

252. *Studies of Ionisation in Non-aqueous Solvents. Part III. The Formation of Certain Sulphides in Methyl and in Ethyl Alcohol.*

By WILLIAM L. GERMAN and THOMAS W. BRANDON.

The reactions between sodium sulphide and a number of metal salts have been studied in methyl and in ethyl alcohol with the aid of conductivity titrations. Unlike the reactions in water, complete double decomposition with precipitation of the metal sulphide does not always take place, the products in these cases being compounds of this sulphide with the original salt.

THE reactions between hydrogen sulphide and metal salts in non-aqueous liquids have been investigated by Naumann and his collaborators (*Ber.*, 1899, **32**, 999; 1909, **42**, 3790; 1910, **43**, 314), who passed the gas into certain salts dissolved in ether, methyl or ethyl acetate, aceto- or benzo-nitrile, acetone, or pyridine. Analysis of the precipitates showed that in some cases complete formation of the metal sulphide did not take place. Curtis and Burns (*J. Amer. Chem. Soc.*, 1917, **39**, 33) similarly used *isoamyl* alcohol as solvent; they did not record analyses of the precipitates, but noted mercaptan formation as a result of reaction between the alcohol and hydrogen sulphide.

A series of reactions between sodium sulphide and conveniently soluble salts has now been studied in anhydrous methyl and ethyl alcohols. Sodium sulphide was used in preference to hydrogen sulphide to avoid mercaptan formation. The ionisation of sodium sulphide is less in the alcohols than in water and this probably explains the fact that, of the reactions studied, only with silver, cadmium, and copper salts did complete double decomposition take place to form the sulphide. In the other cases compounds of the salt and the metal sulphide were precipitated of the type $(RCl_2)_x(RS)_y$, where R is a bivalent metal. The solubility products of cobalt and nickel sulphides in water are much greater than those of copper, silver, and cadmium sulphides, and if a parallel relationship exists in the alcohols then the failure to obtain these sulphides is explained. Mercuric chloride might, on this reasoning, be expected to give mercuric sulphide. Anomalous behaviour of mercury compounds is not, however, uncommon, and in water the sulphide is not formed until a considerable excess of hydrogen sulphide has been added, the initial products ranging from white to yellow and brown in colour.

EXPERIMENTAL.

The alcohols were purified and the anhydrous salts made as previously described (Part I; *J.*, 1938, 1027). The conductivities of the pure solvents at 25° were: methyl alcohol, 8.30×10^{-6} mho; ethyl alcohol, 5.71×10^{-7} mho. Anhydrous sodium sulphide was prepared from a good sample of the colourless nonhydrate (Sabatier, *Ann. Chim. Phys.*, 1881, **22**, 66). Tests showed it to be free from sulphate and to contain only slight traces of thiosulphate (Found: S, 40.3. Calc.: S, 41.0%). Solutions of this substance gave no smell of mercaptan even on refluxing with the alcohols, though a slight smell appeared after several days. A white solid

was deposited on standing which contained sodium sulphate (Found : Na, 32.1; SO₄, 32.5; other S, 10.8%).

In order to gain an insight into the relative dissociation of sodium sulphide in the two alcohols and in water, the conductivities of sulphide solutions of comparable concentrations were measured. The solutions were prepared by shaking the sulphide with the alcohols, filtering in a dry atmosphere, and standardising immediately. The values are given below.

Sodium sulphide in water at 25°.

c	0.062	0.0155	0.003875	0.000969	0.000485
Λ	156	165	166.5	170	174.5
Λ/Λ_{∞}	0.81	0.858	0.860	0.880	0.91
f_{\pm} (calc.)	0.49	0.702	0.838	0.915	0.939

The value for Λ_{∞} , viz., 192, was obtained by plotting \sqrt{c} against Λ and extrapolating to zero concentration, using the values over a concentration range of 1.0—0.05 obtained by Jellinek and Czerwinski (*Z. physikal. Chem.*, 1922, **102**, 438). The values of the mean activity coefficient were calculated from the simple Debye-Hückel expression $-\log f_{\pm} = 0.505Z_+Z_-\sqrt{\mu}$, where Z_+ and Z_- are the valencies of the ions and μ is the ionic strength. At the higher dilutions the agreement between the values of the mean activity coefficient and the conductance ratio is satisfactory.

