

LIQUID HYDROGEN SULPHIDE AS AN IONIZING MEDIUM.—By H. RITCHIE CHIPMAN, M. A., PH. D., and D. MCINTOSH, M. A., D. Sc., Dalhousie University, Halifax, N. S.

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Qualitative measurements of conductivities in liquefied hydrogen sulphide were made by Walker, McIntosh and Archibald², and a few organic substances were found to be good conductors. All these compounds were basic, and it was naturally concluded that sulphides were formed in solution. In an extensive investigation of the properties of hydrogen sulphide by Steele, McIntosh and Archibald², some quantitative determinations were carried out, but no inorganic salt could be found to carry the current appreciably.

In 1925 Quam and Wilkinson³ examined certain reactions in the liquid sulphide, and made some conductivity measurements. In only a few cases were values for other than saturated solutions given, so we have thought it well to examine the conducting power of certain solutions over a suitable concentration range.

Among the compounds mentioned by Quam and Wilkinson are several inorganic substances of particular interest, and of these antimony trichloride and iodine show the greatest conductivity. We have examined these and also studied the conducting power of a number of others which we thought likely to give interesting results.

The hydrogen sulphide was made from hydrochloric acid and ferrous sulphide in a Richard's generator of the usual type. It was washed, then dried with calcium chloride and phosphorus pentoxide, and liquefied by means of carbon dioxide and ether. For qualitative experiments it was liquefied in test tubes, but in the quantitative determinations directly in the conductivity cell.

1. Trans. Chem. Soc. (London) 85, (1904).
2. Trans. Royal Soc. (A) 205, 99, (1905).
3. J. A. C. S. 47, 103, 989, (1925).

REACTIONS IN THE LIQUID SULPHIDE.

Small quantities of the solute were put into the liquid, stirred, and the conductivity measured with a dip electrode. The following results were obtained:

Iodine immediately dissolved forming a beautiful reddish purple solution. It showed a relatively high conductivity.

Sulphur dioxide, made from sodium sulphite and dried with phosphorus pentoxide, was passed through the liquid. No visible reaction took place. A reaction, however, occurred in the gas phase, since sulphur was deposited. The solution did not conduct.

Diphenylamine and phenyl hydrazine were very soluble, but the liquids possessed no conducting power.

Urea and brucine were slightly soluble. The solutions did not conduct.

Meta-phenylenediamine chlorhydrate and glyocoll were either insoluble or only slightly soluble. The solutions showed no conductivity.

Tripopylamine and iso-tributylamine were very soluble and formed good conducting solutions. They were further examined.

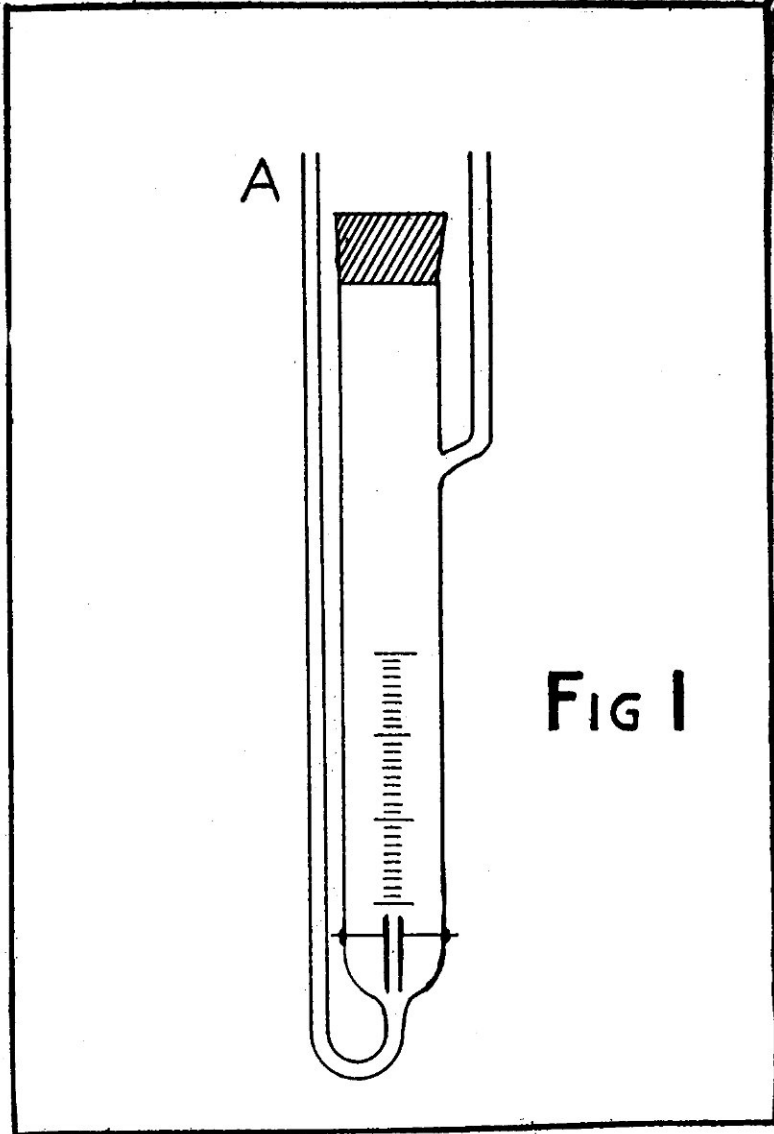
Phosphorus tri- and pentachlorides were soluble but gave no conduction.

