are of particular interest since they seem to indicate a fine structure for the transition. All curves show the inflection on the left side just below the maximum, at a temperature of −38.53 ± 0.10°. That this point has not been observed before is no doubt due to the fact that it would be extremely difficult to detect by any means other than photographic. Its significance is not quite clear. Pauling has suggested[4a] that possibly molecular rotation sets in first about one directional axis in the crystal, and then later about other axes. This seems to be the case for hydrogen bromide which shows three transitions at −184.1, −160.1, and −156.1°. It is possible that this inflection marks the inception of rotation of the NH_4^+ ion about one axis, and that the maximum at −38.12 ± 0.10° marks the inception of rotation about all possible axes.

The transition observed for ammonium arsenate falls in the expected temperature range for rotation of the ammonium ion. The transitions in the dichromate and primary phosphate do not fall in the expected temperature range, and further that of the phosphate is somewhat more gradual than the others observed. If they are due to rotation of the ammonium ion, other factors must be at work in these cases which hinder the motion until higher temperatures are reached. The rotation of an atom group in a crystal may be blocked by its size, or the presence of other atom groups.[5] The possibility of hydrogen bond formation in the case of ammonium compounds of the oxy acids also presents itself as a factor in hindering rotation. Investigation of this factor is underway.

The following ammonium salts were also studied but no transitions were observed in them: chromate, borate, carbonate, nitrate, oxalate, persulfate, secondary phosphate, and tartrate. Crenshaw and Ritter[6] also report no transition for the oxalate, but found a well defined one for ammonium nitrate at −60.4°. Our failure to locate the ammonium nitrate transition we feel to be due to our inability to cool the sample far enough below the transition to be certain to freeze out the molecular rotation. This will be investigated further.

Acknowledgment.—We are indebted to the Northwest Scientific Association for a grant which made possible the building of the photographic recording device.

Summary

A series of ammonium compounds has been investigated in the temperature range −70 to +40° for thermal transitions which might be due to rotation of the ammonium ion. The following transitions were observed: chloride, −30.54 ± 0.10°; bromide, −38.12 ± 0.10°; iodide, −41.65 ± 0.20°; sulfate, −49.71 ± 0.20°; arsenate, −56.02 ± 0.10°; dichromate, −2.40 ± 0.20°; and primary phosphate, +18.9 ± 2.5°. The transition in the bromide seems to show a fine structure. The following exhibited no transitions: borate, carbonate, chromate, nitrate, oxalate, persulfate, secondary phosphate, and tartrate.

MOSCOW, IDAHO RECEIVED JUNE 16, 1937

[CONTRIBUTION FROM THE PHYSICAL CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Potential of the Silver–Silver Thiocyanate Electrode

BY J. N. PEARCE AND LOTHROP SMITH

Any slightly soluble salt of a metal may form, potentially, a good electrode, provided the electrode is perfectly reversible and the metallic salt is stable in solution. In this paper we present briefly the results obtained from a study of the silver–silver thiocyanate electrode.

Materials and Apparatus.—The silver thiocyanate was prepared by mixing dilute solutions of silver nitrate and potassium thiocyanate in the dark. The product was washed thoroughly and stored under conductivity water.

All solutions of potassium thiocyanate were prepared on the weight molal basis, free from dissolved oxygen, and were stored under hydrogen.

The silver crystals were prepared in the manner described by Pearce and Wirth.[1]

All other materials were purified by approved methods.

The electrodes were prepared by a method similar to that described by Linhart.[2] Each half-cell contained either four or five individual electrodes. As a reference, a second cell of each type was kept in the thermostat under exactly parallel conditions. Immediately before and after each determination of electromotive force, the electrodes used were checked against those of the reference cells. All electrodes checked within 0.01 mv. in every case.

A large oil thermostat regulated at 25° was used, and

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[1] Pearce and Wirth, THIS JOURNAL, **55**, 3569 (1933).

[2] Linhart, *ibid.*, **41**, 1175 (1919).

the entire cell system was kept under hydrogen pressure at all times.

The amalgam dropping electrodes were essentially of the type described by Lewis and Kraus,[3] and the calomel cells were of the same multiple electrode type as the silver–silver thiocyanate cells.

The cells measured were of two general types: first, Ag/AgSCN, KSCN (0.1 *m*)/KHg_x–KHg_x/KSCN (m_2), AgSCN/Ag, with amalgam dropping electrodes; and, second, Ag/AgSCN, KSCN (0.1 *m*)/KSCN (m_2), AgSCN/Ag, with a flowing junction of modified Lamb and Larson type.[4] In addition, cells containing 0.1 *M* potassium thiocyanate solution were compared with calomel electrodes in 0.1 *m* potassium chloride.