Owing to the difficulties of accurately measuring conductivities in very dilute solutions and to the fact that sodium sulphide is not very soluble in methyl and ethyl alcohols, it was not possible satisfactorily to extrapolate the conductivity values to get values of Λ_{∞} . Consequently, values of the mean activity coefficient were calculated from the simple Debye-Hückel expression, and no attempt was made to compare them with conductivity ratios. In the alcohols at 25° this expression reduces to $-\log f_{\pm} = Z_+Z_-A\sqrt{\mu}$. The values of the constant A are : in methyl alcohol 2.117, in ethyl alcohol 2.818 (cf. Buckley and Hartley, *Phil. Mag.*, 1929, **8**, 320). These values are given below :

Sodium sulphide in methyl alcohol at 25°.

c	0.070	0.035	0.0175	0.00875	0.00438	0.002188	0.001094	0.000547
Λ	53.7	58.8	60.0	66.3	69.8	70.5	74.0	78.5
f_{\pm} (calc.)	0.042	0.107	0.206	0.327	0.454	0.573	0.668	0.757

Sodium sulphide in ethyl alcohol at 25°.

c	0.0693	0.0347	0.0174	0.0087	0.0044	0.0022	0.0011	0.00055
Λ	18.7	21.5	24.5	26.4	27.2	29.6	32.3	35.5
f_{\pm} (calc.)	0.015	0.052	0.123	0.227	0.348	0.474	0.590	0.689

In these tables c refers to concentration in eqivs. per l. Although the use of the simple Debye-Hückel expression may not be entirely justifiable in alcoholic solutions, the values of the mean activity coefficient deduced in the more dilute solutions are probably sufficiently accurate to justify the conclusion that sodium sulphide is less ionised in these solvents than in water. This would also be expected from the fact that the dielectric constants of the alcohols are lower than that of water, *i.e.*, the dissociating power is less.

For the titrations, the finely ground anhydrous sulphide was well shaken with the alcohol, and the filtered solution was standardised and used immediately. The conductivity apparatus was the same as that used in Part I (*loc. cit.*). The conductivity results are shown in Figs. 1 and 2, which refer respectively to the reactions in methyl and in ethyl alcohol. In these diagrams the specific conductivities are plotted against molecules of sulphide added.

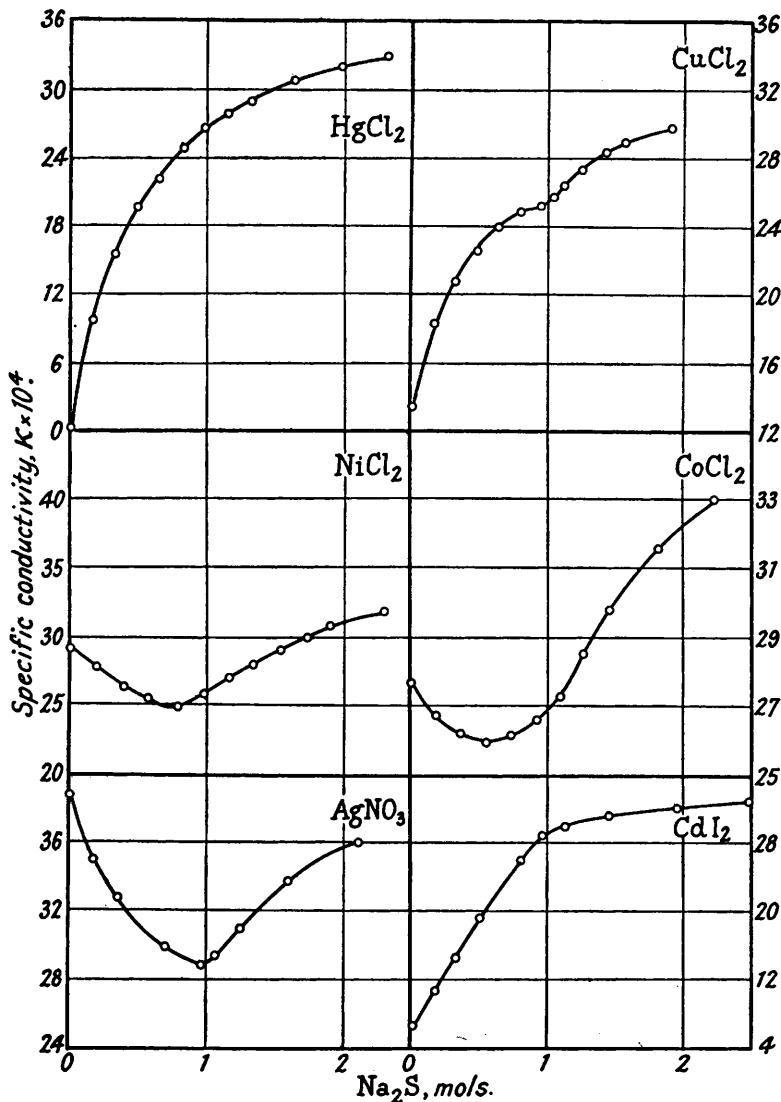
The precipitates for analysis were well washed with the appropriate alcohol, but as several of them were difficult to dissolve, *aqua regia* being necessary in some cases, only the ratio of metal to sulphur was determined.

