

Studies on the electrochemical and thermodynamic behaviour of tin-tin sulphide electrode in the presence of sulphide ions

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Abstract. Tin-tin sulphide (Sn-SnS) electrode has been prepared. Statistical analysis indicates that this electrode is stable and reproducible. It has been found that the electrode can be used in the quantitative determination of S^{2-} in the presence of foreign ions such as F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} and NO_3^- . The potential of the electrode in the presence of S^{2-} has been measured by setting up the following type of cell: Sn-SnS/ S^{2-} (saturated) KCl/Hg₂Cl₂, Hg. The electrode shows Nernstian response to pS ($-\log[S^{2-}]$) over the range 7.09 to 12.26. The electrode also shows the Nernstian response to pH in the range 7.54 to 11.98 at constant pS. Values of E^0 , $(\partial E^0/\partial T)_P$ and various thermodynamic functions, viz., ΔG^0 , ΔH^0 and ΔS^0 for the electrode reaction, $Sn_{(s)} + S^{2-}_{(aq)} \rightleftharpoons SnS_{(s)} + 2e$, have been determined. Besides, the standard free energy of formation (ΔG_f^0) and solubility product constant (K_{sp}) of SnS in aqueous medium at $25 \pm 0.1^\circ C$ have also been determined.

Keywords. Tin-tin sulphide electrode; sulphide ions; thermodynamic behaviour.

1. Introduction

In continuation to earlier publications (Sharma and Singh (in press)) we now report our results of investigation on the electrochemical and thermodynamic behaviour of Sn-SnS electrode in the presence of sulphide ions under different experimental conditions.

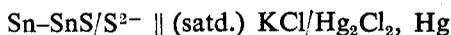
2. Experimental

The tin-tin sulphide (Sn-SnS) electrode was prepared by the same general method as reported in earlier publications (Sharma and Singh). All the chemicals used were of analytical reagent grade. Stock solutions were prepared in double distilled water. A series of Britton Robinson (BR) buffers of pH 7.54 to 11.98

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were prepared. The pH values of the solutions were checked before use by Philips pH-meter (PR 9405) to confirm their pH as mentioned in the literature (Britton 1956). Higher pH values (12.80 and 13.60) were maintained by the addition of normal solution of sodium hydroxide. Stock solutions of sodium sulphide were prepared by dissolving reagent grade $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ in double distilled water, and standardised by Bethge (1954) method. A series of stock solutions of Na_2S were prepared keeping the ionic strength constant at 0.02 M by addition of an appropriate volume of NaNO_3 . pH readings were converted to hydrogen ion concentration.

The potential of the electrode in solutions containing S^{2-} was measured at $25 \pm 0.1^\circ \text{C}$ by setting up the following type of cell :



3. Results and discussion

Sn-SnS electrode was prepared six times under identical conditions and each time its potential was measured in well-stirred aqueous Na_2S solutions of different concentrations (6.0×10^{-6} , 4.0×10^{-5} , 6.0×10^{-4} and 2.9×10^{-3} M) at $25 \pm 0.1^\circ \text{C}$. The results indicated that the variation in the value of electrode potential was within the limits of standard deviation (1.8×10^{-3}) which shows that the potential of the electrode is reproducible.

The potential of Sn-SnS electrode was measured in aqueous Na_2S solutions of different concentrations (6.0×10^{-6} , 4.0×10^{-5} , 6.0×10^{-4} and 2.9×10^{-3} M) at $25 \pm 0.1^\circ \text{C}$. It was found that the potential of the electrode became constant within one minute of its immersion in well-stirred solutions. It is thus inferred that the electrode attains equilibrium potential rapidly.

The potential of Sn-SnS electrode was measured in aqueous solutions of Na_2S of different concentrations (6.0×10^{-6} , 4.0×10^{-5} , 6.0×10^{-4} and 2.9×10^{-3} M) after an interval of one month at $25 \pm 0.1^\circ \text{C}$. It was found that the potential of the electrode remained steady up to 10 months. This study reveals that the electrode is fairly stable if handled carefully and kept in double distilled water after use. However, if the electrode was allowed to remain in the atmosphere for a few hours it began to give erratic readings.

