[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

The Silver–Silver Thiocyanate Electrode[1,2]

BY CECIL E. VANDERZEE AND WAYNE E. SMITH[3]

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Successful techniques have been established for the preparation of silver–silver thiocyanate electrodes which are stable in dilute acid and reproducible to 0.1 mv. or better. Studies have been made of the potential of the cell Pt–$H_2(g)$|$HClO_4(m_1)$, $KSCN(m_2)$|AgSCN(s)–Ag at several temperatures over a range of concentrations ($m_1 \doteq m_2$, up to 0.018 molal). Over the temperature range of 5 to 45°, the standard potentials of the cell follow the relation $E^0 = 0.08949 - 1.00 \times 10^{-4}(t - 25°) - 1.61 \times 10^{-6}(t - 25°)^2$ where t = °C. and E^0 is in absolute volts. The silver–silver thiocyanate electrodes studied were of the thermal electrolytic type, and were characterized by stability over a period of several months with no drift in potential, stability with respect to motion and agitation in air-free electrolyte, lack of hysteresis in heating and cooling cycles and also in concentration cycles. The hydrogen electrodes behaved normally, reaching equilibrium quickly and remaining steady with little evidence of poisoning. Replicate electrodes usually agreed within 0.05 mv.

Although the silver–silver halide electrodes have been the subject of many investigations, no careful study has been made of the silver–silver thiocyanate electrode, and no study has been made in a thermodynamically reversible cell free of a liquid junction. Early and fragmentary studies[4–9] were aimed at evaluation of the solubility product of the silver thiocyanate; the later and more complete investigations by Pearce and Smith[10] and Aditya and Prasad[11] sought to obtain the standard potential of the electrode. The Pearce and Smith electrodes were an intimate mixture of electrolytic silver and precipitated silver thiocyanate; those of Aditya and Prasad were essentially of the "third kind," consisting of silver–silver iodide electrodes equilibrated with the thiocyanate solution. Both these later studies involved a calomel electrode; Pearce and Smith calculated the liquid junction potential by the Lewis and Sargent equation, while Aditya and Prasad employed a saturated salt bridge to reduce the effect. By estimating activity coefficients, Pearce and Smith obtained −0.0947 v. at 25° for the standard oxidation potential of the silver–silver thiocyanate electrode, while Aditya and Prasad, using an extrapolation based on the Debye–Hückel equation, obtained −0.0878 v. at 30°. Recently Cave and Hume[12] obtained −0.0921 v. by recalculation of Pearce and Smith's data.

Prasad and co-workers[11,13] resorted to their modified "third kind" electrodes after they were unsuccessful in attempts to prepare reproducible silver–silver thiocyanate electrodes by either the wholly electrolytic or thermal-electrolytic method. Scatchard and co-workers[14] prepared wholly electrolytic electrodes which showed interagreement to 0.1 to 0.3 mv., but made no study of the standard potential.

The objectives of the present work were to establish techniques for preparing reproducible silver–silver thiocyanate electrodes of the thermal-electrolytic type, analogous to the silver–silver chloride electrodes, and to explore the stability and behavior of these electrodes in acidic solutions, at the same time exploring the behavior of the hydrogen electrode in the presence of the thiocyanate ion. The ultimate goal was the determination of the standard potential of the cell

$$H_2(g)|HClO_4(m_1),\ KSCN(m_2)|AgSCN(s)\text{–}Ag \quad (1)$$

in which the reaction

$${}^1/{}_2H_2(g) + AgSCN(s) \longrightarrow H^+ + SCN^- + Ag \quad (2)$$

is occurring.

The mixed electrolyte was chosen in preference to a single solution of thiocyanic acid in order to facilitate the preparation of fresh uncontaminated cell solution. A preparative procedure involving dilution of a concentrated solution of thiocyanic acid would run the risk of decomposition products of the acid being present, since the rate of decomposition increases rapidly with concentration, and it seems prudent to avoid this risk as much as possible in studies of the behavior of the electrodes. For the most concentrated solutions studied in this work (0.02 m) no decomposition of thiocyanic acid could be detected within a week, and in the most dilute solutions, none was evident over a period of several months. However, measurements with all solutions were made without unnecessary delay.