Sodium Sulphide and Silver Nitrate.—In both solvents the conductivity fell rapidly as sodium sulphide was added to the silver solution, but rose again after the addition of 1 mol. of sulphide. The normal sulphide was therefore formed. It was black and heavy, and precipitation was apparently complete.

Sodium Sulphide and Cadmium Iodide.—A rise of conductivity characterised this reaction in both solvents until 1 mol. of sodium sulphide had been added, after which further addition of reagent caused little conductivity change. The cadmium sulphide, CdS, thus formed, settled immediately as a yellow precipitate, leaving a clear supernatant liquid.

Sodium Sulphide and Copper Chloride.—In ethyl alcohol the first rise in conductivity on addition of sulphide solution was accompanied by the formation of a brown precipitate of indefinite composition containing chloride, that obtained by adding 0.5 mol. of sodium sulphide to 1 mol. of copper chloride having the ratio $\text{Cu} : \text{S} = 1 : 2.56$ (Found : Cu, 18.1; S, 23.2%). The conductivity then fell as this substance reacted with further amounts of sulphide until 1 mol. of sulphide had been added, whereupon the values rose again. Hence, the black pre-

FIG. 1.



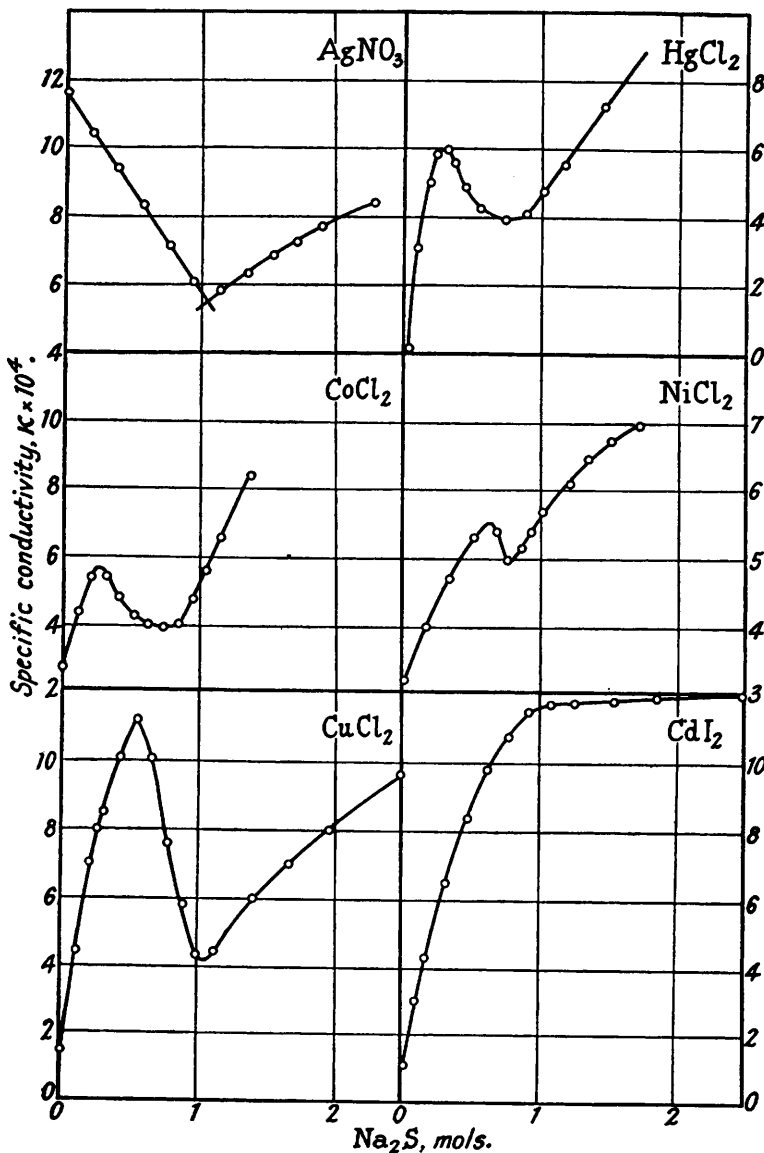
cipitate formed was CuS . Precipitation appeared to be complete, all colour having gone from the supernatant liquid.