Hydrogen chloride and iodide were easily soluble in the liquified sulphide. The former conducted very slightly.

Freshly distilled antimony chloride was quite soluble, but reacted with the solvent. It gave a good conducting solution and will be referred to later.

The conductivity apparatus consisted of an ordinary Wheatsone bridge system with a Leeds and Northup potentiometer as the slide wire. A microphone hummer and a special telephone proved very satisfactory. A Dewar flask with solid carbon dioxide as a refrigerant served as a constant temperature bath.

The conductivity cell was of the form shown in the diagram (Fig. I). The electrodes were platinum, about one centimeter square, and were three millimeters apart. They were platinized in the ordinary way.

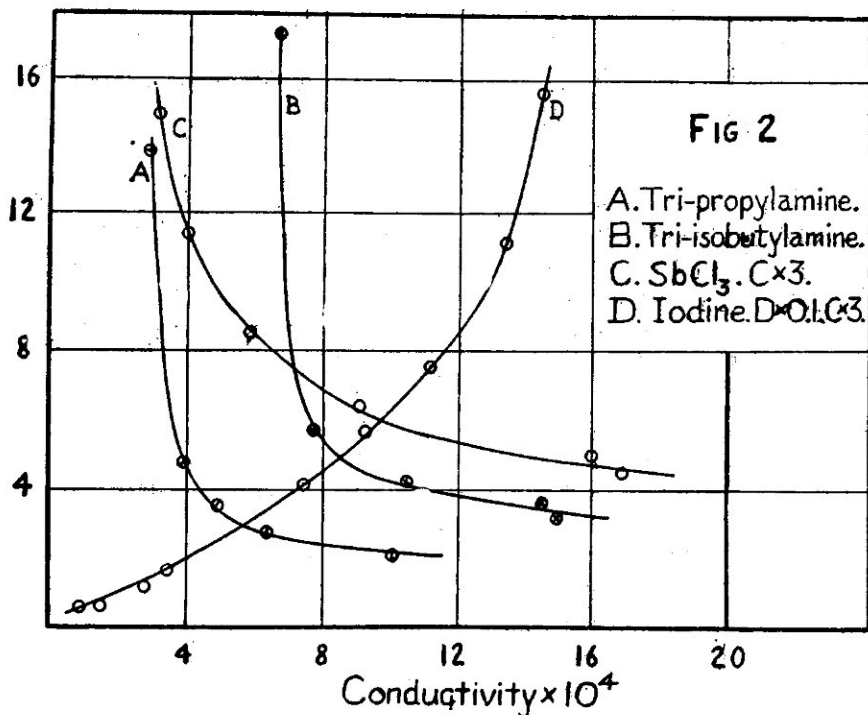


In making measurements the cell was filled with a suitable amount of liquid, a weighed amount of the solute was introduced, and the solution stirred by cold air passed slowly through the tube A, by means of the pump designed by O. Maass. There was very little evaporation, so that this method of stirring was quite suitable for quantitative measurements. After the substance was introduced, the solution was stirred by two strokes of the pump and the resistance was measured. This was repeated until a constant resistance was obtained.

The results are given in the following tables and shown on the curves (Fig. 2).

