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SOLUBILITY DATA SERIES

Volume 3

SILVER AZIDE, CYANIDE, CYANAMIDES, CYANATE, SELENOCYANATE AND THIOCYANATE — *Solubilities of Solids*

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Editor-in-Chief

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FOREWORD

If the knowledge is
undigested or simply wrong,
more is not better

How to communicate and disseminate numerical data effectively in chemical science and technology has been a problem of serious and growing concern to IUPAC, the International Union of Pure and Applied Chemistry, for the last two decades. The steadily expanding volume of numerical information, the formulation of new interdisciplinary areas in which chemistry is a partner, and the links between these and existing traditional subdisciplines in chemistry, along with an increasing number of users, have been considered as urgent aspects of the information problem in general, and of the numerical data problem in particular.

Among the several numerical data projects initiated and operated by various IUPAC commissions, the *Solubility Data Project* is probably one of the most ambitious ones. It is concerned with preparing a comprehensive critical compilation of data on solubilities in all physical systems, of gases, liquids and solids. Both the basic and applied branches of almost all scientific disciplines require a knowledge of solubilities as a function of solvent, temperature and pressure. Solubility data are basic to the fundamental understanding of processes relevant to agronomy, biology, chemistry, geology and oceanography, medicine and pharmacology, and metallurgy and materials science. Knowledge of solubility is very frequently of great importance to such diverse practical applications as drug dosage and drug solubility in biological fluids, anesthesiology, corrosion by dissolution of metals, properties of glasses, ceramics, concretes and coatings, phase relations in the formation of minerals and alloys, the deposits of minerals and radioactive fission produces from ocean waters, the composition of ground waters, and the requirements of oxygen and other gases in life support systems.

The widespread relevance of solubility data to many branches and disciplines of science, medicine, technology and engineering, and the difficulty of recovering solubility data from the literature, lead to the proliferation of published data in an ever increasing number of scientific and technical primary sources. The sheer volume of data has overcome the capacity of the classical secondary and tertiary services to respond effectively.

While the proportion of secondary services of the review article type is generally increasing due to the rapid growth of all forms of primary literature, the review articles become more limited in scope, more specialized. The disturbing phenomenon is that in some disciplines, certainly in chemistry, authors are reluctant to treat even those limited-in-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection - as far as numerical data are concerned - is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books, and other tabulated and graphical compilations - as they exist today, are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to advancement of science is at least questionable. Additionalyy, the change which is taking place in the generation of new and diversified numerical data, and the rate at which this is done, is not reflected in an increased third-level service. The emergence of new tertiary literature sources does not parallel the shift that has occurred in the primary literature.

With the status of current secondary and tertiary services being as briefly stated above, the innovative approach of the *Solubility Data Project* is that its compilation and critical evaluation work involve consolidation and reprocessing services when both activities are based on intellectual and scholarly reworking of information from primary sources. It comprises compact compilation, rationalization and simplification, and the fitting of isolated numerical data into a critically evaluated general framework.

The *Solubility Data Project* has developed a mechanism which involves a number of innovations in exploiting the literature fully, and which contains new elements of a more imaginative approach for transfer of reliable information from primary to secondary/tertiary sources. *The fundamental trend of the Solubility Data Project is toward integration of secondary and tertiary services with the objective of producing in-depth critical analysis and evaluation which are characteristic to secondary services, in a scope as broad as conventional tertiary services.*

Fundamental to the philosophy of the project is the recognition that the basic element of strength is the active participation of career scientists in it. Consolidating primary data, producing a truly critically-evaluated set of numerical data, and synthesizing data in a meaningful relationship are demands considered worthy of the efforts of top scientists. Career scientists, who themselves contribute to science by their involvement in active scientific research, are the backbone of the project. The scholarly work is commissioned to recognized authorities, involving a process of careful selection in the best tradition of IUPAC. This selection in turn is the key to the quality of the output. These top experts are expected to view their specific topics dispassionately, paying equal attention to their own contributions and to those of their peers. They digest literature data into a coherent story by weeding out what is wrong from what is believed to be right. To fulfill this task, the evaluator must cover *all* relevant open literature. No reference is excluded by design and every effort is made to detect every bit of relevant primary source. Poor qualiry or wrong data are mentioned and explicitly disqualified as such. In fact, it is only when the reliable data are presented alongside the unreliable data that proper justice can be done. The user is bound to have incomparably more confidence in a succinct evaluative commentary and a comprehensive review with a complete bibliography to both good and poor data.

It is the standard practice that any given solute-solvent system consists of two essential parts: I. Critical Evaluation and Recommended Values, and II. Compiled Data Sheets.

The Critical Evaluation part gives the following information:
(i) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;
(ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;
(iii) a graphical plot of recommended data.

The compilation part consists of data sheets of the best experimental data in the primary literature. Generally speaking, such independent data sheets are given only to the best and endorsed data covering the known range of experimental parameters. Data sheets based on primary sources where the data are of a lower precision are given only when no better data are available. Experimental data with a precision poorer than considered acceptable are reproduced in the form of data sheets when they are the only known data for a particular system. Such data are considered to be still suitable for some applications, and their presence in the compilation should alert researchers to areas that need more work.

The typical data sheet carries the following information:
(i) components - definition of the system - their names, formulas and Chemical Abstracts registry numbers;
(ii) reference to the primary source where the numerical information is reported. In cases when the primary source is a less common periodical or a report document, published though of limited availability, abstract references are also given;
(iii) experimental variables;
(iv) identification of the compiler;
(v) experimental values as they appear in the primary source. Whenever available, the data may be given both in tabular and graphical form. If auxiliary information is avialable, the experimental data are converted also to SI units by the compiler.

Under the general heading of Auxiliary Information, the essential experimental details are summarized:

(vi) experimental method used for the generation of data;
(vii) type of apparatus and procedure employed;
(viii) source and purity of materials;
(ix) estimated error;
(x) references relevant to the generation of experimental data as cited in the primary source.

This new approach to numerical data presentation, developed during our four years of existence, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of 15 years ago to refrain from unnecessary publication has not achieved much. The literature is still, in 1978, cluttered with poor-quality articles. The Weinberg report (in "Reader in Science Information", Eds. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that "admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint..." We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

If we succeed in that aim, even partially, we have then done our share in protecting the scientific community from unwanted and irrelevant, wrong numerical information.

A. S. Kertes

December, 1978

PREFACE TO THE VOLUME

The uninegative ions CN^-, OCN^-, SCN^-, $SeCN^-$, and N_3^- have historically been referred to as *pseudohalides*. This term was introduced by Birckenbach and Kellermann (*Ber.* 1925, *58B*, 786; *58B*, 2377) who discovered similarities in chemical behavior between the pseudohalides and halides. In addition to the above pseudohalides, this volume includes solubility data for the silver salts of the related ions cyanamide (CN_2^{2-}), dicyanamide ($N(CN)_2^-$), and methyl tricyanamide ($C(CN)_3^-$). Pseudohalides not included in this volume because of the absence from the literature of solubility data for their silver salts are: tellurocyanate ($TeCN^-$), isocyanate (ONC^-), and azidothiocarbonate ($SCSN_3^-$). Silver halides (except AgF) and pseudohalides are characterized by their low intrinsic solubilities and a tendency to dissolve in solutions containing excess anion. With the exception of AgCN, the tendency to dissolve by the formation of complex ions is markedly dependent upon the nature of the solvent. $Ag(CN)_n^{1-n}$ complexes (particularly for $n = 2$) are highly stable in all solvents whereas the analogous complexes for the remaining pseudohalides are generally less stable in protic solvents than in aprotic solvents. Because of the influence of complex ion formation on the solubility of these silver salts, the evaluator has presented detailed analyses of the complex solubilities for those cases where sufficient data exist.

Owing to the very low solubility of silver halides and pseudohalides, their solubilities are conveniently described in terms of appropriate equilibrium constants. Concentration equilibrium constants can be used to calculate thermodynamic equilibrium constants since activity coefficients can readily be calculated in dilute solutions.

The most common mechanism for the dissolution of a silver pseudohalide, AgX, is by the formation of mononuclear complexes according to

$$AgX(s) + (n-1)X^- \rightleftarrows AgX_n^{1-n} \qquad K_{sn} \qquad [1]$$

where K_{sn} is the solubility formation constant. For example, taking $n = 0$, 1, 2 eq [1] can, respectively, be written as

$$AgX(s) \rightleftarrows Ag^+ + X^- \qquad K_{s0} \qquad [2]$$

$$AgX(s) \rightleftarrows AgX(aq) \qquad K_{s1} \qquad [3]$$

$$AgX(s) + X^- \rightleftarrows AgX_2^- \qquad K_{s2} \qquad [4]$$

In several solvents included in this volume, K_{s1} values have generally been found to be small ($\leqslant 10^{-7}$ mol kg^{-1}). The presence of AgX in solution is, however, not always negligible since its concentration may be comparable to the concentrations of all other mononuclear complexes depending upon the magnitudes of K_{s0} and K_{s2}. For the case where $K_{s2} << 1$ and no added salts are present, the solubility of AgX is given by

$$c_{Ag} \simeq K_{s0}^{1/2} + K_{s1} \qquad [5]$$

and for typical values of 10^{-9} to 10^{-16} mol kg^{-1} for K_{s0}, the concentration of soluble AgX may be highly significant. In those solvents where $K_{s2} \geqslant 1$, the equilibrium between solid and solution can also be expressed by

$$2AgX \rightleftarrows Ag^+ + AgX_2^- \qquad [6a]$$

Eq [6a] may be written in the equivalent form (consistent with the older literature)

$$Ag(AgX_2)(s) \rightleftarrows Ag^+ + AgX_2^- \qquad [6b]$$

To differentiate between the solubility products for reactions [2] and [6], the following definitions are used throughout this volume:

$$K_{s0}(AgX) = [Ag^+][X^-] \qquad [7]$$

and

$$K_{s0}(AgAg(X)_2) = [Ag^+][AgX_2^-] \qquad [8]$$

where the brackets, [ ], signify concentrations.

Additional equilibrium constants which are useful in treating the solubility of AgX in terms of mononuclear complexes are the overall formation or stability constants β_n, and the stepwise formation constants K_n. These equilibrium constants are defined by the following general reactions:

$$Ag^+ + nX^- \rightleftarrows AgX_n^{1-n} \qquad \beta_n \qquad [9]$$

and

$$AgX_n^{1-n} + X^- \rightleftarrows AgX_{n+1}^{-n} \qquad K_{n+1} \qquad [10]$$

The above formation constants and solubility products are related by

$$K_{s0}(AgX) = \{K_{s0}(AgAg(X)_2)/\beta_2\}^{1/2} \qquad [11]$$

$$\beta_n = K_1K_2.......K_n \qquad [12]$$

$$\beta_n = K_{sn}/K_{s0}(AgX) \qquad [13]$$

$$K_{sn} = K_{s0}(AgX)\ K_1K_2.....K_n \qquad [14]$$

$$K_n = K_{sn}/K_{s(n-1)} \qquad [15]$$

Polynuclear complexes are not common in dilute solutions containing excess salt, but can form in concentrated Ag^+ or X^- solutions: thus

$$mAg^+ + nX^- \rightleftarrows Ag_mX_n^{m-n} \qquad \beta_{mn} \qquad [16]$$

Mixed-ligand complexes are also of importance under certain conditions:

$$mAg^+ + nX^- + n'Y^- \rightleftarrows (Ag_mX_nY_{n'})^{m-n-n'} \qquad \beta_{mnn'} \qquad [17]$$

Species Y may be neutral such as in the complex $Ag(NH_3)(SCN)$.

Although no definitions were given to specify the effect of using activities or concentrations in the above equilibrium constants, extreme care is taken in the texts to insure that all equilibrium constants are properly defined. Thermodynamic equilibrium constants are denoted by a superscript, e.g. K_{s0}^o, whereas concentration equilibrium constants are denoted simply by K_{s0}. The evaluator has converted all appropriate quantities to S.I. units in the critical evaluations. In the descriptions of experimental methods and source and purity of materials in the compilations, the compilers have, for the most part, retained the units employed in the original investigations: e.g. m for mol kg^{-1} and M for mol dm^{-3}. When possible the solubility data tabulated in the compilations have been converted to S.I. units.

Associates and members of IUPAC Subcommittee V.6.1 are gratefully acknowledged for their many valuable suggestions. In particular, I would like to acknowledge the inputs of H.L. Clever, R. Cohen-Adad, C. Kalidas, A.S. Kertes, K. Loening, J.W. Lorimer, Y. Marcus, G.H. Nancollas, and H. Ohtaki. I would also like to thank in advance those readers who, in future, point out to me any errors in the compilations and evaluations, and any literature which may have been overlooked.

Fair Haven, New Jersey, December 1978 Mark Salomon

INTRODUCTION TO THE SERIES ON SOLUBILITY OF SOLIDS IN LIQUIDS

Nature of the Project

The Solubility Data Project (SDP) has as its aim a comprehensive search of the literature for solubilities of gases, liquids, and solids in liquids or solids. Data of suitable precision are compiled on data sheets in a uniform format. The data for each system are evaluated, and where data from different sources agree sufficiently, recommended values are proposed. The evaluation sheets, recommended values, and compiled data sheets are published on consecutive pages.

This series of volumes includes solubilities of solids of all types in liquids of all types.

Definitions

A *mixture* (1,2) describes a gaseous, liquid, or solid phase containing more than one substance, when the substances are all treated in the same way.

A *solution* (1,2) describes a liquid or solid phase containing more than one substance, when for convenience one of the substances, which is called the *solvent* and may itself be a mixture, is treated differently than the other substances, which are called *solutes*. If the sum of the mole fractions of the solutes is small compared to unity, the solution is called a *dilute solution*.

The *solubility* of a substance B is the relative proportion of B (or a substance related chemically to B) in a mixture which is saturated with respect to solid B at a specified temperature and pressure. *Saturated* implies the existence of equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a metastable substance is usually greater than that of the corresponding stable substance. (Strictly speaking, it is the activity of the metastable substance that is greater.) Care must be taken to distinguish true metastability from supersaturation, where equilibrium does not exist.

Either point of view, mixture or solution, may be taken in describing solubility. The two points of view find their expression in the quantities used as measures of solubility and in the reference states used for definition of activities and activity coefficients.

The qualifying phrase "substance related chemically to B" requires comment. The composition of the saturated mixture (or solution) can be described in terms of any suitable set of thermodynamic components. Thus, the solubility of a salt hydrate in water is usually given as the relative proportion of anhydrous salt in solution, rather than the relative proportions of hydrated salt and water.

Quantities Used as Measures of Solubility

1. *Mole fraction* of substance B, x_B:

$$x_B = n_B / \sum_{i=1}^{c} n_i \qquad (1)$$

where n_i is the amount of substance of substance i, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole per cent* of B is 100 x_B.

2. *Mass fraction* of substance B, w_B:

$$w_B = m'_B / \sum_{i=1}^{c} m'_i \qquad (2)$$

where m'_i is the mass of substance i. *Mass per cent* of B is 100 w_B. The equivalent terms weight fraction and weight per cent are not used.

3. *Solute mole (mass) fraction* of solute B (3,4):

$$x_{S,B} = n_B / \sum_{i=1}^{c'} n_i = x_B / \sum_{i=1}^{c'} x_i \qquad (3)$$

where the summation is over the solutes only. For the solvent A, $x_{S,A} = x_A$. These quantities are called *Jänecke mole (mass) fractions* in many papers.

4. *Molality* of solute B (1,2) in a solvent A:

$$m_B = n_B/n_A M_A \qquad \text{SI base units: mol kg}^{-1} \tag{4}$$

where M_A is the molar mass of the solvent.

5. *Concentration* of solute B (1,2) in a solution of volume V:

$$c_B = [B] = n_B/V \qquad \text{SI base units: mol m}^{-3} \tag{5}$$

The terms molarity and molar are not used.

Mole and mass fractions are appropriate to either the mixture or the solution points of view. The other quantities are appropriate to the solution point of view only. In addition of these quantities, the following are useful in conversions between concentrations and other quantities.

6. *Density*: $\rho = m/V$ SI base units: kg m^{-3} (6)

7. *Relative density*: d; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol $d^{t}_{t'}$ will be used for the density of a mixture at t°C, 1 atm divided by the density of water at t'°C, 1 atm.

Other quantities will be defined in the prefaces to individual volumes or on specific data sheets.

Thermodynamics of Solubility

The principal aims of the Solubility Data Project are the tabulation and evaluation of: (a) solubilities as defined above; (b) the nature of the saturating solid phase. Thermodynamic analysis of solubility phenomena has two aims: (a) to provide a rational basis for the construction of functions to represent solubility data; (b) to enable thermodynamic quantities to be extracted from solubility data. Both these aims are difficult to achieve in many cases because of a lack of experimental or theoretical information concerning activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve critical evaluation of a large body of data that is not directly relevant to solubility. The following discussion is an outline of the principal thermodynamic relations encountered in discussions of solubility. For more extensive discussions and references, see books on thermodynamics, e.g., (5-10).

Activity Coefficients (1)

(a) *Mixtures*. The activity coefficient f_B of a substance B is given by

$$RT\,\ell n(f_B x_B) = \mu_B - \mu_B^* \tag{7}$$

where μ_B is the chemical potential, and μ_B^* is the chemical potential of pure B at the same temperature and pressure. For any substance B in the mixture,

$$\lim_{x_B \to 1} f_B = 1 \tag{8}$$

(b) *Solutions*.

(i) *Solute substance*, B. The molal activity coefficient γ_B is given by

$$RT\,\ell n(\gamma_B m_B) = \mu_B - (\mu_B - RT\,\ell n\, m_B)^{\infty} \tag{9}$$

where the superscript $^{\infty}$ indicates an infinitely dilute solution. For any solute B,

$$\gamma_B^{\infty} = 1 \tag{10}$$

Activity coefficients y_B connected with concentration c_B, and $f_{x,B}$ (called the *rational activity coefficient*) connected with mole fraction x_B are defined in analogous ways. The relations among them are (1,9):

$$\gamma_B = x_A f_{x,B} = V_A^*(1 - \sum_s c_s) y_B \tag{11}$$

or

$$f_{x,B} = (1 + M_A \sum_s m_s)\gamma_B = V_A^* y_B/V_m \tag{12}$$

or

$$y_B = (V_A + M_A \sum_s m_s V_s)\gamma_B/V_A^* = V_m f_{x,B}/V_A^* \tag{13}$$

where the summations are over all solutes, V_A^* is the molar volume of the pure solvent, V_i is the partial molar volume of substance i, and V_m is the molar volume of the solution.

For an electrolyte solute $B \equiv C_{\nu+}A_{\nu-}$, the molal activity is replaced by (9)

$$\gamma_B m_B = \gamma_\pm^{\nu} m_B^{\nu} Q^{\nu} \tag{14}$$

where $\nu = \nu_+ + \nu_-$, $Q = (\nu_+^{\nu_+}\nu_-^{\nu_-})^{1/\nu}$, and $\gamma_\pm$ is the mean ionic molal activity coefficient. A similar relation holds for the concentration activity $y_B c_B$. For the mol fractional activity,

$$f_{x,B}\, x_B = \nu_+^{\nu_+} \nu_-^{\nu_-} f_\pm^{\nu} x_\pm^{\nu} \tag{15}$$

The quantities x_+ and x_- are the ionic mole fractions (9), which for a single solute are

$$x_+ = \nu_+ x_B/[1+(\nu-1)x_B]; \qquad x_- = \nu_- x_B/[1+(\nu-1)x_B] \tag{16}$$

(ii) *Solvent, A:*

The *osmotic coefficient*, ϕ , of a solvent substance A is defined as (1):

$$\phi = (\mu_A^* - \mu_A)/RT\, M_A \sum_s m_s \tag{17}$$

where μ_A^* is the chemical potential of the pure solvent.

The *rational osmotic coefficient*, ϕ_x, is defined as (1):

$$\phi_x = (\mu_A - \mu_A^*)/RT \ln x_A = \phi M_A \sum_s m_s/\ln(1 + M_A \sum_s m_s) \tag{18}$$

The activity, a_A, or the activity coefficient f_A is often used for the solvent rather than the osmotic coefficient. The activity coefficient is defined relative to pure A, just as for a mixture.

The Liquid Phase

A general thermodynamic differential equation which gives solubility as a function of temperature, pressure and composition can be derived. The approach is that of Kirkwood and Oppenheim (7). Consider a solid mixture containing c' thermodynamic components i. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^{c'} x_i'(S_i'dT - V_i'dp + d\mu_i) = 0 \tag{19}$$

A liquid mixture in equilibrium with this solid phase contains c thermodynamic components i, where, usually, c > c'. The Gibbs-Duhem equation for the liquid mixture is:

$$\sum_{i=1}^{c'} x_i(S_i dT - V_i dp + d\mu_i) + \sum_{i=c'+1}^{c} x_i(S_i dT - V_i dp + d\mu_i) = 0 \tag{20}$$

Eliminate $d\mu_1$ by multiplying (19) by x_1 and (20) x_1'. After some algebra, and use of:

$$d\mu_i = \sum_{j=2}^{c} G_{ij}dx_j - S_i dT + V_i dp \tag{21}$$

where (7)

$$G_{ij} = (\partial\mu_i/\partial x_j)_{T,P,x_i \neq x_j} \tag{22}$$

it is found that

$$\sum_{i=2}^{c'}\sum_{j=2}^{c}(x_i' - x_i x_1'/x_1)G_{ij}dx_j - (x_1'/x_1)\sum_{i=c'+1}^{c}\sum_{j=2}^{c} x_i G_{ij}dx_j$$

$$= \sum_{i=1}^{c'} x_i'(H_i - H_i')dT/T - \sum_{i=1}^{c'} x_i'(V_i - V_i')dp \tag{23}$$

where

$$H_i - H_i{}' = T(S_i - S_i{}') \tag{24}$$

is the enthalpy of transfer of component i from the solid to the liquid phase, at a given temperature, pressure and composition, and H_i, S_i, V_i are the partial molar enthalpy, entropy, and volume of component i. Several special cases (all with pressure held constant) will be considered. Other cases will appear in individual evaluations.

(a) *Solubility as a function of temperature.*
Consider a binary solid compound A_nB in a single solvent A. There is no fundamental thermodynamic distinction between a binary compound of A and B which dissociates completely or partially on melting and a solid mixture of A and B; the binary compound can be regarded as a solid mixture of constant composition. Thus, with c = 2, c' = 1, $x_A{}' = n/(n+1)$, $x_B{}' = 1/(n+1)$, eqn (23) becomes

$$(1/x_B - n/x_A)\{1 + (\frac{\partial \ell n f_B}{\partial \ell n x_B})_{T,P}\}dx_B = (nH_A + H_B - H_{AB}^{*})dT/RT^2 \tag{25}$$

where the mole fractional activity coefficient has been introduced. If the mixture is a non-electrolyte, and the activity coefficients are given by the expression for a simple mixture (6):

$$RT\ \ell n\ f_B = wx_A{}^2 \tag{26}$$

then it can be shown that, if w is independent of temperature, eqn (25) can be integrated (cf. (5), Chap. XXIII, sect. 5). The enthalpy term becomes

$$nH_A + H_B - H_{AB}^{*} = \Delta H_{AB} + n(H_A - H_A{}^{*}) + (H_B - H_B{}^{*})$$

$$= \Delta H_{AB} + w(nx_B{}^2 + x_A{}^2) \tag{27}$$

where ΔH_{AB} is the enthalpy of melting and dissociation of one mole of pure solid A_nB, and $H_A{}^*$, $H_B{}^*$ are the molar enthalpies of pure liquid A and B. The differential equation becomes

$$R\ d\ \ell n\{x_B(1-x_B)^n\} = -\Delta H_{AB}\ d(\frac{1}{T}) - w\ d(\frac{x_A{}^2 + nx_B{}^2}{T}) \tag{28}$$

Integration from x_B,T to $x_B = 1/(1+n)$, T = T*, the melting point of the pure binary compound, gives:

$$\ell n\{x_B(1-x_B)^n\} \simeq \ell n\{\frac{n^n}{(1+n)^{n+1}}\} - \{\frac{\Delta H_{AB}^{*} - T^*\Delta C_p^{*}}{R}\}\ (\frac{1}{T} - \frac{1}{T^*})$$

$$+ \frac{\Delta C_p{}^{*}}{R}\ \ell n(\frac{T}{T^*}) - \frac{w}{R}\{\frac{x_A + nx_B}{T} - \frac{n}{(n+1)T^*}\} \tag{29}$$

where $\Delta C_p{}^*$ is the change in molar heat capacity accompanying fusion plus decomposition of the compound at temperature T*, (assumed here to be independent of temperature and composition), and ΔH_{AB}^* is the corresponding change in enthalpy at T = T*. Equation (29) has the general form

$$\ell n\{x_B(1-x_B)^n\} = A_1 + A_2/T + A_3\ell nT + A_4(x_A{}^2 + nx_B{}^2)/T \tag{30}$$

If the solid contains only component B, n = 0 in eqn (29) and (30).

If the infinite dilution standard state is used in eqn (25), eqn (26) becomes

$$RT\ \ell n\ f_{x,B} = w(x_A{}^2 - 1) \tag{31}$$

and (27) becomes

$$nH_A + H_B - H_{AB} = (nH_A{}^* + H_B{}^{\infty} - H_{AB}^{*}) + n(H_A - H_A{}^*) + (H_B - H_B{}^{\infty}) = \Delta H_{AB}^{\infty} + w(nx_B{}^2 + x_A{}^2 - 1) \tag{32}$$

where the first term, ΔH_{AB}^{∞}, is the enthalpy of melting and dissociation of solid compound A_nB to the infinitely dilute state of solute B in solvent A; H_B^{∞} is the partial molar enthalpy of the solute at infinite dilution. Clearly, the integral of eqn (25) will have the same form as eqn (29), with $\Delta H_{AB}^{\infty}(T^*)$, $\Delta C_p^{\infty}(T^*)$ replacing ΔH_{AB}^* and $\Delta C_p{}^*$ and $x_A{}^2 - 1$ replacing $x_A{}^2$ in the last term.

If the liquid phase is an aqueous electrolyte solution, and the solid is a salt hydrate, the above treatment needs slight modification. Using rational mean activity coefficients, eqn (25) becomes

$$R\nu(1/x_B-n/x_A)\{1+(\partial \ln f_{\pm}/\partial \ln x_{\pm})_{T,P}\}dx_B/\{1+(\nu-1)x_B\}$$

$$= \{\Delta H^{\infty}_{AB} + n(H_A-H_A{}^*) + (H_B-H_B^{\infty})\}d(1/T) \qquad (33)$$

If the terms involving activity coefficients and partial molar enthalpies are negligible, then integration gives (cf. (11)):

$$\ln\left\{\frac{x_B^{\nu}(1-x_B)^n}{1+(\nu-1)x_B{}^{n+\nu}}\right\} = \ln\left\{\frac{n^n}{(n+\nu)^{n+\nu}}\right\} - \left\{\frac{\Delta H^{\infty}_{AB}(T^*)-T^*\Delta C_p{}^*}{R}\right\}\left(\frac{1}{T} - \frac{1}{T^*}\right)+ \frac{\Delta C_p^*}{R}\ln(T/T^*) \qquad (34)$$

A similar equation (with $\nu=2$ and without the heat capacity terms) has been used to fit solubility data for some $MOH=H_2O$ systems, where M is an alkali metal; the enthalpy values obtained agreed well with known values (11). In many cases, data on activity coefficients (9) and partial molal enthalpies (8,10) in concentrated solution indicate that the terms involving these quantities are not negligible, although they may remain roughly constant along the solubility temperature curve.

The above analysis shows clearly that a rational thermodynamic basis exists for functional representation of solubility-temperature curves in two-component systems, but may be difficult to apply because of lack of experimental or theoretical knowledge of activity coefficients and partial molar enthalpies. Other phenomena which are related ultimately to the stoichiometric activity coefficients and which complicate interpretation include ion pairing, formation of complex ions, and hydrolysis. Similar considerations hold for the variation of solubility with pressure, except that the effects are relatively smaller at the pressures used in many investigations of solubility (5).

(b) *Solubility as a function of composition.*
At constant temperature and pressure, the chemical potential of a saturating solid phase is constant:

$$\mu^*_{A_nB} = \mu_{A_nB}(\text{sln}) = n\mu_A + \mu_B \qquad (35)$$

$$= (n\mu^*_A + \nu_+\mu_+{}^{\infty}+\nu_-\mu_-{}^{\infty}) + nRT \ln f_A x_A$$

$$+ \nu RT \ln \gamma_{\pm} m_{\pm} Q_{\pm} \qquad (36)$$

for a salt hydrate A_nB which dissociates to water, (A), and a salt, B, one mole of which ionizes to give ν_+ cations and ν_- anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute, $f_A = x_A = 1$, and the quantity K^0_{so} in

$$\Delta G^{\infty} \equiv (\nu_+\mu_+{}^{\infty}+\nu_-\mu_-{}^{\infty}+n\mu^*_A-\mu_{AB}{}^*)$$

$$= -RT \ln K^0_{so}$$

$$= -RT \ln Q^{\nu}\gamma_{\pm}{}^{\nu}m_+{}^{\nu_+}m_-{}^{\nu_-} \qquad (37)$$

is called the *solubility product* of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of K^0_{so} can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt $C_{\nu_+}A_{\nu_-}\cdot nH_2O$ in the presence of other solutes is given by eqn (36) as

$$\nu \ln\{m_B/m_B(0)\} = -\nu\ln\{\gamma_{\pm}/\gamma_{\pm}(0)\} - n \ln(a_{H_2O}/a_{H_2O}(0)) \qquad (38)$$

where a_{H_2O} is the activity of water in the saturated solution, m_B is the molality of the salt in the saturated solution, and (0) indicates absence of other solutes. Similar considerations hold for non-electrolytes.

The Solid Phase

The definition of solubility permits the occurrence of a single solid phase which may be a pure anhydrous compound, a salt hydrate, a non-stoichiometric compound, or a solid mixture (or solid solution, or "mixed crystals"), and may be stable or metastable. As well, any number of solid phases consistent with the requirements of the phase rule may be present. Metastable solid phases are of widespread occurrence, and may appear as polymorphic (or allotropic) forms or crystal solvates whose rate of transition to more stable forms is very slow. Surface heterogeneity may also give rise to metastability, either when one solid precipitates on the surface of another, or if the size of the solid particles is sufficiently small that surface effects become important. In either case, the solid is not in stable equilibrium with the solution. The stability of a solid may also be affected by the atmosphere in which the system is equilibrated.

Many of these phenomena require very careful, and often prolonged, equilibration for their investigation and elimination. A very general analytical method, the "wet residues" method of Schreinemakers (12) (see a text on physical chemistry) is usually used to investigate the composition of solid phases in equilibrium with salt solutions. In principle, the same method can be used with systems of other types. Many other techniques for examination of solids, in particular X-ray, optical, and thermal analysis methods, are used in conjunction with chemical analyses (including the wet residues method).

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A brief description of the data sheets has been given in the FOREWORD; additional explanation is given below.

Guide to the Compilations

The format used for the compilations is, for the most part, self-explanatory. The details presented below are those which are not found in the FOREWORD or which are not self-evident.

Components. Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The formula is given either in terms of the IUPAC or Hill (13) system and the choice of formula is governed by what is usual for most current users: i.e. IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

(a) saturating components;
(b) non-saturating components in alphanumerical order;
(c) solvents in alphanumerical order.

The saturating components are arranged in order according to a 18-column, 2-row periodic table:

Columns 1,2: H, groups IA, IIA;
3,12: transition elements (groups IIIB to VIIB, group VIII, groups IB, IIB);
13-18: groups IIIA-VIIA, noble gases.
Row 1: Ce to Lu;
Row 2: Th to the end of the known elements, in order of atomic number.

Salt hydrates are generally not considered to be saturating components since most solubilities are expressed in terms of the anhydrous salt. The existence of hydrates or solvates is carefully noted in the texts, and CA Registry Numbers are given where available, usually in the critical evaluation. Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the critical evaluation.

Original Measurements. References are abbreviated in the forms given by *Chemical Abstracts Service Source Index* (CASSI). Names originally in other than Roman alphabets are given as transliterated by *Chemical Abstracts*.

Experimental Values. Data are reported in the units used in the original publication, with the exception that modern *names* for units and quantities are used; e.g., mass per cent for weight per cent; mol dm^{-3} for molar; etc. Both mass and molar values are given. Usually, only one type of value (e.g., mass per cent) is found in the original paper, and the compiler has added the other type of value (e.g., mole per cent) from computer calculations based on 1976 atomic weights (14). Errors in calculations and fitting equations in original papers have been noted and corrected, by computer calculations where necessary.

Method. Source and Purity of Materials. Abbreviations used in *Chemical Abstracts* are often used here to save space.

Estimated Error. If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on the papers by Ku and Eisenhart (15).

Comments and/or Additional Data. Many compilations include this section which provides short comments relevant to the general nature of the work or additional experimental and thermodynamic data which are judged by the compiler to be of value to the reader.

References. See the above description for Original Measurements.

Guide to the Evaluations

The evaluator's task is to check whether the compiled data are correct, to assess the reliability and quality of the data, to estimate errors where necessary, and to recommend "best" values. The evaluation takes the form of a summary in which all the data supplied by the compiler have been critically reviewed. A brief description of the evaluation sheets is given below.

Components. See the description for the Compilations.

Evaluator. Name and date up to which the literature was checked.

Critical Evaluation

(a) Critical text. The evaluator produces text evaluating *all* the published data for each given system. Thus, in this section the evaluator review the merits or shortcomings of the various data. Only published data are considered; even published data can be considered only if the experimental data permit an assessment of reliability.

(b) Fitting equations. If the use of a smoothing equation is justifiable, the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets.

(c) Graphical summary. In addition to (b) above, graphical summaries are often given.

(d) Recommended values. Data are *recommended* if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are reported as *tentative* if only one set of measurements is available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as *doubtful* if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value in those instances where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are *rejected*. However references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

(e) References. All pertinent references are given here. References to those data which, by virtue of their poor precision, have been rejected and not compiled are also listed in this section.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in S.I. units (1,16) when the data can be accurately converted.

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December, 1978

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CONTENTS

COMPONENTS:	EVALUATOR:
(1) Silver azide; AgN_3; [13863-88-2] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION:

Papers dealing with the solubility of AgN_3 in aqueous solutions can be divided into three groups: those which report direct determinations of the solubility (1,2), those utilizing e.m.f. measurements (1,3,4), and those in which the standard potential of the Aq,AgN_3 electrode has been determined (5-7).

Solubility Measurements

Leden and Schöön (1) carried out detailed measurements on the solubility of AgN_3 in NaN_3 solutions in which the total silver concentration, C_{Ag}, was determined by titration with standard NaBr, by radioassay involving ^{110}Ag, and by e.m.f. measurements. All measurements were carried out at 298 K and a constant ionic strength of 4 mol dm^{-3} ($NaClO_4$ was used to adjust the ionic strength). The data were fit graphically to

$$C_{Ag} = \sum_{0}^{4} K_{sn}[N_3^-]^{n-1} \qquad [1]$$

where

$$K_{sn} = K_{s0}(AgN_3)\beta_n \qquad [2]$$

No experimental evidence was found which suggested the presence of polynuclear complexes. Using the solubility data only, the results are:

$$K_{s0}(AgN_3) = 1.61 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

$\beta_1 = 3.1 \times 10^2 \text{ mol}^{-1} \text{ dm}^3$ $\quad$ $K_{s1} = 5.0 \times 10^{-7} \text{ mol dm}^{-3}$

$\beta_2 = 1.6 \times 10^4 \text{ mol}^{-2} \text{ dm}^6$ $\quad$ $K_{s2} = 2.6 \times 10^{-5}$

$\beta_3 = 1.5 \times 10^4 \text{ mol}^{-3} \text{ dm}^9$ $\quad$ $K_{s3} = 1.9 \times 10^{-5} \text{ mol}^{-1} \text{ dm}^3$

$\beta_4 = 1.5 \times 10^3 \text{ mol}^{-4} \text{ dm}^{12}$ $\quad$ $K_{s4} = 2.6 \times 10^{-6} \text{ mol}^{-2} \text{ dm}^6$

The solubility of AgN_3 in concentrated NH_3 solutions was studied by Piechowicz (2) at 293 K. A considerable amount of important information was not reported in this work (e.g. details on analysis, and purity of materials), and the uncertainties in the experimental values cannot be estimated. Since K_{s0} and K_{sn} values are small, it would appear that the solubility of AgN_3 in NH_3 solutions can be described by

$$AgN_3(s) + 2NH_3 \rightleftarrows Ag(NH_3)_2^+ + N_3^- \qquad [3]$$

$$C_{Ag} = [N_3^-] = [Ag(NH_3)_2^+] \qquad [4]$$

E.m.f. Measurements

These measurements are based on e.m.f.'s of concentration cells. The e.m.f. of a concentration cell with transference is given by

$$E = (RT/F)(\ln 10)\log(a_{Ag^+}/a'_{Ag^+}) + E_j \qquad [5]$$

where a'_{Ag^+} is the activity of Ag^+ in the reference solution, and E_j is the liquid junction potential. If the ionic strength is the same in both half cells, then the activity term can be replaced by a concentration term. The liquid junction potential may however be large (1 - 10 mV) unless a neutral salt is present in large excess compared to the concentrations of KN_3 and $AgNO_3$. This appears to be the case in the work of Riesenfeld and Müller (3) whose value of E = 0.377 V at 291 K leads to $K_{s0} = 3.0 \times 10^{-9}$. The solubility which is taken as $(K_{s0})^{1/2} = 5.5 \times 10^{-5}$ mol dm^{-3} is clearly in error

COMPONENTS:	EVALUATOR:
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CRITICAL EVALUATION: (continued)

since it is much too high in 0.1M NaN_3 solutions (see detailed calculations below). A value for K^{o}_{s0} at 291K cannot be calculated from these data since mean molar activity coefficients, $y_\pm$, at this temperature and high ionic strength (1 mol dm^{-3}) are not available or calculable.

Using a potentiometric titration technique Courtot-Coupez and Madec (4) determined $K_{s0} = 10^{-8.3}$ mol^2 dm^{-6} at 298 K in 0.01 mol dm^{-3} azide solution and a constant ionic strength of 0.11 mol dm^{-3}. To estimate K^{o}_{s0} the evaluator has computed $y_\pm$ from the Davies equation (8)

$$\log y_\pm = -A\mu^{1/2}/(1 + \mu^{1/2}) + 0.3A\mu \qquad [6]$$

For $\mu = 0.11$ and $A = 0.5116$ dm^3 mol^{-1} at 298.2 K, $y_\pm = 0.775$ and $K^{o}_{s0} = K_{s0}y_\pm^2 = 3.0 \times 10^{-9}$ mol^2 dm^{-6}. Considering the uncertainty in K_{s0} to be at least ±10%, the computed K^{o}_{s0} value is in acceptable agreement with the recommended value of 2.82×10^{-9} (see below).

The e.m.f. measurements of Leden and Schöön in 4 mol dm^{-3} solutions using a mercurous sulfate reference electrode leads to equilibrium constants slightly different than those obtained from the solubility measurements. Since the standard deviations in the equilibrium constants are larger when determined from e.m.f. data, the values obtained from the solubility measurements are given preference.

Standard Electrode Potentials

Four determinations of $E^{o}_{c}(Ag,AgN_3)$ have been reported (5 - 7, 9). A second paper by Brouty (9) has been rejected. This paper reports measurements on the two concentration cells

I Tl(Hg, 2 phase)/TlN_3(xM)//KCl(satd)//KCl(0.1 M)/AgCl,Ag

and

II $AgAgN_3$/TlN_3(xM)//KCl(satd)//KCl(0.1M)/AgCl,Ag

The e.m.f.'s of these two concentration cells should, when added algebraically and correcting for E_j, equal the e.m.f. of the cell

$$\text{Tl(Hg, 2 phase) / TlN}_3\text{ (xM) / AgN}_3\text{,Ag} \qquad [7]$$

The sum of the e.m.f.'s of the two concentration cells give E values for cell [7] which differ from those values reported for direct measurements on this cell (6). Part of the problem is due to the assumption that the liquid junction potentials are zero in the concentration cells, but calculations by the evaluator using the Henderson equation yield E_j values of 1 to 2 mV. In the earlier paper (6) the standard potential for cell [7] at 298 K was calculated incorrectly by the author, and a recalculation by the compiler gave $E^{o}_{c}(AgN_3,Ag) = 0.2934 \pm 0.0010$ V (abs). This leads to a calculated value of $(2.81 \pm 0.13) \times 10^{-9}$ mol^2 dm^{-6} for K^{o}_{s0}.

Taylor and Nims (5) evaluated $E^{o}_{m}(Ag,AgN_3)$ for five temperatures between 278 and 318 K: their values appear to be too low by about 6%. The most likely source of error is probably due to the neglect of the small liquid junction potential: it is unlikely that the E_j's in their experimental cells are zero over the range of m = 0.01 to 0.1 mol kg^{-1}. The error of ± 0.08% in K^{o}_{s0} reported by the compiler is based on the experimental reproducibility. An additional error of +0.5 mV due to the E_j would increase K^{o}_{s0} by about 4%.

The measurements by Suzuki (5) appear to have been carried out with care given to the purity of materials, and the evaluation of liquid junction potentials. The standard electrode potential of the Ag,AgN_3 electrode as a function of temperature was given by the author as

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Water; H_2O; [7732-18-5]

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CRITICAL EVALUATION: (continued)

$$E^{o}_{c}(Ag,AgN_3)/V = 0.2933 - 2.75 \times 10^{-4}(t-25) - 4.15 \times 10^{-6}(t-25)^2 \qquad [8]$$

The E^o values were determined for five temperatures from 293 to 313 K. Using the equation

$$\log(K^{o}_{s0}/mol^2dm^{-6}) = (E^{o}_{Ag,AgN_3} - E^{o}_{Ag,Ag^+})/(RT/F)\ln 10 \qquad [9]$$

the compiler calculated K^{o}_{s0} as a function of temperature and using the least squares method, fit the data to the following equation

$$\log(K^{o}_{s0}/mol^2\ dm^{-6}) = -3588/(T/K) + 3.481 \quad (\sigma = \pm 0.003) \qquad [10]$$

Recommended Values at 298.2 K

1. Solubility product constant. Considering the excellent agreement between the values obtained from the E^o data of Brouty and Suzuki, the following values at 298.2 K are recommended:

$$K^{o}_{s0}/mol^2\ dm^{-6} = (2.82 \pm 0.02) \times 10^{-9} \qquad [11a]$$

$$K^{o}_{s0}/mol^2\ kg^{-2} = (2.83 \pm 0.02) \times 10^{-9} \qquad [11b]$$

The latter value was calculated from $(K^{o}_{s0}/mol^2dm^{-6})/d^2_o$ where d_o is the density of pure water at 25°C ($0.99707\ kg\ m^{-3}$).

2. Recommended standard thermodynamic functions at 298.2 K. The standard thermodynamic functions for the reaction

$$AgN_3(s) \rightleftarrows Ag^+ + N_3^-$$

based on volume units are:

$$\Delta G^{o}_{s0} = 48.80 \pm 0.02\ kJ\ mol^{-1} \qquad [12]$$

$$\Delta H^{o}_{s0} = 69.7 \pm 0.6\ kJ\ mol^{-1} \qquad [13]$$

$$\Delta S^{o}_{s0} = 70.1 \pm 2.0\ JK^{-1}\ mol^{-1} \qquad [14]$$

$$\Delta C^{o}_{p} = 210 \pm 58\ JK^{-1}\ mol^{-1} \qquad [15]$$

The errors reported above are standard deviations (computed by the evaluator) based on the experimental error of ± 0.2 mV in the E^o values.

COMPONENTS:	EVALUATOR:
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CRITICAL EVALUATION: (continued)

Tentative Values

1. Solubility product and thermodynamic functions at 293 - 313 K.

The tentative values are based soley on the work of Suzuki. Tentative values for K°_{s0} are given in eq [10]. Taking $\Delta E^\circ = E^\circ_c(Ag,AgN_3) - E^\circ_c(Ag,Ag^+)$, the evaluator used a least squares curve fitting technique and obtained the following results:

$$\Delta E^\circ/V = -1.0480 + 2.910 \times 10^{-3}(T/K) - 3.66 \times 10^{-6}(T/K)^2 \qquad [16]$$

$$\Delta G^\circ_{s0}/kJ\ mol^{-1} = 101.11 - 0.2808(T/K) + 3.53 \times 10^{-4}(T/K)^2 \qquad [17]$$

$$\Delta H^\circ_{s0}/kJ\ mol^{-1} = 101.1 - 3.53 \times 10^{-4}(T/K)^2 \qquad [18]$$

$$\Delta S^\circ_{s0}/JK^{-1}\ mol^{-1} = 280.8 - 0.707(T/K) \qquad [19]$$

$$\Delta C^\circ_p/JK^{-1}\ mol^{-1} = -0.71(T/K) \qquad [20]$$

The standard deviations for the least squares fit to eqs [16] and [17] are negligible: the major error is due to the experimental reproducibility in the measured e.m.f.'s: hence the errors in eqs [17] - [20] are identical to those given in eqs [12] - [15].

2. Stability constants at 298.2 K. Since AgN_3 forms mononuclear complexes in concentrated azide solutions, the determination of the stability constants is important for understanding the total solubility of the salt. Values of K_{s0}, β_n, and K_{sn} for n = 1-4 are taken from the data of Leden and Schöön in 4 mol dm^{-3} solutions. Since the mean molar activity coefficient is not known in this highly concentrated solution, it was estimated by the compiler from

$$y_\pm = (K^\circ_{s0}/K_{s0})^{1/2} = (2.82/1.61)^{1/2} = 1.33$$

The standard stability constant for $AgN_3(aq)$ was estimated from

$$\beta^\circ_1 = \beta_1 y_{AgN_3}/y_\pm^{2} \simeq \beta_1/y_\pm^{2} \qquad [21]$$

and probably represents a minimum value since y_{AgN3} for the neutral AgN_3 species is most likely greater than unity. The remaining stability constants β_n for n $\geq$ 2, were calculated from a similar relationship:

$$\beta^\circ_n = \beta_n/y_\pm^{2} \qquad [22]$$

Eq [22] is exact for n = 2, and very approximate for n = 3,4, It should be pointed out the K_{s2} (cf eq [2]) is identical to K°_{s2} if one assumes that the activity coefficients for $Ag(N_3)_2^-$ and N_3^- are identical. The results of these calculations are given below.

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CRITICAL EVALUATION: (continued)

constant	experimental value (μ = 4 mol dm^{-3})	standard state value (μ = 0)
$10^9 K_{s0}$/mol^2 dm^{-6}	1.6	2.8
$10^7 K_{s1}$/mol dm^{-3}	5.0	(5.1)**
$10^5 K_{s2}$	2.6	2.6
$10^{-2} \beta_1$/mol^{-1} dm^3	3.1	(1.8)
$10^{-4} \beta_2$/mol^{-2} dm^6	1.6	9.1
$10^{-4} \beta_3$/mol^{-3} dm^9	1.2	(0.7)
$10^{-3} \beta_4$/mol^{-4} dm^{12}	5	(3)
$10^5 K_a$/mol dm^{-3}*		1.91

*Acid dissociation constant for HN_3: value obtained from reference 10.