In methyl alcohol the conductivity rose initially, and the curve showed a break after the addition of 1 mol. of sulphide. Copper sulphide, CuS , was therefore formed.

Sodium Sulphide and Mercuric Chloride.—In methyl alcohol there was a rapid rise in conductivity and the curve was continuous. The precipitate initially was white, but subsequently it turned brown and finally black as more sulphide was added. The compounds were indefinite, that obtained on adding 1 mol. of sulphide to 1 mol. of mercuric chloride having the ratio $\text{Hg} : \text{S} = 1.07 : 1.0$ (Found : Hg, 83.6; S, 12.5%).

In ethyl alcohol there was a similar behaviour, the initial maximum in the conductivity curve corresponding to the formation of a white substance $\text{HgCl}_2 \cdot 2\text{HgS}$ (Found: Hg, 79.6; S, 8.4%; Hg : S = 1.52 : 1.0). This substance is also formed when hydrogen sulphide is passed into aqueous solutions of mercuric chloride. The final rise in conductivity in ethyl alcohol occurred before the addition of 1 mol. of sulphide was completed. The black compound precipitated was thus of indefinite composition and contained halogen. That formed by

FIG. 2.



adding 1 mol. of sulphide to 1 mol. of mercuric chloride had the ratio Hg : S = 1.15 : 1. Naumann (*loc. cit.*) found that in other solvents, *e.g.*, ether, methyl and ethyl acetates, and acetone, hydrogen sulphide precipitated $\text{HgCl}_2 \cdot 2\text{HgS}$.

Sodium Sulphide and Cobalt Chloride.—In methyl alcohol there was a fall in conductivity until about 0.5 mol. of sulphide had been added, followed by a rise on further addition. The shape of the curve indicates that considerable solvolysis took place. A black substance of indefinite composition was precipitated, that prepared by adding 1 mol. of sulphide to 1 mol.

of cobalt chloride having the ratio $\text{Co} : \text{S} = 1.39 : 1$ (Found : Co, 35.4; S, 13.9%). Precipitation was incomplete, the supernatant liquid remaining blue.

In ethyl alcohol the initial conductivity rise was accompanied by precipitation of an indefinite black substance, that prepared by adding 0.25 mol. of sulphide to 1 mol. of cobalt chloride having $\text{Co} : \text{S} = 1.74 : 1.0$ (Found : Co, 26.8; S, 8.4%). Subsequent addition of sulphide caused first a fall in conductivity, and then a rise after the addition of less than 1 mol. Precipitation was incomplete, the filtrate remaining coloured, and the substance precipitated after the addition of 1 mol. of sulphide was indefinite and again contained chloride (Found : Co, 30.6; S, 14.7%; $\text{Co} : \text{S} = 1.13 : 1.0$).

Sodium Sulphide and Nickel Chloride.—Here again indefinite compounds were obtained. In methyl alcohol the initial fall in conductivity stopped when less than 1 mol. of sulphide had been added. A black precipitate was formed in which the ratio $\text{Ni} : \text{S}$ was 1.51 : 1 (Found : Ni, 37.0; S, 13.4%).

In ethyl alcohol there were two breaks in the conductivity curve, corresponding to the formation of substances of indefinite composition. The black substance prepared by adding 1 mol. of sulphide to the nickel chloride solution had a ratio $\text{Ni} : \text{S} = 1.13 : 1.0$ (Found : Ni, 35.2; S, 17.0%). In both alcohols the indefinite substance contained halogen.

The authors' thanks are due to the Chemical Society and to the Dixon Fund of London University for grants.

WOOLWICH POLYTECHNIC, S.E. 18.

[Received, July 2nd, 1940.]