3.1. Electrochemical behaviour of Sn-SnS electrode vis-a-vis its use in the quantitative determination of sulphide ion concentration.

A series of aqueous solutions of Na_2S of different concentrations ranging from 6.0×10^{-6} to 4.0×10^{-3} M were prepared keeping the ionic strength constant at 0.02 M. The potential of the electrode (v. SCE) was measured as a function of $[\text{S}^{2-}]$ at $25 \pm 0.1^\circ \text{C}$. The pH of the solutions was measured with the help of Philips pH-meter (PR 9405) and $[\text{S}^{2-}]$ was calculated at different $[\text{S}^{2-}]$, according to the procedure reported in earlier publication (Sharma and Singh (in press)). The plot of $E_{\text{sn-sns}}$ vs $\log [\text{S}^{2-}]$ is linear (figure 1). The electrochemical equation to this linear plot (figure 1) has been obtained as under :

$$E_{\text{sn-sns}} = -0.610 - 0.030 \log [\text{S}^{2-}] \quad (1)$$

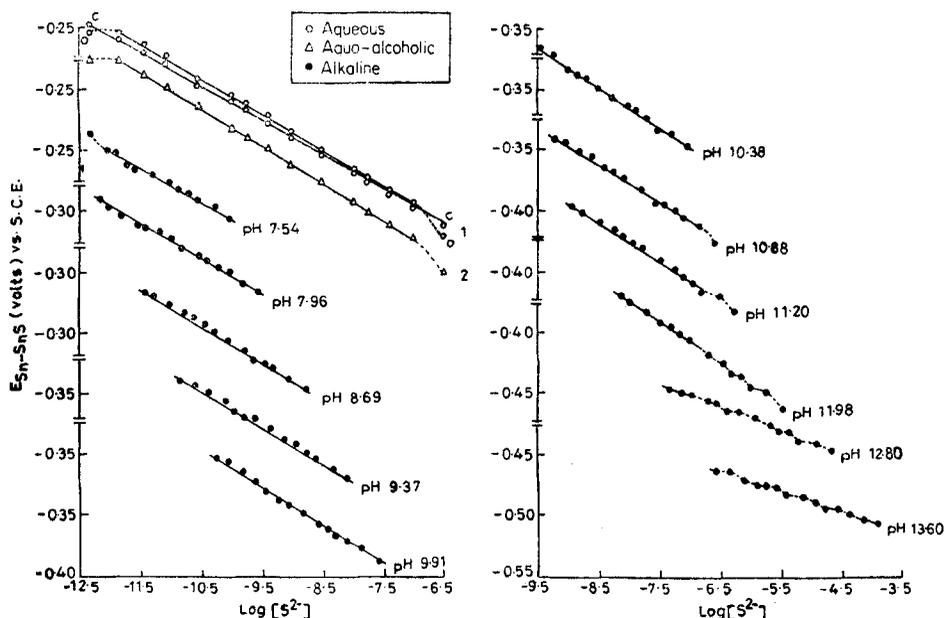


Figure 1. Plots of $E_{\text{Sn-SnS}}$ (volts) vs SCE against $\log [S^{2-}]$ in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54–13.60) media at $25 \pm 0.1^\circ \text{C}$. (O = observed) (C = calculated).

where the intercept potential value -0.610 V at $\log [S^{2-}] = 0$ is the algebraic sum of the standard electrode potential (E^0) of Sn–SnS electrode and that of SCE from which E^0 of the electrode works out to be -0.851 V at $25 \pm 0.1^\circ \text{C}$.