**Values in parenthesis are estimates.

Solubility of AgN_3 in Aqueous Solutions at 298.2 K

In the pure binary AgN_3/H_2O system, the intrinsic solubility of AgN_3, c_{Ag}, is given by

$$c_{Ag} = [Ag^+] + \sum_1^n K^o_{sn} [N_3^-]^{n-1} \qquad [23]$$

and

$$c_{Ag} = [N_3^-] + [HN_3] + \sum_1^n nK^o_{sn}[N_3^-]^{n-1} \qquad [24]$$

Since the solubility is very small in the pure binary system, all activity coefficients are taken as unity. Equating these equations and solving for $[Ag^+]$,

$$[Ag^+]^2 = K^o_{s0}\{1 + K^o_{s2} + [H^+]/K^o_a\} \qquad [25]$$

Elimination of $[Ag^+]^2$ from the above equation is accomplished with

$$[H^+] - K_w/[H^+] = - [H^+][N_3^-]/K^o_a \qquad [26]$$

which yields the following polynominal:

COMPONENTS:	EVALUATOR:
(1) Silver azide; AgN_3; [13863-88-2] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION: (continued)

$$[H^+]^5 + [H^+]^4K_a^o \{1 + K_{s2}^o - K_{s0}^o/K_a^{o2}\} - [H^+]^3\ 2K_w - [H^+]^2 2K_a^oK_w\{1 + K_{s2}^o\}$$

$$+ [H^+]K_w^2 + K_a^oK_w^2 + K_a^oK_w^2(1 + \beta_2) = 0 \qquad [27]$$

Eq [27] was solved iteratively to give $[H^+] = 5.14 \times 10^{-8}$ mol dm^{-3}, and from eq [25], $[Ag^+] = 5.32 \times 10^{-5}$ mol dm^{-3}. From eq [23]

$$c_{Ag} = [Ag^+] + [AgN_3] + [Ag(N_3)_2^-] = [Ag^+] + [AgN_3] = 5.37 \times 10^{-5} \text{mol-dm}^{-3} \qquad [28]$$

Note that $[AgN_3] = K_{s1}^o = 5 \times 10^{-7}$ which constitutes ∿ 1% of the total solubility. Consideration of $Ag(N_3)_2^-$ would increase c_{Ag} by 0.01% and, along with the higher complexes, can be neglected. If hydrolysis is ignored,

$$c_{Ag} = (K_{s0}^o)^{1/2} + K_{s1} = 5.36 \times 10^{-5} \text{ mol dm}^{-3} \qquad [29]$$

Hence in the binary system, hydrolysis accounts for ∿ 0.2% of the solubility and can also be neglected.

In solutions in excess azide, activity coefficients cannot be ignored. Combining eq [23] with

$$c_{Ag} + c = [N_3^-] + [HN_3] \quad + \sum_1^n nK_{sn}\ [N_3^-]^{n-1} \qquad [30]$$

gives

$$[N_3^-]^2\{1 + K_{s2} + [H^+]/K_a\} - c[N_3^-] - K_{s0} = 0 \qquad [31]$$

In eqs [30] and [31] , c is the concentration of added salt (e.g. NaN_3), and n is taken as = 1, 2 for ease of calculation. Note that concentration equilibrium constants are now being employed. Combining eq [31] with [26] gives

$$[H^+]^5 + [H^+]^4K_a(1 + K_{s2} + c/K_a - K_{s0}/K_a^2) - [H^+]^3\ 2K_w - [H^+]^2\Big\{2K_wK_a$$

$$(1 + K_{s2} + c/2K_a)\Big\} + [H^+]K_w^2 + K_w^2K_a(1 + K_{s2}) = 0 \qquad [32]$$

Assuming c = 0.1 mol dm^{-3}, and calculating $y_\pm$ from the Davies equation (cf. eq [6] above), eqs [32] and [31] were solved iteratively and the results are $[H^+] = 2.27 \times 10^{-9}$ and $[N_3^-] \simeq 0.1$ mol dm^{-3}. The solubility of AgN_3 is

$$c_{Ag} = [AgN_3] + K_{s0}/[N_3^-] + K_{s2}[N_3^-] = 5 \times 10^{-7} + 5 \times 10^{-8} + 2.85 \times 10^{-6} \qquad [33]$$

$$= 3.40 \times 10^{-6} \text{ mol dm}^{-3}$$

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

June 1978

CRITICAL EVALUATION: (continued)

AgN_3 (aq) now accounts for 15% of the total solubility and the major species in solution is $Ag(N_3)_2^-$. As c increases, the contribution of AgN_3 (aq) to the total solubility will decrease. If hydrolysis is neglected, $[N_3^-]$ can be calculated directly from eq [31] yielding a value of 0.1 mol dm^{-3} which, when used in eq [33] gives $c_{Ag} = 3.40 \times 10^{-6}$ mol dm^{-3} which is only 0.3% higher than the value calculated above. Since hydrolysis can be neglected, it is fairly easy to determine if the neglect of higher complexes in the above treatment is valid. From eqs [23] and [30]

$$\sum_{3}^{4}(n-1)K_{sn}[N_3^-]^n + [N_3^-]^2(1 + K_{s2}) - c\,[N_3^-] - K_{s0} = 0 \qquad [34]$$

Taking c = 0.1 it is found that $[N_3^-] \simeq 0.1$ and from

$$c_{Ag} = [AgN_3] + [Ag^+] + [Ag(N_3)_2^-] + [Ag(N_3)_3^{2-}] + [Ag(N_3)_4^{3-}]$$

$$= 5 \times 10^{-7} + 5 \times 10^{-8} + 2.85\times10^{-6} + 5 \times 10^{-7} + 2 \times 10^{-8} \qquad [35]$$

c_{Ag} now equals 3.95×10^{-6} mol dm^{-3} and the higher complexes must therefore be considered in solutions of excess azide.

Adding NH_3 in a concentration c to the binary AgN_3/H_2O system can also be adequately described neglecting the hydrolysis of N_3^-. We use eq [4] with the following

$$c = [NH_3] + [NH_4^+] + 2[Ag(NH_3)_2^+] \qquad [36]$$

$$K_N^o = [Ag(NH_3)_2^+]/\{[Ag^+][NH_3]^2\} = 1.07 \times 10^7 \text{ mol}^{-2} \text{ dm}^6 \qquad [37]$$

and

$$K_b^o = [NH_4^+][OH^-]/[NH_3] = 1.78 \times 10^{-5} \text{ mol dm}^{-3} \qquad [38]$$

Values of K_N^o and K_b^o were taken from reference 11. If $c \gg c_{Ag}$, then we can make the assumption that $[NH_4^+] \cong (cK_b^o)^{1/2}$ and the NH_3 concentration is obtained from

$$[NH_3]\{1 + 2(K_{s0}^o K_N^o)^{1/2}\} - c + (cK_b^o)^{1/2} = 0 \qquad [39]$$

Taking c = 0.17 mol dm^{-3} eq [39] gives $[NH_3] = 0.13$ and from eqs [4] and [37]

$$[Ag^+] = \{(K_{s0}^o/[NH_3]^2\,K_N^o)\}^{1/2} = 1.3 \times 10^{-7} \text{ mol dm}^{-3} \qquad [40]$$

The solubility is

$$c_{Ag} = [N_3^-] = K_{s0}^o/[Ag^+] = 2.2 \times 10^{-2} \text{ mol dm}^{-3} \qquad [41]$$

COMPONENTS:	EVALUATOR:
(1) Silver azide; AgN_3; [13863-88-2] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION: (continued)

The experimental value (2) of c_{Ag} at 293 K in 0.17 mol kg^{-1} NH_3 solution is 0.03 mol kg^{-1}. The difference between the observed and calculated value cannot be due to the neglect of $Ag(N_3)_2^-$ since

$$[Ag(N_3)_2^-] = K_{s2}K_{s0}^{o}/[Ag^+] = 4 \times 10^{-7} \text{ mol dm}^{-3}$$

or to the fact that the calculations employ volume units whereas the experimental data are based on weight units. The difference is probably due to the neglect of the formation of soluble $Ag(N_3)(NH_3)$. The existence of this type of mixed-ligand complex and evaluation of its formation constant K_{s111} is discussed in detail in the evaluations for the aqueous AgSCN and AgCN systems.

REFERENCES:

1. Leden, I.; Schöön, N.-H. *Trans Chalmers Univ. Technol. Gothenburg* 1954, *No. 144*, 3.
2. Piechowicz, T. *Bull. Soc. Chim. Fr.* 1971, 1566.
3. Riesenfeld, E.H.; Müller, F. *Z. Elektrochem.* 1935, *41*, 87.
4. Courtot-Coupez, J.; Madec, C. *Bull. Soc. Chim. Fr.* 1971, 4621.
5. Taylor, A.C.; Nims, L.F. *J. Am. Chem. Soc.* 1938, *60*, 262.
6. Brouty, M.-L. *C.R. Acad. Sci.* 1942, *214*, 258.
7. Suzuki, S. *J. Chem. Soc. Jpn.* 1952, *73*, 150.
8. Davies, C.W. *Ion Association.* Butterworths. London. 1962.
9. Brouty, M.-L. *C.R. Acad. Sci.* 1942, *214*, 480.
10. Albert, A.; Serjeant, E.P. *Ionization Constants of Acids and Bases.* Methuen. London. 1962.
11. Bjerrum, J. *Metal Ammine Formation in Aqueous Solution.* P. Haase and Son. Copenhagen. 1941.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Sodium azide; NaN_3; [26628-22-8]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Riesenfeld, E.H.; Müller, F.

Z. Elektrochem. 1935, *41*, 87-92.

VARIABLES:

One temperature: 18°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The solubility was determined from the e.m.f., E_1, of the cell

$$Ag,AgN_3/NaN_3(0.1M),\ KNO_3(1M)//AgNO_3(0.1M),\ KNO_3(1M)/Ag \qquad [1]$$

Based on the experimental value of E_1 = 0.377V at 18°C, the authors report

$$c_{Ag} = 8.43 \times 10^{-3}\ g\ dm^{-3} = 5.62 \times 10^{-5}\ mol\ dm^{-3}$$

The exact significance of this result is not clear since calculation of c_{Ag} from $(K_{s0})^{1/2}$ is an approximation for the pure binary system: it is meaningless to use this approximation in solutions containing a large excess of azide. Using the author's data, the compiler calculates

$$K_{s0}(AgN_3) = 3.0 \times 10^{-9}\ mol^2\ dm^{-6}$$

The authors also report e.m.f. measurements on the cell

$$Ag,AgN_3/NaN_3(1M)//KCl(0.1M)/Hg_2Cl_2,Hg \qquad [2]$$

The e.m.f. data for this cell, E_2, are reported versus the normal hydrogen electrode, and no reference is given as to the potentials of the 0.1 mol dm^{-3} calomel versus the normal hydrogen electrode. The results are:

$$E_2 = 0.372V \text{ at } 0^{\circ}C \quad : \quad E_2 = 0.384V \text{ at } 21^{\circ}C$$

Since the activity coefficients and liquid junction potentials involved in these measurements are unknown, the compiler did not attempt to calculate a K_{s0} from these data.

AUXILIARY INFORMATION

METHOD:

Experimental and computational details are not given. The $[Ag^+]$ in 0.1 mol dm^{-3} NaN_3 can be calculated from

$$\log[Ag^+] = \log[Ag^+]_r - E_1/(RT/F)\ln 10$$

where $[Ag^+]_r$ is the concentration in the $AgNO_3$ reference solution. Taking $(RT/F)\ln 10 = 0.0578$ at 18°C, the compiler calculates

$$[Ag^+] = 3.0 \times 10^{-8}\ mol\ dm^{-3}$$

$$K_{s0} = [Ag^+][N_3^-] = 3.0 \times 10^{-9}\ mol^2 dm^{-6}$$

COMMENTS AND/OR ADDITIONAL DATA:

If an error of ±1mV is assumed for E_1, then the contribution of the liquid junction potential, E_j, is negligible since E_j is probably less than 0.5mV. The calculation of K_{s0} taking $[N_3^-]$ = 0.1 mol dm^{-3} implies that the formation of complex species is negligible.

SOURCE AND PURITY OF MATERIALS:

Ag,AgN_3 electrode prepared by cleaning a 10 cm^2 Ag foil in concentrated aqueous NH_3 followed by anodization in 1 mol dm^{-3} NaN_3 at 2.11 mA for 16.5 h. No other details were given.

ESTIMATED ERROR:

Based on an assumed error of ±1mV in E_1, the average error in K_{s0} is $\pm 1 \times 10^{-10}$ mol^2 dm^{-6}.

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Sodium azide; NaN_3; [26628-22-8]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Taylor, A.C.; Nims, L.F. *J. Am. Chem. Soc.* 1938, *60*, 262-4.

VARIABLES:

Temperature: range 5 to 45°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The authors report the solubility for 25°C as

$$c_{Ag} = (K^{o}_{s0})^{1/2} = 5.1 \times 10^{-5}\ \text{mol dm}^{-3}$$

The compiler has taken the original data and calculated the solubility product as a function of temperature using the equation

$$\log(K^{o}_{s0}/\text{mol}^2\ \text{kg}^{-2}) = (E^{o}_{Ag,AgN_3} - E^{o}_{Ag,Ag^+})F/RT\ln 10$$

t/°C	E^{o}_{cell}/V	E^{o}_{Ag,AgN_3}(abs)*/V	E^{o}_{Ag,Ag^+}(abs)**/V	$10^9 K^{o}_{s0}$/mol^2 kg^{-2}
5	0.0620	0.2960	0.8188	0.337
15	0.0657	0.2943	0.8090	0.994
25	0.0695	0.2920	0.7993	2.66
35	0.0733	0.2890	0.7894	6.54
45	0.0772	0.2855	0.7791	15.16

*Converted to absolute volts by the compiler.
**Data from reference 1 and converted to absolute volts by the compiler.

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

Ag,AgCl/NaCl(m)//NaN_3(m)/AgN_3,Ag

over the temperature range of 5 to 45 °C. The symbol // represents the saturated KCl salt bridge, and the molalities varied from 0.01 to 0.1 mol/kg. The e.m.f. of this cell is given by

$$E_{cell} = E^{o}_{Ag,AgN_3} - E^{o}_{Ag,AgCl}$$

$$(RT/F)\ \ln\ (m_{N_3}\gamma_{\pm}/m_{Cl}\gamma'_{\pm}) + E_j$$

where $\gamma_{\pm}$ is the mean molal activity coefficient and E_j is the liquid junction potential. Seven measurements (six for 5°C) at each temp showed E_{cell} to be independent of concentration to within ±0.01mV (compiler): the reproducibility after temperature change was within ±0.2mV. All solutions were made up in triplicate and analysed gravimetrically for Na as the

SOURCE AND PURITY OF MATERIALS:

Commercial NaN_3 was twice recrystallized from water by adding ethanol, redissolved, filtered through charcoal, and recrystallized from water using acetone. Gravimetric analysis as Na_2SO_4 was termed "satisfactory." NaCl was recrystallized twice from water, and KCl for the salt bridge was c.p. grade. Both the Ag,AgN_3 and Ag,AgCl electrodes were of the thermal-electrolytic type (2).

ESTIMATED ERROR:

E.m.f.'s: reproducibility = ±0.2mV.
K^{o}_{s0}: σ ≈ ±0.08% (compiler).
Temperature: not specified.

REFERENCES:

1. Owen, B.B., Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233.
2. Harned, H.S. *J. Am. Chem. Soc.* 1929, *51*, 416.
3. Harned, H.S.; Ehlers, R.W. *J. Am. Chem. Soc.* 1933, *55*, 2179.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Sodium azide; NaN_3; [26628-22-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Taylor, A.C.; Nims, L.F. *J. Am. Chem. Soc.* 1938, *60*, 262-4.

COMMENTS AND/OR ADDITIONAL DATA:

There is some ambiguity concerning the actual concentration units used. The authors prepared their solutions volumetrically and report the solubility of AgN_3 in mol dm^{-3}. On the other hand they state that the Ag electrodes were anodized in 0.1 molal NaN_3, use the symbol "m" for concentration, and employ $E^o_{Ag,AgCl}$ values based on molal units. It appears to this compiler that the authors report E_{cell} values based on molal units.

The standard potential for the Ag,AgN_3 electrode as a function of temperature were fit by the authors to the following equation:

$$E^o_{Ag,AgN_3} = E^o_{Ag,AgN_3}(25^oC) - 2.62 \times 10^{-4}(t - 25) - 3.13 \times 10^{-6}(t - 25)^2$$

The compiler used the least squares method to fit the K^o_{s0} data to the following equation:

$$\log(K^o_{s0}/mol^2\ kg^{-2}) = -3654/(T/K) + 3.674 \qquad (\sigma = \pm\ 0.007)$$

where σ is the standard deviation for the precision of the least squares fit (the correlation coefficient is 1.000).

Due to the observation that E_{cell} is independent of concentration, the authors assume $E_j = 0$. This assumption is not strictly valid and it is probable that the liquid junction potential is around 0.2 to 0.5mV. For E_j = 0.5mV, the K_{s0} values in the data table would be about 4% higher.

AUXILIARY INFORMATION

METHOD:

sulfate, and by potentiometric titration with $AgNO_3$ for determination of azide and chloride. Using published data for $E^o_{Ag,AgCl}$ (3) the standard potentials for the Ag,AgN_3 electrode were calculated by assuming $E_j = 0$ and the ratio of concentrations and activity coefficients equals unity. Hence

$$E_{cell} = E^o_{cell} = E^o_{Ag,AgN_3} - E^o_{Ag,AgCl}$$

The solubility product of AgN_3 was calculated at 25°C from the relation

$$\log K^o_{s0}(AgN_3) = \log K^o_{s0}(AgCl) + (E^o_{Ag,AgN_3} - E^o_{Ag,AgCl})F/RT\ln 10$$

using previously published data for $K^o_{s0}(AgCl)$ (4).

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

4. Brown, A.S.; MacInnes, D.A. *J. Am. Chem. Soc.* 1935, *57*, 459.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Thallium azide; TlN_3; [13847-66-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Brouty, M.-L. *C.R. Acad. Sci.* 1942, *214*, 258-61.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

E.m.f. measurements were made on the cell

$$Tl(Hg,\ 2\ phase)\ /\ TlN_3(xM)\ /\ AgN_3,Ag \qquad [1]$$

and the experimental results along with some calculated functions are:

TlN_3 /mol dm^{-3}	E_1/V	E_1'/V	E_1°/V
0.0145	0.8535	0.6360	0.6272
0.0096	0.8740	0.6351	0.6279
0.0072	0.8878	0.6345	0.6278
0.0051	0.9036	0.6339*	0.6268
0.0029	0.9327	0.6329*	0.6282
0.0023	0.9435	0.6325*	0.6275
0.0019	0.9532	0.6321*	0.6275
0.0012	0.9785	0.6314*	0.6300
0.0010	0.9878	0.6310*	0.6303

In this table E_1 is the observed e.m.f. and the functions E_1' and E_1° are defined below. To evaluate the solubility product for AgN_3, the compiler first calculated the standard potential of cell [1], E_1°, and then the standard electrode potential of the Ag,AgN_3 electrode with respect to the standard hydrogen electrode: the compiler's results are:

$$E^{\circ}_{Ag,AgN_3} = 0.2934 \pm 0.0010\ V\ (abs)$$

$$K^{\circ}_{s0}(AgN_3) = (2.81 \pm 0.13) \times 10^{-9}\ mol^2\ dm^{-6}$$

AUXILIARY INFORMATION

METHOD:

The e.m.f. of cell [1] is given by

$$E_1 = E_1^{\circ} - (2RT/F)(\ln 10)\log(My_{\pm}) \qquad [2]$$

where M is the molarity and $y_{\pm}$ is the mean molar activity coefficient. Within the framework of the limiting law, E_1° can be obtained by plotting E_1 against the square root of the ionic strength, $\mu^{1/2}$, and extrapolating to $\mu = 0$: E_1' is defined by

$$E_1' = E_1 + (2RT/F)(\ln 10)\log M \qquad [3]$$

The author's extrapolation gives E_1° = 0.6298 V(int), but inspection of the E' terms in the above table shows that those points marked with an asterisk (*) were incorrectly calcd by the author. Using the Davies equation (1) for $y_{\pm}$,

$$\log y_{\pm} \quad -A\mu^{1/2}/(1 + \mu^{1/2}) + 0.3A\mu \qquad [4]$$

the compiler calculated the E_1° values given in the table above using eq [2]. Since the E_1° values are independent of

SOURCE AND PURITY OF MATERIALS:

TlN_3 prepared by pptn from a soln of NaN_3 and $TlNO_3$, and followed by recrystallization. Doubly distilled water of specific conductance 1.5 x 10^{-6} ohm^{-1} cm^{-1} was used. Tl amalgam prepared by dissolving pure Tl in Hg under a slightly acidic soln of $TlNO_3$ under an atmosphere of N_2. The Ag,AgN_3 electrodes were prepared by the thermal-electrolytic method.

ESTIMATED ERROR:

E.m.f.'s: ±0.2 mV (author)

K°_{s0}: see compiler's calcn of the standard deviation above.

Temperature: not specified.

REFERENCES:

1. Davies, C.W. *Ion Association.* Butterworths. London. 1962.
2. Cowperthwaite, I.A.; La Mer, V.K.; Barksdale, J. *J. Am. Chem. Soc.* 1934, *56*, 544.
3. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2223.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Thallium azide; TlN_3; [13847-66-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Brouty, M.-L. *C.R. Acad. Sci.* 1942, *214*, 258-61.

COMMENTS AND/OR ADDITIONAL DATA:

There are two problems associated with the author's evaluation of E_1^o. First the computed values of E_1' from eq [3] are in error as pointed out above: the original incorrect values are presented in the data table above. The correct values of E_1' exhibit no dependence on concentration, and it was for this reason that the compiler used equations [2], [4], [5], and [6] to re-evaluate the original data. In addition to computing incorrect E_1' values, Brouty plots this variable against $\mu^{1/2}$ which is valid within the framework of the Debye-Hückel limiting law, but she takes μ = 2M which is clearly in error.

AUXILIARY INFORMATION

METHOD:

concentration, the compiler has taken the average final value

$$E_1^o = 0.6296 \pm 0.0010 \text{ V} = 0.6298 \text{ V (abs)}$$

The standard potential of the Ag,AgN_3 electrode is given by

$$E^o_{Ag,AgN_3} = E_1^o - E^o_{Tl,Tl^+} \qquad [5]$$

and finally

$$\log K^o_{s0}(AgN_3) = (E^o_{Ag,AgN_3} - E^o_{Ag,Ag^+})/(RT/F)\ln 10 \qquad [6]$$

Values of E^o_{Tl,Tl^+} and E^o_{Ag,Ag^+} taken from references 2 and 3 and converted to absolute volts by the compiler are, respectively, -0.3364 V and 0.7993 V.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Potassium azide; KN_3; [20762-60-1]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Suzuki, S. *J. Chem. Soc. Jpn.* 1952, *73*, 150-3.

VARIABLES:

Temperature: range of 20-40°C

PREPARED BY:

Hitoshi Ohtaki and Mark Salomon

EXPERIMENTAL VALUES: The author reports a value of 2.88 x 10^{-9} mol^2 dm^{-6} for the solubility product at 25°C. Using the author's e.m.f. data, the compilers have recalculated K^o_{s0} as a function of temp using the equation

$$\log K^o_{s0} = (E^o_{Ag,AgN_3} - E^o_{Ag,Ag^+})F/RT \ln 10$$

t/°C	E^o_{cell}/V*	E^o_{Ag,AgN_3}/V**	E^o_{Ag,Ag^+}/V***	$10^9K^o_{s0}/mol^2\ dm^{-6}$
20	0.0687	0.2947	0.8042	1.75
25	0.0706	0.2934	0.7992	2.82
30	0.0724	0.2919	0.7942	4.50
35	0.0741	0.2902	0.7891	7.00
40	0.0760	0.2883	0.7840	10.68

* Uncorrected for liq junction potential (E_j = 0.0003 V at all temps).

** Corrected for E_j and converted to absolute volts by the compilers.

*** From (1) and converted to abs volts and molar units by the compilers.

The compilers have fit the data for $\log K^o_{s0}$ by least squares to

$$\log(K^o_{s0}/mol^2\ dm^{-6}) = -3588/(T/K) + 3.481 \quad (\sigma = \pm 0.003)$$

where σ is the standard deviation of the precision of the least squares fit, and the correlation coefficient for this fit is 1.0000. Converting the above K_{s0} to molal units ($K/mol^2kg^{-2} = K/mol^2dm^{-6}/d_o^2$ where d_o = density of water), the compilers arrived at the following relation:

$$\log(K^o_{s0}/mol^2\ kg^{-2}) = -3612/(T/K) + 3.564 \quad (\sigma = \pm 0.003)$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$Ag,AgCl/KCl(0.05M)//KN_3(0.05M)/-AgN_3,Ag$$

The e.m.f. of this cell is given by

$$E_{cell} = E^o_{Ag,AgN_3} - E^o_{Ag,AgCl} - (RT/F)\ln\{[N_3^-]\ \gamma_{\pm}/[Cl^-]\gamma'_{\pm}\} + E_j$$

E_j was calcd from the Henderson eqn and equals 0.0003V for all temps, and the logrithmic term is assumed to equal unity since the concentrations in both sides of the cell are identical. E^o_{Ag,AgN_3} was given by

$$E^o_{Ag,AgN_3} = 0.2933-2.75\times10^{-4}(t-25) - 4.15 \times 10^{-6}(t-25)^2$$

E^o_{AgAgCl} values as a function of temp were obtained from the work of Harned and Ehler (2).

SOURCE AND PURITY OF MATERIALS:

KN_3 prepared from KOH and HN_3 and purified by the method of Dennis and Benedict (3). HN_3 was prepared by addition of dilute H_2SO_4 to NaN_3. Both electrodes were of the thermal-electrolytic type.

ESTIMATED ERROR:

E.m.f. stable to ±0.2mV for several days, but varied in duplicate runs by ±2mV. Stnd deviation in K^o_{s0} based on this latter error is ±0.8% (compilers)

REFERENCES:

1. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233.
2. Harned, H.S.; Ehler, R.W. *J. Am. Chem. Soc.* 1933, *55*, 2174.
3. Dennis, L.M.; Benedict, C.H. *J. Am. Chem. Soc.* 1898, *20*, 225.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Sodium azide; NaN_3; [26628-22-8]

(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Leden, I.; Schöön, N.-H. *Trans. Chalmers Univ. Technol. Gothenburg* 1954, *No. 144*, 3-17.

VARIABLES:

Concentration of NaN_3 at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: Two experimental techniques were used at a reported temp of 25.00°C. In one method the soly of AgN_3 reported as the total silver content C_{Ag}/mol dm^{-3}, was directly determined in excess NaN_3 solns: the results are given in Table 1. A second e.m.f. method was used to determine the solubility product as a function of NaN_3 concentration, and the results are given in Table 2. The ionic strength of all solns were maintained at 4 mol dm^{-3} with $NaClO_4$.

TABLE 1. Solubility of AgN_3 in excess azide solns at an ionic strength of 4M.

$[NaN_3]$/mol dm^{-3}	$10^6 C_{Ag}$
4.0	1600
3.2	900
2.0	250
1.0	65
0.5	26
0.3	11.5
0.2	7.2
0.16	5.5
0.1	3.2
0.038	1.0
0.01	0.8
0.003	1.0
0.001	1.9
0	40.2

TABLE 2. K_{s0} as a function of $[NaN_3]$ in 4M solns. *Variation in E^o due to use of different Ag,AgI electrodes.
**Points used to calc average K_{s0}.

$[NaN_3]$/mol dm^{-6}	E_1/V	E^o/V*	$10^9 K_{s0}$
4.0	0.4565	-0.0828	3.0
3.2	0.4505	-0.0828	3.1
2.0	0.4397	-0.0829	2.9
1.0	0.4336	-0.0816	2.0
0.2	0.3914	-0.0829	1.9**
0.01	0.3090	-0.0823	2.4
0.001	0.2587	-0.0823	1.7**
0	0.1793	-0.0828	1.4**

AUXILIARY INFORMATION

METHOD:

Solns were prepared isothermally at 25.00°C by rotation of NaN_3(xM), $NaClO_4$(4-x)M and excess of solid AgN_3. Equil attained in < 1 week ascertained by duplicate analysis after 4 and 7 days. Satd solns separated from excess solid by thermostatic filtration and analysed for total Ag, C_{Ag}, by two methods. For $[NaN_3] > 0.1$ mol dm^{-3}, NaCN was added to aliquots of the filtrate and Ag electrodeposited on a Pt rod: the Ag was dissolved in HNO_3, buffered with CH_3COONa, and Ag^+ titrated potentiometrically with 0.01 mol dm^{-3} NaBr. Limit of detection of C_{Ag} by this method was about 10^{-6}mol/ dm^3. For $[NaN_3] < 0.1$ mol dm^{-3}, aliquots of the filtrate were added to a soln of 0.1 mol dm^{-3} $AgNO_3$ with excess NaCN and C_{Ag} determined by radioassay (^{110}Ag). In another set of experiments the satd solns were analysed by e.m.f. measurements and the soly product determined in a series of solns of varying $[NaN_3]$. The cells studied were

SOURCE AND PURITY OF MATERIALS:

$NaClO_4$ (G.F. Smith) solns were filtered and tested for Cl^-: solns were analysed by converting to $HClO_4$ with H^+ ion exchange resin and titrating with NaOH. NaN_3 (Merck, puriss) solns filtered and analysed by the Mohr method. $AgClO_4$ prepared by pptn of the oxide from $AgNO_3$ solns followed by dissolution in $HClO_4$. AgN_3 was pptd from solns of NaN_3 and $AgClO_4$. For the radiochemical experiments, AgN_3 was pptd from a soln of NaN_3 and

ESTIMATED ERROR:

Solubility: nothing specified.

K_{s0}: $\sigma = \pm 13\%$(authors): ±25% (compiler)

Temperature: ± 0.02°C

REFERENCES:

1. Brown, A.S. *J. Am. Chem. Soc.* 1934, *56*, 646.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Sodium azide; NaN_3; [26628-22-8]

(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Leden, I.; Schöön, N.-H. *Trans. Chalmers Univ. Technol Gothenburg* 1954, *No. 144*, 3-17.

COMMENTS AND/OR ADDITIONAL DATA:

In 4 mol dm^{-3} soln the soly of AgN_3 in excess NaN_3 given by

$$c_{Ag} = \sum_{-1}^{3} k'_n [N_3^-]^n \qquad [5]$$

where k'_n is the stepwise formation constant for the reactions

$$AgN_3(s) + nN_3^- = Ag(N_3)_{1+n}^{-n} \qquad [6]$$

The relation between the k'_n's and the overall formation constants, β_n, is

$$k'_n = K_{s0}\beta_{n+1} \qquad [7]$$

The data in Table 1 were analysed graphically and the resulting β_n values are given in Table 3 below (note $k'_{-1} = K_{s0}$). From the e.m.f. measurements the constants K_{s0}, β_3 and β_4 were evaluated (the latter two by a graphical method). The authors report a value of $K_{s0} = (1.6 \pm 0.2) \times 10^{-9}$ mol/dm^3 from the data in Table 2, but the compiler calculates a value of $(1.7 \pm 0.3) \times 10^{-9}$ from these data.

TABLE 3 Equilibrium constants obtained from solubility data and e.m.f. measurements (ionic strength is constant at 4 mol/dm^3

method	10^9K_{s0}	$10^{-2}\beta_1$	$10^{-4}\beta_2$	$10^{-4}\beta_3$	$10^{-3}\beta_4$
soly	1.61±0.2	3.1±0.6	1.6±0.3	1.5±0.5	5±1
e.m.f.	1.67±0.3**			0.8±0.5	4.7±1

* Units are K_{s0} = mol^2/dm^6 ; β_n are mol^{-n} dm^{3n}

** calcd by compiler as discussed above: author's value is (1.6±0.2) x 10^{-9}

AUXILIARY INFORMATION

METHOD:

$$\mathrm{Ag,AgN_3} \left| \begin{array}{l} \mathrm{Ag(N_3)_{1+n}^{-n}} \\ \mathrm{NaN_3(xM)} \\ \mathrm{NaClO_4(4-x)M} \end{array} \right\| \begin{array}{l} \mathrm{NaClO_4(4M)} \\ \mathrm{Hg_2SO_4(satd)} \end{array} \Big| - \mathrm{Hg_2SO_4,Hg} \qquad [1]$$

and

$$\mathrm{Ag,AgI} \left| \begin{array}{l} \mathrm{AgClO_4(xM)} \\ \mathrm{NaClO_4(4-x)M} \end{array} \right\| \begin{array}{l} \mathrm{NaClO_4(4M)} \\ \mathrm{Hg_2SO_4(satd)} \end{array} \Big| - \mathrm{Hg_2SO_4,Hg} \qquad [2]$$

The e.m.f. of cell [1] is given by

$$E_1 = E^o - (RT/F)\ln[Ag^+] \qquad [3]$$

where E^o is determined from e.m.f. measurements on cell [2] and the soly product calculated from

$$K_{s0} = [Ag^+]\,[N_3^-] \qquad [4]$$

SOURCE AND PURITY OF MATERIALS:

$AgNO_3$ containing a small amount of ^{110}Ag. Ag,AgBr and Ag,AgI electrodes prepared as in reference 1. The method of preparation of the Ag,AgN_3 electrode is not given.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Ammonia; NH_3; [7664-41-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Piechowicz, T. *Bull. Soc. Chim. Fr.* 1971, 1566-7.

VARIABLES:

Concentration of NH_3 at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The authors reported composition in weight % and were converted to mol/kg by the compiler. All solutions are saturated with AgN_3.

$[NH_3]$/wt %	c_{Ag}/wt %	$[NH_3]$/mol kg^{-1}	c_{Ag}/mol kg^{-1}
0.28	0.37	0.17	0.03
1.25	2.08	0.76	0.144
1.28	2.16	0.78	0.149
1.79	3.14	1.11	0.220
3.15	6.56	2.05	0.485
3.54	7.42	2.33	0.556
3.74	7.94	2.49	0.600
5.61	13.08	4.05	1.073
5.67	13.03	4.10	1.069
6.64	16.55	5.08	1.437
9.91	29.84	9.66	3.304
10.93	35.69	12.02	4.461
12.24	44.29	16.53	6.797

AUXILIARY INFORMATION

METHOD:

Solutions were prepared isothermally at 20°C by agitating a soln of excess AgN_3. A sealed 3-neck flask was used for the studies, and the pressure within the flask was maintained at atmospheric pressure (1,2). When equilibrium was attained (no details given), an aliquot for analysis was filtered through a cotton filter into a tared pipet which was provided with two stopcocks. The soln was weighed and analysed for silver by titration with NH_4SCN, and for NH_3 by "distillation and titration" (no further details were given, but the compiler assumes that the distillate was titrated with stnd acid). Analysis of the solid phase (no details given) showed it to be AgN_3.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temperature: ± 0.05°C

Nothing else specified.

REFERENCES:

1. Schutze, H.; Piechowicz, T. *Helv. Chim. Acta* 1943, *26*, 242.
2. Guyer, A.; Piechowicz, T. *Helv. Chim. Acta* 1944, *27*, 858: 1945, *28*, 401.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Tetraethylammonium azide; $(C_2H_5)_4NN_3$; [993-20-4]
(3) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]
(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Courtot-Coupez, J.; Madec, C. *Bull. Soc. Chim. Fr.* 1971, 4621-5.

VARIABLES:

Composition of solvent at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Temperature is 25°C and units of K_{s0} are mol^2/dm^6, and dm^6/mol^2 for β_2. Composition of the solvent is given in mole fraction of dimethyl sulfoxide (x_{DMSO}). The ionic strength is constant at about 0.1 mol/dm^3.

x_{DMSO}	$-\log K_{s0}(AgN_3)$	$\log \beta_2$
0	8.3	
0.05	8.1	
0.1	7.9	
0.2	7.6	
0.3	7.4	
0.4	7.2	
0.6	6.9	
0.8	6.7	6.8
0.9	6.9	7
0.95	7.1	7.4

AUXILIARY INFORMATION

METHOD:

The soly products and stability consts were calcd from potentiometric titrn data using the cell

$$Ag/Et_4NN_3(xM),\ Et_4NClO_4(0.1M)/ref$$

where Et = C_2H_5 and the reference electrode is

$$Ag/AgClO_4(0.01M),\ Et_4NClO_4(0.1M)//\ Et_4NClO_4(0.1M)//$$

0.1M $AgClO_4$ was titrated into the xM azide soln at 25°C. Et_4NClO_4 was used to maintain the ionic strength at a about 0.1 mol/dm^3.

SOURCE AND PURITY OF MATERIALS:

Doubly distilled water and pharmaceutical grade $(CH_3)_2SO$ were mixed prior to use. $(C_2H_5)_4NN_3$ was prepared by mixing $(C_2H_5)_4Cl$ and NaN_3 in absolute ethanol. The salt was recrystallized from alcohol and dried under vacuum at room temp. $(C_2H_5)_4ClO_4$ was recrystallized, and BDH $AgClO_4$ was used as received.

ESTIMATED ERROR:

Nothing specified, but precision in the equilibrium constants is probably about ±0.1 log units (compiler).

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Pyridine; C_5H_5N; [110-86-1]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Piechowicz, T. *Bull. Soc. Chim. Fr.* 1971, 1566-7.

VARIABLES:

Solvent composition at 20 and 60°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The authors reported the compositions in weight %. The compiler converted the soly of AgN_3 to mol/kg.

$t/^{\circ}C$	$[H_2O]$/wt %	$[C_5H_5N]$/wt %	c_{Ag}/wt %	$c_{Ag}/mol\ kg^{-1}$
20	0.0	66.8	33.2	3.32
20	2.2	70.9	26.9	2.46
20	8.1	75.6	16.3	1.30
20	24.7	69.0	6.3	0.45
20	49.7	48.5	1.8	0.12
60	0.0	76.5	23.5	2.05
60	2.4	78.3	19.3	1.60
60	8.5	78.7	12.8	1.00
60	24.8	69.0	6.2	0.44
60	49.6	48.4	2.0	0.14

AUXILIARY INFORMATION

METHOD:

Solutions were prepared isothermally by agitating a soln containing an excess AgN_3 in a sealed 3-necked flask. Atmospheric pressure was maintained in the flask (1,2). When equilibrium was attained (no details given), an aliquot for analysis was filtered through a cotton filter into a tared pipet which was provided with two stopcocks. The soln was weighed and analysed for silver by titration with NH_4SCN. The weight of the solvent was determined by difference. The water content was determined prior to the addition of AgN_3 by a Karl Fischer titration. Analysis of the solid phase (no details given) showed it to be AgN_3.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temperature: ±0.05°C.

Nothing else was specified.

REFERENCES:

1. Schutze, H.; Piechowicz, T. *Helv. Chim. Acta* 1943, *26*, 242.
2. Guyer, A.; Piechowicz, T. *Helv. Chim. Acta* 1944, *27*, 858: 1945, *28*, 401.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Tetraethylammonium azide; $(C_2H_5)_4NN_3$; [993-20-4]

(3) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0]

(4) Acetonitrile; C_2H_3N; [75-05-8]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.05 mol/dm^3

$\log K_{s0}(AgN_3) = -9.6$: $K_{s0}(AgN_3) = 2.5 \times 10^{-10}\ mol^2/dm^6$

AUXILIARY INFORMATION

METHOD:

The soly product was determined from potentiometric titrn data using the cell

$Ag/Et_4NN_3(0.05M)//AgNO_3(0.014M)/Ag$

where Et = C_2H_5 and // is a salt bridge of satd tetraethylammonium picrate. 0.05M $AgNO_3$ was titrated into the azide soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titration.

SOURCE AND PURITY OF MATERIALS:

Acetonitrile was purified by a conventional method (1). Analar grade $AgNO_3$ and NaN_3 were used as received. Tetraethylammonium azide was prepared from the bromide and NaN_3, recrystallized from an organic solvent, washed with ether, and dried in vacuo at 20-80°C.

COMMENTS AND/OR ADDITIONAL DATA:

The titration curve was not sharply defined. Ppts appeared after 10-20% of the theoretical amount of $AgNO_3$ was added. A well defined inflection point was obtained at the end point, but very small inflections were noticed in the region of 10-25% titration. The curves were treated as though $Ag(N_3)_2^-$ was not present.

ESTIMATED ERROR:

Nothing specified, but precision in $\log K_{s0}$ is probably about ±0.1 log units.

REFERENCES:

1. Coetzee, J.F.; Cunningham, G.P.; McGuire, D.K.; Padmanabhau, G.R. *Anal. Chem.* 1962, *34*, 1139.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver azide; AgN_3; [13863-88-2] (2) Sodium azide; NaN_3; [26628-22-8] (3) Sodium nitrate; $NaNO_3$; [7631-99-4] (4) Dimethylacetamide; C_4H_9NO; [127-19-5]	Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12
VARIABLES:	PREPARED BY:
One temperature: 25°C	Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.01 mol/dm^3. The soly of AgN_3 in excess azide was determined to be governed by the following reactions:

$$2AgN_3(s) \rightleftarrows Ag^+ + Ag(N_3)_2^- \qquad K_{s0}(Ag\ Ag(N_3)_2) = 4.0 \times 10^{-10}\ \text{mol}^2/\text{dm}^6$$

$$AgN_3(s) \rightleftarrows Ag^+ + N_3^- \qquad K_{s0}(AgN_3) = 1.6 \times 10^{-11}\ \text{mol}^2/\text{dm}^6$$

$$Ag^+ + 2N_3^- \rightleftarrows Ag(N_3)_2^- \qquad \beta_2 = 1.6 \times 10^{12}\ \text{dm}^6/\text{mol}^2$$

AUXILIARY INFORMATION

METHOD:

The soly products and stability const were determined potentiometric titrn data using the cell

$$Ag/NaN_3(0.01M)//AgNO_3(0.02M)/Ag$$

where // is a salt bridge composed of a satd soln of tetraethyammonium picrate. 0.01M $AgNO_3$ was titrated into the azide soln which was exposed to the atmosphere. The cell was thermostated at 25°C and stirred magnetically during the titration. The titration showed two well-defined plateaus from which the constants β_2 and $K_{s0}(Ag\ Ag(N_3)_2)$ were calcd. The soly product for AgN_3 was calcd from

$$K_{s0}(AgN_3) = \{K_{s0}(Ag\ Ag(N_3)_2)/\beta_2\}^{1/2}$$

SOURCE AND PURITY OF MATERIALS:

Dimethylacetamide was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and NaN_3 were used as received.

ESTIMATED ERROR:

Nothing specified, but precision in the equilibrium constants is probably $\leqslant \pm 10\%$.

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Sodium azide; NaN_3; [26628-22-8]

(3) Sodium nitrate; $NaNO_3$; [7631-99-4]

(4) Dimethylformamide; C_3H_7NO; [68-12-2]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.D.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.01 mol/dm^3. The solubility of AgN_3 in excess azide was determined to be governed by the following reactions:

$2AgN_3(s) \rightleftarrows Ag^+ + Ag(N_3)_2^-$	$K_{s0}(Ag\ Ag(N_3)_2) = 7.9 \times 10^{-11}\ mol^2/dm^6$
$AgN_3(s) \rightleftarrows Ag^+ + N_3^-$	$K_{s0}(AgN_3) = 1.0 \times 10^{-11}\ mol^2/dm^6$
$Ag^+ + 2N_3^- \rightleftarrows Ag(N_3)_2^-$	$\beta_2 = 7.9 \times 10^{11}\ dm^6/mol^2$

AUXILIARY INFORMATION

METHOD:

The soly products and stability const were determined from potentiometric titrn data using the cell

$$Ag/NaN_3(0.01M)//AgNO_3(0.024M)/Ag$$

where // is a salt bridge containing a satd soln of tetraethylammonium picrate. 0.01M $AgNO_3$ was titrated into the azide soln which was exposed to the atmosphere. The cell was thermostated at 25°C and stirred magnetically during the titration. The titration showed two well-defined plateaus from which the constants β_2 and $K_{s0}(Ag\ Ag(N_3)_2)$ were calcd. The soly product for AgN_3 was calcd from

$$K_{s0}(AgN_3) = \{K_{s0}(AgAg(N_3)_2)/\beta_2\}^{1/2}$$

SOURCE AND PURITY OF MATERIALS:

Dimethylformamide was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and NaN_3 were used as received.

ESTIMATED ERROR:

Nothing specified, but precision in the equilibrium constant is probably $\leqslant \pm 10\%$.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Silver azide; AgN_3; [13863-88-2] (2) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0] (3) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1] (4) Dimethyl sulfoxide; C_2H_6SO; [67-68-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. March 1978

CRITICAL EVALUATION:

The determination of the soly product $K_{s0}(AgN_3)$ and the stability constant β_2 for the reactions

$$AgN_3(s) \rightleftarrows Ag^+ + N_3^- \qquad K_{s0}(AgN_3)$$

$$Ag^+ + 2N_3^- \rightleftarrows Ag(N_3)_2^- \qquad \beta_2$$

has been reported by Parker et. al. (1) and L'Her et. al. (2). Both sets of results were carried out in dimethyl sulfoxide solns of constant ionic strength, μ. Parker's work involves tetraethylammonium nitrate as the inert electrolyte, and his results are (298 K)

$$K_{s0}(AgN_3) = 3.2 \times 10^{-7}\ mol^2\ dm^{-6} \quad (\mu = 0.05\ mol\ dm^{-3})$$

$$\beta_2 = 1.0 \times 10^7\ mol^{-2}\ dm^6$$

Using tetraethylammonium perchlorate (0.1M soln) as the inert electrolyte, L'Her's results are (295 K)

$$K_{s0}(AgN_3) = 3.2 \times 10^{-8}\ mol^2 dm^{-6} \quad (\mu = 0.11\ mol\ dm^{-3})$$

$$\beta_2 = 1.0 \times 10^8\ mol^{-2}\ dm^6$$

Correcting these equilibrium constants for activity effects using the equations

$$K^o_{s0} = K_{s0}\ y^2_{\pm} \qquad \text{and} \qquad \beta^o_2 = \beta_2/y^2_{\pm}$$

causes a greater divergence between the two sets of data, and the nature of this difference therefore lies elsewhere. In the above equations, $y_\pm$ is the mean molar activity coefficient which can be calculated from various forms of the Debye-Hückel equation.

According to L'Her the N_3^- ion is a weak base in dimethyl sulfoxide and the stability of the complexes are therefore a function of the acidity of the medium. L'Her has shown (in the same paper) that the weak base CH_3COO^- in dimethylsulfoxide is greatly effected by the nature of the supporting electrolyte ($LiClO_4$ compared to $(C_2H_5)_4NClO_4$)); i.e. the strong acid Li^+ acts to increase K_{s0} and decrease β_2. Both Parker and L'Her were careful to eliminate acidic impurities in the solvent, and since the only acids present in both sets of experiments were Ag^+ and $(C_2H_5)_4N^+$, the reason for the differences in their results must again lie elsewhere. It is doubtful that the differences are due to computational methods since they were similar and should not therefore diverge to such a large extent. The fact that the temperatures are different does not explain the differences in the two results unless L'Her's work involves a much lower temperature than that assumed by the compiler.

In summary it appears to this evaluator that one set of data cannot be recommended over another at the time of this writing.