Experimental

Materials.—Throughout the work, conductivity water, freshly distilled and collected near its boiling point, was used for recrystallizations, preparing solutions, all final washings and rinsings of glassware, and other purposes related to the work.

All weighings were corrected to vacuum.

The cell solutions were prepared by delivering a weighed amount of perchloric acid stock solution, accurately standardized on a molal basis, into a known weight of water (about 2 kg.), and then adding a weighed amount of solid potassium thiocyanate which had been prepared as a primary standard. The water was freed of dissolved oxygen by bubbling hydrogen or nitrogen through it for some time before preparing the solution.

The stock solution of perchloric acid was prepared by diluting 70% Baker and Adamson reagent grade perchloric acid (maximum chloride content 0.001%) with conductivity water. Tests for chlorate and similar oxidants were negative.

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[1] From the Ph.D. thesis of Wayne E Smith, University of Nebraska, 1955.

[2] Presented before the Division of Physical and Inorganic Chemistry, 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September 14, 1955.

[3] Minnesota Mining and Manufacturing Company Fellow, 1953–1955; Dow Chemical Company Fellow, 1954–1955.

[4] F. W. Kuster and A. Thiel, *Z. anorg. Chem.*, **33**, 129 (1902).

[5] H. Ley and K. Schafer, *Z. Elektrochem.*, **8**, 694 (1902).

[6] G. Bodlander and R. Fittig, *Z. physik. Chem.*, **39**, 597 (1902).

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[8] R. Abegg and H. J. Cox, *Z. physik. Chem.*, **46**, 1 (1903).

[9] A. Kirschner, *ibid.*, **79**, 245 (1912).

[10] J. N. Pearce and L. Smith, THIS JOURNAL, **59**, 2063 (1937).

[11] S. Aditya and B. Prasad, *J. Ind. Chem. Soc.*, **29**, 293 (1952).

[12] G. C. B. Cave and D. N. Hume, THIS JOURNAL, **75**, 2893 (1953).

[13] R. N. Parida, S. Aditya and B. Prasad, *J. Ind. Chem. Soc.*, **29**, 377 (1952).

[14] G. Scatchard, I. H. Scheinberg and S. H. Armstrong, Jr., THIS JOURNAL, **72**, 540 (1950).

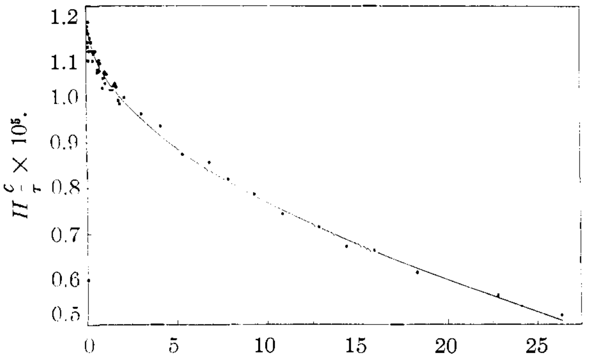

Fig. 5.—Light scattering data for isoionic human serum mercaptalbumin in dist. H_2O plotted in the usual manner.

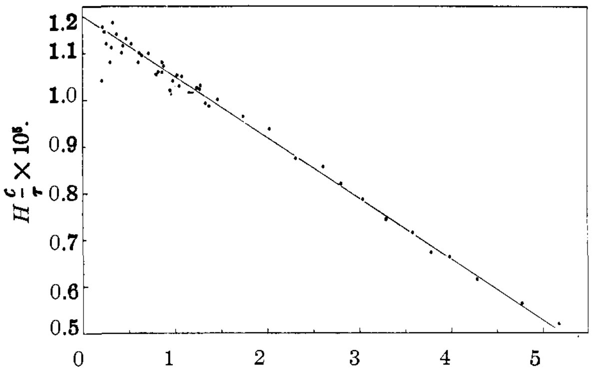

Fig. 6.—Data of Fig. 5 plotted as a function of the square root of protein concentration.