The resulting data are given in Table I.

TABLE I

ELECTROMOTIVE FORCE VALUES AND TRANSFERENCE NUMBERS FOR SOLUTIONS OF POTASSIUM THIOCYANATE

m	E_t volt	*E* volt	T_c
0.01	0.0596	0.1121	0.552
.05	.0160	.0311	.524
.10	.0000	.0000	.514
.50	− .0426	−1.0853	.495
1.00	− .0548	(−0.1036)	

Because of the increasing solubility of silver thiocyanate and the resulting instability of the amalgam electrode, it was found necessary to use potassium thiocyanate solution which was not saturated with silver thiocyanate in the cell containing the 1.0 *m* electrolyte.

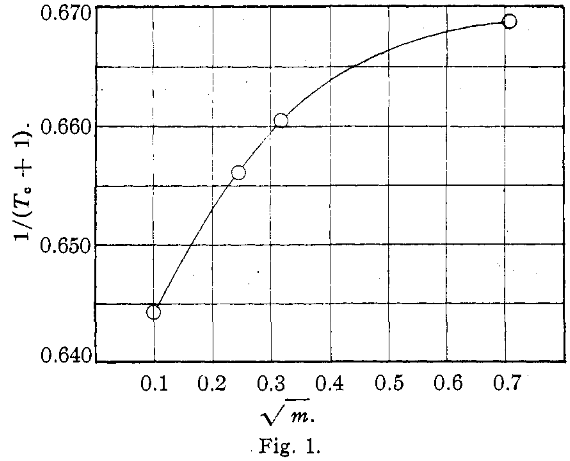

Fig. 1.

Difficulty was experienced with the amalgam electrodes, due to abrupt deflections of the galvanometer. These could be compensated to a considerable extent and the effect minimized by adjusting the amalgam flow to give simultaneous formation of amalgam drops in the two electrodes. Since this effect was only observed when dealing with solutions of potassium thiocyanate, it was attributed to reaction of complex silver thiocyanate ions with the amalgam. Because of this complicating factor, no attempt has been made to calculate mean activity coefficients for potassium thiocyanate from the data.

However, since calculation of the transference number of the potassium ion depends upon comparison of the same cells with and without liquid junction, that calculation has been made.

Taylor[5] gives the following expression for the case of a cell containing one electrolyte, and involving concentrations m_1 and m_2.

$$E_t = \int_{m_1}^{m_2} dE_t - \int_{m_1}^{m_2} T_1 dE = T_1 E$$

where E_t is the electromotive force of the cell with ion-transference, *E* is that of the cell without transference, and T_1 is the mean transference number between the two concentrations. For calculation of the transference number of the cation for a given concentration of electrolyte, the above equation becomes

$$dE_t/dE = T_c$$

Using the determined values of E_t and *E*, numerical coefficients were found by the method of least squares and the equation differentiated to give T_c. The resulting values are given in Table I.

In order to observe the effect of possible complex silver thiocyanate formation on the transference number of potassium ion, the corresponding values of $1/(T_c + 1)$ were plotted against $\sqrt{m}$, in the manner of Jones and Dole.[6] If T_c follows the Debye–Hückel relation, this plot should give a straight line. Increase in the concentration of silver thiocyanate complex with concentration should compensate the decrease in T_c to some extent, and the curve should be concave to the $\sqrt{m}$ axis. This is observed in Fig. 1.

Single Electrode Potentials

In calculating the liquid junction potential for the silver–silver thiocyanate–calomel cell combination, the method of Lewis and Sargent[7] was employed, utilizing the equivalent conductance data of Noyes and Falk.[8] Subtracting the potential difference of 0.00185 thus obtained, from the e. m. f. of the cell Ag/AgSCN, KSCN (0.1 *m*)/KCl (0.1 *m*), Hg_2Cl_2/Hg ($E = 0.17765$), we obtain for the same cell without ion-transference,

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(3) Lewis and Kraus, THIS JOURNAL, **32**, 1459 (1910).

(4) Lamb and Larson, *ibid.*, **42**, 239 (1920).

(5) Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

(6) Jones and Dole, THIS JOURNAL, **51**, 1073 (1929).

(7) Lewis and Sargent, *ibid.*, **31**, 363 (1909).