REFERENCES:

1. Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703.
2. Le Démézet, M.; Madec, D.; L'Her, M. *Bull. Soc. Chim. Fr.* 1970, 365.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Tetraethylammonium azide; $(C_2H_5)_4NN_3$; [993-20-4]

(3) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0]

(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.05 mol dm^{-3}; temperature is 25°C.

$$\log K_{s0}(AgN_3) = -6.5 \quad ; \quad K_{s0}(AgN_3) = 3.2 \times 10^{-7}\ mol^2\ dm^{-6}$$

$$\log K_{s0}(AgAg(N_3)_2) = -6.2; \quad K_{s0}(AgAg(N_3)_2 = 6.3 \times 10^{-7}\ mol^2\ dm^{-6}$$

The titration curve showed two well-defined plateaus corresponding to

$$Ag^+ + 2N_3^- \rightleftarrows Ag(N_3)_2^- \qquad \beta_2 = 1.0 \times 10^7\ mol^{-2}\ dm^6$$

$$Ag^+ + Ag(N_3)_2^- \rightleftarrows 2AgN_3(s) \qquad K = 1.6 \times 10^6\ mol^{-2}\ dm^{6*}$$

The soly product of AgN_3, $K_{s0}(AgN_3)$, is then obtained from

$$\log K_{s0}(AgN_3) = -1/2 \log(K\beta_2)$$

*Note: $K = [K_{s0}(AgAg(N_3)_2)]^{-1}$

AUXILIARY INFORMATION

METHOD:

The soly product and related equilibrium constants were determined from potentiometric titration data. E.m.f. measurements were made on the cell

$$Ag/Et_4NN_3\ (0.05M)//AgNO_3\ (0.01M)/Ag$$

where Et = C_2H_5 and // is a salt bridge containing satd tetraethylammonium picrate. A 0.05M $AgNO_3$ soln was titrated into the azide soln which was exposed to the atmosphere. The cell was thermostated and magnetically stirred during the titration.

SOURCE AND PURITY OF MATERIALS:

Dimethyl sulfoxide was dried with No. 4A molecular sieves and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and NaN_3 were used as received. Et_4NN_3 was prepd from the bromide and NaN_3, recrystallized from an organic solvent, washed with ether, and dried in vacuum at 20 - 80°C.

ESTIMATED ERROR:

Nothing specified, but precision in equilibrium constants is probably ±0.1 log units.

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Tetraethylammonium azide; $(C_2H_5)_4NN_3$; [993-20-4]
(3) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]
(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Le Démézet, M.; Madec, C.; L'Her, M.

Bull. Soc. Chim. Fr. 1970, 365-9.

VARIABLES:

One temperature; probably 22°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.11 mol dm^{-3}, and the temperature is about 22°C.

$$\log K_{s0}(AgN_3) = -7.5 \quad ; \quad K_{s0}(AgN_3) = 3.2 \times 10^{-8}\ mol^2\ dm^{-6}$$

Nowhere in the paper do the authors state the experimental temperature. Since they use a factor of 0.058 in the Nernst equation, the compiler assumes that this corresponds to room temp (22°C) as described in a previous paper. (1) The factor 2.3RT/F = 0.0586 at 22°C whereas the authors use their experimental value (1) of the Nernst slope. The ionic strength is about 0.11 mol dm^{-3}, and the uncertainty is due to the uncertainty in the concentration of the $AgClO_4$ titrant (a 0.05M soln was used in ref 1).

The authors were also able to characterize the following equilibrium:

$$Ag^+ + 2N_3^- \rightleftarrows Ag(N_3)_2^-$$

$$\log(\beta_2/mol^{-2}\ dm^6) = 8.0$$

AUXILIARY INFORMATION

METHOD:

The soly product and stability constant were calcd from potentiometric titration data obtained from the cell

$$Ag/Et_4NN_3(0.01M),\ Et_4NClO_4(0.1M)//-$$

$$LiCl(0.1M),\ AgCl_2^-(0.001M)/Ag$$

where Et = C_2H_5. The azide soln was titrated with $AgClO_4$ soln probably at about 22°C. The equilibrium constants were calcd from various sections of the titration curve.

SOURCE AND PURITY OF MATERIALS:

Commercial Et_4NClO_4, Et_4NCl, KN_3, and $(CH_3)_2SO$ were used, but no details on purification are given. Et_4NN_3 was prepared by dissolving KN_3 and Et_4NCl in absolute alcohol and separating the resulting soln from the insoluble KCl. It is likely that all reagents were purified as described in reference 1.

ESTIMATED ERROR:

Nothing specified, but precision in equilibrium constants is probably ±0.1 log units.

REFERENCES:

1. Courtot-Coupez, J.; L'Her, M.
Bull. Soc. Chim. Fr. 1969, 675.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Sodium azide; NaN_3; [26628-22-8]
(3) Sodium nitrate; $NaNO_3$; [7631-99-4]
(4) Tetraethylammonium azide; $(C_2H_5)_4NN_3$; [993-20-4]
(5) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0]
(6) Formamide; CH_3NO; [75-12-7]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1969, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength was varied from 0.05 - 0.1 mol/dm^3

$\log K_{s0}(AgN_3) = -7.7$; $K_{s0}(AgN_3) = 2.0 \times 10^{-8}$ mol^2/dm^6

AUXILIARY INFORMATION

METHOD:

The soly product was calcd from potentiometric titration data using the cell

$Ag/MN_3/(xM)//AgNO_3(0.01M)/Ag$

where // is a satd tetraethylammonium picrate salt bridge, and MN_3 is either tetraethylammonium- or sodium azide. 0.05 or 0.1M $AgNO_3$ was titrated into 0.05 or 0.1M azide soln which was exposed to the atmosphere. The cell was thermostated at 25°C and stirred magnetically during the titration.

COMMENTS AND/OR ADDITIONAL DATA:

The titration curves showed only one inflection point indicating that the formation of $Ag(N_3)_2^-$ is negligible under the described experimental conditions.

SOURCE AND PURITY OF MATERIALS:

Formamide was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and NaN_3 were used as received. Tetraethylammonium azide was prepared from the bromide and NaN_3, recrystallized from an organic solvent, washed with ether, and dried in vacuo at 20-80°C.

ESTIMATED ERROR:

Nothing is specified, but precision in $\log K_{s0}$ is probably about ±0.1 log units.

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Sodium azide; NaN_3; [26628-22-8]
(3) Sodium nitrate; $NaNO_3$; [7631-99-4]
(4) Hexamethylphosphorotriamide; $C_6H_{18}N_3OP$; [680-31-9]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* <u>1967</u>, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.05 mol/dm^3. The solubility of AgN_3 in excess azide was determined to be governed by the following reactions:

$$2AgN_3(s) \rightleftarrows Ag^+ + Ag(N_3)_2^- \qquad K_{s0}(AgAg(N_3)_2) = 2.0 \times 10^{-6}\ mol^2\ /dm^6$$

$$AgN_3(s) \rightleftarrows Ag^+ + N_3^- \qquad K_{s0}(AgN_3) = 2.8 \times 10^{-9}\ mol^2\ /dm^6$$

$$Ag^+ + 2N_3^- \rightleftarrows Ag(N_3)_2^- \qquad \beta_2 = 2.5 \times 10^{11}\ dm^6\ /mol^2$$

AUXILIARY INFORMATION

METHOD:

The soly products and stability const were determined from potentiometric titration data using the cell

$$Ag/NaN_3(0.05M)//AgNO_3(0.01M)/Ag$$

where // is a salt bridge containing a satd soln of tetraethylammonium picrate. 0.05M $AgNO_3$ was titrated into the azide soln which was exposed to the atmosphere. The cell was thermostated at 25°C and stirred magnetically during the titration. The titration curve showed two well-defined plateaus from which the constants β_2 and $K_{s0}(AgAg(N_3)_2)$ were calcd. The soly product for AgN_3 was calcd from

$$K_{s0}(AgN_3) = \{K_{s0}(AgAg(N_3)_2)/\beta_2\}^{1/2}$$

SOURCE AND PURITY OF MATERIALS:

Hexamethylphosphorotriamide was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and NaN_3 were used as received.

ESTIMATED ERROR:

Nothing specified, but precision in the equilibrium constants is probably $\leqslant \pm 10\%$.

REFERENCES:

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Sodium azide; NaN_3; [26628-22-8]
(3) Sodium nitrate; $NaNO_3$; [7631-99-4]
(4) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0]
(5) Methanol; CH_4O; [67-56-1]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.01 mol/dm^3

$\log K_{s0}(AgN_3) = -11.2$: $K_{s0}(AgN_3) = 6.3 \times 10^{-12}$ mol^2/dm^6

AUXILIARY INFORMATION

METHOD:

The soly product was calcd from potentiometric titrn data using the cell

$Ag/MN_3(0.01M)//AgNO_3(0.0062M)/Ag$

where // is a satd tetraethylammonium picrate salt bridge, and MN_3 is either tetraethylammonium- or sodium azide. 0.01M $AgNO_3$ was titrated into the azide soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titration.

SOURCE AND PURITY OF MATERIALS:

Methanol was purified as described elsewhere (1). Analar grade NaN_3 and $AgNO_3$ were used as received. Tetraethylammonium azide was prepared from the bromide and NaN_3, recrystallized from an organic solvent, washed with ether and dried in vacuo at 20-80°C.

ESTIMATED ERROR:

Nothing specified, but precision in $\log K_{s0}$ probably $\sim \pm 0.1$ log units.

COMMENTS AND/OR ADDITIONAL DATA:

The titration curve showed only one inflection indicating that the formation of $Ag(N_3)_2^-$ is insignificant under the described experimental conditions.

REFERENCES:

1. Clare, B.W.; Cook, D.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1966, *88*, 1911.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]

(2) Pyridine; C_5H_5N; [110-86-1]

ORIGINAL MEASUREMENTS:

Piechowicz, T. *Bull. Soc. Chim. Fr.* 1971, 1566-7.

VARIABLES:

Temperature: range 15 to 80°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The author reported composition in weight %, and conversions to molality were made by the compiler.

$t/^\circ C$	c_{Ag}/wt %	$c_{Ag}/\mathrm{mol\ kg^{-1}}$
15.0	34.7	3.55
20.0	33.18	3.313
20.0	33.22	3.319
20.0	33.23	3.320
30.0	31.2	3.03
40.0	28.9	2.71
50.0	25.9	2.33
60.0	23.5	2.05
70.0	20.8	1.75
80.0	18.4	1.50

AUXILIARY INFORMATION

METHOD:

Solutions were prepared isothermally by agitating a soln containing excess AgN_3 in a sealed 3-necked flask. The pressure within the flask was maintained at atm pressure (1,2). When equilibrium was attained (no details given), an aliquot for analysis was filtered through a cotton filter into a tared pipet which was provided with two stopcocks. The soln was weighed and analysed for silver by titration with NH_4SCN. Analysis (no details given) of the solid phase showed it to be AgN_3.

SOURCE AND PURITY OF MATERIALS:

The water content of the anhydrous pyridine was 0.05% (by wt) as determined by Karl Fischer titration. No other details were given.

ESTIMATED ERROR:

Soly $\sigma \simeq \pm 0.004$ mol/kg at 20°C (compiler)
Temperature: ±0.05°C
Nothing else is specified.

REFERENCES:

1. Schutze, H.; Piechowicz, T. *Helv. Chim. Acta* 1943, *26*, 242.
2. Guyer, A.; Piechowicz, T. *Helv. Chim. Acta* 1944, *27*, 858: 1945, *28*, 401.

COMPONENTS:

(1) Silver azide; AgN_3; [13863-88-2]
(2) Sodium azide; NaN_3; [26628-22-8]
(3) Sodium nitrate; $NaNO_3$; [7631-99-4]
(4) N-methyl-2-pyrrolidinone; C_5H_9NO; [872-50-4]

ORIGINAL MEASUREMENTS:

Virtanen, P.O.I.; Kerkela, R.

Suomen Kem. 1969, *B42*, 29-33.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.01 mol/dm^3

$$\log K_{s0}(AgN_3) = -10.91 \quad : \quad K_{s0}(AgN_3) = 1.23 \times 10^{-11}\ mol^2/dm^6$$

In excess azide, the soly is increased due to the formation of $Ag(N_3)_2^-$. The overall formation constant of this complex was determined to be

$$\log\beta_2 = 12.60 \quad : \quad \beta_2 = 3.98 \times 10^{12}\ dm^6/mol^2$$

AUXILIARY INFORMATION

METHOD:

The soly product and stability const were calcd from potentiometric titrn data obtained from the cell

$$Ag/AgNO_3(0.01M)//KCl(1M)// - AgNO_3(0.01M)/Ag$$

One side of this cell was titrated with 0.01M NaN_3. The titration curve showed two equivalent points, and the equilibrium constants were calcd by a graphical method.

SOURCE AND PURITY OF MATERIALS:

Technical grade solvent was distilled through a Vigreux column under vacuo, and 80% was retained for use. Water content was < 0.002M (Karl Fischer titrn), and a conductometric titn of the acidified solvent with stnd NaOH confirmed the absence of amino acid impurities. Commercial reagent grade NaN_3 was dried at an "appropriate" temperature. Polished silver wire electrodes were used.

ESTIMATED ERROR:

K_{s0}: nothing specified, and a precision ~ ±0.05 log units can be assumed (compiler).

Temp: ±0.02°C.

COMMENTS AND/OR ADDITIONAL DATA:

In calculating K_{s0} and β_2, it was assumed that $AgNO_3$ was completely ionized. If $AgNO_3$ is not completely ionized, the authors point out that $\log K_{s0}$ may be more negative by as much as 0.2 to 0.3 log units.

REFERENCES:

COMPONENTS:

(1) Silver cyanamide; Ag_2CN_2; [3384-87-0]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

August 1978

CRITICAL EVALUATION:

The two results for K_{s0} (Ag_2CN_2) in water at 298 K are so divergent that it is clear that at least one of the studies is in serious error. Since the work of Sato and Sato ignores hydrolysis, it is highly probable that their K_{s0} is in error due to the overestimation of the CN_2^{2-} concentration. It is also clear from the work of Kitaev et. al. that the CN_2^{2-} concentration is small due to its hydrolysis, and the evaluator would give preference to this latter work.

REFERENCES:

1. Sato, M.; Sato, M. *J. Electrochem. Soc. Jpn.* 1954, *22*, 411.
2. Kitaev, G.A.; Bol'shchikova, T.P.; Yatlova, L.E. *Zh. Neorg. Khim.* 1971, *16*, 3173.

COMPONENTS:

(1) Silver cyanamide; Ag_2CN_2; [3384-87-0]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sato, M., Sato, M.

J. Electrochem. Soc. Jpn. 1954, *22*, 411-17.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Hitoshi Ohtaki

EXPERIMENTAL VALUES:

$$C_{Ag} = 2.62 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_{SO} = 7.23 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$Ag/Ca(HCN_2)_2$, H_2CN_2, $Ag_2CN_2(s)$//Satd NH_4NO_3//Satd NH_4NO_3//0.1M $AgNO_3$/Ag

The concentration of Ag^+ (x) in the cell is determined from

$$E = (RT/nF) \ln (c_1/c_2)$$

$$= 0.059 \log (0.081/x)$$

where c_1 is the concentration of free Ag^+ in the reference half-cell (0.1M $AgNO_3$) and $c_2 = x$, the degree of dissociation of $AgNO_3$ in 0.1M soln being assumed to be 0.81 (without any reference). The emf value obtained was 0.4667 V. The liquid junction potential in the cell was neglected. Activity of Ag^+ ion in the soln, a_{Ag}, is estimated to be $9.84 \cdot 10^{-10}$ by using a cell having a 0.1M KCl-Hg_2Cl_2 calomel electrode as a reference half-cell.

SOURCE AND PURITY OF MATERIALS:

$CaCN_2$ and H_2CN_2 are prepared and purified according to Sugino and Kanayama (1). The method of preparation of Ag_2CN_2 crystals is not described. Purity of the materials are not given.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Sugino, K.; Kanayama, M. *J. Electrochem. Soc. Jpn.* 1940, *8*, 250.

COMPONENTS:

(1) Silver cyanamide; Ag_2CN_2; [3384-87-0]

(2) Nitric acid; HNO_3; [7697-37-2]

(3) Potassium nitrate; KNO_3; [7757-79-1]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kitaev, G.A.; Bol'shchikova, T.P.; Yatlova, L.E. *Zh. Neorg. Khim.* 1971, *16*, 3173-4.

VARIABLES:

pH at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at approximately 1 mol dm^{-3}.

$$K_{s0}(Ag_2CN_2) = 3.98 \times 10^{-24}\ mol^3\ dm^{-3}.$$

The solubility, S, varies as a function of pH according to

$$\log S = \log [Ag_2CN_2]_{sat} = (2/3)\log[H^+] - (1/3)\log(0.5K_c/K_{s0})$$

where (1)

$$H_2CN_2 \rightleftarrows 2H^+ + CN_2^{2-} \qquad K_c = 7.95 \times 10^{-23}\ mol^2\ dm^{-6}$$

AUXILIARY INFORMATION

METHOD:

Solid Ag_2CN_2 was placed in 1M KNO_3 solutions and equilibrated at 25°C (no details given). The pH was adjusted with HNO_3. The solution was analysed for Ag^+ with thiocyante (2).
The soly product is defined by

$$K_{s0}(Ag_2CN_2) = [Ag^+]^2[CN_2^{2-}]$$

Since H_2CN_2 is a weak acid, the soly product was calculated from

$$K_{s0}(Ag_2CN_2) = (0.5)\ S^3(K_c/\beta_c)$$

where S is the measured solubility and

$$\beta_c = [H^+]^2 + K_{a1}\ [H^+] + K_c$$

The value for the first disociation constant of H_2CN_2 is (1,3)

$$K_{a1} = 5.25 \times 10^{-11}\ mol\ dm^{-3}$$

SOURCE AND PURITY OF MATERIALS:

Ag_2CN_2 prepd by adding a 25% NH_3 soln to 0.5M Ag-salt soln until the hydroxide completely redissolved. To this a soln of cyanamide (H_2CN_2) was added which precipitated the (yellow) Ag_2CN_2. The ppt was collected on a filter and "thoroughly washed free of excess cyanamide and ammonia."
No other details were given.

ESTIMATED ERROR:

Nothing specified

REFERENCES:

1. Bol'shchikova, T.P. *Candidates Thesis*. Sverdlovsk. 1969.
2. Lur'e, Yu, Yu. *Spravochnik po Analiticheskoi Khimii*. Izd. Khimya, Moscow, 1965.
3. Albert, A.; Serjeant, E.P., *Ionization Constants of Acids and Bases*. Methuen. London. 1962. (translated into Russian, 1964.)

COMPONENTS:

(1) Silver dicyanamide; $AgN(CN)_2$;

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Birckenbach, L.; Hüttner, K.

Z. Anorg. Chem. 1930, *190*, 1-26.

VARIABLES:

One temperature: 18°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$$C_{Ag} = 3.7 \times 10^{-5} \text{ mol dm}^{-3}$$

$$K_{s0}(AgN(CN)_2) = (C_{Ag})^2 = 1.4 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$Ag/AgN(CN)_2(sat)//KNO_3(con)//-$$
$$AgNO_3(0.1M)/Ag$$

The solubility of $AgN(CN)_2$, S, is obtained from the relation

$$\log S = \log C_1 - EF/(RT \ln 10)$$

where C_1 is the $[Ag^+]$ in 0.1M $AgNO_3$ and is evaluated using a value of 0.82 (no reference given) for the degree of dissociation* of $AgNO_3$. The observed e.m.f. was reported as 0.1929 V.

*See additional discussion in the COMMENTS section below.

SOURCE AND PURITY OF MATERIALS:

$AgN(CN)_2$ prepared (1) by refluxing a stoichiometric mixture of Ag_2CN_2 and BrCN for 3 days. To separate $AgN(CN)_2$ from AgBr, the mixed ppt was treated with con NH_3 soln, the insol AgBr removed by filtration, and $AgN(CN)_2$ pptd by addition of HNO_3. This process was repeated, and the salts analysed (2) as 99.7% pure by dissolving in hot con H_2SO_4 followed by potentiometric titration with KI soln. Freshly distilled water was used.

ESTIMATED ERROR:

Solubility: not specified.

E.m.f.: not specified

Temperature: ∿2°C

REFERENCES:

1. Birckenbach, L.; Hüttner, K. *Z. Anorg. Chem.* 1930, *190*, 38.
2. Hüttner, K. Knappe, S. *Z. Anorg. Chem.* 1930, *190*, 27.
3. Kirschner, A. *Z. Physik. Chem.* 1912, *79*, 245.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver dicyanamide; $AgN(CN)_2$; (2) Water; H_2O; [7732-18-5]	Birckenbach, L.; Hüttner, K. *Z. Anorg. Chem.* <u>1930</u>, *190*, 1-26.

COMMENTS AND/OR ADDITIONAL DATA:

One aspect of this work which is not clear is concerned with the temperature of the measurement. On page 6 of this paper, the authors give a value of 18°C, whereas in the table on page 26 the temperature is given as 18 to 20°C. In their calculations using the Nernst equation, they use (RT/F) ln 10 = 0.0576 which corresponds to a temperature of 17.1°C.

It should be noted that the concentration of a satd soln of $AgN(CN)_2$ is given as ∿ 4 x 10^{-5} mol dm^{-3}, and it is therefore fairly certain that a large liquid junction potential exists.

In computing C_1 as 0.1 x 0.82, the authors refer to the number 0.82 as the "Aktivitätsfaktor" which is misleading because 0.82 is probably the degree of disociation, α. Similar values for α can be found in much of the older European literature (e.g. see reference 3). The mean molar activity coefficient for 0.1M $AgNO_3$ is approximately 0.73 (4).

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

1. Robinson, R.A.; Stokes, R.H. *Electrolyte Solutions*. Butterworths. London. <u>1959</u>.

COMPONENTS:

(1) Methyl tricyanamide argentate; $AgC(CN)_3$;

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Birckenbach, L.; Hüttner, K.

Z. Anorg. Chem. 1930, *190*, 1-26.

VARIABLES:

One temperature: 18°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$$c_{Ag} = 6.7 \times 10^{-5} \text{ mol dm}^{-3} .$$

$$K_{s0}(AgC(CN)_3) = (c_{Ag})^2 = 4.6 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$Ag/AgC(CN)_3(sat)//KNO_3(con)//AgNO_3(0.1M)/Ag$$

The solubility of $AgC(CN)_3$, S, is obtained from the relation

$$\log S = \log C_1 - EF/(RT \ln 10)$$

where C_1 is the $[Ag^+]$ in 0.1M $AgNO_3$ and is evaluated using a value of 0.82 (no reference is given) for the degree of dissociation* of $AgNO_3$. The observed e.m.f. was reported as 0.1779 V.

*See additional discussion in the COMMENTS section below.

SOURCE AND PURITY OF MATERIALS:

$AgC(CN)_3$ prepared as described previously (1). The salt analysed (2) as 99.8% pure by dissolving in hot con H_2SO_4 followed by potentiometric titration with KI. Freshly distilled water was used.

ESTIMATED ERROR:

Solubility: not specified.
E.m.f.'s: not specified.

Temperature: $\sim 2^{\circ}$C.

REFERENCES:

1. Birckenbach, L.; Hüttner, K. *Ber.* 1929, *62*, 157.
2. Hüttner, K.; Knappe, S. *Z. Anorg. Chem.* 1930, *190*, 27.
3. Kirschner, A. *Z. Physik. Chem.* 1912, *79*, 245.

COMPONENTS:

(1) Methyl tricyanamide argentate; $AgC(CN)_3$;

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Birckenbach, L.; Hüttner, K.
Z. Anorg. Chem. 1930, *190*, 1-26.

COMMENTS AND/OR ADDITIONAL DATA:

One aspect of this work which is not clear is concerned with the temperature of the measurement. On page 6 of this paper, the authors give a value of 18°C, whereas in the table on page 26 the temperature is given as 18 to 20°C. In their calculations using the Nernst equation, they use (RT/F)ln 10 = 0.0576 which corresponds to a temperature of 17.1°C.

It should be noted that the concentration of a satd soln of $AgC(CN)_3$ is given as $\sim 7 \times 10^{-5}$ mol dm^{-3}, and it is therefore fairly certain that a large liquid junction potential exists.

In computing C_1 as 0.1×0.82, the authors refer to the number 0.82 as the "Aktivitätsfactor" which is misleading because 0.82 is probably the degree of dissociation, α. Similar values for α can be found in much of the older European literature (e.g. see reference 3). The mean molar activity coefficient for 0.1M ($AgNO_3$) is approximately 0.73 (4).

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

4. Robinson, R.A.; Stokes, R.H.
Electrolyte Solutions.
Butterworths. London. 1959.

COMPONENTS:	EVALUATOR:
(1) Silver cyanate; AgOCN; [3315-16-0] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ U.S.A. October 1978

CRITICAL EVALUATION: Of the three experimental studies available (1-3), two are associated with some uncertainty as to the exact temperature used (1,3): it is probable that the latter study (3) employed a temperature of 293 K. Since Birckenbach and Hüttners' result also includes an uncertainty due to the neglect of the liquid junction potential, their data will not be considered in the discussions below.

Lodzinska and Sinda suggested that several sources of errors in C_{Ag} in solutions of excess OCN^- arise due to the reactions

$$HOCN + H_2O = NH_3 + CO_2$$

$$HOCN + NH_3 = CO(NH_2)_2$$

$$KOCN + 2H_2O = KHCO_3 + NH_3$$

They conclude that the extent of these reactions in excess OCN^- is large enough that the ternary system does not reach equilibrium, and that calculations of the stability constant β_2 (e.g. as in ref 2) are therefore incorrect. However these authors claim that in the binary $AgOCN/H_2O$ system, the above reactions are slow enough to permit thermodyamically significant C_{Ag} values to be determined. In a subsequent study on the hydrolysis of NaOCN (4), it was found that the hydrolysis of dilute (up to about 0.2 mol dm^{-3}) NaOCN solutions was negligible for periods of several hours at temperatures up to 323 K. There is no doubt that NaOCN and KOCN solutions hydrolyse to produce NH_3 (2-4): the major disagreement lies, essentially, in the rates of hydrolysis. Veys (4) has shown that the rate of hydrolysis is acid catalysed, and that small amounts of acid will increase the rate by about a factor of 30. Based on Veys' careful work, the rate of hydrolysis observed by Lodzinska and Sinda in their most dilute KOCN solution (0.2 mol dm^{-3}) appears too rapid. It appears to this evaluator that the data of Cohen-Adad are not subject to any error due to the neglect of hydrolysis in the determination of C_{Ag}. In fact, the data from references (2) and (3) appear to be complimentary. Using this data, the evaluator has been able to estimate the enthalpy of solution (ΔH^o_{so}), and the resulting value is very reasonable when compared to ΔH^o_{so} for AgN_3, AgCN, AgSeCN, and AgSCN (see the critical evaluations for these aqueous systems). On this basis, the evaluator suggests that these data can be designated as tentative.

TENTATIVE VALUES

In addition to the tentative values presented in the table below, several provisional values based on calculations by the evaluator are also given. Units are mol dm^{-3} for C_{Ag}, and mol^2 dm^{-6} for K^o_{so}. The C_{Ag} data apply to the pure (binary) $AgOCN/H_2O$ system.

T/K	Reference	10^4C_{Ag}	$10^7K^o_{so}(AgOCN)$	$10^8K^o_{so}(AgAg(OCN)_2)$	K^o_{s2}
293	3	4.11	$1.5^{a,b}$	$0.7^{a,b}$	$0.5^{a,c}$
303	2	7.4^a	4.8	2.3	0.048

a. Calculated by the evaluator (see below).
b. Provisional value.
c. Highly provisional value

SOLUBILITY OF AgOCN IN PURE WATER

In the binary $AgOCN/H_2O$ system, hydrolysis is neglected and all activity coefficients are assumed to equal unity. The solubility of AgOCN under these conditions is given by

$$C_{Ag} = [Ag^+] + K^o_{so}(AgOCN) \quad K^o_{s2}/[Ag^+] \qquad [1]$$

and

$$C_{Ag} = K^o_{so}(AgOCN)/[Ag^+] + 2K^o_{so}(AgOCN) \quad K^o_{s2}/[Ag^+] \qquad [2]$$

COMPONENTS:	EVALUATOR:
(1) Silver cyanate; AgOCN [3315-16-0] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. October 1978

CRITICAL EVALUATION: (Continued)

Eliminating c_{Ag} between eqs [1] and [2].

$$[Ag^+]^2 = K^o_{so}(AgOCN)\ (1 + K^0_{s2}) \qquad [3]$$

Using Cohen-Adad's data for 303 K, eq [3] yields $[Ag^+] = 7.09 \times 10^{-4}$ mol dm^{-3}, and from eq [1]

$$c_{Ag} = 7.09 \times 10^{-4} + 0.32 \times 10^{-4} = 7.42 \times 10^{-4} \text{ mol dm}^{-3}$$

At 303 K the species $Ag(OCN)_2^-$ thus constitutes some 4% of the total solubility of AgOCN in pure water. Assuming this fraction is the same for 293K, we can estimate the following for 293K:

$$[Ag^+] \simeq c_{Ag}(7.09/7.42) = 3.93 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[Ag(OCN)_2^-] = c_{Ag} - [Ag^+] = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[OCN^-] = c_{Ag} - 2[Ag(OCN)_2^-] = 3.74 \times 10^{-4} \text{ mol dm}^{-3}$$

Using these concentrations, and assuming all activity coefficients are unity, the equilibrium constants for 293 K were calculated and entered in the above table. The heat of solution was calculated from the two K^o_{so} (AgOCN) values at 293 and 303 K, and the result is $\Delta H^o_{so} = 86$ kJ/mol. While this value is consistent with those generally found for the silver pseudohalides as mentioned above, it is in serious disagreement with the value of 54.9 kJ/mol calculated from heats of formation data (5).

REFERENCES:

1. Birckenbach, L.; Hüttner, K. *Z. Anorg. Chem.* 1930, *190*, 1.
2. Cohen-Adad, R. *Compt. Rend.* 1954, *238*, 810: *Thèses*. Université D'Alger. 1954.
3. Lodzinskia, A.; Sinda, F. *Roczniki Chem.* 1964, *38*, 117.
4. Veys, P. *Thèses*. Université De Lyon. 1968.
5. Wagman, D.D.; Evans, W.H.; Parker, V.B.; Halow, I.; Bailey, S.M.; Schumm, R.H. *U.S. National Bureau of Standards TN-270-3*. 1968; *TN-270-4*. 1969.

COMPONENTS:

(1) Silver cyanate; AgOCN; [3315-16-0]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Birckenbach, L.; Hüttner, K.

Z. Anorg. Chem. 1930, *190*, 1-26.

VARIABLES:

One temperature: 18°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$$c_{Ag} = 4.8 \times 10^{-4} \text{ mol dm}^{-3}$$

$$K_{s0}(\text{AgOCN}) = (c_{Ag})^2 = 2.3 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$\text{Ag/AgOCN(sat)//KNO}_3\text{(con)// - AgNO}_3\text{(0.1M)/Ag}$$

The soly of AgOCN, S, is obtained from the relation

$$\log S = \log C_1 - EF/(RT\ln 10)$$

where C_1 is the[Ag^+] in 0.1M $AgNO_3$ and is evaluated using a value of 0.82 (no reference given) for the degree of dissociation* of $AgNO_3$. The observed e.m.f. was reported as 0.1284 V.

*See additional discussion in the COMMENTS section below.

SOURCE AND PURITY OF MATERIALS:

Presumably AgOCN prepared by precipitation from solutions of $AgNO_3$ and KOCN, washed with alcohol, ether, and dried in a desiccator (1). Silver analysis indicated a purity of 99.6%. KOCN was prepared by the method of Cranston and Livingston. (2)

Freshly distilled water was used.

ESTIMATED ERROR:

Solubility: not specified.

E.m.f.: not specified.

Temperature: ∿2°C (compiler).

REFERENCES:

1. Hüttner, K.; Knappe, S. *Z. Anorg. Chem.* 1930, *190*, 27.
2. Cranston; Livingston. *J. Chem. Soc.* 1926, 501.
3. Kirschner, A. *Z. Physik. Chem.* 1912, *79*, 245.

COMPONENTS:

(1) Silver cyanate; AgOCN; [3315-16-0]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (Continued)

Birckenbach, L.; Hüttner, K.

Z. Anorg. Chem. 1930, *190*, 1-26.

COMMENTS AND/OR ADDITIONAL DATA:

One aspect of this work which is not clear is concerned with the temperature of the measurement. On page 6 of the paper the authors give a value of 18°C, whereas in the table on page 26 the temperature is given as 18 to 20°C. In their calculations using the Nernst equation, they use (RT/F) ln 10 = 0.576 which corresponds to a temperature of 17.1°C.

It should be noted that the concentration of a satd soln of AgOCN is given as $\sim 5 \times 10^{-4}$ mol dm^{-3}, and it is therefore fairly certain that a large liquid junction potential exists.

In computing C_1 as 0.1 x 0.82, the authors refer to the number 0.82 as the "Aktivitätsfaktor" which is misleading because 0.82 is probably the degree of dissociation, α. Similar values for α can be found in much of the older European literature (e.g. see ref 3). The mean molar activity coefficient of 0.1M $AgNO_3$ is approximately 0.73 (4).

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

4. Robinson, R.A.; Stokes, R. H. *Electrolyte Solutions.* Butterworths. London. 1959.

COMPONENTS:

(1) Silver cyanate; AgOCN; [3315-16-0]

(2) Sodium cyanate; NaOCN; [917-61-3]

(3) Water; H_2C; [7732-18-5]

ORIGINAL MEASUREMENTS:

Cohen-Adad, R. *Comptes Rend.* 1954, *238*, 810-12.[1]

VARIABLES:

Concentration of NaOCN at 30°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: α is the fraction of Ag^+ and the concentration of OCN^- was calcd by the compiler from $[OCN^-] = (1 - \alpha)\mu$ where μ is the ionic strength. Units of $[OCN^-]$ and C_{Ag} are mol dm^{-3}.

α	$10^3[OCN^-]$	10^3C_{Ag}	α	$10^3[OCN^-]$	10^3C_{Ag}
0.0885	3.081	3.380	0.6937	0.520	1.697
0.0978	3.395	3.763	0.8195	0.287	1.589
0.1405	2.294	2.669	0.864	0.347	2.550
0.1800	1.813	2.211	0.906	0.233	2.476
0.2611	1.370	1.854	0.924	0.246	3.240
0.5692	0.668	1.550			

The data were used (see below) to calc the thermodynamic equilibrium constants.

$$K^o_{s0}(AgAg(OCN)_2) = 2.3 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

$$\beta^o_2 = 1.0 \times 10^5 \text{ mol}^{-2} \text{ dm}^6$$

$$K^o_{s0}(AgOCN) = \sqrt{(K^o_{s0}(AgAg(OCN)_2)/\ \beta^o_2\ )} \quad = 4.8 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

Note that the equilibrium constant K^o defined below is equal to $\left(K^o_{s0}(AgAg(OCN)_2)\right)^{-1}$. Also note that in satd solns, $\mu = C_{Ag}$.

AUXILIARY INFORMATION

METHOD:

The titrn of NaOCN with $AgNO_3$ followed conductometrically, and a sharp break in the titrn curve occurred at saturation. Soly prod $K^o_{s0}(AgOCN) = [Ag^+] \times [OCN^-]\ y^2_{\pm}$ was found to depend upon [NaOCN] thereby indicating presence of a complex species. Complex identified as $Ag(OCN)^-_2$ from equiv cond determinations of non-satd solns where α was varied at const ionic strength: the continuous variation method of Job(2) confirmed the stoichiometry of the complex. For the reactions (in satd solns)

$$Ag^+ + 2OCN^- \rightleftarrows Ag(OCN)^-_2 \qquad \beta_2$$

and

$$Ag^+ + Ag(OCN)^-_2 \rightleftarrows 2AgOCN(s) \qquad K$$

mass balance considerations lead to

$$C_{Ag} = A/\sqrt{(1-\alpha)[\alpha - B(1-\alpha)y_{\pm}]}$$

where

$$A^2 = \left\{2 + (K^o\beta^o_2)^{-\frac{1}{2}}\right\}K^o \quad : B = K^o/A^2$$

Values of A and B determined from the C_{Ag} and α data in the above table, and the mean activity coeff calcd from

$$\log y_{\pm} = -0.51\mu^{1/2}.$$

SOURCE AND PURITY OF MATERIALS:

NaOCN prepared by the method of Hackspill and Grandadam (3): it was recrystallized twice and analysis by potentiometric titrn with $AgNO_3$ indicated a purity > 99%. Distilled water was used. No other details given.

ESTIMATED ERROR:

Nothing specified. Since the values of A and B were not given, the compiler could not estimate the stnd deviations in K_{s0} and β_2.

REFERENCES:

1. Cohen-Adad, R. *Thèses.* L'Université D'Alger. 1954.
2. Job. *Thèses.* Paris. 1921; *Les methodes physiques appliquees à la Chimie.* Dion. Paris. 1926.
3. Hackspill, Grandadam. *Ann. Chim.* 1926, *5*, 218.

COMPONENTS:

(1) Silver cyanate; AgOCN; [3315-16-0]
(2) Potassium cyanate; KOCN; [590-28-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lodzinska, A.; Sinda, F. *Roczniki Chem.* 1964, *38*, 117-21.

VARIABLES:

One temperature: probably 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

TABLE 1 Solubility of AgOCN (C_{Ag}) in KOCN Solutions

[KOCN]/mol dm^{-3}	$10^3 C_{Ag}$/mol dm^{-3}
0	0.4106
0.20	4.38
1.02	6.98
1.44	8.14
1.83	9.78

AUXILIARY INFORMATION

METHOD:

For the binary AgOCN/H_2O system, equil was attained by shaking (no other details given), and C_{Ag} detd by a Volhard titrn. For the ternary system, the concn of the initial KOCN soln was determined by titrn with $AgNO_3$. Dried AgOCN was added to the KOCN soln and the mixture shaken for 4-6 h. No details were given. C_{Ag} was detd by a Volhard titrn. Authors stated that reproducibility was satisfactory, but no data were given which indicate the magnitude of the experimental error. Temperature of system during equilibrium not specified, but in another part of the paper concerning the spectroscopy of the mixed solns, the authors state that the measurements were performed at 20°C. It appeared to the compiler that reference to this temperature pertains only to the spectroscopic measurements: it is possible that this statement refers to all measurements.

SOURCE AND PURITY OF MATERIALS:

KOCN prepared by fusing K_2CO_3 with urea: further purification, if carried out, was not indicated. AgOCN prepared by mixing solutions of $AgNO_3$ and KOCN. The ppt was dried to constant weight: further purification, if carried out, was not specified. The source and purity of the water was not described.

ESTIMATED ERROR:

Reproducibility said to be within exptl error, but numerical data were not given.

REFERENCES:

COMPONENTS:

(1) Silver cyanate; AgOCN; [3315-16-0]

(2) Potassium cyanate; KOCN; [590-28-3]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Lodzinska, A.; Sinda, F. *Roczniki Chem.* 1964, *38*, 117-21.

COMMENTS AND/OR ADDITIONAL DATA:

A plot of log C_{Ag} against log KOCN using the data in Table 1 results in a curve with a slope of about 0.5 which, according to the authors, indicates the presence of complexes of varying composition. Upon standing for two weeks, an intense odor of NH_3 was detected from the ternary system. This was attributed to the hydrolysis of KOCN according to

$$KOCN + H_2O = KHCO_3 + NH_3$$

The authors measured the NH_3 concentration in KOCN/H_2O mixtures as a function of time, and the results are given in Table 2. The concentration of NH_3 was determined spectroscopically at 420 mμ using the Nessler reagent. The measurements were carried out at 20°C. Determination of $[NH_3]$ in the ternary system, AgOCN/KOCN/H_2O, was not carried out because of pptn of AgI (due to the Nessler reagent). The authors state that equilibrium in the ternary system is never attained, and that there is a continuous but slow increase in C_{Ag} (due to formation of $Ag(NH_3)_n^+$ complexes). The measured C_{Ag} values after 4-6 h of shaking are, however, claimed to be accurate within the limits of experimental error: no quantitative information was given which would permit the estimation of the exptl error.

TABLE 2 $[NH_3]$ in KOCN/H_2O Solutions as a Function of Time

	$10^3[NH_3]$/mol dm^{-3}			
[KOCN]/mol dm^{-3}	5 min	2 h	4 h	25 h
0.2	0.196	0.234	0.358	0.785
1.0	0.818	1.89	4.47	15.1
1.4	1.07	3.25	6.20	17.2
1.8	1.22	3.05	4.97	27.4

COMPONENTS:	EVALUATOR:
(1) Silver cyanide; AgCN; [506-64-9] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. September 1978

CRITICAL EVALUATION:

The solubility of AgCN in aqueous solutions has been studied by direct solubility measurements (1-10,37) and by e.m.f. methods (11-21). No attempts to measure the standard half-cell potential of the Ag,AgCN electrode have been reported since AgCN is highly soluble in CN^- solutions. In saturated AgCN solutions, the principal species formed is the argentocyanide ion:

$$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad [1a]$$

Because of the high stability of the argentocyanide ion, equilibrium [1a] is often written in the equivalent form

$$AgAg(CN)_2(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad [1b]$$

To distinguish the solubility product of reaction [1] from reaction [3] below, we define

$$K_{s0}(AgAg(CN)_2) = [Ag^+][Ag(CN)_2^-] \qquad [2]$$

and the solubility product for the equilibrium

$$AgCN(s) \rightleftarrows Ag^+ + CN^- \qquad [3]$$

is defined by

$$K_{s0}(AgCN) = [Ag^+][CN^-] \qquad [4]$$

Direct Solubility Measurements

1. The binary $AgCN/H_2O$ system. The paper by Böttger (5) represents the singular attempt to measure the solubility in the pure binary system. Considering that the work was published in 1903, the care in purification of all materials is admirable even by todays standards. The distilled water was of high purity: its CO_2 content was quite low owing to the fact that it was stored in flasks with drying tubes containing NaOH and CaO, and the author noted that the conductivity of the water decreased upon storage. The major sources of errors in this study are the estimates of equivalent ionic conductances, his confusion concerning the nature of the chemical equilibria occuring, and a possible unknown error in resistance measurements due to capacitive effects (electrodes were not platinized and the solutions studied had conductivities of the order of 10^{-7} ohm^{-1}, and an experimental precision of about 10^{-8} ohm^{-1}). Böttger concluded that he was measuring two equilibria, [1] and [3] when in fact he was measuring only equilibrium [1]. The average of these two measurements is $K_{s0}(AgAg(CN)_2) = (2.5 \pm 0.3) \times 10^{-12}$ mol^2 dm^{-6} at 293K which is in agreement with the probable value of 2.4×10^{-12} mol^2 dm^{-6}.

2. Studies in the presence of complexing anions. The two earliest works (1,2) involving equilibria of the type

$$MAg(CN)_2 \rightleftarrows M^+ + Ag(CN)_2^- \qquad [5]$$

where M = Na(1) or Tl (2) are devoid of essential experimental details. Normally such papers would be rejected, but they represent the only papers published on the $NaAg(CN)_2$ and $TlAg(CN)_2$ aqueous systems.

Bassett and Corbet (7) reported the only phase study for the ternary $AgCN/KCN/H_2O$ system at 298 K. Several double salts and their hydrates were identified as discussed in the compilation. The reproducibility of the results was not specified, and only one source of error (KOH impurity in the KCN) was mentioned. All solutions containing excess KCN included an unspecified amount of KOH, and considering the effect of pH on the solubility c_{Ag} (9,10), the resulting error in c_{Ag} measured by Bassett and Corbet may be as high as ±5% for a 3% impurity.

Lucas' (6) calculations of $K_{s0}(AgAg(CN)_2)$ at 298 K are based on the relative solubility method, and involve the following equilibria:

COMPONENTS:	EVALUATOR:
(1) Silver cyanide; AgCN; [506-64-9] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. September 1978

CRITICAL EVALUATION: (continued)

$$AgAg(CN)_2(s) + KCl \rightleftarrows KAg(CN)_2 + AgCl(s) \qquad K_I$$

$$AgAg(CN)_2(s) + KBr \rightleftarrows KAg(CN)_2 + AgBr(s) \qquad K_{II}$$

$$AgAg(CN)_2(s) + KSCN \rightleftarrows KAg(CN)_2 + AgSCN(s) \qquad K_{III}$$

Lucas' results for K_{III} are inconsistent with the results for K_I and K_{II}, and his value for K_{III} has been rejected by the evaluator (see also the critical evaluation for the AgSCN/H_2O system). It is possible that the inconsistency in K_{III} is due to the existence in solution of the mixed-ligand complex $Ag(SCN)(CN)^-$: the solid KAg(SCN)(CN) is known (36). The equilibria involving AgCl and AgBr are more reliable as was also found in relative solubility studies on AgSCN/AgCl and AgSCN/AgBr (see reference 22 and the critical evaluation for AgSCN). The evaluator concludes that the K_I and K_{II} values reported by Lucas are of acceptable accuracy. The equilibrium constants K_I and K_{II} are represented by

$$K_I \text{ and } K_{II} = [Ag(CN)_2^-]/[X^-] = K^o_{s0}(AgAg(CN)_2)/K^o_{s0}(AgX) \qquad [6]$$

where X = Cl or Br, and the concentration equilibrium constants K_{s0} have been replaced by the thermodynamic constant K^o_{s0} since it is assumed that the ratio of activity coefficients for $Ag(CN)_2^-$ and X^- is unity. Because Lucas did not have accurate K^o_{s0} values for AgCl and AgBr at the time of his study, the compiler recalculated $K^o_{s0}(AgAg(CN)_2)$ using Lucas' experimental results for K_I and K_{II} and more recent values for $K^o_{s0}(AgCl)$ and $K^o_{s0}(AgBr)$: from reference (23), $K^o_{s0}(AgCl) = 1.754 \times 10^{-10}$ and $K^o_{s0}(AgBr) = 5.35 \times 10^{-13}$ $mol^2\ dm^{-6}$. The resulting average value and the standard deviation based on the sum of the variances in K_I and K_{II} at 298 K is

$$K^o_{s0}(AgAg(CN)_2) = (4.2 \pm 0.5) \times 10^{-12}\ mol^2\ dm^{-6}$$

Randall and Halford (8) studied the solubility of AgCN in HCN solutions at 298 K, and attempted to calculate $K^o_{s0}(AgCN)$ and β^o_2 from a series of related equilibria. β^o_2 was calculated from

$$\beta^o_2 = K^o_{II}/K^2_a K^o_{s0}(AgCl) \qquad [7]$$

where K^o_a is the acid dissociation constant of HCN and K^o_{II} is the equilibrium constant for

$$AgCl(s) + 2HCN(aq) \rightleftarrows 2H^+ + Cl^- + Ag(CN)_2^- \qquad [8]$$

Randall and Halford's result $\beta^o_2 = 2.62 \times 10^{18}$ appears to be in serious error as the most probable value is $3.91 \times 10^{20}\ mol^{-2}\ kg^2$ (see below). It also appears that their K^o_I value for the equilibrium

$$AgCN(s) + HCN \rightleftarrows H^+ + Ag(CN)_2^- \qquad [9]$$

is also in error. An error in K^o_I means that there must exist corresponding errors in the experimental c_{Ag} values. In support of this conclusion, the evaluator has calculated K^o_{II} from eq [7] using more accurate values for β^o_2, K^o_a, and $K^o_{s0}(AgCl)$. The resulting K^o_{II} can then be used to calculate $K^o_{s0}(AgCN)$ and $K^o_{s0}(AgAg(CN)_2)$ from the following relations:

$$K^o_{s0}(AgCN) = K^o_I K^o_a K^o_{s0}(AgCl)/K^o_{II} \qquad [10]$$

and

$$K^o_{s0}(AgAg(CN)_2) = K^o_{s0}(AgCN)^2 \beta^o_2 \qquad [11]$$

COMPONENTS:	EVALUATOR:
(1) Silver cyanide; AgCN; [506-64-9] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. September 1978

CRITICAL EVALUATION: (continued)

Taking $\beta^{\circ}_2 = 3.91 \times 10^{20}$ mol^{-2} kg^2 (the tentative value discussed below), $K^{\circ}_a = 6.184 \times 10^{-10}$ mol kg^{-1} (24), and K°_{s0}(AgCl) = 1.754×10^{-10} mol^2 kg^{-2} (23), the evaluator obtains $K^{\circ}_{\mathrm{II}} = 2.62 \times 10^{-8}$ mol^3 kg^{-3}. If Randall and Halford's K°_{I} value is correct, then one should obtain acceptable values of K°_{s0} from eqs [10] and [11] using the recalculated (and presumably correct) K°_{II} value. The results are K°_{s0}(AgCN) = 1.6×10^{-16} and K°_{s0}($AgAg(CN)_2$) = 9.5×10^{-12} mol^2 kg^{-2}: the former value is larger, and the latter value smaller than the tentative values by about 70%. A corresponding error of ±70% in the experimental C_{Ag} values is thereby indicated.