A plot of the same data as a function of the square root of protein concentration again resulted in very nearly a straight line (Fig. 6). This is represented by the following equation obtained by least squaring of the data

$$H\frac{C_2}{\Delta\tau} = 1.17 \times 10^{-5}(1 - 3.00C_2^{1/2} - 2.97C_2) \quad (8)$$

The standard error of estimate in $H(C_2/\Delta\tau)$ was found to be 0.014×10^{-5}.

In all three proteins, the term in the first power of the concentration makes only a small contribution to $H(C_2/\Delta\tau)$.

Measurements in the Presence of Salt.—A series of measurements was carried out on each preparation of BSA and BMA in solutions of various concentrations of NaCl, ranging from 1×10^{-5} *M* to 1.5×10^{-1} *M* salt. The results obtained with one preparation of each protein are presented in Fig. 7 and 8.

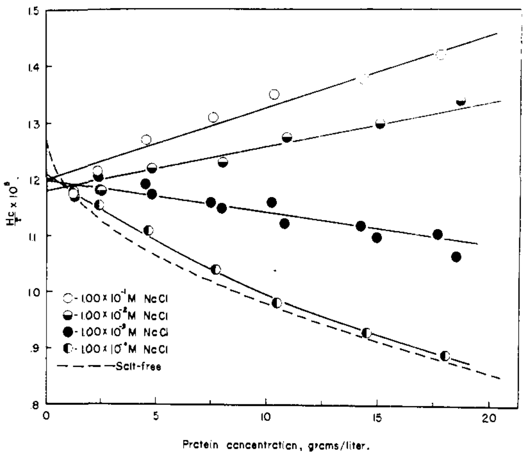

Fig. 7.—Light scattering data of isoionic Armour bovine serum albumin in various concentrations of NaCl.

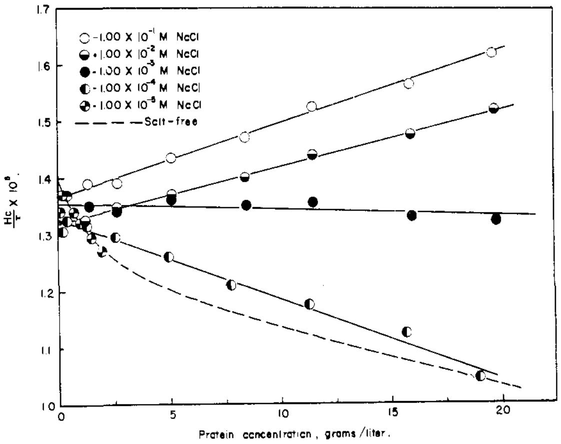

Fig. 8.—Light scattering data of isoionic bovine serum mercaptalbumin in various concentrations of NaCl.

As can be seen, a series of straight lines is obtained at higher salt concentrations when the light scattering data are plotted as a function of the first power of protein concentration. In both cases, the curve obtained in the salt-free solutions is shown by the dotted line. The slopes of these plots are negative at low salt concentrations, becoming increasingly positive with an increase in the concentration of electrolyte. This is in agreement with previous observations[8] and with light scattering theory,[16] since the progressive binding of chloride ions, as the salt concentration rises, results in an increasing negative charge on the protein molecules. It is the swamping out of the attractive force due to fluctuations in charge and the electrostatic repulsion resulting from chloride binding which leads to the positive value of the second virial co-