(8) Noyes and Falk, *ibid.*, **34**, 454 (1912).

$E = 0.1758$ v. Combining this with the value $E = 0.3351$ obtained by Lewis, Brighton, and Sebastian[9] for the 0.1 N calomel electrode, we obtain the potential of the electrode, Ag/AgSCN, KSCN (0.1 m); $E_{298} = -0.1593$ v.

In order to calculate the characteristic "normal electrode potential," E^0, of the thiocyanate electrode, that is, the potential of the electrode when immersed in a solution of unit activity with respect to potassium thiocyanate, we use the relation

$$E = E^0 - RT/nF \ln 1/a_{\text{KSCN}}$$

Substituting numerical values, $E^0_{298} = -0.1593 + 0.05915 \log 1/0.081$, we obtain the value -0.0947 volt.

The above value of E^0 has been verified as follows. Using data from an entirely different set of cells, made up and measured at a time several months previous to the above determination, the following calculations were made. Consider the value of the e. m. f. of the concentration cell with amalgam electrodes, Ag/AgSCN, KSCN (0.01 m)/KHg_x–KHg_x/KSCN (0.10 m), AgSCN/Ag, which is given by the expression $E = 2RT/nF \ln (a_{0.1}/a_{0.01})$, while the potential of the theoretical cell without ion transference, Ag/AgSCN, KSCN (0.01 m)//KSCN (0.1 m), AgSCN/Ag, is/ $E = RT/nF \ln (a_{0.1}/a_{0.01})$. It is apparent that the e. m. f. of the latter cell should be half that of the preceding one, or $E = -0.0561$ v. Combining this with the potential of the 0.1 m potassium thiocyanate electrode, we have, Ag/AgSCN, KSCN (0.01 m)// OH_3^+ / H_2, and making numerical substitutions, $E^0_{298} = -0.2154 + 0.05915 \log 1/0.0091$, we obtain the value 0.0947 for the normal electrode potential, which corresponds to the value obtained by comparing the 0.1 m electrode directly with the corresponding calomel electrode.

In these calculations, since suitable experimentally determined activity coefficients are not available, the modified Debye–Hückel equation of Scatchard[10] has been used to calculate the necessary values. This procedure seems to be justified by vapor pressure studies of solutions of potassium thiocyanate which show that this salt apparently deviates very little in behavior from an ideal solute.[11]

Summary

Electromotive force measurements have been made of a series of cells of the types, [Ag/AgSCN, KSCN (m)/KHg_x/KSCN (0.1 m), AgSCN/Ag], [Ag/AgSCN, KSCN (m) / KSCN (0.1 m), AgSCN/Ag], and [Hg/Hg2Cl_2, KCl (0.1 m)/KSCN (0.1 m), AgSCN/Ag], at 25°.

From these measurements transference numbers for the potassium ion have been calculated, and the potential of the electrode Ag/AgSCN, KSCN ($a = 1$) has been found to be $E^0_{298} = -0.0947$ volt.

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[9] Lewis, Brighton and Sebastian, THIS JOURNAL, **39**, 2245 (1917).

[10] Scatchard, *ibid.*, **47**, 2098 (1925).

[11] Hopson, unpublished doctoral dissertation, 1935.

IOWA CITY, IOWA RECEIVED JULY 28, 1937

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrogen Compounds of Arsenic. I. Preparation of Arsine in Liquid Ammonia. Some Physical Properties of Arsine

BY WARREN C. JOHNSON AND ALPHONSE PECHUKAS

Due to the success in the preparation of the hydrogen compounds of germanium[1] and silicon[2] in liquid ammonia by the action of ammonium salts on magnesium germanides and silicides, respectively, an analogous method was chosen for the preparation of large amounts of arsine required for extensive investigations in this Laboratory. The liquid ammonia method gives high yields of arsine, eliminates objectionable impurities found in the aqueous method and does not produce any other hydrogen compounds of arsenic. In view of the conflicting data in the literature, it appeared advisable to redetermine some of the physical properties of arsine so as to have a control of the purity of the gas to be used in later studies.

Preparation of Arsine.—The arsine was prepared by treating sodium arsenides[3] with ammonium bromide in liquid ammonia by a procedure analogous to that previously described for the preparation of germanes and

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[1] Kraus and Carney, THIS JOURNAL, **56**, 765 (1934).

[2] Johnson and Isenberg, *ibid.*, **57**, 1349 (1935).

[3] Magnesium arsenides were found to give poor yields of arsine; not greater than 25%.