The solubility of AgCN in excess CN^- solutions has been studied in NaOH solutions by Kolthoff and Stock (9), and over a wide range of pH by Gübeli and Côté (10). The data in NaOH solutions are not directly comparable since Kolthoff and Stock studied solutions of varying ionic strength at 296 ±1 K whereas Gübeli and Côté's solutions all contained 1 mol dm^{-3} $NaClO_4$ at a temperature of 298 K: the latter authors' C_{Ag} values were lower than the former authors' values by about 2.9×10^{-3} mol dm^{-3} over the pH range of 13.00 to 13.40. Both papers report β_{111} values for the reaction

$$Ag^+ + OH^- + CN^- \rightleftarrows Ag(OH)(CN)^- \qquad \beta_{111} \qquad [12]$$

(β_{111} = Kolthoff and Stock's K_C, and Gübeli and Côté's K_{11}). Kolthoff and Stock used an incorrect value for β°_2 to calculate β_{111}. Using the tentative value for β°_2 and Kolthoff and Stock's experimental value for K_A (also re-evaluated by the evaluator as discussed below), one obtains from eq [13] a value of $\beta^{\circ}_{111} = 3.9 \times 10^{13}$ mol^{-2} dm^6. If, for the sake of comparison, we

$$\beta^{\circ}_{111} = (K^{\circ}_A\ \beta^{\circ}_2)^{1/2} \qquad [13]$$

assume that the mean molar activity coefficient for NaCN in 1 mol dm^{-3} $NaClO_4$ is given by the mean molal activity coefficient of 1 mol kg^{-1} $NaClO_4$, then $y_{\pm}$ (NaCN) $\simeq \gamma_{\pm}(NaClO_4) \simeq 0.63$ at 298 K (25), then Gübeli and Côté's data give $\beta^{\circ}_{111} = \beta_{111}/y_{\pm}^2 \simeq 1.6 \times 10^{13}$. The difference between Kolthoff and Stock's value and that of Gübeli and Côté's value appears to be too large to attribute to the inaccuracy in $y_{\pm}$, and it is not possible to arrive at a tentative value for this quantity.

It is also of interest to obtain K°_{s0} values from the above works. From Kolthoff and Stock's data, the evaluator first evaluated K°_A using more accurate values for K°_{s0}(AgBr) and the tentative value for β°_2: note that the experimental K°_A value is referred to 296 K and the remaining equilibrium constants refer to 298 K. The evaluator's results are: $K^{\circ}_A = (3.2 \pm 0.8) \times 10^6$ and K°_{s0}(AgCN) = $(1.0 \pm 0.4) \times 10^{-16}$ mol^2 dm^{-6}. Gübeli and Côté's value for K_{s0} can be used to approximate K°_{s0}(AgCN) by assuming $y_{\pm} = 0.63$: the result obtained by the evaluator is 1.1×10^{-16} mol^2 dm^{-6}. Although there appears to be acceptable agreement between these two corrected values, these results cannot be used to assign tentative values since the uncertainties in some of the experimental data and several of the assumptions made to correct to K°_{s0} are of unknown magnitude. They are however useful in support of the tentative values designated below.

3. Cationic Complexes. Hellwig (4) reported the singular value of $[AgCN]_{satd}$ = 0.0091 mol dm^{-3} in 3 mol dm^{-3} $AgNO_3$ solution at 298.4 K.

4. Solubility in NH_3 solutions. It is surprising that the only literature available on the solubility of AgCN in NH_3 solutions date back to the years 1883 (3) and 1904 (6). It appears that one work is in error: e.g. for a 0.3 mol kg^{-1} NH_3 solution, Longi (3) found C_{Ag} = 0.017 mol kg^{-1} at 285 K whereas Lucas (6) found C_{Ag} = 0.011 in 0.3 mol dm^{-3} solution at 298 K. Based on the generally acceptable quality of Lucas' results, the evaluator would give greater weight to this author's results. In the absence of additional studies on this system, rejection of Longi's results is difficult to justify at this time.

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CRITICAL EVALUATION: (continued)

5. E.m.f. studies. The basis of these measurements involves a concentration cell such as

$$\text{Ag/AgCN(satd), CN}^- \text{ // salt bridge // reference electrode} \qquad [14]$$

The first experimental work to be reported on this type of cell is that of Morgan (11) who used the e.m.f. data to determine $[Ag^+]$ and a conductivity method to determine $[CN^-]$. Morgan's result of $K_{s0}(AgAg(CN)_2) = 1 \times 10^{-13}$ at 290.7 K is too low, and his data have been rejected. Linke and Seidell (26) report a solubility of 3.17×10^{-7} for AgCN in water at 290.7 K and cite Abegg and Cox (27) as the source for this value: however Abegg and Cox did not carry out any work on this system, and in fact they are reporting the value of Morgan (i.e. $C_{Ag} = K_{s0}(AgAg(CN)_2)^{1/2}$). Other data which have been rejected because of large errors are: Masaki (12), $K_{s0}(AgCN) = 4.6 \times 10^{-16}$ at 293K; Bicserdy (13), $K_{s0}(AgAg(CN)_2) = 7.8 \times 10^{-8}$ at 297 K; Britton and Dodd (14), $K_{s0}(AgAg(CN)_2) = 5.12 \times 10^{-12}$ at 288 K; Sato and Sato (16), $K_{s0}(AgCN) = 2.2 \times 10^{-11}$ at 298 K; and Chao and Cheng (19, 20), $K^o_{s0}(AgCN) = 2.1 \times 10^{-16}$ and $K^o_{s0}(AgAg(CN)_2) = 1.29 \times 10^{-11}$ mol^2 dm^{-6} at 293 K. It is not clear if Sato and Sato actually measured $K_{s0}(AgCN)$ since they did not present any experimental data for this system: they do not quote any other source, and their value is different from any other found in the literature. Britton and Dodd's study included pH measurements on $KAg(CN)_2$ solutions which demonstrated that $Ag(CN)_2^-$ does not hydrolyse. Having rejected most of the e.m.f. data, we are now left with three papers (15, 17, 18), all of which report K_{s0} and β_n values obtained from potentiometric titration data.

Gauguin's paper (15) is void of so much essential information that the evaluator was considering its rejection. However within the limits of uncertainty of these data compared to others, some agreement exists, and since this work represents one of the few (apparently) acceptable papers available for 293 K, it will not be rejected. Gauguin's $K^o_{s0}(AgAg(CN)_2) = (2.4 \pm 1.0) \times 10^{-12}$ mol dm^{-6} at 293 K agrees well with Böttgers value, and that of Ungerer et. al. (21) whose corrected value is $(2.4 \pm 0.6) \times 10^{-12}$ mol dm^{-3}. Zsakó and Petri's equilibrium constants (18) are generally larger than those of Gauguin.

Azzam and Shimi's results at 298 K (17) are difficult to analyse because their $K^o_{s0}(AgAg(CN)_2)$, β_2, and β_3 values show no concentration dependence over a range of ionic strengths of 0.005 to 1.0 mol dm^{-3}. This surprising behavior is probably due to the large experimental error in the measured e.m.f.'s which, according to the authors were "steady ..... or the variation was less than 10 mV." Their average value of $K_{s0}(AgAg(CN)_2) = (5.8 \pm 0.3) \times 10^{-12}$ mol^2 dm^{-6} is higher than Lucas' value of 4.24×10^{-12} (6), and Gübeli and Côté's value of 1.3×10^{-12} in 1 mol dm^{-3} $NaClO_4$ (10).

Complex Ions

The tendency of silver to form strong complexes with cyanide has long been recognized. One question highly relevant to the solubility of AgCN in solutions containing excess CN^- concerns the nature of the complexes which form. There is no report of soluble AgCN: Zsakó and Petri failed to calculate β_1 and conclude that K_{s1} must be smaller than 4×10^{-7} (18). The early work of Bodländer and Eberlein (28) suggest that both $Ag(CN)_2^-$ and $Ag(CN)_3^{2-}$ are important: no mention of $Ag(CN)_4^{3-}$ was made in the paper, and values of $\beta_2 = 1.14 \times 10^{21}$ mol^{-2} dm^6 and $\beta_3 = 8.85 \times 10^{21}$ mol^{-3} dm^9 were reported for 292 K. Based on the polarization behavior of Ag electrodes in CN^- solutions, Glasstone (29) concluded that $Ag(CN)_2^-$ is the only important anion complex, and that the existence of Ag_2CN^+ and Ag_3CN^{2+} was highly probable. Although there is evidence based on solubility data that AgCN can form cationic complexes (4), the nature of the complexes are unknown, and there is no indication in the literature that cationic complexes form in solutions containing excess CN^-. Britton and Dodd's e.m.f. studies (14)

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CRITICAL EVALUATION: (continued)

lead them to conclude that only $\mathrm{Ag(CN)}_2^-$ is significant, and in related studies Ferrell et. al. (30) conclude that $\mathrm{Ag(CN)}_3^{2-}$ is present only in highly concentrated CN^- solutions. Of the remaining relevant studies discussed above, two do not report the existence of $\mathrm{Ag(CN)}_3^{2-}$ (10, 15), whereas two confirm its existence (17, 18). These latter two papers report β_3 values, in mol^{-3} dm^9, of 9.6 x 10^{21} at 298 K (17), and 6.4 x 10^{21} at 293.6 K (18). No evidence has been cited for the existence of $\mathrm{Ag(CN)}_4^{3-}$ in any of these works, but below other evidence is cited. To determine the relative importance of $\mathrm{Ag(CN)}_3^{2-}$ and $\mathrm{Ag(CN)}_2^-$ in <u>saturated</u> solutions containing excess CN^-, we can define $R_{2,3}$ as

$$R_{2,3} = [\mathrm{Ag(CN)}_2^-]/[\mathrm{Ag(CN)}_3^{2-}] = \beta_2/[\mathrm{CN}^-]\beta_3 \qquad [15]$$

Taking $\beta_2 \simeq 4 \times 10^{20}$ and $\beta_3 \simeq 2 \times 10^{21}$ at 298 K (see below), and a typical $[\mathrm{CN}^-] \simeq 2 \times 10^{-5}$ mol dm^{-3} for a saturated solution of AgCN in 1 mol dm^{-3} KCN, eq [15] yields $R_{2,3} = 1 \times 10^4$. Thus when considering saturated solutions of AgCN in excess CN^-, one can safely assume that the only soluble species present is $\mathrm{Ag(CN)}_2^-$.

Hydrolysis

It may at first seem surprising that the hydrolysis of CN^- has little effect on the solubility of AgCN since the $\mathrm{p}K_a^\circ$ of HCN is 9.2 at 298.2 K (24). The reason for this, as shown below, is that $\mathrm{Ag(CN)}_2^-$ is so stable that the free CN^- concentration is small. In non-saturated solutions where there is a large excess of CN^-, hydrolysis will be important and all three species $\mathrm{Ag(CN)}_n^{1-n}$ for n = 2, 3, 4 may be present in nearly equal amounts. The following studies accounted for hydrolysis in the calculation of β_2 and β_3: 10, 14, 15, 17, 18, 28, 30-33.

Tentative Values

<u>1. Solubility products and formation constants</u>. The difficulty in arriving at a consistent set of K_{s0} and β_n values is that most of the existing data are deficient in information required to define the thermodynamic state, or they are of poor precision. Those papers which specifically define the thermodynamic constant $K_{s0}^\circ(\mathrm{AgAg(CN)}_2)$ are (5, 6, 8, 9, 18, 21) and the data in references (8, 9) have been rejected because of inconsistencies in the data (8) or uncertainty in the temperature (9). The K_{s0} and β_n values of Azzam and Shimi (17) are subject to uncertainty since they are average values based on all data in constant ionic strength solutions of 0.001 to 1.0 mol dm^{-3}. Gauguin's data (15), corrected for $y_\pm$ by the compiler, suffer from uncertainty in the temperature, and the resulting K_{s0}° and β_2° values were accepted because of excellent agreement in K_{s0}° between Böttger (5) and Ungerer et. al. (21). Gübeli and Côté's data were obtained in 1 mol dm^{-3} $\mathrm{NaClO_4}$ solutions, and the calculations of K_{s0}° and β_2° by the evaluator are of marginal significance.

It is clear that a set of recommended values for any of these constants cannot be offered at this time. Since the cyanides of silver play an important role in the understanding of the solution chemistry of the metal, it is of interest to at least attempt to produce a consistent set of tentative values for K_{s0}° and β_n°. In deriving these tentative values, the errors associated with each constant were estimated from the sums of the experimental standard deviation (σ_{exptl}) and the standard deviation obtained from averaging two or more constants (σ_{av}): i.e.

$$\sigma_{\mathrm{total}} = \left\{(\sigma_{\mathrm{exptl}})^2 + (\sigma_{\mathrm{av}})^2\right\}^{1/2}$$

The important constants to be considered are $K_{s0}^\circ(\mathrm{AgCN})$, $K_{s0}^\circ(\mathrm{AgAg(CN)}_2)$, and β_2°. These constants are related by

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$$K_{s0}^{o}(\text{AgCN})\beta_2^{o} = K_{s2}^{o} \cong K_{s2} \qquad [16]$$

$$\beta_2^{o} = (K_{s2}^{o})^2/K_{s0}^{o}(\text{AgAg(CN)}_2) \qquad [17]$$

$$K_{s0}^{o}(\text{AgCN}) = (K_{s0}^{o}(\text{AgAg(CN)}_2)/\beta_2^{o})^{1/2} \qquad [18]$$

As a starting point it is noted that K_{s2}, being defined as $[\text{Ag(CN)}_2^-]/[\text{CN}^-]$, is to a first approximation independent of concentration. The evaluator has chosen the data of Gübeli and Côté (1) and Azzam and Shimi (17) and calculated K_{s2} from eq [17]: the average $K_{s2} = K_{s2}^{o} = (4.1\pm0.7) \times 10^4$ at 298 K. For the value of $K_{s0}^{o}(\text{AgAg(CN)}_2)$ the evaluator uses Lucas' value (6) of $(4.2\pm0.5) \times 10^{-12}$ $\text{mol}^2\ \text{dm}^{-6}$ at 298 K. From eq [18], the tentative value of $K_{s0}^{o}(\text{AgCN})$ at 298 K is $(1.0\pm1.0) \times 10^{-16}$ $\text{mol}^2\ \text{dm}^{-6}$ which is based on the tentative value of $\beta_2^{o} = (3.9\pm0.8) \times 10^{20}$ $\text{mol}^{-2}\ \text{dm}^6$ as obtained from eq [17]. The tentative value for $K_{s0}^{o}(\text{AgCN})$ is in satisfactory agreement with the estimations of the values obtained by the evaluator based on Kolthoff and Stock's data, and Gübeli and Côté's data (see above).

The data at 293 K (5, 15, 18, 21) are much more difficult to analyse. Selecting tentative values at this temperature involves considerably greater uncertainty than for the 298 K values. The data of Gauguin (15), Böttger (5), and Ungerer et. al. (21) have been averaged to obtain the tentative value $K_{s0}^{o}(\text{AgAg(CN)}_2) = (2.4\pm1.0) \times 10^{-12}$ $\text{mol}^2\ \text{dm}^{-6}$. The tentative value of $K_{s2}^{o} = K_{s2} = (4.8\pm2.6) \times 10^4$ was obtained by averaging the values from references (15) and (18). β_2^{o} and $K_{s0}^{o}(\text{AgCN})$ were then calculated from eqs [17] and [18] as was done for the 298 K data.

As mentioned above, Zsakó and Petri place a limit of $K_{s1} < 4 \times 10^{-7}$ mol dm^{-3}. Butler (31) also estimated that $K_{s1} \leqslant 10^{-7}$ mol dm^{-3} based on the assumption that in order to escape detection, [AgCN] must be less than 10% of the minimum solubility of AgCN (i.e. $2K_{s0}(\text{AgAg(CN)}_2)^{1/2}$). In all calculations below, it was assumed that the concentration of AgCN in solution is negligible.

β_3 values obtained from the potentiometric methods referred to above are inconsistent and contain numerous uncertainties. To obtain a consistent set of β_3 and β_4 values, the evaluator used the data of Jones and Penneman (32) in the exact manner used by Butler (31): the only difference between Butler's calculations and those of the evaluator lies in the β_2^{o} values. The data of Jones and Penneman are used because these authors studied non-saturated solutions of high $[\text{CN}^-]$ which gives nearly equal concentrations of the species Ag(CN)_n^{1-n} for n = 2, 3, 4 thereby permitting more accurate calculations of the equilibrium constants. Jones and Penneman recorded a series of infrared spectra on carefully prepared $\text{KAg(CN)}_2/\text{KCN}/\text{H}_2\text{O}$ mixtures "in a constant temperature instrument room at 70°F," (i.e. 294.3 K). Three distinct peaks were identified as arising from Ag(CN)_2^-, Ag(CN)_3^{2-}, and Ag(CN)_4^{3-}. The absorbance coefficients were evaluated and the concentrations for each complex determined which permitted the stepwise formation constants to be calculated. Molar activity coefficients were estimated from

$$\log y_{\pm} = -0.51 z_i^2 \mu^{1/2}/(1 + 0.33 a_o \mu^{1/2}) \qquad [19]$$

where a_o is the distance of closest approach, and values of 0.37 nm and 0.67 nm were taken for CN^- and all complexes, respectively. The average thermodynamic stepwise formation constants were reported as $(K_3^{o})^{-1} = 0.2\pm0.05$ mol dm^{-3}, and $(K_4^{o})^{-1} = 13.4\pm4$ mol dm^{-3}. The overall thermodynamic formation constants were calculated by the evaluator for 293 and 298 K using these constants, the β_2^{o} values in Table 1, and the equation

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CRITICAL EVALUATION: (continued)

$$\beta_n^o = \beta_{n-1}^o K_n^o \qquad [20]$$

It should be pointed out that Ricci (33) arrived at a set of K_{s0}^o and β_n^o values in a manner similar to that employed here. Ricci used Randall and Halford's (8) K_{II}^o (cf. eq [8]) together with an older value of $K_a = 4 \times 10^{-10}$ (34) to calculate β_2^o from

$$\beta_2^o = K_{II}^o/(K_a^2 K_{s0}^o(\mathrm{AgCl})) \qquad [21]$$

TABLE 1 Tentative Values for K_{s0}^o and β_n^o

	293 K		298.2 K	
constant*	volume basis	weight basis	vol basis	wt basis
$10^{16}K_{s0}^o$(AgCN)	0.48±0.27	0.48	1.0±1.0	1.1
$10^{12}K_{s0}^o$(AgAg(CN)$_2$)	2.4±1.0	2.4	4.2±0.5	4.3
$10^{-4}K_{s2}^o$	4.8±2.6	4.8	4.1±0.7	4.1
$10^{-10}\beta_1^o$	<3		<3	
$10^{-20}\beta_2^o$	9.9±2.7	10.0	3.9±0.8	3.9
$10^{-21}\beta_3^o$	4.7±2.8	4.7	2.0±0.8	2.0
$10^{-20}\beta_4^o$	3.5±2.8	3.5	1.5±0.9	1.5
$10^{10}K_a^o$(HCN)	4.36	4.37	6.17	6.18

*All conversions were made from volume to weight units. The relation used was $K_m^o = K_c^o/d_o^{\nu}$ where d_o = density of pure water. The units are:

$$K_{sn} = \mathrm{mol}^{2-n}\ \mathrm{dm}^{3(n-2)} \text{ or } \mathrm{mol}^{2-n}\ \mathrm{kg}^{n-2}$$

$$\beta_n = \mathrm{mol}^{-n}\ \mathrm{dm}^{3n} \text{ or } \mathrm{mol}^{-n}\ \mathrm{kg}^{n}$$

$$K_a = \mathrm{mol\ dm}^{-3} \text{ or } \mathrm{mol\ kg}^{-1}$$

Ricci's value of $\beta_2^o = 7.1 \times 10^{19}$ is clearly in error as are his values of K_{s0}^o(AgCN) $= 1.2 \times 10^{-16}$ and K_{s0}^o(AgAg(CN)$_2$) $= 1.0 \times 10^{-12}$ calculated, respectively, from eqs [10] and [18]. Butler (31) employed a similar method starting with Ricci's value for K_{s0}^o(AgCN), and a non-referenced value of $K_{s2} = 4.2 \times 10^4$ as the basis for his β_n^o values. Butler's results are in close agreement with the tentative values for 298.2 K presented in Table 1.

2. Thermodynamic functions. Due to the large errors associated with the tentative values of the equilibrium constants, it is doubtful that a calculation of ΔC_p^o, which involves double differentiation, would be of any significance. It is also felt that on the basis of two values of ΔG^o (at 293 K and 298 K), a tentative value of ΔH^o is of little significance. The derived ΔH^o values reported in Table 2 below should therefore be regarded as provisional values which demonstrate the need for additional studies on the AgCN/H_2O system. In Table 2, all ΔG^o values were computed for 298.2 K,

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CRITICAL EVALUATION: (continued)

and ΔH^o values were obtained from plots of log K against the reciprocal of the two temperatures. All data are based on volume units.

Solubility of AgCN at 298.2 K

1. The binary system. In the binary AgCN/H_2O system, the intrinsic solubility of AgCN is given by the two mass balance equations

$$C_{Ag} = [Ag^+] + \sum_1^n K^o_{sn}[CN^-]^{n-1} \qquad [22]$$

TABLE 2 Derived Thermodynamic Quantities at 298.2 K

reaction	ΔG^o/kJ mol^{-1}	ΔH^o/kJ mol^{-1}
$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^-$	64.9±0.3	79.5±9.2
$AgCN(s) \rightleftarrows Ag^+ + CN^-$	91.2±6.3	108±38
$AgCN(s) + CN^- \rightleftarrows Ag(CN)_2^-$	-121.6±1.1	-120±38
$AgCN(s) + 2CN^- \rightleftarrows Ag(CN)_3^{2-}$	-115.1±1.8	-120±38

and

$$C_{Ag} = [CN^-] + [HCN] + \sum_1^n nK^o_{sn}[CN^-]^{n-1} \qquad [23]$$

Since C_{Ag} is small, all activity coefficients are assumed to be unity, and the only mononuclear complex that need be considered is $Ag(CN)_2^-$. Equating [22] and [23] yields

$$[Ag^+]^2 = K^o_{s0}(AgCN)\{1 + K^o_{s2} + [H^+][CN^-]/K^o_a\} \qquad [24]$$

Elimination of $[Ag^+]$in this equation is accomplished with

$$[H^+] - K_w/ [H^+] = -[H^+][CN^-]/K^o_a \qquad [25]$$

which yields the polynominal

$$[H^+]^5 + [H^+]^4K^o_a\{1 + K^o_{s2} - K^o_{s0}(AgCN)/K^{o2}_a\} - 2[H^+]^3K_w - 2[H^+]^2K^o_aK_w(1 + K_{s2})$$

$$+ [H^+]K_w^2 + K^o_aK_w^2(1 + K_{s2}) = 0 \qquad [26]$$

In eqs [25] and [26], K_w is the ionization product of water (1×10^{-14} at 298 K). Solving eq [26] by the Newton-Raphson iteration method, it is found that $[H^+] = 9.6 \times 10^{-8}$ mol dm^{-3}, $[Ag^+] = 2.1 \times 10^{-6}$ (eq [24]), and from eq [22], $C_{Ag} = 4.1 \times 10^{-6}$ mol dm^{-3}. The identical result is obtained if hydrolysis is completely neglected, and $C_{Ag} = 2\{K^o_{s0}(AgAg(CN)_2)\}^{1/2}$.

COMPONENTS: (1) Silver cyanide; AgCN; [506-64-9] (2) Water; H_2O; [7732-18-5]	EVALUATOR: Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. September 1978

CRITICAL EVALUATION: (continued)

2. Solutions with excess CN^-. In the presence of excess CN^- the solubility of AgCN is given by eqs [22] and

$$c_{Ag} + c = [CN^-] + [HCN] + \sum_1^n nK_{sn}[CN^-]^{n-1} \qquad [27]$$

where c is the concentration of added salt (e.g. KCN or NaCN), and K^o_{sn} has been replaced by the concentration formation constant K_{sn}. Combining eqs [22] and [27] yields

$$[CN^-]^2\{1 + K_{s2} + [H^+]/K_a\} - c[CN^-] - K_{s0}(AgCN) = 0 \qquad [28]$$

Eliminating $[CN^-]$ between eqs [25] and [28] yields

$$[H^+]^5 + [H^+]^4K_a\{1 + K_{s2} + c/K_a - K_{s0}/K_a^2\} - [H^+]^3 2K_w - [H^+]^2 2K_wK_a\{1 + K_{s2} + c/2K_a\} + [H^+]K_w^2 + K_w^2K_a(1 + K_{s2}) = 0 \qquad [29]$$

Once $[H^+]$ is calculated from eq [29], its value is used in eq [25] to calculate $[CN^-]$, and the solubility of AgCN is obtained from

$$c_{Ag} = \sum_0^n K_{sn}[CN^-]^{n-1} \simeq K_{s2}[CN^-] \qquad [30]$$

Consider solutions of 0.1 and 0.69 mol kg^{-1} KCN which are saturated with AgCN at 298K. The concentration equilibrium constants are obtained from $K_{s0} = K^o_{s0}/\gamma_\pm^2$; $K_a \simeq K^o_a/\gamma_\pm^2$; and $K_{s2} = K^o_{s2}$. Assuming $\gamma_\pm$ values for KCN are equal to those for KI (24), the following results were obtained: for c = 0.1 mol kg^{-1}, $[H^+] = 2.06 \times 10^{-9}$, $[CN^-] = 2.45 \times 10^{-6}$, and $c_{Ag} \simeq 0.1$ mol kg^{-1}. The effect of hydrolysis is small, but not strictly negligible since the pH of the resulting solution is 8.69 (the pH of 0.1 mol kg^{-1} KCN in water at 298 K is 10.89 as calcd by the evaluator). For c = 0.69 mol kg^{-1} KCN, saturation with AgCN yields the following: $[H^+] = 9.20 \times 10^{-10}$ (pH = 9.04), $[CN^-] = 1.69 \times 10^{-5}$, and $c_{Ag} \simeq 0.69$ mol kg^{-1}. The results indicate that the approximation in eq [30] is valid, and that practically all of the added salt complexes with AgCN: i.e. $c_{Ag} \simeq c$. Agreement between these calculated solubilities and the experimental values of Bassett and Corbet (7) is not expected to be very good since the experimental values contain an error due to the presence of KOH impurity as discussed above.

3. Solutions with added HCN. The equilibrium of interest has already been discussed: i.e.

$$AgCN(s) + HCN(aq) \rightleftarrows H^+ + Ag(CN)_2^- \qquad [9]$$

The thermodynamic equilibrium constant for this reaction is $K^o_aK^o_{s2} = (2.6 \pm 0.7) \times 10^{-5}$ mol kg^{-1} as calculated from the data in Table 1 (Randall and Halford (8) report a value of 3.77×10^{-5}). The solubility of AgCN for an initial concentration c of HCN is given by

COMPONENTS: (1) Silver cyanide; AgCN; [506-64-9] (2) Water; H_2O; [7732-18-5]	EVALUATOR: Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. September 1978

CRITICAL EVALUATION: (continued)

$$C_{Ag}^2 + C_{Ag}K_a^oK_{s2}^o - cK_a^oK_{s2}^o = 0 \qquad [31]$$

Activity coefficients are neglected since ionic concentrations are low: thus for c = 0.104 and 0.45 mol kg^{-1}, eq [31] gives C_{Ag} = 0.0016 and 0.0034 mol kg^{-1}, respectively. The corresponding experimental values of Randall and Halford are 0.00204 and 0.00427 mol kg^{-1}.

4. Solubility in NH_3 solutions. Due to the high stability of $Ag(CN)_2^-$, the equations describing the solubility of AgCN in NH_3 solutions must account for the presence of this complex ion. According to the conclusion above that practically all free CN^- will combine to form the $Ag(CN)_2^-$ complex, we can expect the concentration of the complex to be equal to that of $Ag(NH_3)_2^+$. Assuming that only CN^-, $Ag(CN)_2^-$, and $Ag(NH_3)_2^+$ exist when excess AgCN is added to a NH_3 solution of concentration c, the mass balance requirements give

$$C_{Ag} = [Ag(CN)_2^-] + [Ag(NH_3)_2^+] \qquad [32]$$

and

$$C_{Ag} = [CN^-] + 2[Ag(CN)_2^-] \qquad [33]$$

Eliminating C_{Ag} yields

$$K_{s0}^o(AgCN)(1 + K_{s2}^o) - K_N^o[NH_3]^2[Ag^+]^2 = 0 \qquad [34a]$$

or, upon rearranging,

$$[Ag^+] = (K_{s0}^o/K_N^o)^{1/2}(1 + K_{s2}^o)^{1/2}/[NH_3] \qquad [34b]$$

The additional relationships required are the mass balance on NH_3 species,

$$c = [NH_3] + [NH_4^+] + 2[Ag(NH_3)_2^+] \qquad [35]$$

and the two equilibria

$$K_N^o = [Ag(NH_3)_2^+]/[Ag^+][NH_3]^2 = 1.07 \times 10^7 \text{ mol}^{-2} \text{ dm}^6 \qquad [36]$$

and

$$K_b^o = [NH_4^+][OH^-]/[NH_3] = 1.75 \times 10^{-5} \text{ mol dm}^{-3} \qquad [37]$$

Values of K_N^o and K_b^o were obtained from reference (35). The hydrolysis of CN^- is negligible in this system, and assuming $[NH_4^+] \approx (cK_b^o)^{1/2}$ (cf. ref 33) the ammonia concentration at equilibrium is obtained from

$$[NH_3] = \{c - (cK_b^o)^{1/2}\}/\ \{1 + 2(K_{s0}^o(AgCN)K_N^o)^{1/2}\} \qquad [38]$$

$[Ag^+]$ is now calculated from eq [34] and the solubility from eq [32]: i.e.

$$C_{Ag} = K_{s0}^o(AgCN)K_{s2}^o/[Ag^+] + K_N^o[NH_3]^2[Ag^+] \qquad [39]$$

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

September 1978

CRITICAL EVALUATION: (continued)

All attempts to compute C_{Ag} from eq [39] gave results which were 4-5 times smaller than Lucas' experimental values. If Lucas' data are reliable, which they appear to be, then failure to obtain reasonable values of C_{Ag} from eq [39] must be due to the initial assumptions. This difficulty is eliminated if, as suggested by Lucas, one considers the soluble species $Ag(NH_3)(CN)$ which forms according to

$$AgCN(s) + NH_3(aq) \rightleftarrows Ag(NH_3)(CN) \qquad K_{s111} \qquad [40]$$

The new relations required are

$$c = [NH_3] + [NH_4^+] + [Ag(NH_3)(CN)] + 2[Ag(NH_3)_2^+]$$

and (obtained from the above eq and eq [34b])

$$[NH_3] = \left\{c - (cK_b^o)^{1/2}\right\} \Big/ \left\{1 + K_{s111} + 2(K_{s0}^o K_N^o)^{1/2}(1 + K_{s2}^o)^{1/2}\right\} \qquad [41]$$

$[Ag^+]$ is again computed from eq [34b] and the solubility of AgCN is given by

$$C_{Ag} = K_{s0}^o(AgCN)K_{s2}^o/[Ag^+] + K_{111}[NH_3] + K_N^o[NH_3]^2[Ag^+] \qquad [42]$$

By a trial and error method using Lucas' experimental data, it was found that $K_{s111} = 0.023$. Lucas' K_2^o for the equilibrium

$$2Ag(NH_3)(CN)(aq) \rightleftarrows Ag(CN)_2^- + Ag(NH_3)_2^+$$

is related to K_{s111} by

$$K_2^o = K_N^o K_{s0}^o(AgAg(CN)_2)/4K_{s111}^{o2} \qquad [43]$$

REFERENCES:

1. Baup, S. *Ann. Chim. Phys.* 1858, *53*, 462.
2. Fronmüller, C. *Ber.* 1878, *11*, 91.
3. Longi, A. *Gazz. Chim. Ital.* 1883, *13*, 87.
4. Hellwig, K. *Z. Anorg. Chem.* 1900, *25*, 157.
5. Böttger, W. *Z. Physik. Chem.* 1903, *46* 521.
6. Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193.
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8. Randall, M.; Halford, J.O. *J. Am. Chem. Soc.* 1930, *52*, 178.

COMPONENTS:	EVALUATOR:
(1) Silver cyanide; AgCN; [506-64-9] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

CRITICAL EVALUATION: (continued)

9. Kolthoff, I.M.; Stock, J.T. *J. Am. Chem. Soc.* 1956, *78*, 2081.
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36. Sergeeva, A.N.; Semenishin, D.I.; Mazepa, A.V. *Zh. Neorg. Khim.* 1973, *18*, 2956.
37. Noonan, E.C. *J. Am. Chem. Soc.* 1948, *70*, 2915.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium dicyanatoargentate; $NaAg(CN)_2$; [2140-69-3] (2) Water; H_2O; [7732-18-5]	Baup, S. *Ann. Chim. Phys.* <u>1858</u>, *53*, 462 - 8.
VARIABLES:	**PREPARED BY:**
One temperature: 20°C	Mark Salomon

EXPERIMENTAL VALUES:

$$c_{Ag} = 20 \text{ g}/100 \text{ g } H_2O$$

$$c_{Ag} = 1.09 \text{ mol kg}^{-1} \text{ (compilers calcn)}$$

AUXILIARY INFORMATION

METHOD:

Nothing specified.

COMMENTS AND/OR ADDITIONAL DATA:

The major objective of this paper was to establish the stoichiometry of the salt. The solubility was simply mentioned as one of several physical properties.

SOURCE AND PURITY OF MATERIALS:

$NaAg(CN)_2$ was pptd from a satd soln of NaCN and AgCN. The NaCN was prepared by dissolving $Na_4Fe(CN)_6$ with 1/2 equivalent of Na_2CO_3 (solvent not specified, but compiler assumes it to be water). No other details were given. The author states that the $NaAg(CN)_2$ crystals were anhydrous

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Thallium dicyanoargentate (silver thallium cyanide); AgCN·TlCN;

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fronmüller, C. *Ber.* 1878, *11*, 91-5.

VARIABLES:

Two temperatures: 0°C and 16°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

	solubility	
t/°C	g/kg solvent	mol kg^{-1}*
0	47	0.13
16	74	0.20

*Calculated by compiler

AUXILIARY INFORMATION

METHOD:

Nothing specified.

SOURCE AND PURITY OF MATERIALS:

The double salt was prepared by adding AgCN to a solution of TlCN. The resulting crystals were analysed and presumably found to be satisfactory. No other details were given.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Ammonia; NH_3; [7664-41-7]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Longi, A. *Gazz. Chim. Ital.* 1883, *13*, 87-89.

VARIABLES:

Temperature and concentration of NH_3

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

	solvent			AgCN saturated solutions	
t/°C	wt % NH_3	specific gravity	g AgCN in 100 g solvent	$[NH_3]$/mol kg^{-1}*	c_{Ag}/mol kg^{-1}*
12	0.5	0.998	0.231	0.30	0.017
18	10	0.96	0.519	6.52	0.043

*Calculated by compiler

AUXILIARY INFORMATION

METHOD:

Nothing specified. Most likely the author analysed for AgCN gravimetrically by evaporation of a saturated solution, or by addition of HNO_3 to affect precipitation.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

COMMENTS AND/OR ADDITIONAL DATA:

This paper is a discourse on the methods of separation and identification of CN^-, Cl^-, Br^-, I^-, and IO_3^- mixtures by precipitation with $AgNO_3$, and redissolution with acid and NH_3.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Silver nitrate; $AgNO_3$; [7761-88-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hellwig, K. *Z. Anorg. Chem.* 1900, *25*, 157-88.

VARIABLES:

Solubility determined in 3 mol dm^{-3} $AgNO_3$ at 25.2°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

In 3 mol dm^{-3} $AgNO_3$ solution at 25.2°C

$$[AgCN]_{satd} = 0.0091 \text{ mol dm}^{-3}$$

AUXILIARY INFORMATION

METHOD:

Solutions prepared by adding AgCN to a highly concentrated $AgNO_3$ solution until saturated was achieved. These solutions were thermostated and water added in steps to precipiate AgCN. After each dillution aliquots were taken for analysis. Only one result for 3M $AgNO_3$ was reported. Equilibrium was carried out in sealed glass flasks which were mechanically agitated in the water bath. Aliquots for analysis were taken after 4 h (the author states equil is attained within 2 h). All samples withdrawn from the flasks were filtered through a wad of cotton wool directly into a pipet which was kept at 25.2°C. Water was added to the contents of the pipet to ppt all the AgCN which was collected in a Gooch crucible on an asbestos mat. The ppt was washed and dried to const weight. The wash water and mother liquor were combined and $AgNO_3$ determined by Volhard titration.

SOURCE AND PURITY OF MATERIALS:

The water used in the experiments was repeatedly distilled and boiled prior to use. The AgCN was prepared by precipitation followed by washing (no other details given).

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Böttger, W. *Z. Physik. Chem.* 1903, *46*, 521-619.

VARIABLES:

One temperature: 19.96°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Böttger reports two values for the solubility of AgCN, c_{Ag}.

1. In terms of AgCN:

$$c_{Ag} = [AgCN]_{sat} = 1.64 \times 10^{-6} \text{ equiv dm}^{-3}$$

$$K_{s0} = (c_{Ag})^2 = 2.69 \times 10^{-12} \text{ equiv}^2 \text{ dm}^{-6}$$

2. In terms of $Ag{\cdot}Ag(CN)_2$:

$$c_{Ag} = [AgAg(CN)_2]_{sat} = 1.50 \times 10^{-6} \text{ equiv dm}^{-3}$$

$$K_{s0} = (c_{Ag})^2 = 2.25 \times 10^{-12} \text{ equiv}^2 \text{ dm}^{-6}$$

At these low concentrations, it may be assumed that activity coefficients are unity and that thermodynamic equilibrium constants have been evaluated.

AUXILIARY INFORMATION

METHOD:

The soly was determined by conductivity measurements using the equation

$$c_{Ag} = 1000\kappa(\text{salt})/(\lambda_+^o + \lambda_-^o) \qquad [1]$$

where λ_+^o and λ_-^o are the equiv conductances of Ag^+ and the anion (ohm^{-1} cm^2 equiv^{-1}) at infinite dilution. κ (salt) is the specific conductance ($\text{ohm}^{-1}\text{cm}^{-1}$) of the satd solns and is evaluated from

$$\kappa(\text{salt}) = \kappa(\text{soln}) - \kappa(H_2O) \qquad [2]$$

where κ(soln) is the specific conductance of the satd soln and $\kappa(H_2O)$ is that for pure water. The conductivity cells which employed Pt electrodes were designed to prevent entrapment of air bubbles. After sealing, the entire cell was immersed in a water bath and rotated. Equil taken when conductivity remained const within experimental error (usually within 20-30 min). The bridge and thermometer were calibrated, and the cell constants determined by using 0.010M KCl solution.

SOURCE AND PURITY OF MATERIALS:

Analytically pure (Merck) chemicals used. Salts prepared by method of Wagner (1): $AgAg(CN)_2$ probably by pptn from $KAg(CN)_2$ and $AgNO_3$ solns, and AgCN by pptn from $AgNO_3$ and KCN solns. Both ppts soaked, agitated and H_2O changed several times a day for several days. KCl purified by pptn from a satd aq soln with alcohol (3 times). Laboratory distilled water was redistilled from an all tin-plated still and stored in a flask fitted with a drying tube with NaOH and CaO.

ESTIMATED ERROR:

Solubility: ±9-12% (compiler)

Resistance measurements: ±0.006-0.01 x 10^{-6} ohm^{-1}

Temperature: ±0.01 - 0.02°C

REFERENCES:

1. Wagner, *Ber. d. Ver. Deut. Natur. und Arzte* 1902.
2. Kohlrausch, F. *Sitzungsber. d. Akad d. Wissench.* 1902, *42*, 1031.
3. Ostwald, *Lehrbuch d. Allgem. Chemie.*
4. Nernst; Lob, *Z. Physik. Chem.* 1888, *2*, 948.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (Continued)

Böttger, W. *Z. Physik. Chem.* <u>1903</u>, *46*, 521-619.

COMMENTS AND/OR ADDITIONAL DATA:

The three experimental values for κ(AgCN) are 0.206×10^{-6}; 0.213×10^{-6}; and 0.170×10^{-6}. Böttger takes an average of 0.194×10^{-6} whereas the compiler calculates $(0.196 \pm 0.023) \times 10^{-6}$. The standard deviations for κ (H_2O) and κ(soln) are, respectively, ±0.002 and $\pm 0.023 \times 10^{-6}$: combining these with the error due to the limit of observation ($\pm 0.008 \times 10^{-6}$) the compiler obtains

$$\kappa(\mathrm{AgCN}) = (0.194 \pm 0.024) \times 10^{-6}\ \mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$$

Similarly for the measurements on silver dicyanoargentate,

$$\kappa(\mathrm{AgAg(CN)_2}) = (0.154 \pm 0.009) \times 10^{-6}\ \mathrm{ohm}^{-1}\ \mathrm{cm}^{-1}$$

based on the experimental values of $\kappa(\mathrm{AgAg(CN)_2}) = 0.144 \times 10^{-6}$, 0.165×10^{-6}, and 0.148×10^{-6}. To evaluate the limiting equivalent conductances at 20°C, Böttger used the relation

$$\lambda^{\circ}(20^{\circ}\mathrm{C}) = \lambda^{\circ}(18^{\circ}\mathrm{C})\ \{1 + \alpha(18 - t)\} \qquad [3]$$

where α = temperature coeff and t = °C. For Ag^+, $\alpha = 0.0229$ (2) and λ°_{+} = (18°C)= 54.5 (recalculated by Ostwald (3) using the original data of Nernst and Lob (4)). For CN^- Böttger estimates λ°_{-}(18°C) = 56 based on data from Ostwald (5) and Bredig (6). The value for α is 0.022 and presumably comes from Kohlrausch (2). For $Ag(CN)_2^-$ at 18°C, Böttger estimates a value of 43.3 based on data from references 5 and 6. The value for $\alpha = 0.024$ for $Ag(CN)_2^-$ was (again presumably) taken from Kohlrausch. From eq [3], the λ° values at 20°C in units of $\mathrm{ohm}^{-1}\ \mathrm{cm}^2\ \mathrm{equiv}^{-1}$ are:

$$\lambda^{\circ}(\mathrm{Ag}^+) = 57.0 \quad ; \quad \lambda^{\circ}(\mathrm{CN}^-) = 58.5 \quad ; \quad \lambda^{\circ}(\mathrm{Ag(CN)_2^-}) = 45.4$$

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

5. Ostwald, *Klassiker.* *23*, 35.
6. Bredig, *Z. Physik. Chem.* <u>1894</u>, *13*, 232-270.

COMPONENTS:
(1) Silver cyanide; AgCN; [506-64-9]
(2) Silver chloride; AgCl; [7783-90-6]
(3) Potassium chloride; KCl; [7447-40-7]
(4) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193-215.

VARIABLES:

Direction from which equilibrium is approached. Temperature is 25°C.

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The equilibrium studied was

$$AgAg(CN)_2(s) + KCl \rightleftarrows KAg(CN)_2 + AgCl(s) \qquad K_I \qquad [1]$$

The solubility product for $AgAg(CN)_2$ is calculated from

$$K_I = [Ag(CN)_2^-]/[Cl^-] = K^o_{s0}(AgAg(CN)_2)/K^o_{s0}(AgCl) \qquad [2]$$

Experimental results are given below (concentrations in mol dm^{-3}).

$[KCl]_{init}$	$[KAg(CN)_2^-]_{init}$	$[KAg(CN)_2]_{equil}$	K_I	$10^{12}K^o_{s0}$*/mol^2dm^{-6}
0.0973	----	0.00250	0.0264	4.65
0.2038	----	0.00519	0.0261	4.54
----	0.101	0.00249	0.0253	4.44

*Recalculated by the compiler: see METHOD.

Average values calculated by the compiler are:

$$K_I = 0.026 \pm 0.006$$

$$K^o_{s0}(AgAg(CN)_2) = (4.5 \pm 0.1) \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$$

$$c_{Ag} = (K^o_{s0})^{1/2}/y_\pm = (2.13 \pm 0.03) \times 10^{-6} \text{ mol dm}^{-3}/y_\pm$$

where $y_\pm$ is the mean molar activity coefficient.

AUXILIARY INFORMATION

METHOD:

Solution of KCl + $Ag{\cdot}Ag(CN)_2$ or AgCl + $KAg(CN)_2$ equilibrated isothermally by shaking 1-2 d (no details on how equil was ascertained). The soln was rapidly filtered and Ag_2S pptd from aliquots with Na_2S. The ppt was washed, dissolved in dil HNO_3, and Ag^+ determined by titrn with NH_4SCN. Using point No 2 as an example, K_I is calcd from

$$K_I = 0.00519/(0.2038 - 0.00519)$$

The author uses Thiel's value (1) of $K_{s0}(AgCl) = 2.0 \times 10^{-10}$ determined in 1M KCl. Assuming $y_\pm \approx 0.60$, $K^o_{s0}(AgCl) = K_{s0}y_\pm^2 = 7 \times 10^{-11}$ which is incorrect. Using the NBS value** $K^o_{s0}(AgCl) = 1.754 \times 10^{-10}$, the compiler recalculated $K^o_{s0}(AgAg(CN)_2)$ from eq [2]. Since a ratio of concentrations is used in eq [2], activity coefficients probably cancel, and the use of $K^o_{s0}(AgCl)$ gives the corresponding standard value $K^o_{s0}(AgAg(CN)_2)$.

**Converted to mol^2 dm^{-6} by compiler.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

K^o_{s0}: $\sigma = \pm 2\%$ (compiler)

Nothing else was specified.

REFERENCES:

1. Kuster, F.W.; Thiel, A. *Z. Anorg. Chem.* 1900, *24*, 25.
2. Wagman, D.D.; Evans, W.H.; Parker, V.B.; Halow, I.; Bailey, S.M.; Schumm, R.H. *U.S. National Bureau of Standards TN-270-3.* 1968; and *TN-270-4.* 1969.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Silver bromide; AgBr; [7785-23-1]
(3) Potassium bromide; KBr; [7758-02-3]
(4) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193-215.

VARIABLES:

Direction from which equilibrium is approached. Temperature is 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The equilibrium studied was

$$AgAg(CN)_2(s) + KBr \rightleftarrows KAg(CN)_2 + AgBr(s) \qquad K_{II} \qquad [1]$$

The solubility product is calculated from

$$K_{II} = [Ag(CN)_2^-]/[Br^-] = K_{s0}^o(Ag\ Ag(CN)_2/K_{s0}^o(AgBr) \qquad [2]$$

The experimental results are given in the table below (concentration units are mol dm^{-3}).