The validity of the above electrochemical equation (1) has been further checked by obtaining the calculated values of potential of Sn–SnS electrode as a function of $\log [S^{2-}]$ by applying the regression analysis (Brown and Sallee 1963). From figure 1 it is evident that the calculated and observed values are almost the same. The variance of electrode potential about $\log [S^{2-}]$ is 7.3×10^{-6} and the standard error is 0.27%. Since these values are very small in comparison with the calculated values of electrode potential it is concluded that the assumed relation is justified. Thus Sn–SnS electrode can be successfully used in the quantitative determination of S^{2-} in given samples.

3.2. Influence of various experimental conditions on the working of tin-tin sulphide electrode

3.2a. *Influence of foreign ions*: The effect of the presence of some foreign ions such as F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , $S_2O_3^{2-}$, SO_4^{2-} , NO_2^- and NO_3^- with their increasing concentrations (1×10^{-6} – $1 \times 10^{-1} \text{ M}$) was investigated on the working of Sn–SnS electrode in $1 \times 10^{-4} \text{ M}$ sodium sulphide solution. The results of the study indicates that there is hardly any difference between the potential of the electrode in the presence and absence of F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} and NO_3^- . But the same is not true in the case of $S_2O_3^{2-}$

and NO_2^- ions. Further the potential of the electrode has also been measured as a function of $[\text{S}^{2-}]$ when present in saturated solutions of the above foreign ions. A perusal of the above study indicates that the electrode shows a Nernstian response to S^{2-} , within the experimental error of the theoretical Nernstian value (0.0296 V), when S^{2-} is present in saturated aqueous solutions of F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} and NO_3^- ions. From this study it follows that Sn-SnS electrode can be successfully used in the quantitative determination of sulphide ions in presence of impurities of F^- , Cl^- , Br^- , I^- , HCO_3^- , CO_3^{2-} , SO_3^{2-} , SO_4^{2-} and NO_3^- ions in the given samples.

3.2b. *Effect of medium* : The working of the electrode was studied in alcoholic solution of Na_2S of varying concentrations ranging from 6.0×10^{-6} to 2.9×10^{-3} M. The potential of Sn-SnS electrode was measured as a function of $[\text{S}^{2-}]$ in 50% (v/v) alcoholic solutions of Na_2S at $25 \pm 0.1^\circ \text{C}$. The plots of $E_{\text{sn-sns}}$ vs $\log [\text{S}^{2-}]$ are linear (figure 1). This shows that the electrode can be successfully used in the quantitative determination of sulphide ion in aquo-alcoholic medium. The electrochemical equation to the linear plot (figure 1) of Sn-SnS electrode can be represented as under :

$$E_{\text{sn-sns}} = -0.640 - 0.031 \log [\text{S}^{2-}] \text{ for } 50\% \text{ (v/v)} \quad (2)$$

The value of E^0 works out to be -0.881 V and the experimental slope value is 0.031 V . The validity of above electrochemical equation is justified by the statistical treatment of data which shows a variance of 8.4×10^{-6} and standard error 0.29% . The electrode was also tried in non-aqueous (100% alcohol) medium but it failed to respond to S^{2-} .

3.2c. *Effect of pH (BR buffer)* : A series of Na_2S solutions of varying concentrations ranging from 6.0×10^{-6} to 2.9×10^{-3} M were prepared in BR buffer (pH 7.54–11.98) and in solution of pH 12.80 and 13.60 ; and $[\text{S}^{2-}]$ was calculated (Sharma and Singh (in press)) at different pH values. The potential of the electrode has been measured as a function of $[\text{S}^{2-}]$ at fixed (controlled) pH values (7.54–13.60). The plots of $E_{\text{sn-sns}}$ vs $\log [\text{S}^{2-}]$ were found to be linear (figure 1). These indicate a Nernstian response with slope of 0.030 V in the pS range 7.09 – 12.26 at $25 \pm 0.1^\circ \text{C}$ and is within the experimental error of the theoretical value given by equation :