TABLE I

LIGHT SCATTERING DATA FOR ISOIONIC SERUM ALBUMIN SOLUTIONS

NaCl concn. (*M*)	Armour BSA Mol. wt.	$\frac{2BM_2^2}{1000}$	β_{22}^*	Bovine mercaptalbumin Mol. wt.	$\frac{2BM_2^2}{1000}$	β_{22}^*
Salt-free	80,900	....	....	69,500[b]	...	...
Salt-free	82,500[a]	....	....	76,000	...	...
1×10^{-5}				72,500	...	...
3×10^{-5}	85,200[a]	−1240	−1255	....	...	...
1×10^{-4}	84,000[a]	−1200	−1215	75,500	−780	−795
3×10^{-4}	82,200	− 880	− 990	....	...	...
1×10^{-3}	83,300[a]	− 445	− 570	73,700	− 75	−200
3×10^{-3}	80,200	175	5	....	...	...
1×10^{-2}	86,600[a]	570	150	76,600	850	430
3×10^{-2}	80,100	725	305	....	...	...
1×10^{-1}	84,200[a]	975	635	75,800	940	600
1.5×10^{-1}	78,400	875	575	....	...	...
Acetate, *p*H 4.8, $\Gamma/2$ = 0.01			....	73,500		
Human mercaptalbumin						
Salt-free:				90,700		
Acetate, *p*H 5.3, $\Gamma/2$ = 0.01				89,900		

[a] Solution remained one week in deionized form at 4°. [b] Different preparation of protein.

TABLE I

POTENTIALS OF THE CELL: $\text{Pt–H}_2\text{(g,1 atm.)}|\text{HClO}_4(m_1), \text{KSCN}(m_2)|\text{AgSCN(s)–Ag}$

Concentrations are on the molality scale and E values are the absolute volts

Run	$m_1 \times 10^3$	$m_2 \times 10^3$	E_{5°, v.	E_{15°, v.	E_{20°, v.	E_{25°, v.	E_{30°, v.	E_{35°, v.	E_{45°, v.
11	0.70648	0.74127	0.43918	0.45141		0.46312		0.47454	0.48578
10	1.4138	1.5270	.40603	.41699		.42744		.43764	.44759
2	2.4648	2.3379				.40307			
5	2.2433	2.5938	.38299	.39319	0.39783	.40279	0.40739	.41236	.42147
4	3.5275	2.7809	.37069	.38005	.38487	.38982	.39422	.39834	.40705
3	3.9429	3.3172				.38276			
6	4.3063	3.6217	.35981	.36906	.37363	.37817	.38250	.38672	.39509
1	5.3128	5.2895	.34573	.35480	.35924	.36377	.36787	.37182	.37966
9	6.2806	6.2094	.33846	.34721		.35545		.36328	.37081
7	7.6919	8.1383	.32755	.33597	.33986	.34383	.34756	.35106	.35825
12	9.9888	10.454	.31566	.32354		.33128		.33825	.34493
8	10.870	10.658			.32517	.32873	.33225	.33558	.34215
13	16.159	18.303	.29117	.29856		.30544		.31173	.31769

they were in fairly close agreement with our thermal-electrolytic electrodes,[22] but were more susceptible to mechanical disturbances and more sluggish in response to thermal changes.

The anodizing conditions described above were obtained from a study of various anodizing conditions in the preliminary phase of the work. The conditions for this step were found to have a marked influence on the behavior of the electrodes. Those prepared in the absence of acid were dark, almost black, and in poor internal agreement. In the presence of acid, for the same current density, light-colored electrodes with better internal agreement were obtained. No studies were made above 0.1 *M* acid concentration, since at higher acidities decomposition products of thiocyanic acid might appear before the electrolysis is completed. The reproducibility of the electrodes improved with increase in thiocyanate concentration; however, those prepared at higher thiocyanate concentrations equilibrate more slowly in the cell solution. The reproducibility was improved as the current density was decreased; however, there appeared to be little advantage in using lower current densities than those recommended above. Likewise, there appeared to be no advantage in a heavier coating of silver thiocyanate.

