Use of the Stannous Sulphide Electrode

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THE method of preparation of the Stannous sulphide electrode has been described.

Reproducibility of the electrode potential and the stability of the electrode have also been studied. Effect of Medium from aqueous to alcohol-water mixture, pH and temperature have also been studied. The posibility of determination of Sulphide ions in highly concentrated solutions (Saturated solution of other salts) like-Sodium Iodide, Sodium-Thiosulphate, Sodium Nitrate, Sodium Nitrite, Sodium Bicarbonate, Sodium Chloride and Sodium Bromide have also been examined. In general the electrode is fairly suitable for analytical purpose using calibration curves.

The stannous sulphide electrode[1-4] has been studied for the determination of some thermodynamic properties. However, no attempt has been made to use this electrode as an indicator electrode. The present paper is, therefore, devoted for finding out the optimum working conditions of this electrode and to the possible use of this electrode in the determination of sulphide ions.

EXPERIMENTAL

Apparatus : PL. 52 Toshniwal potentiometer with BG 11 Ballastic Galvanometer and Lamp-Scale arrangement was used for the emf. determination. The indicator electrode was a stannous sulphide electrode and reference electrode was a saturated calomel electrode. Temperature of the solution was controlled using a thermostatic water bath as described by Chakravarty[5].

Reagents : All the chemicals used were of analytical grade and used without further purification. Stock solution of sodium sulphide was freshly prepared every day.

Preparation of the Sulphide electrode : A platinum wire of diameter 0.25 mm was fused in a pyrex tubing and the assembly was cleaned in concentrated nitric acid, washed with distilled water and ethanol ; It was then dried. Tin was deposited on this cathode by electrolysing a 0.1% stannous chloride solution with low current from a 4 volt battery for half an hour. The electrode was washed with water and kept in saturated hydrogen sulphide solution overnight. The electrode was maintained in conductivity water after use.

The electrode potential was obtained fairly quickly and the equilibrium potential was reached within 60 seconds of immersion of the electrode. The reproducibility of the electrode was with ± 4 mv and on potential drift was observed.

RESULTS AND DISCUSSION

The stannous sulphide electrode was found to be durable if handled with care and without jerks for about an year, provided that this is kept in condnctivity water after use. The electrode responds to the concentration of sulphide ions in solution. It does respond to the solution of hydrogen sulphide but the readings are not stable because of the continuous escape of hydrogen sulphide gas from the solution. Therefore sodium sulphide has been taken as a source for sulphida ion. In this case, solution becomes alkaline and there is no escape of hydrogen sulphide from the solution. The plot of electrode potential vs. log sulphide concentration is linear (Fig. 1) over a range of concentration 10^{-3}—10^{-6} M. The emperical equation of the line has been computed to be

$$E = 0.105 + 0.035 \log [S^{2}]$$

Using this equation the error in the determination of sulphide ion concentration is of the order of 0.66%. The effect of change of medium from aqueous to alcohol-water mixture viz., 25% alcohol, 50% alcohol, 75% alcohol and 100% alcohol on the electrode potential was also studied. The response is linear and the slope of the line varies with the percentage of alcohol content in the medium and is given in the Table 1.

Data recorded in the Table 1 indicate that the slope values slightly increases with the increases of the alcohol content in the solvent. The useful concentration range in which the electrode can suitably work is the same as in the case of aqueous medium i.e. 10^{-3} to 10^{-6} M.

In an acidic solution, sulphide can partly be lost as H_2S gas. So unless this loss is prevented, by

