CLXXXIV.—*Equilibrium between Alcohols and Salts. Part III.*

By Graham Charles Gibson, John O'Leary Driscoll, and William Jacob Jones.

In the present communication (see J., 1926, 318, 321; 1928, 658) are described the conditions of equilibrium between certain sulphates and absolute methyl and ethyl alcohols. Dissociation pressures and the compositions of the solid phases in contact with the saturated solutions have been investigated by Bagster's method (J., 1917, **111**, 494). The products obtained when the anhydrous salts are continuously extracted with warm absolute methyl alcohol have been examined. Methyl-alcoholates of ferrous, zinc and magnesium sulphates have been prepared by dissolving the metal in a solution of sulphuric acid in the absolute alcohol. The density, without correction of the weighings to vacuum, of the methyl alcohol used in the present work was $d_{4^\circ}^{25^\circ}$ 0·78656, and that of the ethyl alcohol 0·78510. The degree of purity of the salts was : $MnSO_4$, 99·7%; $CdSO_4$, 99·9%; Na_2SO_4, K_2SO_4, $(NH_4)_2SO_4$, $CuSO_4$, Ag_2SO_4, $CaSO_4$, $SrSO_4$, $BaSO_4$, $MgSO_4$, $ZnSO_4$, $Al_2(SO_4)_3$, $PbSO_4$, $Th(SO_4)_2$, $CoSO_4$, $NiSO_4$, each 100·0%.

No determinations of solubilities of sulphates in alcohols over ranges of temperature have hitherto been made, but measurements at 18° were carried out by Lobry de Bruyn (*Z. physikal. Chem.*, 1892, **10**, 782), who gave that of copper sulphate as 0·0105 g. of salt per g.

of methyl alcohol, that of magnesium sulphate as 0·0118, that of zinc sulphate as 0·0065, that of cobalt sulphate as 0·0104, and that of nickel sulphate as 0·005. The first investigation of a solid phase in equilibrium with a saturated anhydrous alcoholic solution was that of Klepl (*J. pr. Chem.*, 1882, **25**, 526) in the case of copper sulphate. He stated that under methyl alcohol the solid phase remained white, but this was contradicted by de Forcrand (*Compt. rend.*, 1886, **102**, 551), who obtained greenish-blue crystals of alcoholate. A more thorough investigation of the composition of the solid phases yielded by the copper sulphate and methyl alcohol was made by Auger (*Compt. rend.*, 1906, **142**, 1272), who showed that on extraction with the alcohol the anhydrous salt was converted into an insoluble green basic salt to which he assigned the formula $CuO,3CuSO_4,4CH_3{\cdot}OH$, but when a small quantity of methyl alcohol was saturated with copper sulphate the solid phase consisted of $CuSO_4,CH_3{\cdot}OH$ with only an insignificant proportion of basic salt. The present work has confirmed these observations of Auger, although it should be pointed out that for the basic sulphate the formula $CuO,4CuSO_4,6CH_3{\cdot}OH$ better satisfies the results of the analyses both of Auger and of the authors. Further, Auger, although he gave no quantitative results, stated that he had obtained evidence of very slight basic decomposition in the cases of cobalt and nickel sulphates, and of more considerable decomposition in the case of zinc sulphate. The present experiments, however, have failed to reveal the formation of basic alcoholates of the former two salts, and have proved that only a trace of basic salt is formed by zinc sulphate even on long standing.

EXPERIMENTAL.

Results. In the following tables solubility is given as gram of salt per gram of alcohol, and pressure as mm. of mercury.

Solubility of sulphates in methyl alcohol.

Temp.	Magnesium.	Zinc.	Cadmium.	Thorium.	Manganous.	Cobalt.	Nickel.
15°	0·00276	0·00485	0·00038	0·00029	0·00190	0·00300	0·00061
25	0·00224	0·00428	0·00031	0·00024	0·00114	0·00418	0·00081
35	0·00180	0·00408	0·00026	0·00019	0·00064	0·00419	0·00110
45	0·00153	0·00420	0·00022	0·00014	0·00043	0·00372	0·00157
55	0·00123	0·00463	0·00019	0·00010	0·00029	0·00267	0·00222

The sulphates of sodium, potassium, ammonium, silver, calcium, strontium, and aluminium were all found to have solubilities less than 0·0001 at 25°; barium and lead sulphates less than 0·00001. Owing to the gradual formation of basic salt in systems containing copper sulphate and methyl alcohol, values of the solubility of the normal salt are subject to some uncertainty. When the two components are brought together, the amount of salt dissolved increases at first, then attains a maximum value, and subsequently steadily falls as the sparingly soluble basic salt is being formed. For instance, in a certain experiment at 15°, when the components were shaken together the amount of salt dissolved after 16 days was 0·00525 g. per g.; after 23 days, 0·00731; after 26 days, 0·00763; and after 28 days, 0·00707. In all cases when the maximum is attained, the solid phase in contact with the blue solution is the white, non-alcoholated salt (Found in one case: SO_4, 59·6. Calc. for $CuSO_4$: SO_4, 60·2%). Alcoholation is always subsequent to the attainment of the maximum, the values of which are given below:

Temp.	15°	25°	35°	45°
Gram $CuSO_4/g.CH_3\cdot OH$	0·0076	0·0140	0·0215	0·0290

When anhydrous copper sulphate is wetted with the absolute alcohol and kept at 15° until alcoholation has completely occurred, the solid phase obtained consists of the monoalcoholate of the normal salt, with only a trace of basic salt (Found: SO_4, 49·3. Calc. for $CuSO_4,CH_3\cdot OH$: SO_4, 50·2%) (compare de Forcrand and Auger, *locc. cit.*), but when copper sulphate is preserved in contact with large excess of the alcohol there is ultimately produced the basic alcoholate (Found: Cu, 34·3, 34·5; SO_4, 42·1, 41·9. Calc. for $CuO,4CuSO_4,6CH_3\cdot OH$: Cu, 34·9; SO_4, 42·2%. Calc. for $CuO,3CuSO_4,4CH_3\cdot OH$: Cu, 37·0; SO_4, 42·0%), already analysed and described by Auger, who found Cu, 35·0, 36·0; SO_4, 42·1, 42·2%.

In the following table are given (1) the compositions of the solid phases in equilibrium with the respective saturated solutions between 15° and 55°, and (2) the dissociation pressures of the alcoholates. In the case of each salt the alcoholate given last in the column headed "Solid phase" is the lowest, and dissociates directly to the non-alcoholated salt.

Methyl-alcoholates.

	Salt in solid phase, %.		Dissociation pressure in mm.		
Solid phase.	Found.	Calc.	12°.	16°.	20°.
$MgSO_4,3\frac{1}{2}CH_3\cdot OH$	51·8	51·8	51·5	57·5	63·0
$ZnSO_4,2\frac{1}{2}CH_3\cdot OH$	66·7	66·8	9·0	12·0	15·0
$ZnSO_4,CH_3\cdot OH$	83·3	83·4	—	—	0·5

Both the first two of the above alcoholates crystallise in plates, and the last forms tabular crystals which cleave into plates. Between 15° and 55°, cadmium, thorium, manganous, cobalt, and nickel sulphates exist in equilibrium with their respective saturated solutions as the non-alcoholated salts. In no case was a transition point observed.

Solubility of sulphates in ethyl alcohol.

Temp.	Magnesium.	Zinc.	Cadmium.	Manganous.	Cobalt.	Nickel.
15°	0·00025	0·00038	—	0·00012	0·00017	0·00017
25	—	0·00034	—	—	0·00018	—
35	0·00020	0·00029	0·00027	0·00014	—	0·00020
45	—	—	0·00025	—	0·00023	0·00022
55	0·00016	0·00020	0·00019	0·00021	0·00026	0·00025

The solubilities of calcium, strontium, barium, and lead sulphates in ethyl alcohol at 25° are less than 0·00009. In the cases of all the above sulphates the solid phase in contact with the saturated solution is the non-alcoholated normal salt.

Basic Methyl-alcoholates.—For the purpose of examining the effect of exhaustive treatment with the fresh warm solvent, the anhydrous sulphates of copper, zinc, thorium and cobalt together with absolute methyl alcohol were placed in Soxhlet extractors, which were provided with guard tubes to prevent ingress of moisture, and kept in action continuously for 100 hours. During the extraction the solids were occasionally stirred by hand in order to present fresh surfaces to the solvent. No vestige of basic decomposition was detected in the thorium and cobalt sulphates, and with zinc sulphate the ratio, by weight, of basic to normal sulphate was only 0·0019. With copper sulphate, however, basic decomposition was complete.

Preparation of Sulphate Methyl-alcoholates from the Metals.—To 163 c.c. of concentrated sulphuric acid (*d* 1·840) were added, slowly and with cooling, 230 c.c. of fuming acid (*d* 1·915), whereby there resulted 100% sulphuric acid. One volume of this acid was gradually added to 6 volumes of well-cooled absolute methyl alcohol. The diluted acid was placed in a flask provided with a Bunsen valve, and particles of dried metal were introduced. When excess of metal had been added, the solution was kept for 12 hours and was then quickly filtered. The filtrate was preserved in a vacuum in the presence of phosphoric oxide. The solid which appeared was dried on unglazed porcelain, and then immediately analysed. Iron thus treated yields *ferrous sulphate hemitritamethyl-alcoholate* in transparent granular crystals, which in the mass possess an olive-green tint (Found : Fe, 28·1; SO_4, 48·6. $FeSO_4,1\frac{1}{2}CH_3\cdot OH$ requires Fe, 27·9; SO_4, 48·1%). Magnesium yields the *hemiheptamethyl-alcoholate* (Found : Mg, 11·3; SO_4, 41·6; $CH_3\cdot OH$, 48·2. $MgSO_4,3\frac{1}{2}CH_3\cdot OH$ requires Mg, 10·5; SO_4, 41·3; $CH_3\cdot OH$, 48·2%), and zinc yields the *monoalcoholate* (Found: Zn, 33·3; SO_4, 49·6; $CH_3\cdot OH$, 16·4. $ZnSO_4,CH_3\cdot OH$ requires Zn, 33·8; SO_4, 49·7%; $CH_3\cdot OH$, 16·5%).

THE TATEM LABORATORIES, UNIVERSITY COLLEGE,
CARDIFF.

[*Received, May 25th,* 1929.]