As mentioned previously, Prasad[11,13] and his associates were unable to obtain reproducible electrodes of this type; their anodizing conditions involved electrolysis at 1 milliampere for 6 hr. in 0.75 *M* ammonium thiocyanate. Scatchard and co-workers[14] anodized their silver bases in 0.1 *M* sodium thiocyanate at 0.5 to 2 milliamperes for 2 hr., noting that anodizing for 4 hr. seemed no more advantageous. Their electrodes were sometimes brown and sometimes white, and they state that lower current densities more often produced brown electrodes. Our observations lead us to believe that the presence of acid in the anodizing solution is essential, and its concentration somewhat specific, in order to obtain reproducible and stable silver–silver thiocyanate electrodes. Since the oxidation process during electrolysis may, in addition to oxidation of the silver, also involve some oxidation of thiocyanate ion to thiocyanogen, the presence of acid should serve to suppress the hydrolytic decomposition of this product at the electrode.[23]

Results and Discussion

Treatment of Experimental Data.—The results of the series of cell measurements are tabulated in Table I. Usually the temperature range 25 to 45° would be studied on one day and the 25 to 5° range on the next; differences in E_{25} readings at the beginning and end of a temperature series were seldom greater than 0.1 mv., and were not systematic in sign or magnitude. The cell solution was changed before each temperature series, and sometimes oftener in the anode compartment. Each individual value of e.m.f. represents the average of at least 4 silver–silver thiocyanate electrodes in combination with 4 hydrogen electrodes, except in a few cases where only two hydrogen electrodes were used. The readings at 25° frequently involved as many as eight different silver–silver thiocyanate electrodes and 4 to 6 hydrogen electrodes. The values reported are corrected to one atmosphere partial pressure of hydrogen,[24] and are adjusted to the rounded temperatures when necessary. This adjustment seldom amounted to more than 0.05° and introduced no uncertainty as large as 0.01 mv. The cells reported in Table I represent measurements with some forty silver–silver thiocyanate electrodes.

For the cell as represented in Table I, in which reaction (2) is occurring, the reversible e.m.f. E can be written as

$$E = E^0 - k \log m_1 m_2 \gamma_{\pm}^2$$

where

$$k = 2.3026RT/F \qquad (3)$$

Combining the Hückel equation for activity coefficients[25] with equation 3 and rearranging leads to

$$E'' = E + k \log m_1 m_2 - 2kA\mu^{1/2}/(1 + aB\mu^{1/2}) = E^0 - C\mu \qquad (4)$$

where A and B are the Debye–Hückel constants, a is the mean distance of approach, μ is the ionic strength, and C is an arbitrary constant. No distinction is made between the rational and practical activity coefficients, since at these concentrations the scale term is linear with concentration and is absorbed into the C term. Recent values of k have been tabulated by Swinehart,[26] and Manov, Bates, *et al.*,[27] have computed values of A and B for rounded temperatures.

Graphical methods, usually with simplifying as-

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[22] Two cells of the Pearce and Smith type, equilibrated several days, gave 0.38279 and 0.38285 v. compared with 0.38269 and 0.38273 v. for two electrodes of the thermal-electrolytic type; these data appear as run 3 in Table I. No further studies were made with the Pearce and Smith type.

[23] R. Gauguin, *J. chim. phys.*, **42**, 136 (1945); *Ann. chim.*, [12] **4**, 832 (1949).

[24] A large scale plot of the correction factor $^1/_2k \log 760/(P - p_W)$ against barometric pressure P for rounded temperatures facilitated evaluation of the correction factor.

[25] E. Hückel, *Physik. Z.*, **26**, 93 (1925).

[26] D. F. Swinehart, THIS JOURNAL, **74**, 1100 (1952).