$[KBr]_{init}$	$[KAg(CN)_2]_{init}$	$[KAg(CN)_2]_{equil}$	K_{II}	$10^{12}K_{s0}^o$*/mol^2 dm^{-6}
0.10375	-----	0.09084	7.036	3.76
0.0515	-----	0.04570	7.879	4.21
-----	0.050	0.04387	7.157	3.83

*Recalculated by the compiler: see METHOD.

Average values calculated by the compiler are:

$$K_{II} = 7.4 \pm 0.5$$

$$K_{s0}^o(AgAg(CN)_2) = (3.9\pm0.2) \times 10^{-12}\ mol^2\ dm^{-6}$$

$$c_{Ag} = (K_{s0}^o)^{1/2}/y_\pm = (1.98\pm0.06) \times 10^{-6}\ mol\ dm^{-3}/y_\pm$$

where $y_\pm$ is the mean molar activity coefficient.

AUXILIARY INFORMATION

METHOD:

Mixtures of KBr + $AgAg(CN)_2$ or AgBr + $KAg(CN)_2$ with water equilibrated isothermally with shaking 1-2 d (no details on how equil was ascertained). The soln was rapidly filtered and aliquots taken and Ag_2S pptd with Na_2S. The ppt was washed, dissolved in dilute HNO_3, and Ag^+ determined by titrn with NH_4SCN. Using point No. 1 as an example, K_{II} is calculated from

$$K_{II} = (0.09084/(0.10375-0.09084)$$

The author uses Thiel's value (1) of $K_{s0}(AgBr) = 6.56 \times 10^{-13}$ in 1 mol dm^{-3} KBr. Correcting for activity effects ($y_\pm \approx 0.62$), $K_{s0}^o(AgBr) = K_{s0}y_\pm^2 = 2.52 \times 10^{-13}$ which is clearly in error. The NBS value** for $K_{s0}^o(AgBr) = 5.35 \times 10^{-13}$ and the compiler has used this value (2) to recalculate $K_{s0}^o(AgAg(CN)_2$ from eq [2]. Since a ratio of concentrations is used in eq [2], activity coefficients probably cancel, and the use of $K_{s0}^o(AgBr)$ gives the corresponding standard value $K_{s0}^o(AgAg(CN)_2)$.

**Converted to mol^2dm^{-6} by compiler.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

K_{s0}^o: σ = ± 3% (compiler)

No other details available.

REFERENCES:

1. Kuster, F.W.; Thiel, A. *Z. Anorg. Chem.* 1900, *24*, 25.
2. Wagman, D.D.; Evans, W.H.; Parker, V.B.; Halow, I.; Bailey, S.M.; Schumm, R.H. *U.S. National Bureau of Standards TN-270-3.* 1968, and *TN-270-4.* 1969.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Silver thiocyanate; AgSCN; [1701-93-5]
(3) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]
(4) Potassium thiocyanate; KSCN; [333-20-0]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193-215.

VARIABLES:

Direction from which equilibrium is approached. Temperature is 25°C.

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The equilibrium studied was

$$AgAg(CN)_2(s) + KSCN \rightleftarrows KAg(CN)_2 + AgSCN(s) \quad K_{III} \qquad [1]$$

The solubility product for $AgAg(CN)_2$ is calculated from

$$K_{III} = [Ag(CN)_2^-]/[SCN^-] = K_{s0}^{o}(AgAg(CN)_2)/K_{s0}^{o}(AgSCN) \qquad [2]$$

The experimental results are given below (concentrations in mol dm^{-3}).

$[KSCN]_{init}$	$[KAg(CN)_2]_{init}$	$[KAg(CN)_2]_{equil}$	K_{III}	$10^{12}K_{s0}^{o*}/mol^2\ dm^{-6}$
0.1093	----	0.0827	3.109	3.10
0.0536	----	0.04051	3.095	3.09
----	0.05361	0.04023	3.007	3.00

*Recalculated by the compiler: see METHOD.

Average values calculated by the compiler are:

$$K_{III} = 3.07 \pm 0.06$$

$$K_{s0}^{o}(AgAg(CN)_2) = (3.06 \pm 0.05) \times 10^{-12}\ mol^2\ dm^{-6}$$

$$c_{Ag} = (K_{s0}^{o})^{1/2}/y_{\pm} = (1.75 \pm 0.02) \times 10^{-6}\ mol\ dm^{-3}/y_{\pm}$$

where $y_{\pm}$ is the mean molar activity coefficient.

AUXILIARY INFORMATION

METHOD:

Solutions of KSCN + $AgAg(CN)_2$ or AgSCN + $KAg(CN)_2$ equilibrated isothermally by shaking 1-2 d (no details on how equil was ascertained). The soln was rapidly filtered and Ag_2S pptd from aliquots with Na_2S. The ppt was washed, dissolved in dil HNO_3, and Ag^+ determined by titrn with NH_4SCN. Using point No. 1 as an example, K_{III} is calcd from

$$K_{III} = 0.0827/(0.1093 - 0.0827)$$

The author uses Abegg's value (1) of $K_{s0}(AgSCN) = 1.25 \times 10^{-12}$ which is too high. The compiler used a more accurate value (2) of $K_{s0}^{o}(AgSCN) = 9.97 \times 10^{-13}$ (converted to $mol^2\ dm^{-6}$ by the compiler) to recalculate $K_{s0}^{o}(AgAg(CN)_2)$ from eq [2]. Since a ratio of concentrations is used in eq [2], activity coefficients probably cancel, and the use of $K_{s0}^{o}(AgSCN)$ gives the corresponding standard value $K_{s0}^{o}(AgAg(CN)_2)$.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

K_{s0}^{o}: $\sigma = \pm 2\%$ (compiler)

No other details available.

REFERENCES:

1. Abegg, R.; Cox, A.J. *Z. Physik. Chem.* 1903, *46*, 1.
2. Vanderzee, C.E.; Smith, W.E. *J. Am. Chem. Soc.* 1956, *78*, 721.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Ammonia; NH_3; [7664-41-7]
(3) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]
(4) Silver nitrate; $AgNO_3$; [7761-88-8]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193 – 215.

VARIABLES:

Concentrations of NH_3, $AgNO_3$, and $KAg(CN)_2$ at 25°C.

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

All concentrations in equiv dm^{-3}.

$[NH_3]_{init}$	$[NH_3]_{free}$	$[AgNO_3]_{init}$	$[KAg(CN)_2^-]_{init}$	c_{Ag}
0.09955	0.09297	----	----	0.00329
0.100	0.09354	----	----	0.00323*
0.100	0.09327	----	----	0.00337
0.1973	0.1838	----	----	0.006748
0.1975	0.1843	----	----	0.00660*
0.296	0.276	----	----	0.01065*
0.2993	0.2790	----	----	0.010145
0.3353	0.3127	----	----	0.01331
0.4760	0.4418	----	----	0.017115
0.4950	0.4604	----	----	0.017308*
0.490	0.459	----	0.005	0.01551
0.490	0.4615	----	0.01	0.01422
0.525	0.4813	0.005	----	0.016865
0.525	0.4813	0.015	----	0.016085

*The salt, AgCN, for these studies was a commercial preparation (Kahlbaum); the remaining studies used a salt prepared by the author.

AUXILIARY INFORMATION

METHOD:

No details given: presumably solutions were equilibrated isothermally with shaking. The concentration of free NH_3(n) was calculated from (1)

$$n = p/13.42 \ / \ \text{equiv dm}^{-3}$$

where p is the vapor pressure of NH_3 in mm. The solubility of AgCN for all the entries in the above table was calculated from

$$\text{soly} = ([NH_3]_{init} - [NH_3]_{free})/2$$

For the last two entries in the above table, the soly of AgCN was calcd from

$$\text{soly} = ([NH_3]_{init} - [NH_3]_{free})/2 - [AgNO_3]_{init}$$

Details on methods of analysis were not given.

SOURCE AND PURITY OF MATERIALS:

AgCN was prepared by the author (no details given) or by the firm Kahlbaum. The ammonia was "carefully purified," but again no details were given.

ESTIMATED ERROR:

Based on the two measurements for $[NH_3]_{init}$ = 0.100, av error of ± 5% was calculated by the compiler.

REFERENCES:

1. Locke; Forssall, *Am. Chem. Jour.* 1904, *31*, 287.
2. Bodländer, G.; Fittig, R. *Z. Physik. Chem.* 1902, *39*, 597.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Ammonia; NH_3; [7664-41-7]
(3) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]
(4) Silver nitrate; $AgNO_3$; [7761-88-8]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193 - 215.

COMMENTS AND/OR ADDITIONAL DATA:

The two major equilibria in the system under investigation were

$$AgAg(CN)_2(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad K_{s0} = 4.9 \times 10^{-12}\ mol^2\ dm^{-6}$$

$$Ag(NH_3)_2^+ \rightleftarrows Ag^+ + 2NH_3 \qquad K_N^{-1} = 6.8 \times 10^{-8}\ mol^2\ dm^{-6}$$

where K_{s0} was evaluated by the author in this paper (e.g. see the compilation for the KCl and KBr exchange reactions), and K_N was taken from the work of Bodländer and Fittig (2). Elimination of $[Ag^+]$ from the two equations gives

$$[NH_3]/\alpha c_{Ag} = (K_N K_{s0})^{-\frac{1}{2}} = 117.8 \qquad [1]$$

where α is the degree of dissociation of the ion pair in the equilibrium

$$Ag(NH_3)_2^+ \cdot Ag(CN)_2^- \rightleftarrows Ag(NH_3)_2^+ + Ag(CN)_2^- \qquad K_1$$

Using values of α ranging from 0.96 for the most dilute solution to 0.93 for the most concentrated soln (2), Lucas calcd the quantity $[NH_3]/\alpha c_{Ag}$ using his exptl values, and found that this quantity equaled about 29 instead of the theoretical value of 117.8. He therefore assumed the α values to be wrong and using the exptl data, calcd the α values from

$$\alpha = [NH_3]/(117.8 \times c_{Ag}) \qquad [2]$$

The resulting average value was $\alpha = 0.232 \pm 0.012$. The individual values for α (i.e. for each c_{Ag} determination) gave rise to an additional problem since K_1 for the above equilibrium was no longer constant: K_1 is defined by

$$K_1 = c_{Ag}\alpha^2/(1-\alpha) \qquad [3]$$

Lucas found that if the ion pair equilibrium could be represented as

$$2Ag(NH_3)(CN)(aq) \rightleftarrows Ag(NH_3)_2^+ + Ag(CN)_2^- \qquad K_2$$

a constant value of K_2 was obtained using the calculated α values in the following relation:

$$K_2 = \alpha^2/4(1-\alpha)^2 = 0.023 \pm 0.003 \qquad [4]$$

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Potassium cyanide; KCN; [151-50-8]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Bassett, H.; Corbet, A.S. *J. Chem. Soc.* 1924, *125*, 1660-75.

VARIABLES:

Composition at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition of solution given in g salt/ 100 g solution.

KCN	AgCN	solid phase	KCN	AgCN	solid phase
41.7	0.00	A	20.14	21.66	C
40.77	6.52	A	8.56	16.11	C
39.91	8.14	A	8.05	15.76	D
40.24	10.93	A	8.93	17.73	D
40.44	13.71	B	6.75	13.53	E
37.76	18.92	B	2.36	4.42	E
35.19	25.18	B	1.64	3.27	E
28.43	26.37	C	1.26	2.31	E
26.67	24.71	C	0.0	2.9×10^{-5} (1)	E

A = KCN

B = $K_3Ag(CN)_4 \cdot H_2O$

C = $KAg(CN)_2$ [506-61-6]

D = $KAg_2(CN)_3 \cdot H_2O$

E = AgCN

AUXILIARY INFORMATION

METHOD:

Saturated solutions were prepd isothermally by placing water and excess solid in sealed waxed bottles. Prior, to sealing, the air in the bottles was flushed out with coal gas. The bottles were rotated in a thermostat for 4-5 d. Since the KCN contained KOH impurity, solutions were prepd, when possible, from mixtures of double salts and AgCN. The presence of KOH thus affected the system only for solutions containing excess KCN. Aliquots of soln were removed by suction through asbestos filter into weighed flasks (all at 25°C). Moist solids were pressed on filter paper and weighed. Total Ag in soln and solid determined by boiling in con HNO_3 and weighing as the chloride. To determine KCN in excess AgCN, AgCN was pptd by adding excess 1.0 mol dm^{-3} H_2SO_4 and separated by filtration. The filtrate was titrated with standard 0.5 mol dm^{-3} NaOH (methyl orange), and the total alkalinity calcd from the excess of H_2SO_4. In solutions of excess KCN when KOH was present, KCN was

SOURCE AND PURITY OF MATERIALS:

AgCN prepared in the dark by adding cold KCN soln to $AgNO_3$ until the ppt redissolved. The soln was filtered and AgCN pptd with HNO_3 followed by washing and air drying. The commercial grade of KCN contained as much as 3% KOH. $KAg(CN)_2$ prepared by adding excess AgCN to boiling KCN, decanting, and allowing the soln to cool. $K_3Ag(CN)_4 \cdot H_2O$ was obtained by evaporating a solution containing KCN and AgCN in a 3:1 mole ratio. Water

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Bodländer, G.; Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 192 (this is a non-existent reference, and the authors are probably referring to ref 2).
2. Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Potassium cyanide; KCN; [151-50-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Bassett, H.; Corbet, A.S. *J. Chem. Soc.* 1924, *125*, 1660-75.

COMMENTS AND/OR ADDITIONAL DATA:

The compiler has converted the experimental data into molal units, and the data are given below.

[KCN]/mol kg^{-1}	[AgCN]/mol kg^{-1}	[KCN]/mol kg^{-1}	[AgCN]/mol kg^{-1}
10.98	0.0	5.314	2.780
11.88	0.924	1.745	1.597
11.80	1.170	1.622	1.545
12.65	1.672	1.870	1.806
13.54	2.233	1.300	1.268
13.39	3.262	0.339	0.354
13.64	4.746	0.265	0.257
9.659	4.357	0.201	0.179
8.424	3.796	0.0	2.17×10^{-6}(1)

AUXILIARY INFORMATION

METHOD:

determined by distilling off HCN from the acidified filtrate into an alkaline solution which was then titrated with 0.1M $AgNO_3$ in the presence of NH_3 and KI.

SOURCE AND PURITY OF MATERIALS:

was boiled and cooled in a current of coal gas which was passed through solutions of lead acetate and NaOH.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Hydrogen cyanide; HCN; [74-90-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Randall, M.; Halford, J.O. *J. Am. Chem. Soc.* 1930, *52*, 178-91.

VARIABLES:

Concentration of HCN at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The solubility of AgCN is expressed in terms of the total silver, c_{Ag}, present in solution. Assuming the soluble species is $Ag(CN)_2^-$, then the experimental solubility can be represented by the equilibrium

$$AgCN(s) + HCN \rightleftarrows H^+ + Ag(CN)_2^- \qquad K_I . \qquad [1]$$

All concentrations in the table below are in units of mol kg^{-1}.

[HCN]	c_{Ag}	$-\log K_I$	[HCN]	c_{Ag}	$-\log K_I$
0.0296	9.83×10^{-4}	4.488	0.2275	4.24×10^{-3}	4.100
0.1016	$2.04 \times 10^{-3*}$	4.288	0.2325	3.16×10^{-3}	4.368
0.1596	2.45×10^{-3}	4.422	0.3000	3.75×10^{-3}	4.328
0.1780	3.66×10^{-3}	4.134	0.3625	3.31×10^{-3}	4.508
0.1825	2.46×10^{-3}	4.396	0.4230	4.00×10^{-3}	4.420
0.2124	2.92×10^{-3}	4.394	0.4260	5.11×10^{-3}	4.212
0.2245	2.72×10^{-3}	4.482	0.4465	4.27×10^{-3}	4.390

The authors report an average value of $K_I = 4.45 \times 10^{-5}$ mol kg^{-1}.

Based on the above data, the compiler obtains an average value of

$$K_I = (4.6 \pm 1.5) \times 10^{-5} \text{ mol kg}^{-1}$$

*A misprint in the original paper incorrectly lists this as 2.04×10^{-4}.

AUXILIARY INFORMATION

METHOD:

HCN, benzene, and excess AgCN were placed in stoppered bottles and rotated in a thermostat at 25°C for several days. HCN concentrations in the aq phase were determined by extraction from the benzene and titrated with standard NaOH. CN^- concentrations were determined by placing samples in excess NaOH and titrating to an end point with KI (i.e. method of Liebig). In a few cases, equilibrium was approached from supersaturation.

SOURCE AND PURITY OF MATERIALS:

AgCN was prepared from $AgNO_3$ and KCN. HCN was prepared by adding 9 mol dm^{-3} H_2SO_4 to KCN and collecting the gas in H_2O. No other details were given.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Lewis, J.N.; Randal, M. *Thermodynamics and the Free Energy of Chemical Substances.* McGraw-Hill. N.Y. 1923.
2. Randal, M.; Young, L.E. *J. Am. Chem. Soc.* 1928, *50*, 989.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Hydrogen cyanide; HCN; [74-90-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Randall, M.; Halford, J.O. *J. Am. Chem. Soc.* 1930, *52*, 178-91.

COMMENTS AND/OR ADDITIONAL DATA:

The authors also made three measurements on the equilibrium

$$AgCl(s) + HCN(aq) \rightleftarrows 2H^+ + Cl^- + Ag(CN)_2^- ; \; K^o_{II} = 1.9 \times 10^{-9} \text{ mol}^3 \text{ kg}^{-3} \quad [2]$$

where K^o_{II} was obtained by extrapolating a plot of $-\log K_{II}$ against $\mu^{1/2}$ (μ is the ionic strength). There is enough scatter in this data to question this extrapolated value. Similarly the authors plot $-\log(K_I(av))$ and the average ionic strength (0.0031 mol/kg) "with the aid of the curve for HCl" to obtain $K^o_I = 3.77 \times 10^{-5}$. Combining eq [2] with the dissociation reaction

$$HCN(aq) \rightleftarrows H^+ + CN^- \quad K_a = 2.05 \times 10^{-9} \text{ mol dm}^{-3} \quad [3]$$

results in

$$\beta^o_2 = K^o_{II}/K_a^2 K^o_{s0}(AgCl) = 2.62 \times 10^{18} \text{ mol}^{-2} \text{ kg}^2 \quad [4]$$

where β^o_2 is the overall formation constant for the reaction

$$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^- \quad [5]$$

Combining eqs [1] - [3] gives the solubility product for AgCN:

$$K^o_{s0}(AgCN) = K^o_I \cdot K_a \cdot K^o_{s0}(AgCl)/K^o_{II} = 7 \times 10^{-15} \text{ mol}^2 \text{ kg}^{-2} \quad [6]$$

The values for β^o_2 and $K^o_{s0}(AgCN)$ are certainly in error. The major source of this error is not due to the questionable evaluation of K^o_I or K^o_{II}, but rather to inaccurate thermodynamic data (1,2) for $K^o_{s0}(AgCl)$ and K_a which were available to the authors at the time of this research.

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Potassium cyanide; KCN; [151-50-8]

(3) Potassium nitrate; KNO_3; [7757-79-1]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gauguin, R. *J. Chim. Phys.* 1945, *42*, 28-39.[1]

VARIABLES:

One temperature: probably 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The e.m.f.'s of cell [1] were measured as 0.1 mol dm^{-3} $AgNO_3$ was titrated into a 0.0952 mol dm^{-3} KCN solution.

$$\mathrm{Pt,H_2/KCN(0.0952M)\ /\ Ag} \qquad [1]$$

The titration curve showed three well defined plateaus corresponding to the following electrode reactions:

$$\mathrm{Ag(CN)_2^- + e^- \rightleftarrows Ag + 2CN^-} \qquad E = E_2 + 0.058 \log \left\{[\mathrm{Ag(CN)_2^-}]/[\mathrm{CN^-}]^2\right\} \quad [2]$$

$$\mathrm{AgAg(CN)_2 + e^- \rightleftarrows Ag + Ag(CN)_2^-} \qquad E = E_3 - 0.058 \log[\mathrm{Ag(CN)_2^-}] \quad [3]$$

$$\mathrm{Ag^+ + e^- \rightleftarrows Ag} \qquad E = E_1 + 0.058 \log[\mathrm{Ag^+}] \quad [4]$$

The determined values of E_1, E_2, and E_3 were used to calculate the solubilith product for $Ag{\cdot}Ag(CN)_2$ and the stability constant for $Ag(CN)_2^-$. At an ionic strength of about 0.1 mol dm^{-3} and a temperature of about 20°C, the author reports the following:

$$K_{s0}(\mathrm{AgAg(CN)_2})/\mathrm{mol^2 dm^{-6}} = 10^{-11.4} = (4.0 \pm 0.9) \times 10^{-12}$$

$$\beta_2\ /\ \mathrm{mol^{-2}\ dm^6} = 10^{20.8} = (6.3 \pm 1.2) \times 10^{20}$$

The errors in K_{s0} and β_2 were calculated by the compiler and are standard deviations based on the estimated error of ±0.005 V in the e.m.f. measurements.

AUXILIARY INFORMATION

METHOD:

Experimental details not provided. It appears that a hydrogen reference electrode was used, but details on its construction and use were not given. No temp is specified and it is assumed that it was about 20°C (based on the Nernst factor of 0.058 V used by the author). A glass electrode was used to measure the pH during the titrn: thus from a materials balance and a pK_a = 9.1 for HCN (no reference given), both $[CN^-]$ and $[Ag(CN)_2^-]$ could be calcd at any point on the titrn curve. Based on the definitions of $K_{s0}(AgAg(CN)_2)$ and β_2, the following relations were given:

$$E_2 = E_1 - 0.058 \log \beta_2 \qquad [5]$$

$$E_3 = E_1 + 0.058 \log K_{s0}(\mathrm{AgAg(CN)_2}) \qquad [6]$$

Neglecting the two last data points for the highest $[Ag(CN)_2^-]$, the average of 7 points for E_2 is -0.395±0.002V

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

E.m.f.'s: ±5 mV (est. by compiler)

Temperature: ±1°C (compiler)

REFERENCES:

1. See also Gauguin, R. *Ann. Chim.* 1949, *4*, 832.
2. Davies, C.W. *Ion Association.* Butterworths. London. 1962.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver cyanide; AgCN; [506-64-9] (2) Potassium cyanide; KCN; [151-50-8] (3) Potassium nitrate; KNO_3; [7757-79-1] (4) Water; H_2O; [7732-18-5]	Gauguin, R. *J. Chim. Phys.* 1945, *42*, 28-39.[1]

COMMENTS AND/OR ADDITIONAL DATA:

Using the Davies equation (2),

$$\log y_{\pm} = -A\mu^{1/2}/(1 + \mu^{1/2}) + 0.3A\mu \qquad [7]$$

the compiler calculates a mean molar activity coefficient of $y_{\pm} = 0.782$ at 20°C ($A = 0.507$ $mol^{-1/2}$ $dm^{3/2}$ and $\mu = 0.1$ mol dm^{-3}). The standard equilibrium constants are

$$K^{o}_{s0}(AgAg(CN)_2) = K_{s0}y^2_{\pm} = (2.4\pm1.0) \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$$

$$\beta^{o}_2 = \beta_2/ y^2_{\pm} = (1.0\pm0.2) \times 10^{21} \text{ mol}^{-2} \text{ dm}^6$$

AUXILIARY INFORMATION

METHOD:

(standard deviation in E_2 calculated by the compiler). Neglecting the last two points in the second plateau region for the smallest $[Ag(CN)_2^-]$ values (i.e. for the data in the saturated solns), 9 e.m.f.'s were averaged to give $E_3 = 0.152\pm0.003$ V (standard deviation calcd by the compiler). E_1 was determined from those data points lying on the third plateau (i.e. in solns containing excess $AgNO_3$). Only one data point is given: $E = 0.650$ V for $[Ag^+] = 0.00432$ mol dm^{-3}. Using eq [3] these data give $E_1 = 0.796$ V: however the author reports a value of 0.81 V for E_1. This latter value was used to calculate the equilibrium constants. In another set of experiments, the author measured the e.m.f.'s of cells containing $HClO_4$ with either $KAg(CN)_2$ or saturated AgCN while adding KOH. Both E_2 and E_3 were found to be independent of pH over the range of pH = ∿ 0.3 to 10 (AgOH ppts at pH ⩾ 10).

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Noonan, E.C. *J. Am. Chem. Soc.* 1948, *70*, 2915-8.

VARIABLES:

One temperature: 5.0°C

PREPARED BY:

Mark Salomon and W.A. Van Hook

EXPERIMENTAL VALUES:

The solubility of $KAg(CN)_2$ in H_2O at 5.0°C was reported as

$$c_{Ag} = 1.290 \text{ mol/100 mol } H_2O \text{ } (0.716 \text{ mol kg}^{-1}*)$$

*Compilers' calculation.

AUXILIARY INFORMATION

METHOD:

Nothing specified, but compilers assume method was identical to that for the D_2O systems which are described in detail in this paper. The soly in D_2O was determined by evaporating a weighed sample of satd soln to dryness and weighing the residual salt. All determinations performed in duplicate.

SOURCE AND PURITY OF MATERIALS:

Commercial reagent grade salt was recrystallized at least twice. Treatment of water was not specified, but may be similar to that for D_2O: i.e. distillation from alkaline permanganate.

ESTIMATED ERROR:

Soly: nothing specified, but author indicates a reproducibility of ±0.5% for soly in D_2O.

Temperature: at least ±0.05°C.

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]
(3) Sodium hydroxide; NaOH; [1310-73-2]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kolthoff, I.M.; Stock, J.T. *J. Am. Chem. Soc.* 1956, *78*, 2081-5.

VARIABLES:

Concentrations of $KAg(CN)_2$ and NaOH at room temperature (22-24°C).

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

All concentrations given in mol dm^{-3}. The total soly of AgCN is denoted by S which is the sum of the concentrations of $Ag(CN)_2^-$ and $Ag(CN)(OH)^-$. The initial concentration of potassium dicyanoargentate, $[KAg(CN)_2]_{init}$, is 0.004 mol dm^{-3} in all cases.

$[NaOH]_{init}$	10^3 S	$10^3[Ag(CN)_2^-]_{free}$ *	$10^4[Ag(CN)(OH)^-]$	$10^{16}K_{s0}^o(AgCN)$
0.1	4.12	3.89	2.3	3.0
0.15	4.15	3.85	3.0	2.6
0.2	4.18	3.82	3.6	2.3
0.3	4.26	3.75	5.1	2.2
0.4	4.34	3.67	6.7	2.1
0.5	4.41	3.60	8.1	2.1
0.6	4.54	3.46	10.8	2.3
0.7	4.59	3.41	11.8	2.1
0.8	4.73	3.28	14.5	2.3
0.9	4.84	3.17	16.7	2.4

*Calculated by the compiler from eq [8] in the authors' paper:

$$[Ag(CN)_2^-]_{free} = [Ag(CN)_2^-]_{init} - 1/2[Ag(CN)(OH)^-] \qquad [1]$$

The average value of the standard solubility product at 22-24°C is

$$K_{s0}^o(AgCN) = (2.3 \pm 0.3) \times 10^{-16} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD:

An amperometric titration method was employed using the cell

$$Pt(Ag)/KAg(CN)_2(0.004M),\ NaOH(xM)/ref \qquad [2]$$

where the reference electrode is a satd calomel and Pt(Ag) is a silver plated Pt rotating microelectrode. A potential difference of -0.15 V was maintained between the two electrodes during the addition of $AgNO_3$. As $AgNO_3$ soln was titrated into the cell, the current increases until pptn occurs and at which point, the slope of a plot of current vs $AgNO_3$ abruptly changes. The concentration of added silver at this point is the "turbidity concentration," and the equilibrium existing between the soluble species is

$$Ag^+ + 2OH^- + Ag(CN)_2^- \rightleftarrows 2Ag(OH)(CN)^- \qquad [3]$$

SOURCE AND PURITY OF MATERIALS:

C.p. grade reagents and conductivity water were used to prepare all solns. $KAg(CN)_2$ solns prepared by stoichiometrically combining KCN and $AgNO_3$ solutions. All solns were deoxygenated by means of a stream of N_2.

ESTIMATED ERROR:

Solubility: av ±1% (compiler)
K_{s0}^o: ±44% (authors); ±12% (compiler)
Amperometric endpoint: 1×10^{-5} mol dm^{-3}.
Temperature: 23 ±1°C

REFERENCES:

1. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233.
2. Ricci, J.E. *J. Phys. Colloid Chem.* 1947, *51*, 1375.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver cyanide; AgCN; [506-64-9] (2) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	Kolthoff, I.M.; Stock, J.T., *J. Am. Chem. Soc.* <u>1956</u>, 2081-5.

COMMENTS AND/OR ADDITIONAL DATA:

The equilibrium constant for reaction [3] is given by

$$K_A = [Ag(CN)(OH)^-]^2/[Ag^+][OH^-]^2[Ag(CN)_2^-] = [Ag(CN)(OH)^-]^2\beta_2^{-1}/\left\{[Ag^+]^2 \times [CN^-]^2[OH^-]^2\right\} \qquad [4]$$

where β_2 is the overall formation constant for $Ag(CN)_2^-$. At the turbidity point, the soln is satd and the solid phase is AgCN: hence eq [4] becomes

$$K_A^o = [Ag(CN)(OH)^-]^2\beta_2^{-1}/K_{s0}^2(AgCN)[OH^-]^2 \qquad [5]$$

Experiments were also carried out with additions of KBr in which case the precipitating moiety at the turbidity point is AgBr: hence

$$K_A^o = [Ag(CN)(OH)^-]^2[Br^-]/K_{s0}(AgBr)[OH^-]^2[Ag(CN)_2^-] \qquad [6]$$

Eq [6] was used to evaluate K_A^o at 25±0.1°C taking $K_{s0}^o(AgBr) = 5.0 \times 10^{-13}$ (1). From eq [1], it is seen that $[Ag(CN)(OH)^-]$ is twice the turbidity concentration (t) of $AgNO_3$ minus a correction c for the formation of argentate (AgO^-):

$$[Ag(CN)(OH)^-] = 2t - c$$

This correction is small for solns containing $Ag(CN)_2^-$ (i.e. $c \sim 10^{-6}$ mol dm^{-3}). With the K_A^o value of $3.4 \pm 0.8 \times 10^6$ evaluated for 25°C, the authors compute K_{s0}^o for 22-24°C for each data point listed in the table above (eq [5]). It is assumed that all effects due to activity coefficients cancel in eqs [5] and [6]. The value for β_2 required in eq [5] was taken as 7.1×10^{19} (2). The authors also calculated the equilibrium constants of the following reactions at 25°C:

$$Ag(CN)_2^- + OH^- \rightleftarrows Ag(CN)(OH)^- + CN^- \qquad B$$

$$Ag^+ + OH^- + CN \rightleftarrows Ag(CN)(OH)^- \qquad C$$

$$K_B^o = (K_A^o/\beta_2^o)^{1/2} = 2.27 \times 10^{-7}$$

$$K_C^o = (K_A^o\ \beta_2^o)^{1/2} = 1.6 \times 10^{13}\ mol^{-2}\ dm^6$$

The compiler would like to point out that as a result of the preparation of $AgAg(CN)_2$ from KCN and $AgNO_3$, and the titration of the former with $AgNO_3$, both $NaNO_3$ and KNO_3 may, formally, be considered as additional components in this complex system.

The authors quote an average deviation of ±44% in their $K_{s0}(AgCN)$ value at 22-24°C. However based on the data in the above table, the compiler computes a standard deviation of ±12%. The authors do not describe how they arrived at their average error.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Potassium cyanide; KCN; [151-50-8]
(3) Potassium nitrate; KNO_3; [7757-79-1]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Azzam, A.M.; Shimi, I.A.W. *Z. Anorg. Allg. Chem.* 1963, *321*, 285-92.

VARIABLES:

Ionic strength at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Although the ionic strength was varied from 0.005 to 1.0 mol dm^{-3}, the equilibrium constants vary randomly thereby preventing any extrapolation to zero ionic strength. The data presented below are therefore average values based on the data for each ionic strength. The standard deviation of the average values of each equilibrium constant was calculated by the compiler.

$$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad K_{s0}(Ag\,Ag(CN)_2) = (5.83 \pm 0.25) \times 10^{-12} mol^2 dm^{-6}$$

$$AgCN(s) \rightleftarrows Ag^+ + CN^- \qquad K_{s0}(AgCN) = (1.46 \pm 0.40) \times 10^{-16}\ mol^2\ dm^{-6}$$

$$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^- \qquad \beta_2 = (2.8 \pm 0.3) \times 10^{20}\ mol^{-2}\ dm^6$$

$$Ag^+ + 3CN^- \rightleftarrows Ag(CN)_3^{2-} \qquad \beta_3 = (9.57 \pm 0.02) \times 10^{21}\ mol^{-3}\ dm^9$$

Values for β_3 calculated from those data in the region for [Ag]/[CN] = 1/4.5 to 1/6.5. In the region for [Ag]/[CN] = 1/2.9 to 1/5, both $Ag(CN)_3^{2-}$ and $Ag(CN)_2^-$ were assumed to exist and β_2 evaluated from this data.

AUXILIARY INFORMATION

METHOD:

Equilibrium constants determined by potentiometric titration using the cell

$$Ag/AgNO_3,\ KCN \left|\left| \begin{matrix} NH_4NO_3 \\ \text{agar bridge} \end{matrix} \right|\right| \begin{matrix} \text{satd} \\ \text{calomel} \end{matrix}$$

The initial $AgNO_3$, KCN soln in which [Ag]/[CN] ≈ 1/6 was placed in the cell, thermostated, and titrated with $AgNO_3$. $[Ag^+]$ determined from the Nernst eq and the remaining concentrations calcd from mass balance considerations: the hydrolysis of CN^- was taken into account and K_a for HCN was taken as 7.9×10^{-10}. Equilibrium was taken when the e.m.f. remained steady or when the change was less than 10 mV in 15 min. Five constant ionic strength solns were used where μ = 1.0, 0.25, 0.05, 0.01, and 0.005 mol dm^{-3}. The experiments were repeated two or three times for each ionic strength.

SOURCE AND PURITY OF MATERIALS:

Most of the materials used were of analar grade. The KCN, which lost 0.5% weight upon melting, analysed as 99.5% by volumetric CN analysis. All solutions were prepared with conductivity water.

ESTIMATED ERROR:

An error of ±10 mV in the e.m.f. gives av error of ±30% in the K_{s0} value.
Temperature: not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver cyanide; AgCN; [506-64-9] (2) Potassium cyanide; KCN; [151-50-8] (3) Water; H_2O; [7732-18-5]	Zsakó, J.; Petri, E. *Rev. Roumaine Chim.* 1968, *10*, 571-80.
VARIABLES:	PREPARED BY:
One temperature: 20.5°C	Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength constant at about 0.01 mol dm^{-3}. The results are reported in terms of standard values of the equilibrium constants at 20.5°C.

$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^-$ $\quad K_{s0}^o(Ag\,Ag(CN)_2) = 4.5 \times 10^{-12}\ mol^2\ dm^{-6}$

$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^-$ $\quad \beta_2^o = 7.1 \times 10^{20}\ mol^{-2}\ dm^6$

$Ag^+ + 3CN^- \rightleftarrows Ag(CN)_3^{2-}$ $\quad \beta_3^o = 6.4 \times 10^{21}\ mol^{-3}\ dm^9$

Using the relation

$$K_{s0}^o(AgCN) = \sqrt{K_{s0}^o(AgAg(CN)_2)/\beta_2^o}$$

the compiler has computed the solubility product for AgCN:

$AgCN(s) \rightleftarrows Ag^+ + CN^-$ $\quad K_{s0}^o(AgCN) = 8.0 \times 10^{-17}\ mol^2\ dm^{-6}$

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations with 0.2 mol dm^{-3} $AgNO_3$ were carried out using the cell

Ag/KCN(0.01)//satd calomel

The cell was thermostated and the titrations carried out both with and without stirring. In the latter case, natural gas was passed over the soln during the titrn. The titrn curve showed three distinct pleateaus corresponding to $Ag(CN)_3^{2-}$, $Ag(CN)_2^-$, and the pptn of AgCN according to

$Ag^+ + Ag(CN)_2^- \rightleftarrows 2AgCN(s)$

Equil constants were calcd by Sillén's method (1) and due allowance was made for the hydrolysis of CN^-: K_a for HCN was taken as 4.79×10^{-10} (2). All equil constants were corrected for activity effect by use of the limiting law: $\log y_\pm = -0.508\mu^{1/2}$ where μ is the ionic strength. The reported value for $K_{s0}(AgAg(CN)_2)$ is an average one based on 10 points in the saturated region.

SOURCE AND PURITY OF MATERIALS:

All solutions were prepared from chemically pure reagent grade materials. Analyses were performed by potentiometric titrn (results not given). For reproducible Ag indicator electrodes, Ag wire was plated with Ag from a cyanide bath followed by anodization in 0.2M HCl and cathodized in 0.1M H_2SO_4. The electrodes were washed and stored in a dil soln of $AgNO_3$. Distilled water was, presumably, used.

ESTIMATED ERROR:

Assuming error in the av values is ±1 unit in the last significant figure, standard dev in equil constants is $\leqslant$ 3%. Temp control is ±0.5°C.

REFERENCES:

1. Sillén, L.G. *Acta Chem. Scand.* 1962, *16*, 159.
2. *Sprawochnik Khimika.* Moskau - Leningrad. 1952, *3*, 495.

COMPONENTS:

(1) Silver cyanide; $AgCN$; [506-64-9]

(2) Perchloric acid; $HClO_4$; [7601-90-3]

(3) Sodium cyanide; $NaCN$; [143-33-9]

(4) Sodium hydroxide; $NaOH$; [1310-73-2]

(5) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gübeli, A.O.; Côté, P.A. *Can. J. Chem.* 1972, *50*, 1144-8.

VARIABLES:

NaCN concentration and pH at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: Concentration units employed are mol dm^{-3}. The concentration of $NaClO_4$ in all solutions is 1.0 mol dm^{-3}. The total solubility of silver is expressed in logarithmic form, pAg_{tot}. Similarly the silver ion and total cyanide are expressed as pAg^+ and pCN_{tot}.

TABLE 1. pH < 4

pH	pCN_{tot}	pAg_{tot}	pAg^+
1.85	2.72	5.02	5.73
2.02	2.70	4.90	5.97
2.05	2.57	4.77	6.14
2.12	2.66	4.75	6.01
2.20	2.51	4.55	6.22
2.32	2.59	4.47	6.33
2.72	2.26	3.85	7.10
2.95	2.67	4.06	6.88
3.00	2.83	4.13	6.79
3.05	2.61	3.86	7.10
3.05	2.34	3.67	7.31
3.10	2.72	4.01	6.97
3.12	2.28	3.49	7.50
3.22	2.20	3.36	7.56
3.22	2.21	3.37	7.58
3.35	2.49	3.63	7.31
3.55	2.80	3.92	7.04
3.42	2.65	3.77	7.20
3.42	2.64	3.70	7.51
3.50	2.31	3.23	7.78
3.55	2.20	3.19	7.99

TABLE 2. 4 < pH < 13

pH	pCN_{tot}	pAg_{tot}	pAg^+
5.63	2.45	2.81	8.18
5.70	2.47	2.84	8.09
5.80	2.93	3.34	7.71
6.70	2.40	2.72	8.13
7.05	2.93	3.29	7.53
7.72	2.30	2.67	8.20
8.33	2.47	2.84	8.05
8.50	2.42	2.84	8.08
8.57	2.33	2.67	8.24
8.82	2.48	2.81	8.12
8.95	2.42	2.76	8.18
9.37	2.35	2.69	8.13
9.52	2.33	2.68	8.20
9.72	2.51	2.84	7.93
10.00	2.34	2.70	8.18
10.40	2.46	2.81	8.09
10.62	2.32	2.68	8.24
10.65	2.48	2.82	7.95
10.70	2.50	2.83	7.91
11.17	2.36	2.73	8.18
11.67	2.34	2.68	8.24

AUXILIARY INFORMATION

METHOD:

Saturated solns prepared by mixing solns of $AgClO_4$ with excess NaCN, and the pH adjusted with either $HClO_4$ or NaOH. The $AgClO_4$ contained known amounts of ^{110}Ag. The mixtures were prepared such that the resulting $[NaClO_4]$ was constant at 1.0 mol dm^{-3}. The solns were equilibrated isothermally by agitation for the first several days followed by quiescent equilibration for 4 weeks. Equilibrium was verified by constancy in the total Ag concentration. $[Ag]_{tot}$ was determined in a scintillation counter, and total CN by a spectrophotometric method (1). The pH was measured with a glass / calomel electrode combination. The silver ion concentration was similarly determined by replacing the glass electrode with a silver wire. The pK_a value of HCN was determined using Anderegg's method (2).

SOURCE AND PURITY OF MATERIALS:

All reagents were of a "guaranteed purity" grade, and were dissolved in doubly distilled water. No other details were given.

ESTIMATED ERROR:

Soly: av probably ⩽ ±6% (compiler)

Equil constants: see COMMENTS below.

Temperature: not specified.

REFERENCES:

1. Bark, L.S.; Higson, H.G., *Talanta* 1964, *11*, 621.
2. Anderegg, G. *Helv. Chim. Acta* 1957, *40*, 1022.
3. Kolthoff, I.M.; Stock, J.T. *J. Am. Chem. Soc.* 1956, *78*, 2081.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Perchloric acid; $HClO_4$; [7601-90-3]

(3) Sodium cyanide; NaCN; [143-33-9]

(4) Sodium hydroxide; NaOH; [1310-73-2]

(5) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Gübeli, A.O.; Côté, P.A. *Can. J. Chem.* 1972, *50*, 1144-8.

EXPERIMENTAL VALUES: (continued)

TABLE 3 $pH \geqslant 13$

pH	pCN_{tot}	pAG_{tot}	pAg^+	pAg^f_{tot}*
13.00	2.49	2.79	8.06	3.74
13.05	2.65	2.90	7.92	3.69
13.10	2.76	3.02	7.80	3.65
13.15	2.80	3.04	7.74	3.67
13.20	3.10	3.24	7.38	3.57
13.25	2.59	2.85	7.92	3.46
13.27	2.66	2.93	7.84	3.51
13.30	2.96	3.14	7.50	3.45
13.35	2.99	3.16	7.35	3.38
13.40	3.05	3.18	7.30	3.37

* $[Ag]^f_{tot} = [Ag(CN)(OH)^-] = [Ag]_{tot} - [Ag^+] - [Ag(CN)_2^-]$

COMMENTS AND/OR ADDITIONAL DATA:

The data in Tables 1 - 3 were treated in terms of the following equilibria:

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w$$

$$HCN \rightleftarrows H^+ + CN^- \qquad K_a$$

$$AgCN(s) \rightleftarrows Ag^+ + CN^- \qquad K_{s0}(AgCN)$$

$$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad K_{s0}(AgAg(CN)_2)$$

$$Ag^+ + OH^- + CN^- \rightleftarrows Ag(CN)(OH)^- \qquad K_{11}$$

K_w was taken as 1.0×10^{-14}* and pK_a in 1M $NaClO_4$ was determined by the authors to be 8.95. The values of these equilibrium constants were determined by the authors to be:

$$K_{s0}(AgCN) = (2.9 \pm 0.4) \times 10^{-16}\ mol^2\ dm^{-6}$$

$$K_{s0}(AgAg(CN)_2) = (1.3 \pm 0.2) \times 10^{-12}\ mol^2\ dm^{-6}$$

$$\beta_2 = (1.4 \pm 0.2) \times 10^{20}\ mol^{-2}\ dm^6$$

$$K_{11} = (6.4 \pm 1.2) \times 10^{12}\ mol^{-2}\ dm^6$$

K_{11} is identical to Kolthoff and Stock's K_C (3): the authors do not discuss the differences between their work and that of Kolthoff and Stock.

*For 1 mol dm^{-3} solns, $K_w = K_w^o \gamma_\pm^2$: the authors did use the activity term a_{H^+} in their calculations (obtained from their pH measurements), but all other concentrations were not corrected for activity effects.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]
(2) Silver iodide; AgI; [7783-96-2]
(3) Barium nitrate; $Ba(NO_3)_2$; [10022-31-8]
(4) Potassium cyanide; KCN; [151-50-8]
(5) Potassium iodide; KI; [7681-11-0]
(6) Potassium nitrate; KNO_3 [7757-79-1]
(7) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ungerer, B.; Jurio, R.; Manuele, R.J.

J. Chem. Educ. 1972, *49*, 434-5.

VARIABLES:

[KCN]/[KI] ratio at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The thermodynamic soly product was calcd from

$$\log K^{\circ}_{s0}(\mathrm{AgAg(CN)_2}) = (E_2-E_1)F/(RT\ \ln 10) - \log[\mathrm{I^-}]y_{\pm} + \log[\mathrm{Ag(CN)_2^-}]y_{\pm} + \log K^{\circ}_{s0}(\mathrm{AgI}) \qquad [1]$$

The data and results are summarized in the table (data based on volume units)

titrn no.	$(E_2-E_1)/0.0582$	$-\log[\mathrm{I^-}]y_{\pm}$	$-\log[\mathrm{Ag(CN)_2^-}]y_{\pm}$	$\log K^{\circ}_{s0}(\mathrm{AgAg(CN)_2})$ authors	compiler
1	5.2062	2.1240	2.4931	-11.26	-11.58
2	5.2062	2.1240	2.4922	-11.25	-11.58
3	5.1890	2.1239	2.4904	-11.27	-11.60
4	5.1890	2.1240	2.4912	-11.27	-11.60
5	5.1890	2.1240	2.4912	-11.27	-11.60
6,7	----	----	----	-11.37*	-11.70

*Mean of two values: only other data supplied was [KCN]/[KI] for initial solution = 2.

The average values and standard deviations based on the compilers calculations are:

$$\log\,[K^{\circ}_{s0}(\mathrm{AgAg(CN)_2})/\mathrm{mol^2\ dm^{-6}}] = -11.62 \pm 0.05$$

$$K^{\circ}_{s0}(\mathrm{AgAg(CN)_2}) = (2.4 \pm 0.6) \times 10^{-12}\ \mathrm{mol^2\ dm^{-6}}$$

AUXILIARY INFORMATION

METHOD: Potentiometric titrn with $AgNO_3$. The cell used is given by

$Ag/KCN,\ KI,\ KNO_3,\ Ba(NO_3)_2//$ satd cal

E.m.f.'s measured with L and N 7041 potentiometer at room temp, and solns purged with N_2. pH measurements were also carried out and reported graphically. Three plateaus were obsd: at the end of the 1st plateau $Ag(CN)_2^-$ has formed stoichiometrically, the e.m.f. is E_1, and ionic strength, μ, is 0.0062 mol dm^{-3}. At the end of the 2nd plateau, AgI has completely pptd and pptn of AgCN begins; at this point the e.m.f. is E_2 and μ = 0.0605. Initial solns for titrns 1-5 contained [KCN] = [KI] =0.01. Composition of solns 6, 7 not given. Activity coeff calcd from

$$\log y_{\pm} = -A\mu^{1/2} + Ba\mu \qquad [2]$$

Values of A, B, and a not given. Authors used incorrect value (1) of log $K^{\circ}_{s0}(\mathrm{AgI})$ = -16.093: compiler's calcn uses correct value of -16.421 based on E° data at 20°C (2,3).

SOURCE AND PURITY OF MATERIALS:

Analytical grade reagents used with bidistilled water. $Ba(NO_3)_2$ was added (0.001 mol dm^{-3}) to eliminate carbonates. 99.9% Ag wire used for indicator electrode was cleaned in KCN soln and washed. A potassium nitrate-agar salt bridge was used to separate the study soln from the satd calomel reference electrode.