$$E_{\text{sn-sns}} = \text{constant} - 0.0296 \log [\text{S}^{2-}] \quad (3)$$

where the 'constant' is the sum of standard electrode potentials of the saturated calomel electrode and the standard potential of Sn-SnS electrode. Also the potential of Sn-SnS electrode was measured as a function of pH values (≥ 7.54) keeping the sulphide ion concentration constant. At constant $[\text{S}^{2-}]$, and constant ionic strength 0.02 M (NaNO_3) a plot of $F_{\text{sn-sns}}$ vs pH is linear (figure 2) having an experimental slope of $0.030 \pm 0.004 \text{ V}$ per pH unit. The Sn-SnS electrode can thus be used to measure pH between 7.54–11.98 at given $[\text{S}^{2-}]$. A perusal of this study reveals that Sn-SnS electrode can be successfully used in the quantitative determination of sulphide ion in alkaline medium from pS ($-\log [\text{S}^{2-}]$) 7.09 to 12.26 and in the pH range 7.54 – 11.98.

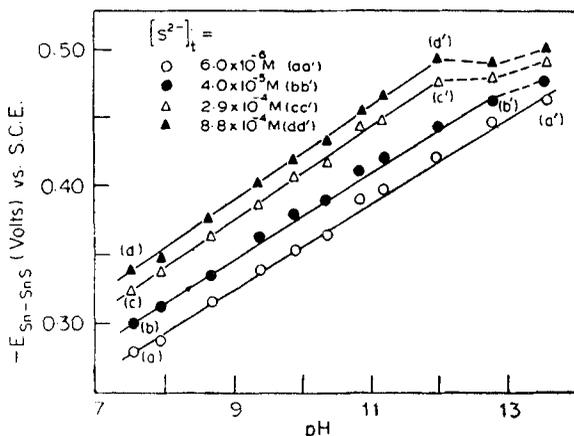


Figure 2. Plots of E_{Sn-SnS} (volts) vs SCE against pH at constant sodium sulphide concentration ($[S^{2-}]_t$).

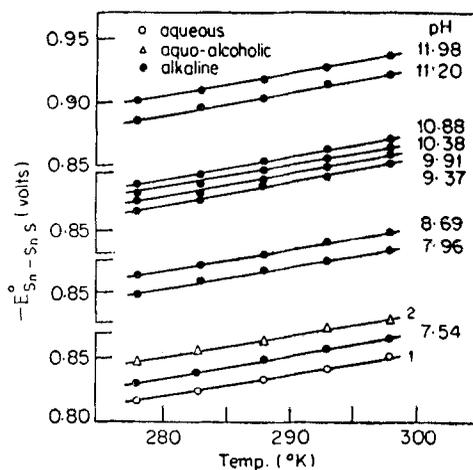


Figure 3. Plots of E_{Sn-SnS}^0 (volts) vs temperature ($^{\circ}K$) in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54-11.98) media containing S^{2-} .

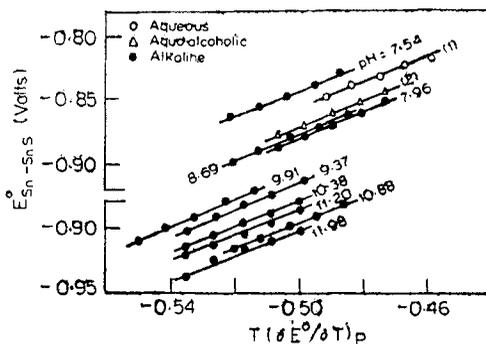


Figure 4. Plots of E_{Sn-SnS}^0 (volts) vs $T(\partial E^0/\partial T)_P$ in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54-11.98) media containing S^{2-} .