[27] G. G. Manov, R. G. Bates, W. J. Hamer and S. F. Acree, *ibid.*, **65**, 1765 (1943).

sumptions,[28,29] are commonly used in the evaluation of E^0. Even when the full equation 4 is used, a choice of the parameter a which gives the best linear relation between E'' and μ is difficult to make from visual examination of the graphs. Therefore, a more objective method was used, which consisted of fitting equation 4 to the data by the method of least squares for several values of a, and then choosing as the best fit the value of a which made the root-mean-square deviation a minimum. This is essentially the method used by Bates and Bower.[30]

In applying the least squares method to the data in Table I, the values of a for best fit lay between 5 and 7.5 Å., the larger values corresponding to the two extreme temperatures, with no significant trend in between. This scatter is probably due to the use of a statistical method with limited data. Since the a parameter is probably almost insensitive to temperature,[31] we therefore sought a single value of a which would minimize the root-mean-square deviations for the whole body of data. The value of a meeting this requirement was very close to 6 Å. Essentially the same value was obtained by seeking the minimum mean deviation.

In Table II are presented the results of the least squares method, taking a equal to 6.0 Å. It should be noted that a variation of 1 Å. in a caused a variation of 0.01–0.02 mv. in E^0, the remaining variation being absorbed in the C-parameter. All of the E^0 values obtained by graphical means fell well within the range of the mean deviation at the respective temperatures. Not much physical significance can be attached to the value 6.0 Å. because of the low concentration range over which it is based.

TABLE II

STANDARD E.M.F. AND OTHER CONSTANTS BY LEAST SQUARES METHOD[a,b]

Temp., °C.	$E^0_{\text{exp.}}$, abs. v.	σ, abs. v. $\times 10^5$	$\bar{d}$, abs. v. $\times 10^5$	C, kg./mole	w	$E^0_{\text{exp}} - E^0_{\text{eq. 5}}$, mv.
5	0.09084	14.4	10.0	−0.050	2	−0.01
15	.09034	15.4	12.0	− .037	2	.00
20	.09001	9.6	8.0	− .031	1	+ .05
25	.08951	8.0	6.3	− .025	3	+ .02
30	.08892	7.9	6.6	− .022	1	− .03
35	.08828	14.7	10.6	− .025	2	− .05
45	.08687	15.0	11.9	− .030	2	+ .02

[a] Calculated with parameter a equal to 6 Å. [b] $\sigma = (\Sigma d^2/n)^{1/2}$; $\bar{d} = \Sigma d/n$.

The standard e.m.f. of the cell (1) in absolute volts can be represented as a function of temperature by the relation

$$E_t^0 = 0.08949 - 1.00 \times 10^{-4}(t - 25^\circ) - 1.61 \times 10^{-6}(t - 25^\circ)^2 \quad (5)$$

The constants in this equation were found by the method of least squares, with the individual E^0 values weighted approximately in proportion to the number of cells on which the E^0 values were based. These weight factors w are shown in Table II, column 6. Deviations of experimental E^0 values from equation 5 are shown in the last column.

Evaluation of Results.—The value of the standard oxidation potential reported by Pearce and Smith (−0.0947 v. at 25°) differs from our value by 5.2 mv.; Cave and Hume's[12] recalculation differs by 2.6 mv. These discrepancies are almost certainly due to the use of estimated activity coefficients and incomplete correction for the junction potential. The value of Aditya and Prasad (−0.0878 v. at 30°)[11] is low, in spite of their attempt to eliminate the junction potential by a salt bridge; the difference, however, (1.1 mv.) is small. Since we found that electrodes of type used by Pearce and Smith agreed within 0.1 mv. with the thermal-electrolytic type, it seems fairly certain that all three types of electrodes, compared under similar conditions, will yield the same potential in a given solution. The completely electrolytic type,[14] anodized under the conditions used in this work, should be equally reliable.