ESTIMATED ERROR:

K°_{s0}: see above

Temperature: ±0.5°C

REFERENCES:

1. Jurio, R.L.; Ungerer, B.; Manuele, R.J. *J. Chem. Educ.* 1971, *48*, 122.
2. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233.
3. Hetzer, H.B.; Robinson, R.A.; Bates, R.G. *J. Phys. Chem.* 1964, *68*, 1929.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium dicyanatoargentate; $NaAg(CN)_2$; [2140-69-3] (2) Ethanol; C_2H_6O; [64-17-5] (3) Water; H_2O; [7732-18-5]	Baup, S. *Ann. Chim. Phys.* 1858, *53*, 462-8.
VARIABLES:	PREPARED BY:
One temperature: 20°C	Mark Salomon

EXPERIMENTAL VALUES:

The solvent is 85% ethanol (presumably by weight)

$$c_{Ag} = 4.2 \text{ g/100 g solvent}$$

$$c_{Ag} = 0.23 \text{ mol kg}^{-1} \text{ (compiler's calculation)}$$

AUXILIARY INFORMATION

METHOD:	SOURCE AND PURITY OF MATERIALS:
Nothing specified.	$NaAg(CN)_2$ was pptd from a satd soln of NaCN and AgCN. The NaCN was prepared by dissolving $Na_4Fe(CN)_6$ with 1/2 equivalent of Na_2CO_3 (solvent not specified, but compiler assumes it to be water). No other details were given. The author states that the $NaAg(CN)_2$ crystals were anhydrous.
COMMENTS AND/OR ADDITIONAL DATA:	ESTIMATED ERROR:
The major objective of this paper was to establish the stoichiometry of the salt. The solubility was simply mentioned as one of several physical properties.	Nothing specified.
	REFERENCES:

COMPONENTS:

(1) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]

(2) Eicosahydrodibenzo [b,k][1,4,7,10,13,16] hexaoxacyclooctadecin (dicyclohexyl-18-crown-6); $C_{20}H_{36}O_6$; [16069-36-6]

(3) 1,4-Dichlorobenzene; $C_6H_4Cl_2$; [95-50-1]

ORIGINAL MEASUREMENTS:

Pedersen, C.J. *J. Am. Chem. Soc.* 1967, *89*, 7017-36

VARIABLES: One temperature: 26°C

PREPARED BY: Mark Salomon

EXPERIMENTAL VALUES:

The solubility of $KAg(CN)_2$ in the presence of an equal molar quantity or excess of dicyclohexyl-18-crown-6 was reported as

$$0.27 \text{ mol dm}^{-3}$$

AUXILIARY INFORMATION

METHOD:

Saturated solutions were prepared by adding $KAg(CN)_2$ to an equimolar or excess quantity of the crown ether in the solvent o-dichlorobenzene. The author did not specify the concentration of the crown ether, and the compiler assumes that the solubility is the same whether equimolar or excess polyether is present.

No other details were given.

SOURCE AND PURITY OF MATERIALS:

Dibenzo-18-crown-6 was first prepared by reacting catechol with bis(2-chloroethyl) ether in aqueous NaOH solutions. Dicyclohexyl-18-crown-6 was prepared by hydrogenation of the former polyether in p-dioxane with RuO_2 catalyst. No other details were given.

ESTIMATED ERROR:

Nothing specified

REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Tetraethylammonium cyanide; $(C_2H_5)_4NCN$; [13435-20-6]

(3) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]

(4) Dimethyl sulfoxide; C_2H_6SO; [67-68-5]

ORIGINAL MEASUREMENTS:

Le Démézet, M.; Madec, C.; L'Her, M.
Bull. Soc. Chim. Fr. 1970, 365-9.

VARIABLES:

One temperature: probably 22°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at about 0.11 mol dm^{-3}. The data are reported in terms of the following equilibrium constants:

$$K_{s0}(AgCN) = 1.3 \times 10^{-15}\ mol^2\ dm^{-6}$$

$$K_{s0}(Ag\ Ag(CN)_2) = 4.0 \times 10^{-7}\ mol^2\ dm^{-6}$$

$$\beta_2 = 2.5 \times 10^{23}\ mol^{-2}\ dm^6$$

$$\beta_{21} = 1.0 \times 10^{15}\ mol^{-2}\ dm^6$$

These constants correspond to the following reactions:

$$AgCN(s) \rightleftarrows Ag^+ + CN^- \qquad K_{s0}(AgCN)$$

$$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad K_{s0}(Ag\ Ag(CN)_2)$$

$$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^- \qquad \beta_2$$

$$2Ag^+ + CN^- \rightleftarrows Ag_2CN^+ \qquad \beta_{21}$$

AUXILIARY INFORMATION

METHOD:

The equilibrium constants were determined from potentiometric titrn data using the cell

$$Ag/Et_4NCN(0.01M),\ Et_4NClO_4(0.1M)//\text{-}LiCl(0.1M),\ AgCl_2^-(0.001M)/Ag$$

where Et= C_2H_5. The cell soln was titrated with $AgClO_4$ soln. $[Ag^+]$ was calcd from the Nernst eq, and the equilibrium constants were calcd using mass balance relationships for $[CN^-]$.

SOURCE AND PURITY OF MATERIALS:

Commercial Et_4NClO_4, Et_4NCl, KCN, and $(CH_3)_2SO$ were used, but no details were given for purification. Et_4NCN prepared by dissolving KCN and Et_4NCl in alcohol, and separating the soln from the insoluble KCl.

COMMENTS AND/OR ADDITIONAL DATA:

Nowhere in the paper do the authors state the experimental temperature. Since they use the factor 0.058 in the Nernst equation which is their experimental value determined elsewhere (1) for 22°C, the compiler assumes the same temperature for the present work. The uncertainty in the total ionic strength is due to the uncertainty in the concentration of the $AgClO_4$ titrate (a 0.5M soln was used in reference 1).

ESTIMATED ERROR:

Nothing specified

REFERENCES:

1. Courtot-Coupet, J.; L'Her, M. *Bull. Soc. Chim. Fr.* 1969, 675.

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Tetraethylammonium cyanide; $(C_2H_5)_4NCN$; [13435-20-6]

(3) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]

(4) Nitromethane; CH_3NO_2; [75-52-5]

ORIGINAL MEASUREMENTS:

Bardin, J.C.; *J. Electroanal. Chem. Interfacial Electrochem.* 1970, *28*, 157-66.[1]

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The data were reported in terms of the following equilibrium constants at varying ionic strength ($\leqslant$ 0.02 mol dm^{-3}):

$$K_{s0}(AgCN) = 1 \times 10^{-24}\ mol^2\ dm^{-6}$$

$$K_{s0}(Ag\ Ag(CN)_2) = 1 \times 10^{-15}\ mol^2\ dm^{-6}$$

$$\beta_2 = 1 \times 10^{34}\ mol^{-2}\ dm^6$$

$$K_{s2} = 1 \times 10^{10}$$

The corresponding reactions are:

$$AgCN(s) \rightleftarrows Ag^+ + CN^- \qquad K_{s0}(AgCN)$$

$$2AgCN(s) \rightleftarrows Ag^+ + Ag(CN)_2^- \qquad K_{s0}(AgAg(CN)_2)$$

$$Ag^+ + 2CN^- \rightleftarrows Ag(CN)_2^- \qquad \beta_2$$

$$AgCN(s) + CN^- \rightleftarrows Ag(CN)_2^- \qquad K_{s2}$$

AUXILIARY INFORMATION

METHOD:

The various equilibria were studied by a potentiometric titration method using the cell

$$Ag/(C_2H_5)_4NCN(0.01M)//reference$$

In this cell, the indicator electrode is a silver wire, and the reference electrode, AgCl,Ag, is the same as that described elsewhere (2). A solution of $AgClO_4$ was titrated into the cell and the Ag^+ concentration determined from the Nernst equation, and the CN^- concentration from mass balance considerations. The cell was enveloped with a water jacket.

SOURCE AND PURITY OF MATERIALS:

$(C_2H_5)_4NCN$ prepd by passing a soln of $(C_2H_5)_4NClO_4$ through a column contng the CN-form Dowex 1X4 ion-exchange resin. The effluent was evap under vac, recryst from methanol, dried at 80°C in vac, and stored in vac. Practical grade CH_3NO_2 washed with aq solns of $NaHCO_3$, and 5% H_2SO_4 and fractionally distilled in vac. The 110°C fraction dried over $CaSO_4$ under N_2 for 3 weeks. Detectable amounts of $C_2H_5NO_2$ and $C_3H_7NO_2$ were present. The maximum H_2O present was 5×10^{-3} mol dm^{-3}.

ESTIMATED ERROR:

Nothing specified

REFERENCES:

1. (a) Bardin, J.-C. *Thèse* Paris. 31 Mai 1972. enregistrée au C.N.R.S. sous le No. AO 7142: (b) Badoz-Lambling, J.; Bardin, J.-C.; *C.R. Acad. Sci.* 1968, *266C*, 95.

2. Cauquis, G.; Serve, D.; *Bull. Soc. Chim. Fr.* 1966, 302.

COMPONENTS:	EVALUATOR:
(1) Silver cyanide; AgCN; [506-64-9] (2) Nitric acid; HNO_3; [7697-37-2] (3) Sulfuric acid; H_2SO_4; [7664-93-9] (4) Hydrogen cyanide; HCN; [74-90-8]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ U.S.A. August 1978

CRITICAL EVALUATION:

Jander and Grüttner determined the solubility of AgCN in anhydrous HCN in the presence of H_2SO_4 and HNO_3. The data were presented graphically, and the temperature was not reported. It appears that the solubility of AgCN in pure HCN is vanishingly small. In fact Linke and Seidell have interpolated values of c_{Ag} from the graphical data, and report numerical values in their compilation.

REFERENCES:

1. Jander, G.; Grüttner, B. *Ber.* 1948, *81*, 107.
2. Linke, W.; Seidell, A. *Solubilities of Inorganic and Metal Organic Compounds*. American Chemical Society. Washington, D.C. 1958, Vol 1.

COMPONENTS: (1) Silver cyanide; AgCN; [506-64-9] (2) Hydrogen fluoride; HF; [7664-39-3]	ORIGINAL MEASUREMENTS: Dove, M.F.A.; Hallett, J.G. *J. Chem. Soc. (A)* 1969, 2781-7.
VARIABLES: One temperature: 20°C	PREPARED BY: Mark Salomon

EXPERIMENTAL VALUES:

$$c_{Ag} \geqslant 3.2 \text{ mol kg}^{-1}$$

AUXILIARY INFORMATION

METHOD: Nothing specified. Solutions of AgCN in HF were found to be stable after several weeks.	SOURCE AND PURITY OF MATERIALS: Anhydrous HF purified by distillation from a nickel vessel into a silver plated cold finger. The specific conductance was 2 x 10^{-5} ohm^{-1} cm^{-1} at 0°C. A commercial grade of AgCN was dried under vacuum at 100°C.
	ESTIMATED ERROR: Nothing specified.
	REFERENCES:

COMPONENTS:

(1) Silver cyanide; AgCN; [506-64-9]

(2) Sulfur dioxide; SO_2; [7446-09-5]

ORIGINAL MEASUREMENTS:

1. Jander, G.; Ruppolt, W. *Z. Physik. Chem.* <u>1937</u>, *179A*, 43-50.
2. Jander, G.; Wickert, K. *Z. Physik. Chem.* <u>1936</u>, *178A*, 57-73.

VARIABLES:

One temperature: 0°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$$C_{Ag} = 0.19 \text{ g kg}^{-1}$$

$$= 0.00142 \text{ mol kg}^{-1} \text{ (compilers calcn)}$$

AUXILIARY INFORMATION

METHOD:

Saturated solns prepared isothermally in an ice-bath. Liquid SO_2 with excess AgCN sealed in a glass tube and rotated in the ice-bath. In the center of the tube a wad of glass wool was placed which served to filter the satd soln by rotating the tube lengthwise through 180°C. The lower half of the tube containing the satd soln was kept in the ice-bath and separated from the upper half by melting the tube just below the glass wool filter. The satd soln was analysed by evaporating the SO_2, taking up the residue in water, and analysing by "known" methods (no details given).

COMMENTS AND/OR ADDITIONAL DATA:

Source paper 2 describes preparation of the solvent and a few details on the method while source paper 1 describes the source of the salts and additional details on the exptl method. Both papers report the same soly data, and indicate that no solvate forms.

SOURCE AND PURITY OF MATERIALS:

Commercial SO_2 of high purity was passed through concentrated H_2SO_4, asbestos wool to remove dust and non-gaseous impurities, P_2O_5, and asbestos wool again. The SO_2 was collected in a vessel cooled with a mixture of CO_2 and ether: it had a specific conductivity of 4.7×10^{-7} ohm^{-1} cm^{-1} (the temperature was not specified). The AgCN used was either prepared by the authors or was a high purity commercial product: it was dried before use.

ESTIMATED ERROR:

Nothing specified

REFERENCES:

COMPONENTS:

(1) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]

(2) Water-d_2; D_2O; [7789-20-0]

ORIGINAL MEASUREMENTS:

Noonan, E.C. *J. Am. Chem. Soc.* 1948, *70*, 2915-8.

VARIABLES:

One temperature: 5.0°C

PREPARED BY:

W.A. Van Hook

EXPERIMENTAL VALUES:

D_2O analysis = D/(D + H) = 0.9086

$$C_{Ag} = 1.015 \text{ mol/100 mol solvent } (0.511 \text{ mol kg}^{-1*})$$

In pure D_2O the calculated** solubility is

$$C_{Ag} = 0.974 \text{ mol/100 mol } D_2O \quad (0.486 \text{ mol kg}^{-1*})$$

*Compiler's calculation.

**Assumption made is that the soly is linearly dependent upon D content.

AUXILIARY INFORMATION

METHOD:

D_2O purity was measured by a density method. Solubility by evaporating a weighed sample of saturated solution to dryness and weighing residual salt. All determinations performed in duplicate.

SOURCE AND PURITY OF MATERIALS:

Commercial reagent grade salt was recrystallized at least twice. Heavy water was treated by distillation from alkaline permanganate and found to have a conductivity of 2 x 10^{-6} mho or better. D/H analysis was by density.

ESTIMATED ERROR:

No estimate of accuracy is possible for this single point. Author indicates a reproducibility of ±0.5%. Temp control at least ±0.05°C

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Silver selenocyanate; AgSeCN; [5169-33-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ U.S.A. January 1978

CRITICAL EVALUATION:

The solubility of AgSeCN in water has been studied in detail by three research groups (1-3). All have used the e.m.f. method to determine the soly, but only the most recent work by Das et. al. (3) completely eliminates liquid junction potentials: this was accomplished by using the method of Owen and King (4).

Waitkins and McCrosky (2) report that their cell potentials decreased with time, and the "equilibrium" e.m.f. values were therefore measured as soon as possible after the salt bridge was introduced to complete the cell. The reason for this instability is not known, but formation of red Se at the Ag electrode was observed.

The value of 4.0 x 10^{-16} mol^2 dm^{-6} for K_{s0} obtained by Birckenbach and Hüttner (1) at 291 K appears to be much too low based on the extrapolated value of 3.7 x 10^{-15} obtained by Das et. al. This latter work is given preference because of the care taken in the experimental techniques, and the elimination of liquid junction potentials. Many experimental details (e.g. temp, purity of materials, technique) are not discussed in the paper Birckenbach and Hüttner: in addition it is clear that a large liquid junction potential probably exists. There is also some question as to whether the soly product determined in (1) is K_{s0} or K_{s0}^{o}. It appears that the authors have evaluated K_{s0} (see the COMMENTS in the compilation).

Smoothing equation

The data of Das et. al. between 298-323 K revised by the compiler were fit by least squares with the following result:

$$\log(K_{s0}^{o}/\mathrm{mol}^2\ \mathrm{kg}^{-2}) = -5535.1\ /(T/K)+4.563 \qquad (\sigma = \pm\ 0.002)$$

The standard deviation was calculated from the differences between the experimental and least squares value by the evaluator. The average error in the experimental soly of ±1.25% (±0.008 log K_{s0} units) is not included in the above σ value. The correlation coefficient for the least squares fit is 1.0000.

Tentative values of K_{s0}^{o} in water

T/K	$10^{14}K_{s0}^{o}$ / mol^2 kg^{-2}	T/K	$10^{14}K_{s0}^{o}$ /mol^2 kg^{-2}
291.15*	0.36	308.15	4.00
293.15*	0.48	313.15	7.75
298.15	1.00	318.15	14.63
		323.15	27.07

*Extrapolated values based on the smoothing equation

Solubility of AgSeCN in Water and Aqueous Solutions

The soly of AgSeCN was observed to increase upon addition of KSeCN (5), $AgNO_3$ and $AgClO_4$ (6). This increase was attributed to the formation of tri-ligand and tetra-ligand mononuclear complexes (5), and bi-, tri-, and tetra-polynuclear complexes (6). For the mononuclear complexes, no tabular data were presented, and most of the experimental work is concerned with AgSeCN in highly concentrated KSeCN solns in which no solid phase is present (5). The results at 293K indicate the important mononuclear complexes to be

$$Ag^+ + 3SeCN^- \rightleftarrows Ag(SeCN)_3^{2-} \qquad \beta_3 \quad 6.21 \times 10^{13}\ \mathrm{mol}^{-3}\ \mathrm{dm}^9$$

$$Ag^+ + 4SeCN^- \rightleftarrows Ag(SeCN)_4^{3-} \qquad \beta_4 \quad \text{not determined}$$

COMPONENTS:	EVALUATOR:
(1) Silver selenocyanate; AgSeCN; [5169-33-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. January 1978

CRITICAL EVALUATION: (continued)

There are no papers dealing with the existence of soluble AgSeCN and Ag(SeCN)$_2^-$; however by analogy to the AgSCN system, and from the experimental evidence for Ag(SeCN)$_3^{2-}$ and Ag(SeCN)$_4^{3-}$, there is a high probability that all Ag(SeCN)$_n^{1-n}$ species for n = 1-4 exist. Using $(K_{s0}^{o})^{1/2}$ as an estimate for the solubility of AgSeCN in pure water is quite likely to be in error by about 10% assuming $K_{s1} \sim 10^{-8}$.

The soly of AgSeCN in aqueous $AgNO_3$ and $AgClO_4$ solns at 293 K is enhanced due to the formation of polynuclear complexes according to (6)

$$2Ag^+ + SeCN^- \rightleftarrows Ag_2SeCN^+ \qquad \beta_{21} = 5 \times 10^{11}\ mol^{-2}\ dm^6$$

$$3Ag^+ + SeCN^- \rightleftarrows Ag_3SeCN^{2+} \qquad \beta_{31} = (1.74 \pm 0.06) \times 10^{12}\ mol^{-3}\ dm^9$$

$$4Ag^+ + SeCN^- \rightleftarrows Ag_4SeCN^{3+} \qquad \beta_{41} = (1.59 \pm 0.70) \times 10^{12}\ mol^{-4}\ dm^{12}$$

The above β_{mn} values are mean values obtained from the soly data for AgSeCN in excess $AgNO_3$ and $AgClO_4$, and have not been corrected for activity effects. Since Golub and Skopenko evidently used the K_{s0} value of Birckenbach and Hüttner to obtain the β_{mn} values, it is evident that they may be in error by the factor $4 \times 10^{-16}/4.9 \times 10^{-15} = 0.0812$ (the value of 4.9×10^{-15} was obtained from the smoothing equation). Thus the corrected β_{mn} values are:

$$\beta_{21} = 4.1 \times 10^{10} \quad ; \quad \beta_{31} = 1.4 \times 10^{11} \quad ; \quad \beta_{41} = 1.3 \times 10^{11}$$

Saturated AgSeCN solutions in excess $AgNO_3$ and $AgClO_4$ prepared at 60 to 70°C precipitated $(Ag_3SeCN)(NO_3)_2$ and $(Ag_2SeCN)(ClO_4)$ upon cooling (6).

REFERENCES:

1. Birckenbach, L.; Hüttner, K. *Z. Anorg. Chem.* 1930, *190*, 1.

2. Waitkins, G.R.; McCrosky, C.R. *J. Am. Chem. Soc.* 1946, *68*, 1385.

3. Das, R.C.; Sahu, G.; Satyanarayana, D.; Misra, S.N. *Electrochim. Acta* 1974, *19*, 887.

4. Owen, B.B.; King, E.J. *J. Am. Chem. Soc.* 1941, *63*, 1711.

5. Golub, A.M.; Pomerants, G.B. *Zh. Neorg. Khim.* 1959, *4*, 769.

6. Golub, A.M.; Skopenko, V.V. *Dokl. Akad. Nauk. S.S.S.R.* 1961, *138*, 601.

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Birckenbach, L.; Hüttner, K.
Z. Anorg. Chem. 1930, *190*, 1-26.

VARIABLES:

One temperature: 18°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Based on molar units at 18°C

$$c_{Ag} = 2.0 \times 10^{-8} \text{ mol dm}^{-3}$$

$$K_{s0} = 4.0 \times 10^{-16} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$Ag/AgSeCN(satd)//KNO_3(con)//-AgNO_3(0.1M)/Ag$$

The soly of AgSeCN in the left hand side of this cell is obtained from

$$\log C_2 = \log C_1 - EF/2.3RT$$

where C_1 is the $[Ag^+]$ in 0.1M $AgNO_3$ and is evaluated using a value of 0.82 (no reference is given) for the degree of dissociation* of $AgNO_3$ in this soln. The observed e.m.f., E, was found to equal 0.3810 V.

Since the soly of AgSeCN is C_2, the soly product, K_{s0}, is obtained as $(C_2)^2$.

*See the COMMENTS section below.

SOURCE AND PURITY OF MATERIALS:

AgSeCN was precipitated, presumably, from $AgNO_3$ and an alkali metal selenocyanate as discussed in another paper (1). Analysis was performed by dissolving the salt in hot concentrated H_2SO_4 followed by potentiometric titration which 0.1M KBr. Freshly distilled water was used.

ESTIMATED ERROR:

Solubility: not specified
e.m.f.'s: not specified
Temperature: ± 2°C (compiler)

REFERENCES:

1. Hüttner, K.; Knappe, S. *Z. Anorg. Chem.* 1930, *190*, 27.
2. Kirschner, A. *Z. Physik. Chem.* 1912, *79*, 245.
3. Robinson, R.A.; Stokes, R.H. *Electrolyte Solutions*. Butterworths. London. 1959. 2nd edition.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver selenocyante; AgSeCN; [5169-33-5] (2) Water; H_2O; [7732-18-5]	Birckenbach, L.; Hüttner, K. *Z. Anorg. Chem.* 1930, *190*, 1-26.

COMMENTS AND/OR ADDITIONAL DATA:

One aspect of this work which is not clear is concerned with the temperature of the measurement. On page 6 of this paper, the authors give a value of 18°C, whereas in the table on page 26, the temperature is given as 18 to 20°C. In their calculations using the Nernst equation, they use 2.3RT/F = 0.0576 which corresponds to a temperature of 17.1°C.

It should be noted that the concentration of a satd soln of AgSeCN is given as $\sim 10^{-8}$ mol dm^{-3}. Since the salt bridge is composed of a concentrated soln of KNO_3, and the reference electrode employs a 0.1M $AgNO_3$ soln, it is fairly certain that a large liquid junction potential exists.

In computing C_2 from log(0.1 x 0.82) - E/0.0576, the authors refer to the number 0.82 as the "Aktivitätsfaktor" which is misleading because 0.82 is probably the degree of disociation, α. Similar values for α can be found in much of the older European literature (e.g. see reference 2). If 0.82 is truly associated with the mean molar activity coefficient, $y_\pm$, then an error has been introduced into the calcn of the soly product since $y_\pm$ is closer to 0.73(3).

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]

(2) Potassium selenocyanate; KSeCN; [3425-46-5]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Waitkins, G.R.; McCrosky, C.R. *J. Am. Chem. Soc.* 1946, *68*, 1385-6.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Four measurements were made at 25°C using molar units:

[KSeCN]/ mol dm^{-3}	[$AgNO_3$]/ mol dm^{-3}	E/V	$10^{15}K^{\circ}_{s0}$
0.0894	0.1363	0.7081	7.1
0.0935	0.0856	0.7008	6.5
0.0958	0.3183	0.7288	6.6
0.0644	0.1340	0.6988	7.4

The average value is

$$K^{\circ}_{s0} = (6.9 \pm 0.4\ ) \times 10^{-15}\ mol^2\ dm^{-6}$$

The error in K°_{s0} is the standard deviation of the experimental average, and was calculated by the compiler.

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$\underset{\text{satd}}{Ag/AgSeCN},\ \underset{a_1}{KSeCN}//\underset{\substack{\text{satd}\\ \text{in agar}}}{KNO_3}//\underset{a_2}{AgNO_3}/Ag$$

The cell was thermostated at 25°C. The solns were prepared by weighing KSeCN into a fixed amount of water, adding 1 drop of 0.1M $AgNO_3$ (or 10 ml 0.001M $AgNO_3$), and permitting the cell, without the salt bridge, to equilibrate for 10-15 h. The salt bridge was connected and the initial e.m.f. (within the first 15 s) was taken as the equilibrium value. The cell e.m.f. decreased with time, and after a few minutes a layer of red Se could be observed on the Ag electrode.

SOURCE AND PURITY OF MATERIALS:

KSeCN was thrice recrystallized from absolute ethanol and dried at 100 to 105°C. The source and purity of the remaining materials was not specified.

ESTIMATED ERROR:

Solubility product: see above
E.m.f.'s: unknown (See METHOD)
Temperature: ±0.1°C.

REFERENCES:

1. Harned, H.S. *J. Am. Chem. Soc.* 1929, *51*, 416.
2. Robinson, R.A. *J. Am. Chem. Soc.* 1935, *57*, 1161.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver selenocyante; AgSeCN; [5169-33-5] (2) Potassium selenocyanate; KSeCN; [3425-46-5] (3) Water; H_2O; [7732-18-5]	Waitkins, G.R.; McCrosky, C.R. *J. Am. Chem. Soc.* 1946, *68*, 1385-6.

COMMENTS AND/OR ADDITIONAL DATA:

The e.m.f. of the experimental cell is given by

$$E = -(RT/F)\ \ln\left\{ K^{\circ}_{s0}/[(a_{SeCN})_1(a_{Ag^+})_2]\right\} + E_j$$

where $(a_{SeCN})_1$ is the activity of $SeCN^-$ in the left hand side of the cell, $(a_{Ag^+})_2$ is the activity of Ag^+ in the reference (right hand side) half-cell, and E_j is the liquid junction potential. The activity coefficients for KSeCN were assumed to equal the mean of those for KBr and KI (1,2). The authors calculated K°_{s0} from the above equation assuming $E_j = 0$.

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium selenocyanate; KSeCN; [3425-46-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Das, R.C.; Sahu, G.; Satyanarayana, D.; Misra, S.N. *Electrochim. Acta* 1974, *19*, 887-90.

VARIABLES:

Temperature: range 35 to 50°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$t/^{\circ}C$	E°_{m}/V	$10^{14}K^{\circ}_{s0}/mol^2\ kg^{-2}$
25*	0.2515	0.977
35	0.2454	3.89
40	0.2423	7.59
45	0.2394	14.79
50	0.2360	27.54

*Determined by extrapolation

The E°_{m} values in the above table are the standard molal e.m.f.'s for the experimental cell.

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$\text{Ag,AgCl}\Big/\begin{matrix}\text{KCl }(xm)\\ \text{KNO}_3(1-x)m\end{matrix}\ \Big/\Big/\ \begin{matrix}\text{KSeCN }(xm)\\ \text{KNO}_3\ (1-x)m\end{matrix}\Big/\text{AgSeCN,Ag}$$

where // is the liq junction, m is the total molality, and x is a fraction. The standard potentials of the cell were evaluated by the method of Owen and King (1) which effectively eliminates the liquid junction potentials. The e.m.f.'s were measured at 35, 40, 45, and 50°C. Four values of m from 0.04 to 0.07 mol kg^{-1} were used with x varying from 1.0 to 0.2 in steps of 0.1. A double extrapolation was used to evaluate E°_{m}. The measured e.m.f.'s for constant m was first extrapolated to $x \to 0$. The resulting $E_{x=0}$ values were then plotted against m and E°_{m} obtained by extrapolation to $m \to 0$.

SOURCE AND PURITY OF MATERIALS:

Ag,AgSeCN electrodes were prepd by electrolytic deposition of $SeCN^-$ onto spongy Ag, the latter prepd by the thermal method. Ag,AgCl electrodes were prepd in a similar fashion. All chemicals were AR grade and, in most cases, recrystallized. Triply distilled water was used.

ESTIMATED ERROR:

K_{s0}: σ = ±0.005 log units (compiler)
E.m.f. values: ±0.3 mV, average
Temperature: ±0.1°C

REFERENCES:

1. Owen, B.B.; King, E.J. *J. Am. Chem. Soc.* 1941, *63*, 1711.
2. Bates, R.G.; Bower, V.E. *J. Res. Nat. Bur. Stand.* 1954, *53*, 282.
3. Lewis, G.N.; Randall, M. *Thermodynamics*. McGraw-Hill. N.Y. 1952.

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium selenocyanate; KSeCN; [3425-46-5]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Das, R.C.; Sahu, G.; Satyanarayana, D.; Misra, S.N. *Electrochim. Acta* 1974, *19*, 887-90.

COMMENTS AND/OR ADDITIONAL DATA:

Converting Owen's data for the Ag,Ag^+ electrode (5) to absolute volts, the compiler has recalculated the K^o_{s0}'s. The results given below.

$t/^oC$	$E^o_{Ag,AgSeCN}/V^*$	$E^o_{Ag,Ag^+}/V^*$	$10^{14}K^o_{s0}/mol^2\ kg^{-2}$
25	-0.0291**	0.7993	0.992
35	-0.0298	0.7894	4.00
40	-0.0302	0.7844	7.75
45	-0.0311	0.7791	14.63
50	-0.0315	0.7743	27.07

* Converted to absolute volts

** Extrapolated E^o value

The data in the above table were fit by least squares to

$$\log(K^o_{s0}/mol^2\ kg^{-2}) = -5535.09/\ (T/K) + 4.563 \quad (\sigma = \pm\ 0.002)$$

where σ is the standard deviation for the precision of the fit to the obsd K_{s0}, and the correlation coefficient for this fit is 1.0000. From the slope of this relation a standard enthalpy change of 105.97 kJ mol^{-1} is obtained for the reaction

$$AgSeCN(s) \rightleftarrows Ag^+ + SeCN^-$$

AUXILIARY INFORMATION

METHOD:

The solubility products were calcd from the standard half-cell potentials using the relation

$$\ln K^o_{s0} = (E^o_{Ag,AgSeCN} - E^o_{Ag,Ag^+})F/RT$$

The $E^o_{Ag,AgCl}$ and E^o_{Ag,Ag^+} values required for these calculations were obtained from the literature (2-4).

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

4. Latimer, W.M. *Oxidation Potentials*. Prentice-Hall, N.Y. 1952.

5. Owen, B.B.; Brinkley, S.R. *J. Am. Chem.* 1938, *60*, 2233.

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]

(2) Silver nitrate; $AgNO_3$; [7761-88-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Golub, A.M.; Skopenko, V.V. *Dokl. Akad. Nauk. S.S.S.R.* 1961, *138*, 601-4.

VARIABLES:

Concentration of $AgNO_3$ at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

All concentrations are in units of mol dm^{-3} at 20°C.

$[AgNO_3]$	c_{Ag}	10^{-3} Ø
0.736	3.75×10^{-4}	0.069
1.192	1.00×10^{-3}	0.298
1.521	1.49×10^{-3}	0.566
1.728	2.12×10^{-3}	0.914
1.860	2.50×10^{-3}	1.16
2.097	3.45×10^{-3}	1.81
2.687	6.36×10^{-3}	4.26
3.022	8.48×10^{-3}	6.39

Each value of the soly of AgSeCN is an average one based on two or three determinations. The function Ø is defined on the following page.

AUXILIARY INFORMATION

METHOD:

A series of $AgNO_3$ solns were satd with freshly prepared AgSeCN at a constant temp of 20°C. When equilibrium was reached, the solid phase (AgSeCN) was separated by filtration and Ag and Se determined in the filtrate. For this purpose an aliquot was treated with HNO_3 and the total Ag was determined gravimetrically as the chloride: Se was determined argentometrically. (1) The soly experiments were repeated two or three times.

SOURCE AND PURITY OF MATERIALS:

AgSeCN was prepared by an exchange reaction between analytical grade $AgNO_3$ and KSeCN (99%). The purity of the water was not specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Hahn, H.; Viohl, V. *Z. Anal. Chem.* 1956, *149*, 50.
2. Cave, G.C.B.; Hume, D.N. *J. Am. Chem. Soc.* 1953, *75*, 2892.
3. *Chemist's Handbook.* Moscow. 1952. Volume 3.

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]

(2) Silver nitrate; $AgNO_3$; [7761-88-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Golub, A.M.; Skopenko, V. V.

Dokl. Akad. Nauk S.S.S.R. 1961, *138*, 601-4.

COMMENTS AND/OR ADDITIONAL DATA:

Although the soly experiments were repeated two or three times, the authors report only the average value for each $AgNO_3$ concentration, and it is therefore not possible to estimate any errors.

A graphical method was used to evaluate the stability constants for polynuclear species. The function $\Psi_{m1} = \phi / [Ag^+]^m$ was extrapolated to zero $[Ag^+]$ and the intercept is taken as the formation constant β_{m1}. The function ϕ is defined by (2)

$$\phi = S[Ag^+]/K_{s0}$$

where S is the soly, and the soly product was taken (3) as $K_{s0} = 4 \times 10^{-16}$ mol^2 dm^{-6}. The authors' results are:

$2Ag^+ + SeCN^- = Ag_2SeCN^+$ $\beta_{21} = 5 \times 10^{11}$ mol^{-2} dm^6

$3Ag^+ + SeCN^- = Ag_3SeCN^{2+}$ $\beta_{31} = 1.8 \times 10^{12}$ mol^{-3} dm^9

$4Ag^+ + SeCN^- = Ag_4SeCN^{3+}$ $\beta_{41} = 1.1 \times 10^{12}$ mol^{-4} dm^{12}

Although the authors quote a Handbook (3) for the value of K_{s0} at 20°C, it is most likely that this value comes from the work of Birckenbach and Hüttner (4) which was performed at about 18°C: in any case this value is probably too small by a factor of 10 (see the CRITICAL EVALUATION).

A 3 mol dm^{-3} $AgNO_3$ soln was satd with AgSeCN at 60-70°C and filtered. Upon cooling the filtrate produced stable crystals which analysed as $(Ag_3SeCN)(NO_3)_2$.

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

4. Birckenbach, L.; Hüttner, K. *Z. Anorg. Chem.* 1930, *190*, 1.

COMPONENTS:

(1) Silver selenocyanate; AgSeCN; [5169-33-5]

(2) Silver perchlorate; $AgClO_4$; [7783-93-9]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Golub, A.M.; Skopenko, V. V. *Dokl. Akad. Nauk S.S.S.R.* 1961, *138*, 601-4.

VARIABLES:

Concentration of $AgClO_4$ at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

All concentrations are in units of mol dm^{-3} at 20°C.

$[AgClO_4]$	c_{Ag}	10^{-13} ∅
1.045	1.10×10^{-3}	0.287
1.305	1.98×10^{-3}	0.645
1.381	2.12×10^{-3}	0.731
1.796	4.35×10^{-3}	1.949
1.943	6.61×10^{-3}	3.20
2.093	7.01×10^{-3}	3.66
3.008	2.24×10^{-2}	16.7

Each value of the soly of AgSeCN is an average one based on two or three determinations. The function ∅ is defined on the following page.

AUXILIARY INFORMATION

METHOD:

A series of $AgClO_4$ solns were satd with freshly prepared AgSeCN at a constant temp of 20°C. When equilibrium was reached, the solid phase (AgSeCN) was separated by filtration and Ag and Se determined in the filtrate. For this purpose an aliquot was treated with HNO_3 and the total Ag was determined gravimetrically as the chloride: Se was determined argentometrically. (1). The soly experiments were repeated two or three times.

SOURCE AND PURITY OF MATERIALS:

AgSeCN was prepared by an exchange reaction between analytical grade $AgNO_3$ and KSeCN (99%). $AgClO_4$ was prepd by converting $AgNO_3$ to the oxide followed by soln in c.p. grade $HClO_4$. The $AgClO_4$ was recrystallized before use. The purity of the water used was not specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Hahn, H.; Viohl, V. *Z. Anal. Chem.* 1956, *149*, 50.
2. Cave, G.C.B.; Hume, D.N. *J. Am. Chem. Soc.* 1953, *75*, 2892.
3. *Chemist's Handbook*. Moscow. 1952. volume 3.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver selenocyanate; AgSeCN; [5169-33-5] (2) Silver perchlorate; $AgClO_4$; [7783-93-9] (3) Water; H_2O; [7732-18-5]	Golub, A.M.; Skopenko, V. V. *Dokl. Akad. Nauk S.S.S.R.* 1961, *138*, 601-4.

COMMENTS AND/OR ADDITIONAL DATA:

Although the soly experiments were repeated two or three times, the authors report only the average value for each $AgClO_4$ concentration, and it is therefore not possible to estimate any errors.

A graphical method was used to evaluate the stability constants for polynuclear species. The function $\psi_{m1} = \phi\,[Ag^+]^m$ was extrapolated to zero $[Ag^+]$ and the intercept taken as the formation constant β_{m1}
The function ϕ is defined by (2)

$$\phi = S[Ag^+]/K_{s0}$$

where S is the soly and the soly product was taken (3) as $K_{s0} = 4 \times 10^{-16}$ $mol^2\ dm^{-6}$. The authors' results are:

$2Ag^+ + SeCN^- = Ag_2SeCN^+$ $\quad \beta_{21} = 5 \times 10^{11}\ mol^{-2}\ dm^6$

$3Ag^+ + SeCN^- = Ag_3SeCN^{2+}$ $\quad \beta_{31} = 1.7 \times 10^{12}\ mol^{-3}\ dm^9$

$4Ag^+ + SeCN^- = Ag_4SeCN^{3+}$ $\quad \beta_{41} = 2.1 \times 10^{12}\ mol^{-4}\ dm^{12}$

Although the authors quote a Handbook (3) for the value of K_{s0} at 20°C, it is most likely that this value comes from the work of Birckenbach and Hüttner (4) which was performed at about 18°C: in any case this value is probably too small by a factor of 10 (see the CRITICAL EVALUATION).

A 3 mol dm^{-3} $AgClO_4$ soln was satd with AgSeCN at 60-70°C and filtered. Upon cooling the filtrate produced crystals which analysed as $(Ag_2SeCN)(ClO_4)$.

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

4. Birckenbach, L.; Hüttner, K.
K. Anorg. Chem. 1930, *190*, 1.

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION:

The number of studies concerned with the direct determination of the solubility of AgSCN (1-27) far outnumber those based on e.m.f. measurements (28-38,52), and the determination of standard electrode potentials (39-42). Recommended values for the solubility product and related thermodynamic functions are based entirely on the latter work. The most reliable values for stability and formation constants for complex ions are those obtained from the solubility studies. The decision of whether to classify these latter constants as recommended or tentative values proved to be a difficult task. The evaluator decided to recommend a consistent set of formation constants despite the fact that they are associated with large standard deviations.

Solubility Studies

1. Studies not involving complexation of AgSCN. Most of these studies involve the direct determination of the solubility (3,6,14,20,22,24). The papers by Whitby (22) and Fioroni and Magno (24) have been rejected. The former work reports little information on the colorimetric determination of the solubility, C_{Ag}, and the value of $C_{Ag} = 1.5 \times 10^{-6}$ mol dm^{-3} at 294 K is too high. The latter work reports $K_{s0} = 10^{-12.8}$ based on a coulometric titration method: no temperature is given in this paper, and this value of K_{s0} appears to be much too small (it corresponds to the 283 K value). Other works (25-28) were rejected for similar reasons. Böttger's determination of C_{Ag} and K_{s0} at 293 K (3) and 373 K (6) constitute the first satisfactory values for these quantities.

The determination of C_{Ag} by Dash, Mohanty, and Panda (2) based on analysis of Ag^+ by titration with KCl was performed with extreme care. However their results for C_{Ag} at zero ionic strength appear to be in error by at least ±5% and as much as ±60% depending upon temperature. Their errors are reflected in the resulting thermodynamic functions for the reaction

$$\mathrm{AgSCN(s)} \rightleftarrows \mathrm{Ag^+ + SCN^-} \qquad [1]$$

Their results for $\Delta H^o_{s0} = 65.5$ kJ mol^{-1} and $\Delta S^o_{s0} = -10.4$ JK^{-1}mol^{-1} are clearly in error as discussed below.

The relative solubility studies (5, 7) both employ a slightly soluble silver salt, AgX, in equilibria of the type

$$\mathrm{AgX(s) + KSCN} \rightleftarrows \mathrm{KX + AgSCN(s)} \qquad [2]$$

The equilibrium constant for this reaction is given by

$$K = [X^-]/[SCN^-] = K^o_{s0}(AgX)/K^o_{s0}(AgSCN) \qquad [3]$$

Note that standard K^o_{s0} values are used in eq [3] since it is assumed that activity coefficients cancel. Lucas (5) made a poor choice of AgCN for AgX: his high results are undoubtably due to the complexity of CN^- in solution. Hill's choice of AgCl and AgBr leads to excellent values of K^o_{s0}(AgSCN) after recalculation using correct values of K^o_{s0} for AgCl and AgBr (see the compilations). Vanderzee and Smith (41) claim that Hill's K_{s0}'s are dependent upon ionic strength, but inspection of the original data in the compilations does not reveal any such dependence.

Without specifying details, Cave and Hume (14) used a nephelometric method to determine $C_{Ag} = (1.1 \pm 0.03) \times 10^{-6}$ mol kg^{-1} at 298 K. This value is slightly high, and is probably due to the presence of AgSCN(aq). An extimate of AgSCN(aq) can be obtained from these data using the following equation:

$$[AgSCN] = K^o_{s1} = c^o_{Ag} - (K^o_{s0})^{1/2} = (10 \pm 3) \times 10^{-8} \text{ mol kg}^{-1} \qquad [4]$$

The recommended value of $K^o_{s0} = 1.003 \times 10^{-12}$ mol^2 kg^{-2} was used in eq [4].

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION: (continued)

2. Studies in the presence of complexing anions. A number of papers have been published which deal with the solubility of AgSCN in excess SCN^- solutions (1,4,8,10 - 18): two other papers report the effect of SO_3^{2-} (34) and $S_2O_3^{2-}$ (19) on the solubility of AgSCN. In most cases direct comparisons cannot be made because of the various experimental conditions employed (e.g. concentration units, ionic strength, supporting electrolyte, and temperature).

The complex ternary system AgSCN-KSCN-H_2O has received considerable attention (1,4,8,10,13,15,17,18,21). The detailed phase relationships were studied by Foote (4) and Occleshaw (10). The results for C_{Ag} in both papers are in excellent agreement, but slight differences exist as to the regions of [KSCN] in which the various solid phases are present. Both papers report the existence of several double salts, and significantly find no evidence for the existence of any hydrate. Although Hellwig (1) and Randall and Halford (8) employed different concentration units, their results appear to be in satisfactory agreement. The latter authors calculated K_{s2} values for the reaction

$$\mathrm{AgSCN(s) + SCN^- \rightleftarrows Ag(SCN)_2^-} \qquad [5]$$

and found that the formation constant K_{s2} varied by a factor of 10 over the concentration range of [KSCN] = 0.3 - 1.2 mol kg^{-1}. These authors correctly concluded that higher complexes of the type $Ag(SCN)_n^{1-n}$ for $n > 2$ were present.

Golub's study (17) of the quaternary AgSCN-KSCN-KNO_3-H_2O system at a constant ionic strength of 1.8 mol dm^{-3} at 293 K included, in addition to the determination of C_{Ag}, the evaluation of β_4 by the potentiostatic method. The author claims that the major soluble species is $Ag(SCN)_4^{3-}$, and computes K_{s4} = 0.145 mol^{-2} dm^6. That an error is involved in this value is easily demonstrated by his value of $K_{s0} = 4.05 \times 10^{-12}$ mol^2 dm^{-6} at 293 K which is larger than the value in 2.2 mol kg^{-1} solutions at 298 K (see table 1 below). Golub calculated K_{s0} from

$$K_{s0} = K_{sn}/\beta_n \qquad [6]$$

and the error in K_{s4} most likely is due to the neglect of other complex ions. In a similar study of this quaternary system at 293 K, Gyunner and Yakhkind (18) report $Ag_3(SCN)_6^{3-}$ to be the major species in solution. However, as pointed out in the compilation, evidence for the absence of $Ag(SCN)_3^{2-}$ and $Ag(SCN)_4^{3-}$ is weak, and the computed value of K_{s36} cannot be supported. The C_{Ag} values in these two papers (17, 18) differ by at least 20% and cannot therefore be attributed to the small difference in ionic strengths (1.8 mol dm^{-3} (17) compared to 2.0 mol dm^{-3} (18)). This quaternary system was studied by Cave and Hume (14) at 298 K at a constant ionic strength of 2.2 mol kg^{-1}. Graphical analysis of their data for $0.06 \leqslant$ [KSCN] $\leqslant 2.2$ mol kg^{-1} resulted in values for the formation constants K_{s2}, K_{s3}, and K_{s4}. The values obtained (see Table 1 below) are in agreement with those from two other studies (16, 21).

Using a turbidimetric method, Težak and coworkers (13, 15, 23) carried out detailed studies on the solubility of AgSCN at 293 K in KSCN solutions in which $0.01 \leqslant$ [KSCN] $\leqslant 1.2$ mol dm^{-3}. The last paper (23) contains only graphical data and will not be considered in this evaluation. Graphical analysis of the data resulted in high values for K_{s3} and K_{s4} (15, 43). The errors in these calculations are due to the neglect of $Ag(SCN)_2^-$ in the low concentration region, and the fact that for the higher [KSCN] regions, both $Ag(SCN)_3^{2-}$ and $Ag(SCN)_4^{3-}$ are present in nearly equal amounts so that the graphical procedure of considering only one species at a time in a particular [KSCN] region is clearly inapplicable. Woolley (21) measured C_{Ag} by radioassay in the quaternary AgSCN-KSCN-$KClO_4$-H_2O system in which [KSCN] varied from about 10^{-6} to 10^{-1} mol dm^{-3} at 298 K. Using a relative least squares technique, the data were fit to the equation

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

June 1978

CRITICAL EVALUATION: (continued)

$$c_{Ag} = \sum_{0}^{n} K^{o}_{sn}[SCN^-]^{n-1}\ y_{\pm}^{n-1} \qquad [7]$$

where $y_\pm$ is the mean molar activity coefficient calculated from the extended Debye-Hückel equation. Although Woolley's value for K^o_{s0} is too large, it has little effect on the remaining K_{sn} values since most measurements were made for $10^{-4} \leqslant [KSCN] \leqslant 10^{-1}$. The values for K^o_{sn} (n = 1, 2, 3) are in satisfactory agreement with those of Leden and Nilsson (16) and with those of Cave and Hume (14) for n = 2,3.

Two studies (10, 16) have reported the solubility of AgSCN in NaSCN solutions. Occleshaw's study (10) is concerned with the phase relationships, and reports a number of double salts as well as the hydrate $NaSCN{\cdot}AgSCN{\cdot}2H_2O$. Leden and Nilsson's work (16), carried out at 298 K in the presence of $NaClO_4$ to maintain a constant ionic strength (μ), is mainly concerned with the determination of formation and stability constants. For solutions in which μ = 4 mol dm^{-3}, the double salt $NaSCN{\cdot}AgSCN{\cdot}2H_2O$ is the solid phase for $[NaSCN] \geqslant 0.5$ mol dm^{-3}. The formation constants were evaluated graphically using K_{s0} values obtained from e.m.f. measurements (33). The results, along with those of other investigators, are given in Table 1.