	Dilution	Equivalent Conductivity $\times 10^4$
Tri-isobutylamine	17.2	6.42
	5.6	7.55
	4.10	10.1
	3.27	14.2
	2.71	14.6
Tri-propylamine	13.7	2.72
	4.61	3.65
	3.32	4.61
	2.65	6.01
	1.93	9.58
Iodine	156.5	4.86
	110.0	4.43
	77.1	3.67
	61.5	3.01
	44.2	2.27
	18.7	1.08
	13.7	0.87
	5.4	0.42
	3.3	0.28
	2.2	0.21

Dilution.



The conductivity curves for the amines in liquid hydrogen sulphide exhibit a form which is just opposite to that of the curves for electrolytes in aqueous solutions, that is, the conductivity increases with the concentration. Similar results were obtained for the organic substances which were examined by Steele, McIntosh and Archibald¹, and they show that this indicates the formation of a complex compound between the solute and the solvent. All the organic substances which have been found to possess conducting power when in solution in hydrogen sulphide are basic, and it would not be surprising to find evidence of compound formation. The substituted amines which have been investigated therefore behave

1. Loc. cit.

in a similar manner to all other organic substances which have been found to give conducting solutions in hydrogen sulphide.

Iodine in liquid hydrogen sulphide behaves exactly as an electrolyte in aqueous solutions, as its conductivity increases with increasing dilution and apparently tends towards a maximum value. In their paper on conductivities in liquid hydrogen sulphide, Quam and Wilkinson state that they investigated the conductivity of iodine in that solvent and reach the conclusion that the current is carried by positive and negative ions of iodine. In support of this they state that they made a transport experiment on a solution of iodine and obtained no evidence of a change in concentration at either electrode. They therefore hold to the opinion expressed by Walden that the iodine is dissociated into positive and negative ions and apparently does not form a compound with the solvent. An attempt was made to find evidences of compound formation or chemical reaction. A strong solution of iodine in liquid hydrogen sulphide was prepared and the hydrogen sulphide distilled off into water. No traces of hydrogen iodide could be found in the resulting solution and the iodine was left in the tube as a mass of small crystals. Apparently iodine does not react with liquid hydrogen sulphide, nor does its solution deposit compounds on cooling. Iodine is the only one of the halogens which shows appreciable conduction in hydrogen sulphide, and there seems to be no good reason why a liquid having a low di-electric constant should be able to cause dissociation. Mention may be made here of the fact that bromine and chlorine show affinity for ether, alcohol, etc., at low temperatures and form compounds; iodine does not.

The investigation of the conductivity of antimony chloride yielded a most interesting result. As this substance is an inorganic salt it might be expected that its conductivity curve would have the form common to all electrolytes in aqueous solutions. It was found however that the curve has the opposite forms. It would therefore be suspected that the antimony trichloride formed a complex compound with the hydrogen sulphide. Quam and Wilkinson investigated this reaction by

sealing up some antimony trichloride with liquid hydrogen in a tube and leaving them for some time. They state that the salt was readily soluble and remained as a clear solution, but that on evaporation or cooling a yellow solid separated which they suspected to be a mixture of antimony sulphochloride, SbSCl , and antimony trisulphide. It was noticed that all the chloride did not dissolve, but on the addition of a further amount the conduction increased. On filtering the solution and analysing it, approximately seventy-five per cent. was found to dissolve.

To obtain evidence of a chemical reaction a solution of the trichloride in hydrogen sulphide was allowed to evaporate, and the gas was passed through water. Hydrogen chloride was found in the distillate, showing that the sulphide and chloride had reacted. We hope in the future to examine this reaction more fully, and to make molecular weight determinations of the substances mentioned in this paper by the freezing—and boiling-point methods.

SUMMARY

1. An apparatus has been constructed to measure the conductivity of substances in liquid hydrogen sulphide, and a satisfactory method of stirring the solution has been devised.

2. The conductivity of fifteen substances in liquid hydrogen sulphide has been examined. Of the substances investigated, iodine, tri-isobutylamine, tri-propylamine, and antimony trichloride were found to possess an appreciable conductivity which was measured over a considerable concentration range.

3. It was found that all of these substances acted as if they formed complex compounds with the solvent, with the exception of iodine, which conducted the current in a similar manner to an electrolyte in aqueous solutions.

4. It is concluded that the conductivity of the solutions of the amines and antimony trichloride is due to the dissociation of a compound formed with the hydrogen sulphide, while in the case of the iodine it is due to the dissociation of the iodine into positive and negative ions.