For reaction (2) at 25°, equation 5 leads to $\Delta F^0 = -2064 \pm 3$ cal., $\Delta H^0 = -2750 \pm 30$ cal., $\Delta S^0 = -2.30 \pm 0.10$ cal. deg.$^{-1}$, and $\Delta C_p^0 = -22$ cal. deg.$^{-1}$ Combining these values with data for the silver–silver ion electrode,[32] we obtain for the reaction

$$\text{AgSCN(s)} \longrightarrow \text{Ag}^+ + \text{SCN}^- \quad (6)$$

at 25°, $\Delta F^0 = 16.366$ kcal., $\Delta H^0 = 22.56$ kcal., and $\Delta S^0 = 20.77$ cal. deg.$^{-1}$. From cell data between 18 and 25°, Kirschner[9] found $\Delta H = 21.3$ kcal., and Joannis[33] in a single calorimetric determination found $\Delta H = 22.44$ kcal. at 13.5°, uncorrected for dilution to the reference state. Our data give $\Delta H^0 = 22.72$ kcal. at 13.5°; the correction for dilution, for which data are missing in Joannis' paper, could account for a large part of the difference.

The thermodynamic solubility product, K_{AgSCN}, is of considerable analytical interest. Much of the older data[4–9] is of historical interest only, having been determined with inadequate treatment of activities and junction potentials. Those determinations based on relative solubility[6,8,34,35] involve the least uncertainty in their interpretation. We have re-examined the data of Hill[34], who studied at 25° the equilibria

$$\text{AgCl(s)} + \text{SCN}^- \rightleftharpoons \text{AgSCN(s)} + \text{Cl}^- \qquad K_1 = a_{\text{Cl}^-}/a_{\text{SCN}^-} \quad (7)$$

and

$$\text{AgBr(s)} + \text{SCN}^- \rightleftharpoons \text{AgSCN(s)} + \text{Br}^- \qquad K_2 = a_{\text{Br}^-}/a_{\text{SCN}^-} \quad (8)$$

where the equilibrium constants are ratios of the solubility products of the insoluble silver salts. Extrapolating Hill's data to zero ionic strength, we obtained $K_1 = 170$ and $K_2 = 0.533$. Combining these with K_{AgCl} and K_{AgBr} (1.776×10^{-10} and

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[28] D. I. Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

[29] A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935).

[30] R. G. Bates and V. E. Bower, *J. Research Natl. Bur. Standards*, **53**, 283 (1954).

[31] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, Chap. 11-12.

[32] Circular 500, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards, Washington, D. C., 1952.

[33] A. Joannis, *Ann. chim.*, [5] **26**, 482 (1882).

[34] A. E. Hill, THIS JOURNAL, **30**, 68 (1908).

[35] N. A. Tananaev and N. V. Shcherbina, *J. Applied Chem.* (*U. S. S. R.*), **10**, 545 (1937).

4.96×10^{-13}, respectively,[30,36a,b,c] we obtain K_{AgSCN} equal to 1.05 and 0.93×10^{-12}. These values, based on limited but perhaps the most reliable comparative data in the literature, agree well with our value (1.01×10^{-12}). Cave and Hume[12] by direct analysis found 1.06×10^{-6} *M* for the solubility at 25°, using a nephelometric method; however, it is quite possible that even at such low concentrations, silver thiocyanate is not completely dissociated.

The most reliable criteria of reversible cell behavior are the reproducibility of e.m.f. using electrodes of different types and methods of preparation, and the agreement of the cell data with related calorimetric data. To the extent that such data are available for comparison, those criteria are met for this system.

LINCOLN, NEBRASKA

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[36] (a) B. B. Owen, THIS JOURNAL, **60**, 2229 (1938). (b) B. B. Owen and S. R. Brinkley, Jr., *ibid.*, **60**, 2233 (1938). (c) B. B. Owen and E. J. King, *ibid.*, **63**, 1711 (1941).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ST. LOUIS UNIVERSITY]

On the Alkali Metal Salts Derived from the Diammoniate of Diborane[1]

BY GEORGE W. SCHAEFFER, MAX D. ADAMS[2] AND FRANCIS J. KOENIG, S.J.[2]

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The reaction of an alkali metal with an ammonia solution of the diammoniate of diborane, $B_2H_6 \cdot 2NH_3$, gives upon removal of the solvent the alkali metal borohydride and aminoborine: $M + B_2H_6 \cdot 2NH_3 = \frac{1}{2}H_2 + NH_3 + MBH_4 + BH_2NH_2$. During removal of the solvent, the aminoborine undergoes ammonolysis. The extent of this secondary reaction is dependent upon the metal employed, increasing from potassium through lithium.