TABLE 1 Comparisons of Formation and Stability Constants at 298.15 K

reference	μ = 0			μ = 0.113	μ = 2.2	μ = 4.0
constant	14	16, 33	21	16, 33	14	16, 33
$10^{12}K_{s0}$	1.13	1.08±.02	6.8	1.58±.02	6.75	0.77±.02
$10^{8}K_{s1}$	(10±3)	6±3	1.7±.2	6±3	---	3±2
$10^{4}K_{s2}$	2.77	1.8±.1	1.48±.07	1.8±.1	2.5	1.5±.1
$10^{3}K_{s3}$	4.68	3±2	5.3±.4	6±3	8.0	9±2
$10^{2}K_{s4}$	0.89	0.5±.5	---	4±4	7.9	14±2
$10^{2}K_{s26}$	---	---	---	---	---	1.1±.2
$10^{-4}\beta_1$	---	6±3	(1.7±.2)	4±2	---	4±3
$10^{-8}\beta_2$	2.45	1.7±.2	(1.48±.07)	1.14±.06	0.37	1.9±.2
$10^{-9}\beta_3$	4.14	3±2	(5.6±.4)	4±2	1.2	1.2±.2
$10^{-10}\beta_4$	0.79	0.5±0.4	---	2.5±2	---	18±2
$10^{-22}\beta_{26}$	---	---	---	---	---	2±1

Notes to Table: Data of ref 14 based on weight units; remaining data based on volume units. Values in parenthesis calculated by the evaluator. β_n values from ref 21 calculated from eq [6] taking $K^o_{s0} = 1.00 \times 10^{-12}$ $mol^2\ dm^{-6}$, and K^o_{s1} for ref 14 estimated previously in eq [4].

3. Cationic complexes. Two studies on the solubility of AgSCN in excess $AgNO_3$ have been published (1, 13). No attempts were made to evaluate polynuclear stability constants, β_{mn}. The existence of these complexes is highly probable (43).

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION: (continued)

4. Solubility in NH_3 solutions. The two studies available (2, 9) are not directly comparable due to the different concentration units employed, and the different range in $[NH_3]$. Qualitative agreement is apparent, and both sets of data can be used as a reference guide for c_{Ag} in NH_3 solutions. The attempt by Abegg and Cox (2) to calculate K_{s0} is clearly in error. The source of this error may be the neglect of $Ag(SCN)(NH_3)$ as discussed below. Details on Garrick and Wilson's phase study are given in the compilation.

E.m.f. Measurements

The basis of these measurements is the concentration cell

$$Ag/\ AgNO_3(c_2)\ //\text{salt bridge}//\ KSCN\ (c_1),\ AgSCN(sat)/Ag \qquad [8]$$

Variations of this cell where the Ag/Ag^+ reference electrode on the left hand side is replaced with a suitable alternate reference electrode has also been reported. The e.m.f. of the above cell is given by

$$E = (RT/F)\ \ln\{[Ag^+]_2 y_\pm/[Ag^+]_1 y'_\pm\} + E_j \qquad [9]$$

By adjusting $c_2 = c_1$ the ratio $y_\pm/y'_\pm$ approaches unity, but elimination of the liquid junction potential, E_j, has proved to be difficult. In the earlier works (29 - 32), $[Ag^+]_2$ was calculated as $\alpha[AgNO_3]$ (i.e. αc_2) where α is the dissociation constant of $AgNO_3$: values of α from 0.82 to 0.93 were commonly used. For 0.01 mol dm^{-3} $AgNO_3$ solutions at 298 K, $\alpha = 0.82$ as calculated from the equivalent conductivity ratio Λ/Λ^o (44). E_j contributions have either been ignored (29, 30), assumed to be negligible due to the use of a highly concentrated salt bridge solution (31), or estimated (32) by conventional methods (45). Once $[Ag^+]_1$ is calculated from eq [9], the solubility product can be calculated from

$$K_{s0} = [Ag^+]_1\ \{c_1 - \sum_1^n nK_{sn}[SCN^-]^{n-1}\} \simeq [Ag^+]_1\ c_1 \qquad [10]$$

For dilute solutions of $[KSCN] \leqslant 0.1$ mol dm^{-3}, the total concentration of AgSCN is small compared to c_1 and the above approximation is valid. It has been common practice to assume that the solubility of AgSCN is simply $(K_{s0})^{1/2}$. This is however incorrect since, depending upon the SCN^- concentration, the major soluble species are the $Ag(SCN)_n^{1-n}$ complexes. Kirschner (31) realized this difference and calculated c_{Ag} as $K_{s0}\beta_2\alpha[SCN^-]$: his result for 291 K of $c_{Ag} = 2.5 \times 10^{-4}$ mol dm^{-3} is in close agreement with the observed value of 2×10^{-4} mol dm^{-3} at 293 K (13, 15). This result is however fortuitous since an incorrect value of 5.99×10^9 was used for β_2 (46). Erroneous calculations of $c_{Ag} = (K_{s0})^{1/2}$ were retained in the compilations when used by the various investigators.

Jaenicke's results (28) for K_{s0} at 293, 308, 323, 339 K appear to be consistent with the recommended values (see below). The work was not compiled because the author did not define experimental conditions or the sources and purities of materials. Jaenicke also claims to use the activity term a_{SCN^-} in his calculations of K_{s0}, but recalculation by the evaluator showed that the concn term $[SCN^-]$ was used, and adjustments by the evaluator cannot be made since the ionic strengths are not given. A value of $\Delta H = 22.3$ kcal/mol (93.3 kJ/mol) was reported for reaction [1], and a "normal" ΔH of 21.5 kcal/mol (90.0 kJ/mol). The term "normal" was not defined.

The paper by Ley and Schafer (29) was not compiled since they do not report any quantitative data. All remaining papers (20, 21, 32-38) report K_{s0} values and, with the exception of the values of Leden and Nilsson (33), give qualitative results. Three additional papers (36, 38, 52) have not been compiled because of large errors in the K_{s0} values.

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION: (continued)

Standard Electrode Potentials

Initial attempts (39,40) to measure E^o(Ag,AgSCN) yielded inconsistent results. Additional attempts to reevaluate E^o from these original data have only slightly improved the E^o values: e.g. Cave and Hume's recalculation based on the data of Pearce and Smith (39), and the compiler's correction to the data of Aditya and Prasad (40). Both works probably still contain residual errors in E_j or in activity coefficients since the resulting K^o_{s0} values are still in error. The most consistent results have been obtained by using slightly acidic solutions (41, 42). Vanderzee and Smith's results are in excellent agreement with those of Lal and Prasad over the temperature range of 288-318 K. The resulting K^o_{s0} values agree with those of Böttger (3), Hill (7), and Leden and Nilsson (33). Also of major significance is the fact that these E^o data lead to enthalpy data which are in agreement with those values found by direct measurement (47, 48), and from the temperature dependence of the solubility (6, 31, 34). On this basis, the evaluator concludes that the K^o_{s0} data based on the E^o determinations of Vanderzee and Smith, and Lal and Prasad should constitute the recommended values.

Recommended Values

1. Solubility product constant. The E^o_m(Ag,AgSCN) values from references 41 and 42 were averaged, and K^o_{s0} calculated from

$$\log(K^o_{s0}/\mathrm{mol}^2\ \mathrm{kg}^{-2}) = \{E^o_m(\mathrm{Ag,AgSCN}) - E^o_m(\mathrm{Ag,Ag^+})\}/(RT/F)\ \ln 10 \qquad [11]$$

The recommended data are presented in Table 2. Conversions to volume units were carried out by the evaluator using the equation

$$K^o_{s0}/\mathrm{mol}^2\ \mathrm{dm}^{-6} = (K^o_{s0}/\mathrm{mol}^2\ \mathrm{kg}^{-2})\ d^2_o \qquad [12]$$

where d_o is the density of pure water whose values were obtained from Robinson and Stokes (49). $E^o_m(\mathrm{Ag,Ag^+})$ was obtained from Owen's paper (50) and converted to absolute volts by the compiler.

TABLE 2 Recommended E^o_m(Ag,AgSCN) and K^o_{s0} Values from 278-328K

T/K	E^o_m(Ag,AgSCN)/V	$E^o_m(\mathrm{Ag,Ag^+})$/V	$10^{12}K^o_{s0}/\mathrm{mol}^2\mathrm{kg}^{-2}$	$10^{12}K^o_{s0}/\mathrm{mol}^2\mathrm{dm}^{-6}$
278.15	0.0908	0.8188	0.0645	0.0645
288.15	0.0903	0.8090	0.269	0.269
293.15	0.0900	0.8043	0.523	0.521
298.15	0.0895	0.7993	1.003	0.997
303.15	0.0889	0.7944	1.866	1.850
308.15	0.0883	0.7894	3.41	3.37
318.15	0.0868	0.7791	10.79	10.58
328.15	0.0850	0.7691	31.1	30.2
373.15	----	----	1630.	1500. (provisional)

Notes to Table: Average standard deviation in K_{s0}'s is ±0.4% as calculated from experimental error in the e.m.f.'s of ±0.1 mV. The K^o_{s0} value at 373 K is from reference 6.

The data in Table 2 were fit to the following smoothing equations:

$$\log(K^o_{s0}/\mathrm{mol}^2\mathrm{kg}^{-2}) = -4898/(T/K) + 4.426 \quad \sigma = 0.004 \qquad [13a]$$

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CRITICAL EVALUATION: (continued)

$$\log(K^{\circ}_{s0}/\mathrm{mol}^2\ \mathrm{dm}^{-6}) = -4874/(T/K) + 4.345 \qquad \sigma = \pm 0.006 \qquad [13b]$$

Extrapolation of eq [13b] to 373.15 K yields $K^{\circ}_{s0} = 1.9 \times 10^{-9}\mathrm{mol}^2\mathrm{dm}^{-6}$ which qualitatively confirms Böttger's value obtained from conductivity data.

2. Thermodynamic functions for reaction [1]. The standard thermodynamic functions for reaction [1] were computed from the data in Table 2 for the temperature range of 278-328 K. The recommended values are given in terms of the following smoothing equations which are based on volume units:

$$\{E^{\circ}_c(\mathrm{Ag,AgSCN}) - E^{\circ}_c(\mathrm{Ag,Ag^+})\}/V = -1.0579 + 1.45 \times 10^{-3}(T/K) -9.42 \times 10^{-7}(T/K)^2 \qquad \sigma = \pm 0.0001 \qquad [14]$$

$$\Delta G^{\circ}_{s0}/\mathrm{kJ\ mol}^{-1} = 102.07 - 0.140(T/K) + 9.08 \times 10^{-5}(T/K)^2 \qquad \sigma = \pm 0.01 \qquad [15]$$

$$\Delta H^{\circ}_{s0}/\mathrm{kJ\ mol}^{-1} = 102.1 - 9.08 \times 10^{-5}(T/K)^2 \qquad \sigma = \pm 0.8 \qquad [16]$$

$$\Delta S^{\circ}_{s0}/\mathrm{JK}^{-1}\mathrm{mol}^{-1} = 139.7 - 0.182(T/K) \qquad \sigma = \pm 2.7 \qquad [17]$$

$$\Delta C^{\circ}_p/\mathrm{JK}^{-1}\mathrm{mol}^{-1} = -0.18(T/K) \qquad \sigma = \pm 7.3 \qquad [18]$$

At 298.15 K eq [16] yields $\Delta H^{\circ}_{s0} = 94.0$ kJ mol^{-1}. This value compares favorably with Böttger's quoted value (48) of 100.4 kJ mol^{-1} and his experimental value of 87.5 kJ/mol, Jaenicke's value (28) of 93.1 kJ/mol, and Kirschner's value of 89.1 kJ/mol calcd for the temp range of 291-298 K (31). Joannis' calorimetric determination of $\Delta H^{\circ}_{s0} = 93.89$ kJ/mol at 286.7K is in excellent agreement with the value of 94.6 kJ/mol calcd from eq [16] for this temperature. Since ΔH°_{s0} is a sensitive test for the accuracy of the K°_{s0} determinations, the evaluator recommends its use as a guide to the accuracy of K°_{s0} data reported as a function of temperature. The work of Dash, Mohanty, and Panda (20) certainly involves an error based upon this criteria as discussed above. Klein's data (34) are difficult to interpret since the ionic strength of the solutions are not known: i.e. his value of 82.1 kJ mol^{-1} might be correct for ΔH_{s0} (i.e. at some finite ionic strength), but is quite low for a ΔH°_{s0} value.

3. Stability and formation constants at 298.15K. Inspection of Table 1 indicates acceptable (i.e. within experimental error) agreement for the K°_{s2}, K°_{s3}, K°_{s4} values reported by three different investigators (14, 16, 21), and moderate agreement between K°_{s1} values (16,21). Thus despite the large standard deviations in these formation constants, it seems reasonable to propose a set of recommended values. These were arrived at by averaging those K°_{sn}'s for n = 1-3 obtained by Leden and Nilsson (16) and by Woolley (21). Cave and Hume's data were not used in the averaging computations simply because they do not report any errors in C_{Ag} and K_{sn}: their inclusion would not produce any significant change in computed C_{Ag} values. The tentative value for K°_{s4} was taken from Leden and Nilsson (16). Based on the calculations presented below, it is clear that the recommended set of K_{sn} for n = 1-4 are not sufficient to describe C_{Ag} in solutions of excess SCN^-. Leden and Nilsson (16) and Guynner and Yakhkind (18) find evidence for polynuclear species. The latter evidence for $Ag_3(SCN)_6^{3-}$ is weak since other important soluble species ($Ag(SCN)_3^{2-}$ and $Ag(SCN)_4^{3-}$) were ignored. Leden and Nilsson have determined a K_{s26} value in a 4 mol dm^{-3} medium, and for lack of any other data, this value for K_{s26} is given along with the recommended values below: it must however be regarded as highly provisional. Because of the apparent weaknesses in the calculations of K_{sn} values at 293 K, the evaluator cannot suggest recommended values, nor does he feel that

COMPONENTS:

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(2) Water; H_2O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION: (continued)

tentative values can be given at this time. Thus the recommended values at 298.15 K based on volume units are:

$$K^o_{s0}/\mathrm{mol^2 dm^{-6}} = (9.97 \pm 0.04) \times 10^{-13} \qquad [19]$$

$$K^o_{s1}/\mathrm{mol\ dm^{-3}} = (4 \pm 3) \times 10^{-8} \qquad [20]$$

$$K^o_{s2} = (1.6 \pm 0.2) \times 10^{-4} \qquad [21]$$

$$K^o_{s3}/\mathrm{mol^{-1} dm^3} = (4.2 \pm 2) \times 10^{-3} \qquad [22]$$

$$K^o_{s4}/\mathrm{mol^{-2} dm^3} = (5 \pm 5) \times 10^{-3} \text{ (tentative)} \qquad [23]$$

$$K^o_{s26}/\mathrm{mol^{-2} dm^6} = 0.01 \text{ (highly provisional)} \qquad [24]$$

The stability constants, β^o_{mn}, can be calculated from this data using the equation (cf. eq [6])

$$\beta^o_{mn} = K_{smn}/(K^o_{s0})^m \qquad [25]$$

Solubility of AgSCN in Aqueous Solutions at 298.15 K

1. The binary system. In pure water at 25°C, the solubility of AgSCN is governed by the following relationships:

$$C_{Ag} = [Ag^+] + \sum_1^n K^o_{sn}[SCN^-]^{n-1} \qquad [26]$$

and

$$C_{Ag} = [SCN^-] + \sum_1^n nK^o_{sn}[SCN^-]^{n-1} \qquad [27]$$

Standard equilibrium constants are used since C_{Ag} is small and all activity coefficients are taken as unity. Equating the two relationships, noting that

$$[Ag^+][SCN^-] = K^o_{s0} \qquad [28]$$

we have

$$\sum_1^n (n-1)K^o_{sn}[SCN^-]^n + [SCN^-]^2 - K^o_{s0} = 0 \qquad [29]$$

Using the recommended K^o_{sn}'s, the above equation was solved iteratively to yield $[SCN^-] = 9.98 \times 10^{-7}$ mol dm^{-3}. Thus the only other species present in significant amounts is AgSCN(aq) and the solubility is, from eq [26],

$$C_{Ag} = K^o_{s0}/[SCN^-] + K^o_{s1} = 9.98 \times 10^{-7} + 4 \times 10^{-8} = 1.04 \times 10^{-6} \mathrm{mol\ dm^{-3}} \qquad [30]$$

The contribution of AgSCN(aq) to C_{Ag} of about 4% is small, but significant: other species contribute by less than 0.02%.

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

CRITICAL EVALUATION: (continued)

2. Solutions with excess SCN^-. In the presence of a salt such as KSCN or NaSCN, the equations governing the solubility of AgSCN are, considering only mononuclear species, given by eq [26] and

$$c_{Ag} = [SCN^-] - c + \sum_{1}^{n} nK_{sn}[SCN^-]^{n-1} \qquad [31]$$

where c is the concentration of added salt, and the K_{sn}'s are the concentration values. To evaluate these concentration K_{sn} values, a plot of K_{sn} against $\mu^{1/2}$ was constructed and specific values were interpolated: with the exception of K_{s2} which is assumed to be independent of ionic strength, the data used in this plot were obtained from eqs [19] - [23] and Table 1. Combining eqs [26], [28], and [31] yields

$$\sum_{1}^{n} (n-1)K_{sn}[SCN^-]^n + [SCN^-]^2 - c[SCN^-] - K_{s0} = 0 \qquad [32]$$

If the polynuclear species $Ag_2(SCN)_6^{4-}$ is considered, the analog to eq [32] is

$$4K_{s26}[SCN^-]^5 + \sum_{1}^{n} (n-1)K_{sn}[SCN^-]^n + [SCN^-]^2 - c[SCN^-] - K_{s0} = 0 \qquad [33]$$

and the solubility of AgSCN is given by

$$c_{Ag} = \sum_{0}^{n} K_{sn}[SCN^-]^{n-1} + 2K_{s26}[SCN^-]^4 \qquad [34]$$

Equations [32] and [33] were solved by the Newton-Raphson method, and c_{Ag} calculated from eq [26] or [34]. The results are given in Table 3. The data in this table are of interest for several reasons. First they indicate that for all c values considered, the contributions by mononuclear complexes to c_{Ag} is of prime importance: the contribution by $Ag(SCN)_2^-$ drops off rapidly for c > 0.1 mol dm^{-3} which explains why this complex has escaped detection in several investigations. The polynuclear complex makes important contributions to c_{Ag} for values of c $\geqslant$ 0.1 mol dm^{-3}. The fact that all complexes, except perhaps $Ag(SCN)_2^-$, exist in nearly equal concentrations for c values commonly employed in most investigations adds to the difficulty in the evaluation of the formation constants. The additional fact that Cave and Hume (14) report formation constants for mononuclear complexes in a concentration region where the polynuclear species exists in significant concentrations is another reason their values were not used in the recommended average values for K_{sn}.

3. Solubility in NH_3 solutions. In solutions containing c mol dm^{-3} NH_3 where c $\geqslant$ 0.2, the observed solubility is large enough, and $[SCN^-]$ is small enough, that only complexes involving NH_3 need be considered. As a trial function, it is assumed that only $Ag(NH_3)_2^+$ forms so that

$$c_{Ag} = [SCN^-] = [Ag(NH_3)_2^+] \qquad [35]$$

Equation [35] can be solved with the aid of the following relations:

$$c = [NH_3] + [NH_4^+] + 2[Ag(NH_3)_2^+] \qquad [36]$$

COMPONENTS:	EVALUATOR:
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CRITICAL EVALUATION: (continued)

$$K^\circ_N = [Ag(NH_3)_2^+]/ [Ag^+][NH_3]^2 = 1.07 \times 10^7 \text{ mol}^{-2} \text{ dm}^6 \qquad [37]$$

$$K^\circ_b = [NH_4^+][OH^-]/[NH_3] = 1.78 \times 10^{-5} \text{ mol dm}^{-3} \qquad [38]$$

The values for K°_N and K°_b were taken from Bjerrum's text (51). Assuming $[NH_4^+] = (cK^\circ_b)^{1/2}$, the NH_3 concentration is obtained from

$$[NH_3]\left\{1 + 2(K^\circ_{s0}K^\circ_N)^{1/2}\right\} - c + (cK^\circ_b)^{1/2} = 0 \qquad [39]$$

Taking c = 0.226 mol dm^{-3}, eq [39] gives $[NH_3]$ = 0.223 and $[Ag^+]$ = 1.4 x 10^{-9} mol dm^{-3} as calculated from

$$[Ag^+] = (K^\circ_{s0}/K^\circ_N)^{1/2}/[NH_3] \qquad [40]$$

Computing C_{Ag} from eq [35] gives C_{Ag} = 7.3 x 10^{-4}mol dm^{-3} which is not in satisfactory agreement with the observed value of 1.16 x 10^{-3} mol dm^{-3} (2). This disagreement is not due to the neglect of activity coefficients, $Ag(NH_3)^+$, or mononuclear complexes: e.g. allowing for mononuclear complexes in eqs [35] - [40] gives $[Ag(SCN)_2^-]$ = 1.2 x 10^{-7} mol dm^{-3} >> $[Ag(SCN)_3^{2-}]$ + $[Ag(SCN)_4^{3-}]$. The difference is assumed to be due to the formation of $Ag(SCN)(NH_3)$ according to

$$AgSCN(s) + NH_3(aq) \rightleftarrows Ag(SCN)(NH_3)(aq) \qquad K_{s111} \qquad [41]$$

The solubility of AgSCN is now written as

$$C_{Ag} = [Ag(SCN)(NH_3)] + [Ag(NH_3)_2^+] = [SCN^-] + [Ag(SCN)(NH_3)] \qquad [42]$$

The solution for the concentration of ammonia is

$$[NH_3] = \{c - (cK^\circ_b)^{1/2}\}/\{1 + K_{s111} + 2(K^\circ_{s0}/K^\circ_N)^{1/2}K^\circ_N\} \qquad [43]$$

Taking c = 0.226 mol dm^{-3}, K_{s111} was adjusted to give the observed value of C_{Ag}. The resulting value for K_{s111} is 0.002. Using this value for K_{s111}, C_{Ag} was calculated for various values of c as shown in Table 4.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Water; H_2O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION:

TABLE 3 Calculations of C_{Ag} Based on Equations [26] and [34] at 298.15 K

	results from eq [26]					results from eq [34]			
total $[SCN^-]$ =	0.05	0.10	0.573	0.626	1.066	0.10	0.573	0.626	1.066
10^3K_{s3}	5.35	5.7	6.9	6.95	7.4	5.7	6.9	6.95	7.4
10^2K_{s4}	2.75	3.55	6.4	6.6	8.2	3.55	6.4	6.6	8.2
$[SCN^-]_{equil}$	0.04996	0.0999	0.539	0.582	0.885	0.0998	0.536	0.578	0.869
$10^3[Ag(SCN)_2^-]$	0.008	0.016	0.086	0.093	0.142	0.016	0.086	0.093	0.139
$10^3[Ag(SCN)_3^{2-}]$	0.0134	0.0568	2.00	2.36	5.79	0.057	1.98	2.32	5.59
$10^3[Ag(SCN)_4^{3-}]$	0.003	0.035	10.0	13.0	56.5	0.04	9.84	12.8	53.5
$10^3[Ag_2(SCN)_6^{4-}]$	----	----	----	----	----	0.002	1.81	2.46	12.6
10^3C_{Ag}(calcd)	0.025	0.11	12.1	15.5	62.4	0.11	13.7	17.6	71.8
10^3C_{Ag}(obsd)	----	0.1*	12.4	16.8	85.0	0.1*	12.4	16.8	85.0

Notes to table: $K_{s2} = 1.6 \times 10^{-4}$ and $K_{s26} = 0.01$ are assumed to be independent of ionic strength. Observed C_{Ag} values from Hellwig (1) with the exception of the single point marked with an asterisk (*) which was estimated from the data of Leden and Nilsson (16).

COMPONENTS:	EVALUATOR:
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CRITICAL EVALUATION: (continued)

TABLE 4 Solubility of AgSCN in NH_3 Solutions at 298 K Calculated from Eq [42].

$c/\text{mol dm}^{-3}$ =	0.226	0.4546	0.612	1.449
$[NH_3]_{equil}$	0.222	0.448	0.604	1.432
$10^3[Ag(SCN)(NH_3)]$	0.435	0.878	1.18	2.81
$10^3[Ag(NH_3)_2^+]$	0.725	1.463	1.97	4.68
10^3c_{Ag}(calcd)	----	2.3	3.2	7.5
10^3c_{Ag}(obsd)[2]	1.16	2.14	2.95	7.2

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COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. June 1978

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43. Kratohvil, J.; Težak, B.; Vouk, V.B. *Arhiv. Kem.* 1954, *26*, 191.
44. Shedlovsky, T. *J. Am. Chem. Soc.* 1932, *54*, 1411.
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46. Bodländer, G.; Eberlein, W. *Z. Anorg. Chem.* 1903, *39*, 197.
47. Joannis, A. *Ann. Chim.* 1882, *26*, 482.
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50. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233.
51. Bjerrum, J. *Metal Ammine Formation Constants in Aqueous Solutions.* P. Haase and Son. Copenhagen. 1941.
52. Chao, E.E.; Cheng, K.L. *Anal. Chem.* 1976, *46*, 267.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hellwig, K. *Z. Anorg. Chem.* 1900, *25*, 157-88.

VARIABLES:

Concentration of KSCN at 25.2°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

[KSCN]/ mol dm^{-3}	c_{Ag}/ mol dm^{-3}
0.573	0.0124
0.626	0.0168
1.066	0.0850
1.12	0.0975
1.20	0.120
1.25	0.134

AUXILIARY INFORMATION

METHOD:

Solns were prepd isothermally at 25.2 °C by adding AgSCN to concentrated KSCN solns until saturation was achieved. The solns were thermostated and water added in steps to ppt AgSCN. After each addition of water, aliquots were taken for analysis. Equil was attained in sealed flasks. The flasks were mechanically agitated in a water bath for 4 h (the author states that 2 h was required to reach equilibrium). A calibrated pipet, kept at 25.2°C, was used to withdraw the aliquots. All samples for analysis were filtered through a wad of cotton wool into the pipet. The contents of the pipet were placed in a beaker and water added to ppt all the AgSCN. The solid was washed, dried, and weighed. The wash water was combined with the mother liquor and KSCN determined by titration (presumably by the Volhard method).

SOURCE AND PURITY OF MATERIALS:

The water used in all experiments was repeatedly distilled and boiled prior to use. The AgSCN was prepared by precipitation followed by washing. No other details were given.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Silver nitrate; $AgNO_3$; [7761-88-8]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hellwig, K. *Z. Anorg. Chem.* 1900, *25*, 157-88.

VARIABLES:

One temperature: 25.2°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The author apparently made several determinations of the solubility of AgSCN as a function of $AgNO_3$ concentration: however he only reports the solubility for $[AgNO_3] = 3$ mol/dm^3 at 25.2°C.

$$[AgSCN]_{satd} = 0.00026 \text{ mol dm}^{-3}$$

AUXILIARY INFORMATION

METHOD:

Solutions were prepared by adding AgSCN to highly concentrated solns of $AgNO_3$. Water was added in steps to precipitate AgSCN and equilibrium was carried out by mechanical rotation in sealed flasks in a thermostat. Aliquots were taken for analysis after 4 h (the author states that equilibrium is reached within 2 h). A calibrated pipet which was kept at 25.2°C was used to withdraw the aliquots. All samples were filtered through a wad of cotton wool directly into the pipet. The contents of the pipet were placed in a beaker and water added to ppt the AgSCN. The solid was filtered, washed, and dried to constant weight. The wash water and the mother liquor were combined and $AgNO_3$ determined by a Volhard titration.

SOURCE AND PURITY OF MATERIALS:

The water used in all experiments was repeatedly distilled and boiled prior to use. AgSCN prepared by pptn followed by washing. No other details were given.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Ammonia; NH_3; [7664-41-7]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Abegg, R.; Cox, A.J. *J. Physik. Chem.* 1903, *46*, 1-12.

VARIABLES:

Concentration of NH_3 at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Temperature for all data is 25°C

$[NH_3]$/mol dm^{-3}	c_{Ag}/mol dm^{-3}
0.226	0.00116
0.2794	0.001518
0.4546	0.002139
0.46	0.00237
0.612	0.00295
1.449	0.0072

The solubility product of AgSCN, uncorrected for activity effects, was given as

$$K_{s0}(\text{AgSCN}) = 1.56 \times 10^{-12} \text{ mol}^2/\text{dm}^6$$

AUXILIARY INFORMATION

METHOD:

No experimental details are given. The authors state that the soly of AgSCN was determined by weighing the residue after evaporation of a given volume of solution whose NH_3 content was previously determined. The soly product was determined from the equation

$$K_{s0} = K_{diss} \; c_{Ag}/[NH_3]^2$$

where the dissociation constant, K_{diss} for $Ag(NH_3)_2^+$ is 6.8×10^{-8} mol^2 dm^{-6} and the degree of dissociation, α, of the complex salt $Ag(NH_3)(SCN)$ was taken as 0.95 (both values were obtained from reference 1).

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Bodländer, G.; Fittig, R. *Z. Physik. Chem.* 1902, *39*, 597.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Böttger, W. *Z. Physik. Chem.* 1903, *46*, 521-619.

VARIABLES:

One temperature: 19.96°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The solubility at 19.96°C in pure water is

$$c_{Ag} = 1.37 \times 10^{-4}\ g/dm^3 \quad (8.27 \times 10^{-7}\ mol\ dm^{-3})$$

$$K_{s0}(AgSCN) = (c_{Ag})^2 = 6.84 \times 10^{-13}\ mol^2\ dm^{-6}$$

Assuming the mean molar activity coefficient is equal to unity

$$K_{s0}(AgSCN) = K^o_{s0}(AgSCN)$$

AUXILIARY INFORMATION

METHOD:

A conductivity method was used. The concentration of AgSCN in a satd soln was calcd from

$$[AgSCN]_{sat}=1000\ (AgSCN)/(\lambda^o_+ + \lambda^o_-) \quad [1]$$

where λ^o is the equiv conductance at infinite dilution ($ohm^{-1}cm^2/equiv$), and $\kappa(AgSCN)$ is the specific conductance of the salt ($ohm^{-1}cm^{-1}$). The latter quantity is calcd from

$$\kappa(AgSCN) = \kappa(soln) - \kappa(H_2O) \quad [2]$$

The conductivity cells were designed to prevent the occlusion of air bubbles after sealing. The sealed cells were rotated in a const temp bath. Equil was assumed to have been attained when the conductivity remained const within experimental error (2-3%). Equil was attained in 10-15 minutes. The cond bridge and thermometer were calibrated, and the cell constants determined by using 0.010M KCl soln.

SOURCE AND PURITY OF MATERIALS:

Analytically pure chemicals (Merck) were used. AgSCN was pptd from $AgNO_3$ and KSCN. Ppt 1 was prepared in a dark room, and ppt 2 was prepd in daylight. Both ppts were washed repeatedly for several days and stored in the dark. Discoloration was noted with ppt 2 after 1 h. KCl was purified by pptn from satd aqueous soln by adding alcohol (three times). Distilled water was redistilled from an all tin plated apparatus, and stored

ESTIMATED ERROR:

Solubility: av dev ~ ±6 % (compiler)
Detection limit: ±0.006 to 0.01 x 10^{-6} ohm^{-1}
Temperature: ±0.01 to ±0.02°C

REFERENCES:

1. Kohlrausch, F. *Sitzungsber, d. Akad d. Wissen. Zu Berlin* 1902, *42*, 1031.
2. Ostwald, *Lehrbuch d. Allgem. Chemie.*
3. Nernst; Lob, *Z. Physik. Chem.* 1888, *2*, 948.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Böttger, W.; *Z. Physik. Chem.* 1903, *46*, 521-619.

COMMENTS AND/OR ADDITIONAL DATA:

Results using ppt 2 were high ($\kappa(AgSCN) = 0.126 \times 10^{-6}$) and were discarded. Ppt 1 was used for three series of measurements in which 4 individual determinations of κ(soln) and $\kappa(H_2O)$ were made. The results, from eq [2] are: $\kappa(AgSCN) = (0.101 \pm 0.012) \times 10^{-6}$; $(0.099 \pm 0.007) \times 10^{-6}$, $(0.096 \pm 0.002) \times 10^{-6}$. Böttger used κ(AgSCN) = (0.096 x 10^{-6} in eq [1]. The values for λ_+^o and λ_-^o at 20°C were estimated from the 18°C data using the equation

$$\lambda^o(20^oC) = \lambda^o(18^oC)\ \{1 + \alpha\ \Delta\ t\} \qquad [3]$$

where α = temp coefficient and Δt is the difference in temp in °C. For Ag^+, $\alpha = 0.0229$ (1), $\lambda_+^o(18^oC) = 54.5$ (recalculated by Ostwald (2) using the original data of Nernst and Lob (3)). For SCN^- Böttger gives $\lambda_-^o(18^oC) = 56.63$ and $\alpha = 0.0221$ which presumably comes from one of Kohlrausch's papers (no reference was given). At 20°C Böttger gives the following (in units of $ohm^{-1} cm^2/equiv$)

$$\lambda_+^o = 57.0 \quad ; \quad \lambda_-^o = 59.1$$

To estimate the precision of the soly determination, the compiler summed the squares of the errors in $\kappa(H_2O)$, κ(AgSCN), and the average error due to the limit of detection according to

$$\sigma = \{(0.003^2 + 0.002^2 + 0.008^2)/2\}^{1/2} = \pm 0.006 \times 10^{-6}\ ohm^{-1}\ cm^{-1}$$

This average error (±6.5%) does not include any errors which may be associated with the evaluation of the λ's.

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

in a flask fitted with a drying tube containing NaOH and CaO.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Foote, H.W. *Am. Chem. Jour.* 1903, *30*, 330-44 : *Z. Physik. Chem.* 1903, *46*, 78-86.

VARIABLES:

Composition at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition of solutions given in weight percent.

solution phase			solution phase		
AgSCN	KSCN	solid phase	AgSCN	KSCN	solid phase
0.0	70.38	A	20.41*	50.91	C,D
0.0	70.68	A	20.46	50.55	C,D
9.46	66.44	B,C	20.40	50.81	C,D
8.95	66.80	B,C	20.32	49.43	D
9.56	66.42	B,C	18.34	32.51	D
9.60*	66.46	B,C	16.41	24.68	D
10.62	66.47	C	16.14	23.89	D,B
11.76	61.25	C	16.01	23.83	D,B
13.55	58.34	C	16.05*	23.88	D,B
17.53	53.21	C			

*See discussion under METHOD

A = KSCN

B = AgSCN

C = 2KSCN·AgSCN

D = KSCN·AgSCN [62928-04-5]

AUXILIARY INFORMATION

METHOD:

Weighed amounts of all components placed in a glass tube, heated until (when possible) both salts dissolved, and placed in a Noyes solubility apparatus at 25°C. Aliquots removed for analysis when equilibrium was attained (method of attainment not specified). Solutions analysed for Ag gravimetrically by adding water to ppt AgSCN, filtered, dried at 100-120 °C. Remaining SCN^- in the filtrate was determined by acidifying with HNO_3 and titrating with $AgNO_3$ using ferric alum indicator. By assuming that no hydrates are formed, the solid phase composition could be computed by differences. In several cases which are indicated with an asterisk (*) in the data table above, equilibrium was achieved by adding water to a mixture of solid KSCN or AgSCN with the appropriate double salt.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Foote, H.W. *Am. Chem. Jour.* 1903, *30*, 330-44: *Z. Physik. Chem.* 1903, *46*, 79-86.

COMMENTS AND/OR ADDITIONAL DATA:

The compiler has converted the original data into molal units.

[AgSCN]/mol kg^{-1}	[KSCN]/mol kg^{-1}	[AgSCN]/mol kg^{-1}	[KSCN]/mol kg^{-1}
0.00	24.45	4.29*	18.27
0.00	24.80	4.26	17.94
2.37	28.37	4.27	18.16
2.22	28.34	4.05	16.81
2.40	28.45	2.25	6.81
2.42*	28.57	1.68	4.31
2.79	29.85	1.62	4.10
2.63	23.35	1.60	4.08
2.90	21.36	1.61*	4.09
3.61	18.71		

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium bromide; KBr; [7758-02-3]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Sulfuric acid; H_2SO_4; [7664-93-9]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kuster, F.W.; Thiel, A. *Z. Anorg. Chem.* 1903, *33*, 129-39.

VARIABLES:

Concentrations of KSCN and KBr

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: Solubility data are based on e.m.f. measurements at 25°C on cells containing KSCN and KBr solutions saturated with AgSCN and AgBr. Concentrations given in units of mol/dm^3, and e.m.f.'s (E_1 and E_2) are in V.

[KSCN]*	E_1	E_2**	$10^{12}[Ag^+]$	10^7 S***
0.100	0.122	0.015	13.6	10.8
0.090	0.120	0.017	14.6	11.2
0.070	0.115	0.022	17.8	12.4
0.067	0.112	0.025	19.9	13.1
0.066	0.113	0.024	19.2	12.8
0.067	0.113	0.024	19.2	12.8
0.068	0.113	0.024	19.2	12.8
0.059	0.115	0.022	17.8	12.4
0.060	0.118	0.019	15.8	11.7
0.055	0.119	0.018	15.2	11.4
0.030	0.131	0.006	9.57	9.07
0.000	0.137	0.000	7.59	8.08[1]

*[KBr] = 0.100 - [KSCN] ; **E_2 = 0.137 - E_1 ; *** S = total solubility (AgSCN + AgBr)

In 0.100M KSCN solution,

K_{s0}(AgSCN) = 1.17×10^{-12} mol^2/dm^6 ; S(AgSCN) = 1.08×10^{-6} mol/dm^3

AUXILIARY INFORMATION

METHOD:

The experimental cell is

$Hg,Hg_2Cl_2/KCl(1M)//KNO_3(1M)//KBr(xM)-$
$KSCN(0.1-x),AgBr(sat),KSCN(sat)/Ag$ [1]

The e.m.f.'s of cell [1] were added to give the e.m.f. of cell [2] (E_2):

$Ag/AgX(sat),KX(0.1M) \,\vdots\, KBr(0.1M),-$
$AgBr(sat)/Ag$ [2]

where X = Br or SCN, or a combination of the two anions. The $[Ag^+]_l$ on the left hand side was obtained from

$\log[Ag^+]_l = E_2/0.002K + \log[Ag^+]_r$

The $[Ag^+]_r$ on the right hand side was obtained from the soly product of KBr[1] (= 6.53×10^{-13}) assuming a 0.1M KBr soln is 86% dissociated.[2] All solns were prepd by mixing 0.1M $AgNO_3$ with 1 cm^3 1M KX, 5 cm^3 0.1M H_2SO_4, and 785 cm^3 water. The soly S given in the above table was calculated from

$S^2 = 0.1 \times 0.86 \times [Ag^+]$

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Assuming an uncertainty of ±0.002V in E_1, stnd dev in K_{s0} is ±0.09 x 10^{-12} mol^2 dm^{-6} and ± 0.04 x 10^{-6} mol dm^{-3} for the soly (compiler).

REFERENCES:

1. Kuster, F.W.; Thiel, A. *Z. Anorg. Chem.* 1900, *24*, 25.
2. Nernst, W. *Theoretisch. Chemie.* 1898,

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Silver cyanide; AgCN; [506-64-9]

(3) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]

(4) Potassium thiocyanate; KSCN; [333-20-0]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193-215.

VARIABLES:

Nature of the starting materials

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The author determined the solubility of AgSCN from studies on the following equilibrium reaction:

$$AgAg(CN)_2(s) + KSCN \rightleftarrows KAg(CN)_2 + AgSCN(s)$$

The experimental temperature was 25°C, and all concentrations are in units of mol dm^{-3}; K_{s0} is expressed in $mol^2\ dm^{-6}$.

$[KSCN]_{init}$	$[KAg(CN)_2]_{init}$	$[KAg(CN)_2^-]_{equil}$	c_{Ag}	$10^{12}K_{s0}(AgSCN)$
0.1093	----	0.0827	1.27×10^{-6}	1.61
0.0536	----	0.04051	1.27×10^{-6}	1.62
----	0.05361	0.04023	1.29×10^{-6}	1.67

Av values and their stnd deviations calcd by the compiler are:

$$c_{Ag} = (1.28\pm0.01) \times 10^{-6}\ mol\ dm^{-3}$$

$$K_{s0}(AgSCN) = (1.64\pm0.03) \times 10^{-12}\ mol^2\ dm^{-6}$$

AUXILIARY INFORMATION

METHOD:

The relative soly method was used. Mixtures of KSCN + AgCN or $KAg(CN)_2$ + AgSCN with water were equilibrated isothermally at 25°C with shaking. Equilibrium was attained in 1-2 days (no details given). The soln was rapidly filtered, aliquots taken and Ag_2S pptd with Na_2S. The ppt was washed, dissolved in dilute warm HNO_3, cooled and Ag^+ determined by titration with standard NH_4SCN.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Solubility: see DATA part above.

Nothing else specified.

REFERENCES:

1. Kuster, F.W.; Thiel, A. *Z. Anorg. Chem.* 1903, *33*, 129.
2. Abegg, R.; Cox, A.J. *Z. Physik. Chem.* 1903, *46*, 1.
3. Kuster and Thiel *Z. Anorg. Chem.* 1900, *24*, 25.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Silver cyanide; AgCN; [506-64-9]

(3) Potassium dicyanoargentate; $KAg(CN)_2$; [506-61-6]

(4) Potassium thiocyanate; KSCN; [333-20-0]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Lucas, R. *Z. Anorg. Chem.* 1904, *41*, 193-215.

COMMENTS AND/OR ADDITIONAL DATA:

Neglecting the possible formation of $Ag(SCN)_2^-$ and $Ag(SCN \cdot CN)^-$, the equilibrium constant for the above reaction, K_{III}, is given by

$$K_{III} = [Ag(CN)_2^-]/[SCN^-] = K_{s0}(AgAg(CN)_2)/K_{s0}(AgSCN) \qquad [1]$$

K_{III} is calcd directly from the data in the above table. Lucas' original intent was to calculate $K_{s0}(Ag\ Ag(CN)_2)$ from eq [1] using previously determined values for $K_{s0}(AgSCN)$. However, the only data at 25°C available to Lucas were those of Kuster and Thiel (1), $K_{s0} = 1.17 \times 10^{-12}$, and Abegg and Cox (2), $K_{s0} = 1.56 \times 10^{-12}$. To determine the correct value of $K_{s0}(AgSCN)$, Lucas used the mean value of $K_{s0}(AgAg(CN)_2) = 5.01 \times 10^{-12}$ in eq [1] with the experimental K_{III} values. The latter soly product was determined by Lucas in the same paper compiled elsewhere in this volume) from studies on the exchange reactions

$$AgAg(CN)_2(s) + KCl \rightleftarrows KAg(CN)_2 + AgCl(s) \qquad [2]$$

$$AgAg(CN)_2(s) + KBr \rightleftarrows KAg(CN)_2 + AgBr(s) \qquad [3]$$

Lucas' average value of $K_{s0}(AgSCN) = 1.64 \times 10^{-12}$ is in good agreement with the value of 1.56×10^{-12} found by Abegg and Cox.

Lucas then uses Abegg and Cox's value of $K_{s0}(AgSCN)$ and his experimental K_{III} values (see below) to calculate $K_{s0}(AgAg(CN)_2)$ values. Thus the reader will find another compilation for $K_{s0}(AgAg(CN)_2)$ which uses the same data as given in the above data table.

As an example of how Lucas calculated the K_{III} values, consider the first data point in the above data table:

$$K_{III} = 0.0827/(0.1093 - 0.0827) = 3.109$$

For uninegative ions, K_{III} should be independent of ionic strength since from eq [1], it is seen that mean activity coefficients should cancel. Thus the $K_{s0}(AgSCN)$ value obtained from eq [1] will in fact be the standard value, K°_{s0}, depending upon whether the corresponding $K_{s0}(AgAg(CN)_2)$ is a standard value or the value at a specific ionic strength. In computing this soly product from eqs. [2] and [3], Lucas used the $K_{s0}(AgCl)$ and $K_{s0}(AgBr)$ values of 2.0×10^{-10} (3) and 6.4×10^{-13} (3), respectively. The data from references 1 and 3 involve several assumptions concerning liquid junctions and the degree of dissociation, and are not corrected for activity effects. In the compilations for AgCN based on equations [2] and [3], the compiler has used more recent data for K°_{s0} values for AgCl and AgBr, and has computed the following average value based on Lucas' data:

$$K^{\circ}_{s0}(Ag\ Ag(CN)_2) = (4.3 \pm 0.4) \times 10^{-12}\ mol^2\ dm^{-6}$$

Using this value in eq [1] with Lucas' average $K_{III} = 3.07 \pm 0.06$, the compiler arrives at the value

$$K^{\circ}_{s0}(AgSCN) = (1.4 \pm 0.8) \times 10^{-12}\ mol^2\ dm^{-6}$$

$$c_{Ag} = (K^{\circ}_{s0})^{1/2} = (1.2 \pm 0.4) \times 10^{-6}\ mol\ dm^{-3}$$

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Böttger, W. *Z. Physik. Chem.* <u>1906</u>, *56*, 83-94.

VARIABLES:

One temperature: 100°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

At 100.0°C in pure water,

$$c_{Ag} = 6.4 \times 10^{-3}\ \text{g/dm}^3 \quad (3.9 \times 10^{-5}\ \text{mol/dm}^3)$$

$$K_{s0}(\text{AgSCN}) = (c_{Ag})^2 = 1.5 \times 10^{-9}\ \text{mol}^2/\text{dm}^6$$

Assuming the mean molar activity coefficient is equal to unity,

$$K_{s0}(\text{AgSCN}) = K^{\circ}_{s0}(\text{AgSCN})$$

AUXILIARY INFORMATION

METHOD:

A conductivity method was used. The vessel (1) was Pt-lined with quartz insulation and the second electrode was a Pt-Ir cylinder suspended in the center. The sealed vessel, which could be pressurized, was placed in a xylene temp bath. The concentration of AgSCN in the satd solns was calcd from

$$[\text{AgSCN}]_{sat} = 1000\kappa(\text{AgSCN})/\Lambda \qquad [1]$$

where κ = specific conductance of AgSCN ($\text{ohm}^{-1}\text{cm}^{-1}$) and Λ is the equivalent conductance ($\text{ohm}^{-1}\text{cm}^2$/equiv). Assuming complete dissociation, $\Lambda = \Lambda^{\circ} = \lambda^{\circ}_{+} + \lambda^{\circ}_{-}$. κ(AgSCN) was determd from

$$\kappa(\text{AgSCN}) = \kappa(\text{soln}) - \kappa(H_2O) \qquad [2]$$

Four independent measurements for κ (soln) were made at 100.1°C and were corrected to 100.0°C as described below. The conduct vessel was calibrated at 18 and 99.8°C with 0.01M NaCl.

SOURCE AND PURITY OF MATERIALS:

Commercial c.p. grade materials were used. AgSCN was prepared by pptn from 0.1M solns of $AgNO_3$ and NH_4SCN in the dark. The ppt was stored in distilled water for several weeks being renewed several times daily by decantation.

