364. Silver–Silver Sulphide Electrodes in Alkaline Solutions.

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From e.m.f. measurements at 25° on the cell,

$$\mathrm{Ag,Ag_2S|S^{2-}}\ (m_s)|\mathrm{OH^-}(m_1)||\mathrm{OH^-}(m_1)||\mathrm{OH^-}(m_1)|\mathrm{H_2}(1\ \mathrm{atm.})\mathrm{Pt}$$

the sulphide electrode was found to be irreversible in alkaline solution, obeying the equation $e_0 = b + (\boldsymbol{RT}/n\boldsymbol{F}) \ln m_s$ where $b = 0{\cdot}691$ v and $n = 1{\cdot}61$. The sulphide concentration, m_s, ranged from 10^{-3} to 10^{-6} molal.

Goates *et al.*[1] recently found the standard e.m.f. ($e_0°$) of the $\mathrm{Ag,Ag_2S|S^{2-}}$ electrode to be 0·7125 volt in slightly alkaline solutions. They assumed the electrode reaction to be $2\mathrm{Ag} + \mathrm{S^{2-}} \longrightarrow \mathrm{Ag_2S} + 2e$. They used the cell $\mathrm{Ag,Ag_2S|S^{2-}}$ (x molal)||normal calomel; the e.m.f. of the $\mathrm{Ag,Ag_2S|S^{2-}}$ half cell was given by the Nernst equation as $\varepsilon = \varepsilon° + (\boldsymbol{RT}/n\boldsymbol{F}) \ln a_s$. Sodium sulphide solutions were used and the activity of the sulphide ion was calculated from the hydrolysis equilibrium. From four sodium sulphide concentrations (0·1—0·005 molal) the standard e.m.f. of the $\mathrm{As,Ag_2S|S^{2-}}$ electrode was evaluated.

Using a wide range of $\mathrm{S^{2-}}$ and $\mathrm{OH^-}$ concentrations, we could not obtain results that would correspond to a reversible two-electron process ($n = 2{\cdot}0$). This led to a more detailed study of the electrode system in alkaline solutions.

Experimental

The cell detailed above was set up, the same hydroxyl-ion concentrations being used on each side of the liquid–liquid junction, so that the liquid–liquid potentials could be ignored. The cell was H-shaped, divided into three compartments. The vertical tubes were separated from the central horizontal tube by solid filter-paper plugs. Standardised hydroxide was added to the three compartments, and dry nitrogen passed through to remove all traces of oxygen from the solution to which the sulphide was to be added. The central hydroxide compartment minimised diffusion of sulphide through the cell.

The silver–silver sulphide electrode was prepared by silver-plating a spiral of platinum wire. The silver surface was washed in ammonia solution and then hydrochloric acid, placed in an atmosphere of hydrogen sulphide for 30 min., dried, and finally washed in distilled water. The electrodes were kept under distilled water until used.[2]

Carbonate-free sodium hydroxide solutions of various molalities were used. Pure hydrogen sulphide was bubbled through oxygen-free alkali solutions and the $\mathrm{HS^-}$ concentration determined by measuring the optical density of the solutions at 2300 Å ($\lambda_{\text{max.}}$ $\mathrm{HS^-} = 2300$ Å, and $\varepsilon_{\text{max.}} = 7{\cdot}98 \times 10^3$).[3] The sulphide-ion concentration was evaluated, with allowance for hydrolysis, from the concentration dissociation constant,[3] $[\mathrm{H^+}][\mathrm{S^{2-}}]/[\mathrm{HS^-}] = 1{\cdot}0 \times 10^{-14}$. All the e.m.f. readings were taken at 25° after the cell had reached equilibrium (usually 12 hr.).

Results.—From the e.m.f. readings the potential of the sulphide electrode was obtained relative to the standard hydrogen electrode:

$$e_0 = e + 0{\cdot}0592 \log m_{\mathrm{OH}}\gamma_{\mathrm{OH}}/10^{-14}$$

where e_0 is the e.m.f. relative to standard potential of the hydrogen electrode, e the e.m.f. measured, m_{OH} = sodium hydroxide molality, and γ_{OH} = activity coefficient (assumed equal to the mean molal activity coefficient $\gamma_\pm$ for NaOH).