The arguments which first led to the assignment of the ammonium salt structure,[3] $NH_4BH_3NH_2BH_3$ to the diammoniate of diborane, $B_2H_6 \cdot 2NH_3$, depend in part on the supposed replacement of the ammonium ion with the sodium ion by reaction of the diammoniate of diborane with sodium metal in liquid ammonia. The reaction assumed may be represented by the equation

$$Na + NH_4BH_3NH_2BH_3 = NaBH_3NH_2BH_3 + NH_3 + {}^1/_2H_2 \quad (1)$$

Upon removal of the solvent ammonia, a residue possessing the empirical formula expected from a simple replacement was obtained and the material was therefore assumed to be the sodium salt corresponding to the monoammonium salt formulation of the diammoniate of diborane. In view of recent observations[4] which suggest that the ion $BH_3NH_2BH_3^-$ either does not exist or is unstable with respect to disproportionation into the borohydride ion and aminoborane, it becomes of interest to examine closely the nature of the products that may be isolated from the metal–$B_2H_6 \cdot 2NH_3$ reaction and to determine their relationship to the diammoniate of diborane.

To this end, the reactions of solutions of the diammoniate of diborane $B_2H_6 \cdot 2NH_3$ in liquid ammonia with lithium, sodium and potassium were examined, and the isolation and identification of the reaction products were attempted. Without exception the products were found to be the metal borohydride, polymeric aminoborane and ammonolysis products of aminoborane. The over-all process can be represented by the following two equations: first, the reaction of the metal with the ammonia solution of the diammoniate[5]

$$Li(soln.) + B_2H_6 \cdot 2NH_3(soln.) = LiB_2H_8N(soln.) + {}^1/_2H_2 + NH_3 \quad (2)$$

followed by the removal of the solvent

$$LiB_2H_8N(soln.) = LiBH_4(solid) + BH_2NH_2(polymeric) \quad (3)$$

In the case of lithium and sodium borohydride, it was possible to separate the borohydride from the excess metal and the polymeric aminoborane by use of an appropriate ether solvent. The borohydride was identified by analysis and the composition of the ether-insoluble fraction was inferred by difference and confirmed by direct analyses to be aminoborane. In the cases of sodium and potassium, the identity of the borohydrides was confirmed by X-ray diffraction.

Unless the solvent ammonia was removed at the lowest possible temperatures, ammonolysis of the aminoborane with the production of hydrogen, empirically represented by the following equation, occurred

$$BH_2NH_2 + XNH_3 = BH_{2-x}(NH_2)_{1+x} + XH_2 \quad (4)$$

That the reaction which produced hydrogen was indeed ammonolysis of the aminoborane was indicated by the following observations: (a) the mole ratio of hydrogen produced to ammonia retained was always one; (b) regardless of the extent of the reaction, the diffraction pattern of the borohydride remained unchanged; (c) under comparable conditions, alkali metal borohydrides do not react with ammonia; and (d) the extent of ammonolysis does not appreciably affect the amount of borohydride which can be recovered.

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[1] Presented at the 128th Meeting of the American Chemical Society, Minneapolis, Minnesota, September, 1955.

[2] Taken from theses presented by Max D. Adams in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1955, and by the Rev. Francis J. Koenig, S.J., in partial fulfillment of the requirements for the degree of Master of Science, February, 1955, to the Graduate School of St. Louis University.

[3] H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

[4] G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955).

[5] The formula "LiB_2H_8N" is written only in accord with the stoichiometry and does not imply a structure or a particular species.