3.2d. *Effect of temperature*: The potential of Sn-SnS electrode was measured as a function of $[S^{2-}]$ at different temperatures ranging from 5 – 25°C, at four different concentrations of Na_2S in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54 – 11.98) solutions. From the plots of E_{Sn-SnS} vs $\log [S^{2-}]$ at different temperatures in various media, the values of E^0 of electrode have been obtained at different temperatures. The temperature coefficient, $(\partial E^0/\partial T)$, of E^0 has also been determined from the linear plots of E^0 (volts) vs T (°K) (figure 3), in various media. The corresponding values of $T(\partial E^0/\partial T)_p$ have been calculated and the relationship between $T(\partial E^0/\partial T)_p$ and E^0 in different media containing S^{2-} has been shown in figure 4. The relationship is linear in all the cases in accordance with the equation :

$$E^0 = -\frac{\Delta H^0}{nF} + T\left(\frac{\partial E^0}{\partial T}\right)_p \quad (4)$$

The thermodynamic functions (Daniels and Alberty 1966) ΔH^0 , ΔG^0 and ΔS^0 for Sn-SnS electrode in different media at $25 \pm 0.1^\circ C$ containing S^{2-} , have been calculated and the values listed in table 1.

3.3. The standard free energy of formation (ΔG_f^0) of SnS

The standard free energy of formation, ΔG_f^0 , of SnS can be calculated following the method put forward by Goates *et al* (1951) for the calculation of ΔG_f^0 of Ag_2S . Now, ΔG^0 for Sn-SnS electrode, *i.e.*, for the electrode reaction,

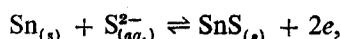


Table 1. Values of various thermodynamic parameters for Sn-SnS electrode in aqueous, aquo-alcoholic (50% v/v) and alkaline (pH 7.54-11.98) solutions of S^{2-} at $25 \pm 0.1^\circ C$.

Medium	ΔG^0 kcal mole ⁻¹	ΔH^0 kcal mole ⁻¹	ΔS^0 e.u.
Aqueous	39.3	16.6	-76.1
Aquo-alcoholic (50% v/v)	40.7	17.3	-78.4
Alkaline (pH)			
7.54	39.9	15.8	-80.8
7.96	40.8	17.4	-78.4
8.69	41.5	17.4	-80.8
9.37	41.6	16.8	-83.1
9.91	42.0	16.6	-85.4
10.38	42.3	17.5	-83.1
10.80	42.4	18.3	-80.8
11.20	42.5	17.7	-83.1
11.98	43.2	18.4	-83.1

is 39.3 kcal mole⁻¹ (*vide* table 1) in aqueous medium. A positive value of ΔG_0 shows that the above electrode reaction is nonspontaneous in the forward direction and that in the backward direction it would be spontaneous with $\Delta G^0 = -39.3$ kcal. Thus,

$$-39.3 = \Delta G_f^0 (\text{SnS}_{(s)}) - [\Delta G_f^0 (\text{Sn}_{(s)}) + \Delta G_f^0 (\text{S}_{(aq)}^{2-})].$$

As ΔG_f^0 of Sn_(s) (element) is zero and taking (Kaye and Laby 1959) ΔG_f^0 for S²⁻ as 20.00 kcal mole⁻¹ (at 25° C) the value of ΔG_f^0 of SnS works out to be -19.3 kcal mole⁻¹. This is in agreement, within the experimental accuracy, with the literature value (Lurie 1975) of -19.7 kcal mole⁻¹.

3.4. Solubility product constant (K_{sp}) of SnS

The solubility product constant, K_{sp} , of SnS can be calculated from the standard free energy change of the reaction :

$\text{SnS} \rightleftharpoons \text{Sn}^{2+} + \text{S}^{2-}$, by means of the expression (Goates *et al* 1951)

$$\ln K_{sp} = \frac{-\Delta G^0}{RT}$$

Since the values of ΔG_f^0 of SnS has already been calculated as -19.3 kcal mol⁻¹ and using the literature values (Kaye and Laby 1959) of ΔG_f^0 for S²⁻ and Sn²⁺ as 20.0 kcal and 6.28 kcal respectively, the value of K_{sp} can be obtained from the above equation. This works out to be 6.1×10^{-25} at $25 \pm 0.1^\circ \text{C}$. This compares fairly well with the literature value (Lurie 1975) 1.0×10^{-25} (at 25° C).

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