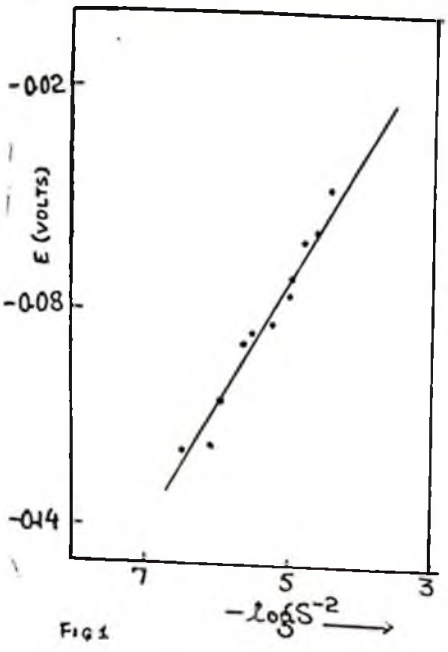


Fig. 1 Plots of E (Volts) vs log S^{-2} in aqueous medinm

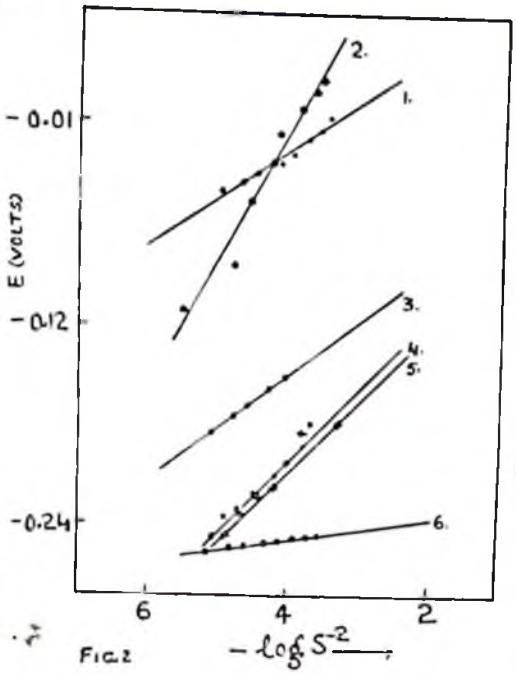


Fig 2 Plots of E (Volts) vs log S^{-1} Curve 1,2 3,4,5, and 6 are at pH 14,13,12,11,10 and 9 respectively

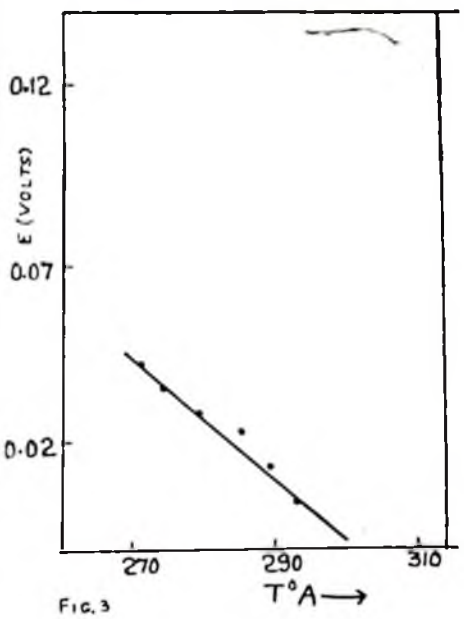


Fig. 3 Plots of E (Volts) vs. temperature In aqueous Sodium sulphide solution

TABLE 1

Percentage of Alcohol in Medium	Slope value	E_o
0	0.035	0.105
25	0.037	0.132
50	0.038	0.160
75	0.041	0.190
100	0.043	0.208

TABLE 2

pH	Slope Value	E_o
14	0.026	+0.081
13	0.066	+0.258
12	0.031	−0.021
11	0.022	−0.066
10	0.027	−0.095
9	0.005	−0.117

suitable cell arrangement S^{2-} cannot be measured with this electrode in acid medium. So the pH, during these measurements, must be maintained in alkaline range. At a given concentration of sulphide, the potential of the electrode was a linear function of pH in the range of pH 9-14. At pH values less than 9, erratic values are observed. The values of electrode potential vs. log sulphide concentration are plotted in Figs. 2. In all cases plotes are linear. Slope of the line for different values of pH are recorded in Table 2.

The results show that in solutions of pH 14, 12, 11 and 10 the slopes are near the Nernstian value. In solutions of pH 13, the slope is higher and in solutions of pH 9, it is lower. Sulphide ion determination can be made fairly accurately in any of these solutions. However, an attempt to correlate the hydrogen ion concentrarion, sulphide ion concentration and the electrode potential into one single equation failed, although in the case of silver -silver sulphide electrode, a relation was obtained by Gurtu[7] between these quantities in the narrow range of pH near the value of 9.

Varying amounts of (upto 10 times the sulphide concentration) of carbonate, bicarbonate, sulphide, sulphite, thiosulphite, nitrite, chloride, bromide and iodide ions, had very little effect on the measured potentials. This shows that the electrode is highly specific and it responds only to sulphide ions. So attempts were made to determine the concentration of sulphide in different saturated salt solutions and and the results are presented is Table 3.

The electrode potential is measured as a function of temperature at a constant concentration of sulphide ion and the results are plotted in Fig. 3. From the slope of the curve, the dE/dT is computed to be -1.7×10^{-3} volts/degree.

TABLE III

Saturated solution of ions	Detectable molar range of sulphide ion concentration		Error %
	From	To	
Iodide	—	—	—
Thiosulphate	—	—	—
Sulphate	—	—	—
Sulphite	1×10^{-3}	1.5×10^{-4}	0.0
Nitrate	1.75×10^{-3}	5×10^{-4}	0.5
Nitrite	2×10^{-3}	1.5×10^{-4}	0.8
Bicarbonate	1.75×10^{-3}	0.2×10^{-4}	0.4
Bromide	1.75×10^{-3}	1.5×10^{-4}	0.2
Chloride	1.75×10^{-3}	0.2×10^{-4}	0.2
Carbonate	—	—	—

CONCLUSION

The above discussion shows that the electrode gives Nernstian response in limited cases only. However, with suitable calibration curves, the electrode can safely be used in aqueous. and alcoholic alkaline solutions. The durability of the electrode and the reproducibility of the electrode potential is fairly good. Temperature dependence of the electrode potential is also small. The concentration range in which sulphide ion can be determined is 10^{-3} to 10^{-6}M.

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