From Robinson and Stokes's data,[4] $\gamma_{\mathrm{NaOH}} = 0{\cdot}681$, 0·690, and 0·723 for 1·20M-, 0·500M-, and 0·250M-NaOH respectively, and calculation from the Debye–Hückel theory gives $\gamma_{\mathrm{NaOH}} = 0{\cdot}891$ for $1{\cdot}20 \times 10^{-2}$M-NaOH.

From the Table of results, by the method of least squares, for the range of sulphide concentrations 10^{-6} to 10^{-3}m, $e_0 = 0{\cdot}691 + (\boldsymbol{RT}/1{\cdot}61\boldsymbol{F}) \log m_s$, with a regression coefficient of 0·997.

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[1] Goates, Cole, Gray, and Faux, *J. Amer. Chem. Soc.*, 1951, **73**, 707.

[2] Martinez, *Chem. Abs.*, 1941, **42**, 4072.

[3] Ellis and Golding, *J.*, 1959, 127.

[4] Robinson and Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 477.

$-e$	m_{OH}	$-\log m_s$	e_0	b ($n =$ 1·61)
0·2266	1·20	2·530	0·5989	0·692
0·2265	1·20	2·491	0·5970	0·689
0·2380	1·20	2·993	0·5855	0·696
0·2496	1·20	3·219	0·5739	0·692
0·2664	1·20	3·665	0·5571	0·692
0·2850	1·20	4·019	0·5385	0·686
0·1964	0·500	2·261	0·6061	0·689
0·2300	0·500	3·171	0·5725	0·689
0·2753	0·500	4·238	0·5272	0·683
0·1902	0·250	2·580	0·5948	0·689
0·1964	0·250	2·921	0·5886	0·696
0·2265	0·250	3·634	0·5585	0·689
0·1940	0·0120	4·668	0·5185	0·690
0·2076	,,	5·070	0·5049	0·693
0·2231	,,	5·590	0·4894	0·670
0·2275	,,	5·590	0·4850	0·691

However, the Nernst equation gives

$$e_0 = e_0{}^\circ + (\boldsymbol{RT}/n\boldsymbol{F}) \ln m_S \gamma_S = e_0{}^\circ + (\boldsymbol{RT}/n\boldsymbol{F}) (\ln \gamma_S + \ln m_S)$$

Comparing this equation with the experimental result, we have

$$e_0{}^\circ + (\boldsymbol{RT}/n\boldsymbol{F}) \ln \gamma_S = 0·691 \; (= b)$$

and since $e_0{}^\circ$ is a defined cell constant, γ_S must be constant, within the experimental error, over the sulphide and hydroxide concentrations used.

Conclusion.—This experimentally derived equation, with an apparent value of $n =$ 1·61, shows that the electrode reaction $Ag,Ag_2S|S^{2-}$ in alkaline solution is irreversible.

In e.m.f. cell work, it is important to show that the cell reaction being considered is a thermodynamically reversible or irreversible process. If it is reversible, the number of electrons involved will be an integer and the free-energy change, ΔG, of such a system can be evaluated from the equation $\Delta G = ne_0{}^\circ \boldsymbol{F}$. If the number of electrons involved in the cell reaction is not an integer the electrode process is irreversible and the free-energy change cannot be evaluated.

As the $Ag,Ag_2S|S^{2-}$ cell reaction in alkaline solutions is irreversible, the free energy of formation of Ag_2S cannot be derived. From a series of only four e.m.f. readings in alkaline solutions Goates *et al.*[1] assumed that the electrode process was reversible and therefrom calculated the free energy of formation of Ag_2S. The present results show that this was not justified.

Despite the irreversibility of the electrode the experimentally derived equation relating e.m.f. and sulphide-ion concentration enables the latter to be measured at high alkalinities. As the electrode is reproducible it can also be used as a reference electrode for the study of sulphide systems.

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