ESTIMATED ERROR:

Solubility: ±2.9% (author).
Temperature: not specified.
Conductivity measurements: $\pm 3 \times 10^{-7}$ ohm^{-1}

REFERENCES:

1. Noyes, A.A.; Coolidge, W.D. *Z. Physik. Chem.* <u>1903</u>, *46*, 325.
2. Böttger, W. *Z. Physik. Chem.* <u>1903</u>, *46*, 521.
3. Quoted by Ostwald. *Lehrbuch der Allgem. Chemie. 2*, 335-439.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Water; H_2O; [7732-18-5]	Böttger, W. *Z. Physik. Chem.* <u>1906</u>, *56*, 83-94.

COMMENTS AND/OR ADDITIONAL DATA:

At room temp (18-22°C) the conductivity of the satd solns was constant within 1-2 minutes after vigorous shaking demonstrating that equilibrium was rapidly attained. However at 100°C the conductivity slowly increased linearly with time, and was attributed to the slow dissolution of impurities. Böttger therefore made two κ(AgSCN) measurements for the first run after 95 and 125 minutes at 100.1°C (κ = 14.76 and 15.18 x 10^{-6} ohm^{-1} cm^{-1}, respectively): the rate of increase is thus 0.84 x 10^{-6} ohm^{-1} cm^{-1}/h. Using this value to correct all four experimental runs, the compiler computes an average value of κ(AgSCN) = (13.79±0.30) x 10^{-6} ohm^{-1} cm^{-1}. $\kappa(H_2O)$ was determined by first making measurements at 46°C and 100°C: the ratio of these two measurements was 1.88±0.08. Before each run, Böttger measured $\kappa(H_2O)$ at 46°C and multiplied this value by the ratio 1.9 to obtain the value of $\kappa(H_2O)$ at 100°C for each of the four experimental runs.

To correct the specific conductivity of AgSCN to 100°C Böttger estimated the temp coefficient by adding the temp coeff of $AgNO_3$ (0.88%) at 100°C obtained by A.C. Melcher (no reference was given) with the value (dS/S)dT calcd from

$$(dS/S)dT = \Delta H_{soln}/2RT^2 = 0.040 \qquad [3]$$

where S is the soly and ΔH_{soln} = 24,000 cal (3). Thus the temp coefficient is 0.04 + 0.009 = 0.049, and the final value for κ(AgSCN) at 100.0°C is 13.7 x 10^{-6} ohm^{-1} cm^{-1}. Böttger gives a value of 13.9 x 10^{-6} which is probably due to a rounding-off error: the compiler can duplicate the κ values for AgCl and AgBr from Böttger's data so that the above difference is not due to an error in calcn by the compiler.

To obtain the equivalent conductivity of AgSCN at 100.0°C Böttger assumes that the ratio ($\Lambda_o(AgNO_3)$ - Λ_o(AgSCN))/$\Lambda_o(AgNO_3)$ is twice as large at 20°C than it is at 100°C: at 20°C this ratio = 4.6%, and at 100°C it equals 2.3%. Using Melcher's value (no reference) $\Lambda_o(AgNO_3)$ = 367 at 100°C, Böttger obtains Λ_o(AgSCN) = 359 ohm^{-1} cm^2/equiv at 100°C.

Combining the solubility of AgSCN at 100°C with the value obtained at 20°C(2) Böttger, using the integrated form of eq [3], calculates a heat of solution, ΔH_{soln}, = 20.92 kcal/mol which is in agreement with the value obtained by Tomsen (3).

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Silver chloride; AgCl; [7783-90-6]
(3) Potassium chloride; KCl; [7447-40-7]
(4) Potassium thiocyanate; KSCN; [333-20-0]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hill, A.E. *J. Am. Chem. Soc.* 1908, *30*, 68-74.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The equilibrium studied was

$$AgSCN(s) + KCl \rightleftarrows AgCl(s) + KSCN \qquad K_A = [SCN^-]/[Cl^-] \qquad [1]$$

Neglecting ion-pair formation, complex ion formation, and activity effects,

$$K^o_{s0}(AgSCN) = K_A \cdot K^o_{s0}(AgCl) \qquad [2]$$

In the table below K_A was obtained from the exptl results of Hill and $K^o_{s0}(AgSCN)$ was calcd by the compiler from eq [2] taking $K^o_{s0}(AgCl) = 1.76 \times 10^{-10}$ mol^2/dm^6 (converted to these units from mol^2/kg^2 by the compiler from the data given in reference 1). The recalculation of $K^o_{s0}(AgSCN)$ by the compiler is necessary because in the original paper, Hill used an incorrect value (2) for $K^o_{s0}(AgCl) = 2.6 \times 10^{-10}$ mol^2/dm^6. μ is the ionic strength in mol/dm^3.

μ	K_A	$10^{13}K^o_{s0}(AgSCN)$
0.1980	0.00527	9.26
0.1940	0.00518	9.10
0.0504	0.00585	10.28
0.0492	0.00573	10.07
0.0101	0.0060	10.54
0.0101	0.0057	10.02

Average values are:

$$K_A = (5.62 \pm 0.33) \times 10^{-3}$$

$$K^o_{s0}(AgSCN) = (9.88 \pm 0.57) \times 10^{-13} \text{ mol}^2 \text{ dm}^6$$

AUXILIARY INFORMATION

METHOD:

A relative soly method was used. Satd solns were prepared isothermally at 25°C. Three solns were prepd starting with AgCl and KSCN, and three more starting with AgSCN and KCl. With stirring equilibrium was stated to be attained in less than 1 h. After 4-6 h the solid phases were allowed to settle and aliquots withdrawn for analysis. The solns were analysed simultaneously for SCN^- and Cl^- by the Volhard method, and separately for SCN^- by colorimetry (no details given).

SOURCE AND PURITY OF MATERIALS:

Ag salts prepd by pptn from hot solns of "pure" $AgNO_3$ and KCl or KSCN, and washed until free of Cl^- and SCN^-. AgCl redissolved in aq NH_3, pptd with HNO_3 and washed. The salts were stored moist in the dark. KCl and KSCN (Kahlbaum, c.p.), the latter free of Cl^-, were used as received. No other details were given.

ESTIMATED ERROR:

Standard deviations given above were calcd by the compiler.

REFERENCES:

1. Wagman, D.; Evans, W.H.; Parker, V.B.; Halow, I.; Bailey, S.M.; Schumm, R.H. *Selected Values of Chemical Thermodynamic Properties. U.S. National Bureau of Standards TN-270-3*, 1968; and *270-4*. 1969.
2. Kohlrausch; Rose, *Z. Physik. Chem.* 1893, *12*, 241.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Silver bromide; AgBr; [7785-23-1]
(3) Potassium bromide; KBr; [7758-02-3]
(4) Potassium thiocyanate; KSCN; [333-20-0]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hill, A.E. *J. Am. Chem. Soc.* 1908, *30*, 68-74.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The equilibrium studied was

$$AgSCN(s) + KBr \rightleftarrows AgBr(s) + KSCN \qquad K_B = [SCN^-]/[Br^-] \qquad [1]$$

Neglecting ion-pair formation, complex ion formation, and activity effects,

$$K^o_{s0}(AgSCN) = K_B \cdot K^o_{s0}(AgBr) \qquad [2]$$

In the table below, K_B was obtained from the exptl results of Hill, and K^o_{s0}(AgSCN) was calcd by the compiler from eq [2] taking K^o_{s0}(AgBr) = 5.31 x 10^{-13} mol^2 dm^6 (converted to these units from mol^2/kg^2 by the compiler from the data given in reference 1). μ is the ionic strength in mol/dm^3

μ	K_B	$10^{13}K^o_{s0}$(AgSCN)
0.1852	1.862	9.88
0.1872	1.815	9.63
0.0477	1.891	10.04
0.0500	1.841	9.77

Average values are:

$$K_B = 1.85 \pm 0.03$$

$$K^o_{s0}(AgSCN) = (9.83 \pm 0.17) \times 10^{-13}\ mol^2\ dm^{-6}$$

AUXILIARY INFORMATION

METHOD:

A relative soly method was used. Satd solns were prepared isothermally at 25°C. Two solns were prepared starting with KBr + AgSCN, and two more with KSCN + AgBr. Ionic strengths were either about 0.05 or 0.2 mol/dm^3. With stirring, equilibrium was stated to be attained in less than 1 h. After 4 h the solid was allowed to settle and aliquots of soln taken for analysis. Total Br^- + SCN^- determined by the Volhard method, and Br^- separately by the method of Rosanoff and Hill (2).

SOURCE AND PURITY OF MATERIALS:

Ag salts prepared by pptn from hot soln of "pure" $AgNO_3$ and KSCN or KBr were washed until free of Br^- or SCN^-. Both salts were stored moist in the dark. KSCN (Kahlbaum, c.p.) free of Cl^-, and KBr (Baker and Adamson, A.R.) were used as received. No other details given.

ESTIMATED ERROR:

Nothing specified by author. Standard deviations given above were calcd by the compiler.

COMMENTS AND/OR ADDITIONAL DATA:

Hill's original intention was to use the K_B value to calc K_{s0}(AgBr) from eq [2]. The value of K_{s0}(AgSCN) was obtained from the studies on the reaction

$$AgSCN(s) + KCl \rightleftarrows AgCl(s) + KSCN \qquad [3]$$

Reaction [3] is compiled elsewhere in this volume.

REFERENCES:

1. Wagman, D.; Evans, W.H.; Parker, V.B.; Halow, I.; Bailey, S.M.; Schumm, R.H. *Selected Values of Chemical Thermodynamic Properties*. U.S. National Bureau of Standards *TN-270-3*. 1968; and *270-4*. 1969.
2. Rosanoff; Hill, *J. Am. Chem. Soc.* 1907, *29*, 1461.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kirschner, A. *Z. Physik. Chem.* <u>1912</u>, *79*, 245-7.

VARIABLES:

Two temperatures: 18 and 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

c_{Ag} is the total solubility of AgSCN in 0.1 mol/dm^3 KSCN.

$t/^{\circ}C$	$c_{Ag}/mol\ dm^{-3}$*	$10^{12}K_{s0}/mol^2\ dm^{-6}$
18	2.5×10^{-4}	0.49 (average of 5 measurements)
25		1.16 (average of 3 measurements)

*Computed value: see COMMENTS AND/OR ADDITIONAL DATA below.

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the cell

$$\overset{C_2}{} \qquad \text{conc} \qquad \overset{C_1}{}$$

$$Ag/AgNO_3(0.1M)//NH_4NO_3//KSCN(.1M)/\text{-}AgSCN,Ag$$

The cell e.m.f.'s were measured at room temp (18°C) and in a regulated water bath at 25°C. Equil e.m.f.'s were recorded after about 2 h when agitation did not change the e.m.f. The av e.m.f.'s were 0.586V at 18°C and 0.578 V at 25°C. The $[Ag^+]$ in the satd soln was calcd from

$$\log C_1 = \log C_2 - EF/2.3RT$$

The author uses dissociation constants of 0.815 and 0.86, resp, for 0.1M $AgNO_3$ and KSCN solns at 18 and 25°C: no reference was given for either of these values.

SOURCE AND PURITY OF MATERIALS:

Silver wire electrodes were cleaned with emery paper followed by ingition. The Ag electrode in the KSCN soln was almost completely covered with solid AgSCN. The electrodes were checked by placing 0.1M $AgNO_3$ soln in both sides of the cell (a zero e.m.f. resulted). No other details were given.

ESTIMATED ERROR:

K_{s0}: $\sigma = \pm 4\%$ (compiler)

Nothing else specified.

REFERENCES:

1. Bodländer, G.; Eberlein, W. *Z. Anorg. Chem.* <u>1903</u>, *39*, 197.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Kirschner, A. *Z. Physik. Chem.* 1912, *79*, 245-7.

COMMENTS AND/OR ADDITIONAL DATA:

The total solubility of AgSCN in excess KSCN was calculated assuming the predominant complex formed is the mononuclear species $Ag(SCN)_2^-$. Using Bodländer and Eberlein's (1) value of 5.99×10^9 for the overall formation constant β_2, the solubility at 18°C was calcd from

$$C_{Ag} = [Ag(SCN)_2^-] = K_{s0}\beta_2[SCN^-] = K_{s0}\beta_2(0.1)(0.86) = 0.00025 \text{ mol/dm}^3$$

The calculation was not repeated for 25°C presumably since the author did not have a value for β_2 at this temperature.

The author calculated the heat of solution of AgSCN from

$$\Delta H = \{RT_1T_2/(T_2-T_1)\}\ln(C_2/C_1) = 21.3 \text{ kcal/mol} = 89.1 \text{ kJ/mol}$$

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Randall, M.; Halford, J.O. *J. Am. Chem. Soc.* 1930, *52*, 178-91.

VARIABLES:

Concentration of KSCN at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]/mol\ kg^{-1}$	$c_{Ag}/mol\ kg^{-1}$
0.312	0.00202
0.564	0.0121
0.870	0.0458
1.124	0.0985

AUXILIARY INFORMATION

METHOD:

KSCN solns of known strength were rotated in bottles containing excess AgSCN in a thermostat (25°C) for several days. The solns were analysed gravimetrically by pptn of AgSCN: this was accomplished by oxidizing the excess SCN^- by heating with 2M HNO_3.

COMMENTS AND/OR ADDITIONAL DATA:

The authors attempted to analyse their data in terms of the equilibrium

$$AgSCN(s) + SCN^- \rightleftarrows Ag(SCN)_2^- \qquad K_{s2}$$

The computed values for K_{s2} varied by a factor of 10 over the range of KSCN concentrations studied, and they concluded that higher complexes of the type $Ag(SCN)_n^{1-n}$ where $n > 2$ were present.

SOURCE AND PURITY OF MATERIALS:

AgSCN was prepared by precipitation from a dilute $AgNO_3$ solution with KSCN in the presence of dilute HNO_3. No other details are given.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Masaki, K. *Bull. Chem. Soc. Jpn.* 1930, *5*, 345-8.

VARIABLES:

One temperature: 18°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Five measurements of the e.m.f. of the experimental cell were made at 18°C in 0.1 mol dm^{-3} solutions.

	e.m.f./V	$10^{11}[Ag^+]$/mol dm^{-3}	$10^{12}K^*_{s0}$/$mol^2 dm^{-6}$	$10^6 c_{Ag}$/mol dm^{-3}
	0.545	1.2	1.3	1.1
	0.550	1.0	1.1	1.0
	0.552	0.9	1.0	0.9
	0.549	1.1	1.0	1.0
	0.551	1.0	1.0	1.0
av	0.549	1.0	1.1	1.0

*Calculated by the compiler.

The experimental errors in the e.m.f.'s are not known, but the above data give a reproducibility of ± 0.003 V. Thus the errors listed below are standard deviations in the reproducibility based on the data in the table. Errors arising from the accuracy of the e.m.f. measurements are unknown. The assumption that $c_{Ag} = [K_{s0}]^{1/2}$ is an approximation for 0.1 mol dm^{-3} SCN^- solns (see the critical evaluation). This data is presented by the compiler only because it was given by Masaki in the original publication.

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made for the cell

$$Ag/AgNO_3(0.01M)//NH_4NO_3(satd)/\text{-}$$
$$KSCN(0.1M),\ AgSCN(satd)/Ag$$

The cells were thermostated at 18°C i the dark, and all readings were taken after 1 hour. The e.m.f. of the above cell is given by

$$\text{e.m.f.} = (0.53)(0.116)\log(0.01\alpha/[Ag^+])$$

where 0.53 is the transport number of NO_3^- (assumed value), and α is the degree of dissociation of $AgNO_3$ in 0.01M soln: α = 0.93 (no reference is given). K_{s0} and solubilities were calculated from

$$\text{solubility} = K_{s0}^{1/2} = (0.1\ x[Ag^+])^{1/2}$$

SOURCE AND PURITY OF MATERIALS:

Water of specific conductivity equal to 1.2 x 10^{-6} ohm^{-1} cm^{-1} was used. AgSCN was prepared by pptn from a soln of KSCN and "purified" $AgNO_3$ followed by washing. Kahlbaum KSCN was recrystallized before use. "Pure" Ag wire electrodes were used.

ESTIMATED ERROR:

E.m.f.'s: ±3 mV (compiler)

K_{s0}: ± 1 x 10^{-13} mol^2 dm^{-6} (compiler)

Temperature: ± 0.1°C

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Ammonia; NH_3; [7664-41-7]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Garrick, F.J.; Wilson, C.L. *J. Chem. Soc.* 1932, 835-41.

VARIABLES:

Concentration of NH_3 at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Concentrations are in mol kg^{-1}; temperature = 25.00°C.

$[NH_3]$	$10^3[AgSCN]$	solid phase
1.026	5.17	A
1.587	8.54	A
1.840	10.01	A
2.178	12.34	A
2.276	12.92	A
2.440	13.76	B
2.581	14.54	B
2.848	15.90	B
2.915	16.35	B
3.049	17.34	B
3.217	17.80	C
3.325	18.42	C
3.684	19.91	C
3.767	20.31	C
4.335	22.84	C
4.504	23.41	C
5.27	27.24	C
5.36	27.71	C
6.60	34.89	C
7.47	40.62	C
8.94	51.8	C
9.91	62.0	C
11.36	79.1	C
14.69	159.6	C

Solid phases:

A = AgSCN

B = ? = $AgSCN \cdot 1/2NH_3 \cdot 1/2H_2O$

C = $AgSCN \cdot NH_3$

AUXILIARY INFORMATION

METHOD:

Equilibrium was attained in several h by mechanically stirring in a thermostat at 25.00°C. Liquid phase samples titrated with HNO_3 using bromophenol blue indicator, and the AgSCN ppt washed, dried at 110°C, and weighed. Each datum point is the mean of two determinations. A plot of $[NH_3]$ against [AgSCN] showed two breaks near $[NH_3]$ = 2.276m and 3.049m. Direct analysis of solid failed due to decomposition. Indirect identification affected by analysis of satd soln with ∿ 10% solid for total NH_3, AgSCN, and H_2O (by difference). Assuming all the water was initially present in soln, the solid phase was identified by mass balance considerations. In the region where $AgSCN \cdot 1/2NH_3 \cdot 1/2H_2O$ is presumed to exist, calculations gave fractional values of NH_3 and the water of hydration is an assumed value.

SOURCE AND PURITY OF MATERIALS:

AgSCN was precipitated from solns of AR grade NH_4SCN and $AgNO_3$. The ppt was washed, and in some cases dried at 110°C.

ESTIMATED ERROR:

Solubility: ±0.4% (reproducibility)

Solid phase analysis: ±1-5%

Temperature: ±0.01°C

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Ammonium thiocyanate; NH_4SCN; [1762-95-4]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Occleshaw, V. J. *J. Chem. Soc.* 1932, 2404-10.

VARIABLES:

Concentration of all components at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition of solutions expressed in weight percent.

solution phase			solution phase		
AgSCN	NH_4SCN	solid phase	AgSCN	NH_4SCN	solid phase
0.00	64.33	A	33.14	44.27	C
3.19	63.37	A	33.29	40.25	C
4.48	62.87	A,B	33.44	36.04	C
4.51	62.70	B	34.10	31.10	C
9.46	57.07	B	35.09	28.19	C,D
17.16	51.42	B	30.88	26.86	D
24.80	48.22	B	14.92	19.57	D
30.38	46.18	B	3.19	10.66	D
33.18	45.13	B,C	0.00002[1]	0.00	D

A = NH_4SCN

B = $5NH_4SCN \cdot AgSCN$

C = $NH_4SCN \cdot AgSCN$; [14038-74-5]

D = AgSCN

AUXILIARY INFORMATION

METHOD:

Mixtures containing an excess of one or both salts shaken at 40°C and then thermostated at 25°C: equilibrium established by duplicate analysis at 2 day intervals. The total SCN^- was determined gravimetrically by precipitating AgSCN with a slight excess of $AgNO_3$. The total Ag content was determined by heating an aliquot with con HNO_3, evaporating to near dryness, adding water, and titrating with standard NH_4SCN (Volhard method).

The compiler assumes that the solid phases were analysed by the method of residues.

SOURCE AND PURITY OF MATERIALS:

A.R. grade NH_4SCN was used as received. AgSCN residues from previous studies were dissolved in aqueous NH_4SCN, filtered, precipitated with water, washed with water, ethanol, and air-dried at 120°C. Distilled water was used.

ESTIMATED ERROR:

Solubility: $\leqslant \pm 2\%$ (reproducibility)

Temperature: ±0.05°C

REFERENCES:

1. Masaki, K. *Bull. Chem. Soc. Jpn.* 1930, *5*, 345.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Ammonium thiocyanate; NH_4SCN; [1762-95-4]

(3) Water; H_2O; [7732-18-5]

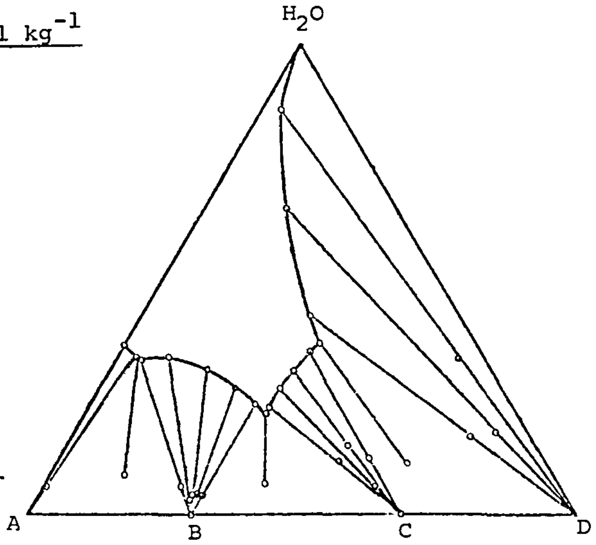
ORIGINAL MEASUREMENTS: (continued)

Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404-10.

COMMENTS AND/OR ADDITIONAL DATA:

The compiler has converted the original data into molal units. These conversions, along with the phase diagram, are presented below.

[AgSCN]/mol kg^{-1}	[NH_4SCN]/mol kg^{-1}
0.00	23.69
0.57	24.90
0.83	25.30
0.83	25.12
1.70	22.40
3.29	21.50
5.54	23.48
8.84	25.74
7.58	19.98
6.60	15.51
5.90	11.74
5.76	10.09
4.40	8.35
1.37	3.92
0.22	1.63
---	0.0



AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Occleshaw, V.J. *J. Chem. Soc.* 1932, 2402-10.

VARIABLES:

Concentration of all components at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition of solutions expressed in weight percent.

solution phase		
AgSCN	KSCN	solid phase
0.00	70.89	A
5.12	68.77	A
9.19	66.88	A,B
9.22	66.31	B
11.78	61.39	B
13.06	59.29	B
16.12	55.21	B
18.74	52.13	B
20.57	50.53	B
20.56*	54.09	C
20.58	50.01	C
20.28	47.72	C
20.04	43.02	C
19.24	35.88	C
16.68	25.40	C
16.10	23.15	C,D
11.39	20.98	D
6.69	16.97	D
1.29	9.67	D
0.00002[1]	0.0	D

*metastable

A = KSCN

B = 2KSCN·AgSCN

C = KSCN·AgSCN [62928-04-5]

D = AgSCN

AUXILIARY INFORMATION

METHOD:

Mixtures containing an excess of one or both salts shaken at 40°C and then thermostated at 25°C: equilibrium established by duplicate analysis at 2 day intervals. Inoculation with the solid phase was carried out to prevent the formation of metastable solid phases. Total SCN^- was determined gravimetrically by precipitating AgSCN with a slight excess of $AgNO_3$. Total Ag content was determined by heating an aliquot with con HNO_3, evaporating to near dryness, adding water, and titrating with standard NH_4SCN (Volhard method). The compiler assumes that the solid phases were analysed by the method of residues.

SOURCE AND PURITY OF MATERIALS:

A.R. grade KSCN used as received. AgSCN residues from previous studies were dissolved in aqueous NH_4SCN, filtered, precipitated with water, washed with water, ethanol, and air-dried at 120°C. Distilled water was used.

ESTIMATED ERROR:

Solubility: ≤ ±2% (reproducibility)

Temperature: ±0.05°C

REFERENCES:

1. Masaki, K. *Bull. Chem. Soc. Jpn.* 1930, *5*, 345.
2. Foote, H.W. *Am. Chem. Jour.* 1903, *46*, 79.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

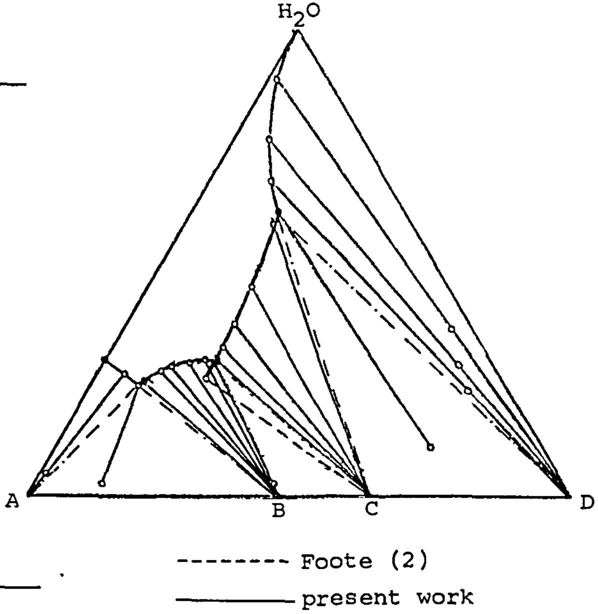
ORIGINAL MEASUREMENTS: (continued)

Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404-10.

COMMENTS AND/OR ADDITIONAL DATA:

The compiler has converted the original data into molal units. These conversions, along with the phase diagram, are presented below.

[AgSCN]/mol kg^{-1}	[KSCN]/mol kg^{-1}
0.00	25.06
1.18	27.10
2.31	28.76
2.27	27.88
2.65	23.54
2.85	22.06
3.39	19.82
3.88	18.41
4.29	17.99
4.89	21.96
4.22	17.50
3.78	15.34
3.27	11.98
2.58	8.23
1.74	4.51
1.60	3.92
1.01	3.19
0.53	2.29
0.09	1.12
---	0.0



AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium thiocyanate; NaSCN; [540-72-7]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404-10.

VARIABLES:

Concentration of all components at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition expressed in weight percent.

solutions			solutions		
AgSCN	NaSCN	solid phase	AgSCN	NaSCN	solid phase
0.00	58.78	A	12.72	54.34	B,C
5.09	56.94	A	12.68	54.36	C
9.80	55.42	A	11.53	48.51	C
12.11	54.76	A,B	11.21	42.49	C
12.14	54.55	A,B	11.14	38.31	C
12.17	54.73	A,B	11.06	25.42	C
12.21	54.80	A,B	12.61	17.24	C,D
12.23	54.78	B	10.09	17.55	D
12.54	54.46	B	1.74	9.19	D
			0.00002[1,2]	0.0	D

A = $NaSCN \cdot 2H_2O$

B = $3NaSCN \cdot AgSCN$

C = $NaSCN \cdot AgSCN \cdot 2H_2O$ [66418-41-5]

D = AgSCN

AUXILIARY INFORMATION

METHOD:

Mixtures of excess AgSCN or NaSCN shaken at 40°C and then thermostated at 25°C: equilibrium established by duplicate analysis at 2 day intervals. Mixtures containing solid NaSCN seeded to prevent formation of metastable mixtures. Total SCN^- analysed by pptn with excess $AgNO_3$. Ag was determined by heating an aliquot with conc HNO_3, evaporating to near dryness, addition of water and titrated by the Volhard method. The compiler assumes that the solid phases were analysed by the method of residues.

SOURCE AND PURITY OF MATERIALS:

AgSCN residues from previous studies dissolved in aq NH_4SCN, filtered and pptd with water. The ppt washed with water, alcohol and air-dried at 120°C. Commercial NaSCN recrystallized several times from water, 96% ethanol, and air-dried at 120°C. Distilled water was used.

ESTIMATED ERROR:

Solubility: $\geq \pm 2\%$ (reproducibility)

Temperature: ± 0.05°C

REFERENCES:

1. Kuster, F.W.; Thiel, A. *Z. Anorg. Chem.* 1903, *33*, 129.
2. Masaki, K. *Bull. Chem. Soc. Jpn.* 1930, *5*, 345.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium thiocyanate; NaSCN; [540-72-7]

(3) Water; H_2O; [7732-18-5]

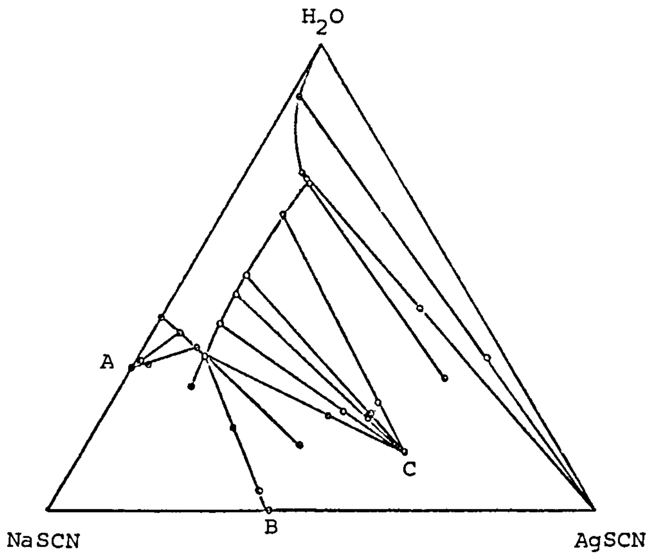
ORIGINAL MEASUREMENTS: (continued)

Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404-10.

COMMENTS AND/OR ADDITIONAL DATA:

The double salts are crystalline, colorless, and have refractive indices between 1.65 and 1.75. The dehydration of $NaSCN \cdot 2H_2O$ was studied at 25°C and there is no indication that the monohydrate exists. The compiler has converted the authors original data into molal units. These conversions, along with the phase diagram, are presented below.

[AgSCN]/mol kg^{-1}	[NaSCN]/mol kg^{-1}
0.00	17.59
0.81	18.50
1.70	19.66
2.20	20.39
2.20	20.20
2.22	20.40
2.23	20.49
2.23	20.48
2.29	20.36
2.33	20.35
2.32	20.34
1.74	14.97
1.46	11.32
1.33	9.35
1.05	4.94
1.08	3.03
0.84	2.99
0.12	1.27
	0.00



COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Barium thiocyanate; $Ba(SCN)_2$; [2092-17-3]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Occleshaw, V.J. *J. Chem. Soc.* 1934, 1892-5.

VARIABLES:

Concentration of all components at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition of solutions expressed in weight percent.

solution phase			solution phase		
AgSCN	$Ba(SCN)_2$	solid phase	AgSCN	$Ba(SCN)_2$	solid phase
0.0	62.1	A	35.79	39.54	1:2:2 , 1:3:2
4.29	61.39	A	35.79	39.02	1:3:2
12.58	58.91	A	35.13	38.41	1:3:2
17.04	57.36	A	34.58	37.49	1:3:2
22.58	55.99	A	34.28	37.13	1:3:2
22.98	55.91	A, 1:1:2	34.01	36.78	1:3:2
23.91	55.20	1:1:2	33.79	36.04	1:3:2 , B
25.01	54.14	1:1:2	27.99	34.50	B
26.35	53.23	1:1:2	23.24	32.20	B
27.89	52.61	1:1:2	14.67	27.00	B
29.17	52.01	1:1:2 and 1:2:2	4.47	18.18	B
29.81	47.74	1:2:2	0.75	9.68	B
31.67	44.28	1:2:2	0.00002[1]	0.00	B
34.70	40.61	1:2:2			

A = $Ba(SCN)_2 \cdot 3H_2O$

B = AgSCN

1:1:2 = $Ba(SCN)_2 \cdot AgSCN \cdot 2H_2O$

1:2:2 = $Ba(SCN)_2 \cdot 2AgSCN \cdot 2H_2O$

1:3:2 = $Ba(SCN)_2 \cdot 3AgSCN \cdot 2H_2O$

AUXILIARY INFORMATION

METHOD:

Mixtures containing an excess of one or both salts shaken at 40°C and then thermostated at 25°C: equilibrium established by duplicate analysis at 2 day intervals. Barium was determined by the Volhard method using standard $AgNO_3$. Total SCN^- determined gravimetrically as AgSCN by precipitation with $AgNO_3$. The amount of AgSCN was obtained by difference. The compiler assumes that the solid phases were analysed by the method of residues.

SOURCE AND PURITY OF MATERIALS:

Commercial $Ba(SCN)_2$ recrystallized several times and dried over $CaCl_2$. AgSCN residues from previous studies were dissolved in aqueous NH_4SCN, filtered, precipitated with water, washed with water, ethanol, and air-dried at 120°C. Presumably distilled water was used.

ESTIMATED ERROR:

Solubility: nothing specified but probably ±2% as in prior work (2).

Temperature: ±0.05°C

REFERENCES:

1. Masaki, K. *Bull. Chem. Soc. Jpn.* 1930, 5, 345.
2. Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Barium thiocyanate; $Ba(SCN)_2$; [2092-17-3]

(3) Water; H_2O; [7732-18-5]

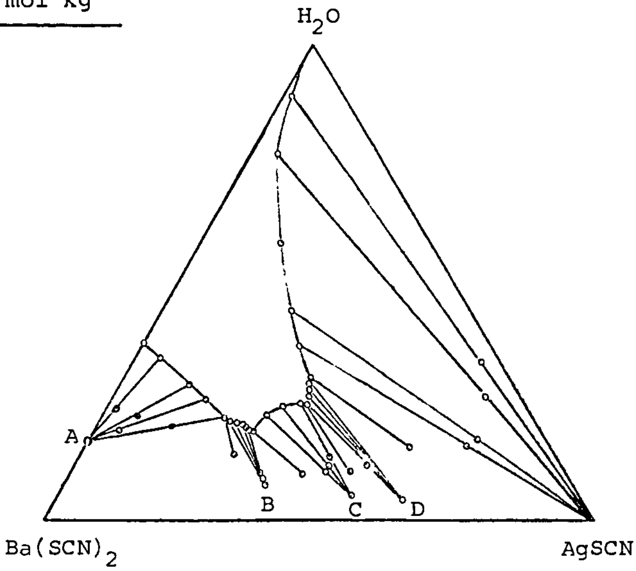
ORIGINAL MEASUREMENTS: (continued)

Occleshaw, V.J. *J. Chem. Soc.* 1934, 1892-5.

COMMENTS AND/OR ADDITIONAL DATA:

The data support the existence of three double salts 1:1:2, 1:2:2, and 1:3:2. No congruent point occurs on the solubility curve of any of these double salts. These double salts have refractive indices greater than 1.65, are anisotropic and biaxial with optical properties that suggest they are monoclinic. The compiler has converted the original data to molal units which are presented below.

[AgSCN]/mol kg^{-1}	$[Ba(SCN)_2]$/mol kg^{-1}
0.00	6.46
0.75	7.06
2.66	8.15
4.01	8.84
6.35	10.31
6.56	10.45
6.90	10.42
7.23	10.24
7.78	10.28
8.62	10.64
9.34	10.90
8.00	8.39
7.94	7.26
8.47	6.49
8.74	6.32
8.56	6.11
8.00	5.73
7.46	5.30
7.23	5.12
7.02	4.97
6.75	4.71
4.50	3.63
3.14	2.85
1.52	1.83
0.35	0.93
0.05	0.43
---	0.0



B = 1:1:2

C = 1:2:2

D = 1:3:2

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Pearce, J.N.; Smith, L. *J. Am. Chem. Soc.* 1937, *59*, 2063-5.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The object of the authors' work was to evaluate the standard molal potential E^o_m, for the Ag,AgSCN half-cell. They did not report a value for the soly product K^o_{s0}(AgSCN), but using their data, the compiler obtains

$$K^o_{s0}(\text{AgSCN}) = 1.24 \times 10^{-12}\ \text{mol}^2/\text{kg}^2$$

Cave and Hume (1) have recalculated K_{s0}(AgSCN) using the original data of Pearce and Smith:

$$K^o_{s0}(\text{AgSCN}) = 1.13 \times 10^{-12}\ \text{mol}^2/\text{kg}^2$$

Based on the compiler's conversion of E^o_m values to absolute volts,

$$K^o_{s0}(\text{AgSCN}) = 1.11 \times 10^{-12}\ \text{mol}^2\ \text{kg}^{-2}$$

AUXILIARY INFORMATION

METHOD:

E.m.f. measurements were made on the following cells at 25°C:

$\text{Ag,AgSCN/KSCN(0.1M)//KCl(0.1m)/-}$
$\text{Hg}_2\text{Cl}_2\text{,Hg}$ [1]

and

$\text{Ag,AgSCN/KSCN(0.1m)//K(Hg)//-}$
$\text{KSCN(0.01m)/AgSCN,Ag}$ [2]

The e.m.f.'s of these cells are written as

$$E_1' = E_1 + E_j = 0.17765\text{V}$$

$$E_2 = (2RT/F)\ln(a_{0.01}/a_{0.1}) = 0.1121\text{V}$$

With those two measurements, the authors calculated the e.m.f.'s of the cells

$\text{H}_2/\text{H}^+(a=1)//\text{KSCN(0.1m)/AgSCN,Ag}$ [3]

and

$\text{H}_2/\text{H}^+(a=1)//\text{KSCN(0.01m)/AgSCN,Ag}$ [4]

using published data (2) for the cell

SOURCE AND PURITY OF MATERIALS:

The authors state that all materials were purified by approved methods. The Ag,AgSCN electrodes appear to have been made by covering crystals of cathodically produced silver with AgSCN as described in ref. 5. Electrical contact was presumably made by physical contact with a Pt wire embedded in the Ag crystals.

ESTIMATED ERROR:

E.m.f. measurements: ±0.01 mV

Nothing else is specified.

REFERENCES:

1. Cave, G.C.B.; Hume, D.N. *J. Am. Chem. Soc.* 1953, *75*, 2893.
2. Lewis; Brighton; Sebastian, *J. Am. Chem. Soc.* 1917, *39*, 2245.
3. Scatchard, G. *J. Am. Chem. Soc.* 1925, *47*, 2098.
4. Lewis; Sargent, *J. Am. Chem. Soc.*

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium thiocyanate; KSCN; [333-20-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Pearce, J.N.; Smith, L. *J. Am. Chem. Soc.* 1937, *59*, 2063-5.

COMMENTS AND/OR ADDITIONAL DATA:

The solubility product of AgSCN at 25°C is obtained from the equation

$$\log K^{\circ}_{s0}(\mathrm{AgSCN}) = (E^{\circ}_{m}(\mathrm{Ag,AgSCN}) - E^{\circ}_{m}(\mathrm{Ag,Ag^+}))/0.05916 \qquad [8]$$

Taking $E^{\circ}_{m}(\mathrm{Ag,Ag^+}) = 0.7991\mathrm{V}$ at 25°C (6) and Pearce and Smith's value for $E^{\circ}_{m}(\mathrm{Ag,AgSCN})$ gives the first entry in the data table above. Cave and Hume (1) pointed out that the E_5 value used by Pearce and Smith is incorrect since it is actually E_5': correcting for the liq junction potential (E_j = 1.8mV as calcd from the Henderson equation), we have $E_5 = E_5' - E_j = 0.3356 - 0.0018 = 0.3338\mathrm{V}$. Introducing this result into eq [6] and taking the mean molal activity coefficient for 0.1m KSCN equal to 0.769 (7), it is found that $E^{\circ}_{m}(\mathrm{Ag,AgSCN}) = 0.0921\mathrm{V}$. Using eq [8] gives $K^{\circ}_{s0}(\mathrm{AgSCN}) = 1.12 \times 10^{-12}\ \mathrm{mol^2/kg^2}$. Cave and Hume report a value of 1.13×10^{-12} which was obtained by correcting the former value for the activity of water in 0.1m KSCN soln (Robinson and Stokes give $a_W = 0.997$): i.e. according to Cave and Hume, A_g^+ exists as the tetrahydrate $\mathrm{Ag^+(H_2O)_4}$, and

$$K^{\circ}_{s0}(\mathrm{AgSCN}) = 1.12 \times 10^{-12}/a_W^4 = 1.13 \times 10^{-12}\ \mathrm{mol^2/kg^2}$$

Finally the compiler has taken Cave and Hume's E°_{m} data and converted them to absolute volts. The results, given below, were used to calculate the results given on the previous page by use of eq [8].

$$E^{\circ}_{m}(\mathrm{Ag,AgSCN}) = 0.0921\ \mathrm{V\ (abs)} \quad ; \quad E^{\circ}_{m}(\mathrm{Ag,Ag^+}) = 0.7993\ \mathrm{V\ (abs)}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$$\mathrm{H_2/H^+(a=1)//KCl(0.1m)/Hg_2Cl_2,Hg} \qquad [5]$$

$$E_5' = E_5 + E_j = 0.3356\mathrm{V}$$

The e.m.f.'s for cells 3 and 4 are:

$$E_3 = E_5 - E_1 = E^{\circ}_{m}(\mathrm{Ag,AgSCN}) - 0.05916\log(a_{\mathrm{KSCN}}) \qquad [6]$$

and

$$E_4 = E_5 + \tfrac{1}{2}E_2 - E_1 = E^{\circ}_{m}(\mathrm{Ag,AgSCN}) - 0.05916\ \log(a_{\mathrm{KSCN}}) \qquad [7]$$

Evaluating the liq junction potential, E_j, for cell [1] by the method of Lewis and Sargent (4), calculating the mean molal activity coefficients (3), and taking E_5 as 0.3356V, both equations [6] and [7] yield $E^{\circ}_{m}(\mathrm{Ag,AgSCN}) = 0.0947\mathrm{V}$.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

1909, *39*, 363.

5. Linhart, G. *J. Am. Chem. Soc.* 1919, *41*, 1175.
6. Latimer, W.M. *Oxidation Potentials.* 2nd Edition Prentice-Hall. New Jersey. 1952.
7. Robinson, R.A.; Stokes, R.H. *Electrolyte Solutions.* Butterworths. London. 1955.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Calcium thiocyanate; $Ca(SCN)_2$; [2092-16-2]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

McKerrow, A.K.; Occleshaw, V.J.; Drabble, F. *J. Chem. Soc.* 1946, *B*, 1 - 5.

VARIABLES:

Concentration of all components at 20°C and 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Composition of solutions expressed in weight percent. The 20°C are marked with an asterisk (*); all other data are at 25°C.

solution phase			solution phase		
AgSCN	$Ca(SCN)_2$	solid phase	AgSCN	$Ca(SCN)_2$	solid phase
0.00	60.20	α-A	31.01	25.15	B,C
4.03	58.80	α-A	30.70	24.52	C
7.49	57.05	α-A	22.88	21.72	C
7.52	57.03	α-A,B	15.42	19.23	C
8.50	55.21	B	11.74	17.33	C
8.26	54.74	B	8.09	15.01	C
10.27	50.76	B	3.42	14.11	C
13.09	44.99	B	0.00002[1]	0.00	C
14.96	41.95	B	0.00*	59.10	β-A
19.22	37.02	B	4.24*	57.27	β-A
25.71	29.12	B	5.19*	56.85	β-A
26.74	37.86	B	7.50*	56.41	β-A
29.79	25.47	B	8.73*	55.44	β-A

A = $Ca(SCN)_2 \cdot 4H_2O$

B = $Ca(SCN)_2 \cdot 2AgSCN \cdot 2H_2O$

C = AgSCN

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures containing an excess of one or both salts shaken at 40°C and then thermostated at 20 or 25°C for periods of up to one week. Equilibrium was established by duplicate analysis at 2 day intervals. Solutions containing solid $Ca(SCN)_2$ were seeded to prevent formation of metastable phases. The removal and separation of solution and solid samples for analysis was carried out at the thermostat temperature. The solid phases were analysed by the method of residues. For the solutions, Ca was determined by the Volhard method using standard $AgNO_3$, and the total SCN^- determined gravimetrically as the Ag salt. The amount of AgSCN was obtained by difference.

SOURCE AND PURITY OF MATERIALS:

Commercial $Ca(SCN)_2$ was recrystallized several times. AgSCN residues from previous studies were dissolved in NH_4SCN, filtered, precipitated with water, washed with water and ethanol, and air-dried at 120°C. Distilled water was used.

ESTIMATED ERROR:

Solubility: not specified but probably ±2% as in prior work (2).
Temperature: 25 ± 0.05°C
20°C not specified.

REFERENCES:

1. Masaki, K. *Bull. Chem. Soc. Jpn.* 1930, *5*, 345.
2. Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Calcium thiocyanate; $Ca(SCN)_2$; [2092-16-2]

(3) Water; H_2O; [7732-18-5]

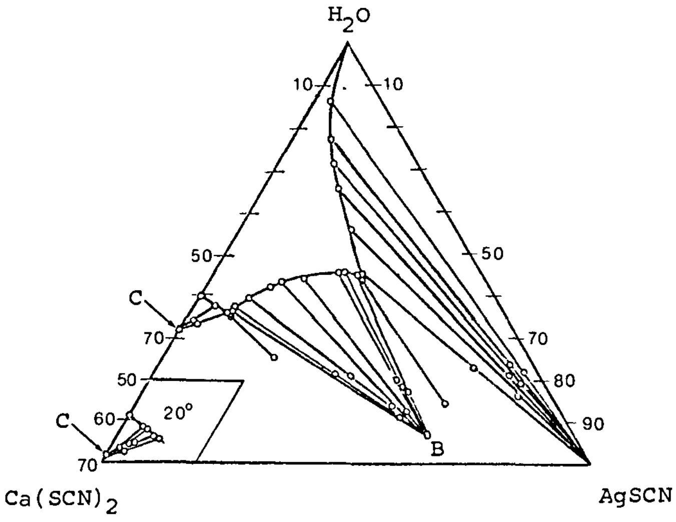
ORIGINAL MEASUREMENTS: (continued)

McKerrow, A.K.; Occleshaw, V.J.; Drabble, F. *J. Chem. Soc.* 1946, *B*, 1-5.

COMMENTS AND/OR ADDITIONAL DATA:

$Ca(SCN)_2$ was found to be dimorphous: the transition point between the α and β phases was determined to be 23.8°C. The compiler has converted the original data into molal units which are given below.

[AgSCN]/mol kg^{-1}	$[Ca(SCN)_2]$/mol kg^{-1}
0.00	9.68
0.65	10.12
1.27	10.30
1.28	10.30
1.41	9.74
1.35	9.47
1.59	8.34
1.88	6.87
2.09	6.23
2.65	5.41
3.43	4.13
3.55	3.93
4.01	3.64
4.26	3.67
4.13	3.50
2.49	2.51
1.42	1.88
1.00	1.56
0.63	1.25
0.25	1.10
----	0.00
0.00*	9.25
0.66*	9.52
0.82*	9.59
1.25*	10.00
1.47*	9.90



COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Stubičan, V.; Težak, B. *Arhiv. Kem.* 1950, *22*, 75-84.

VARIABLES:

Concentration of KSCN at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

All concentrations are in units of mol dm^{-3}.

c_{Ag}	[KSCN]
0.10	1.000
0.05	0.840
0.025	0.707
0.015	0.615
0.010	0.540
0.005	0.441
0.0025	0.352
0.0015	0.281
0.0010	0.259

c_{Ag}	[KSCN]
0.00070	0.233
0.00050	0.200
0.00025	0.150
0.00020	0.105
0.00015	0.094
0.00010	0.080
0.00007	0.056
0.00005	0.050
0.000025	0.025
0.000013	0.019
0.000007	0.010

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubilities were determined turbidimetrically with a Zeiss nephelometer and a Pulfrich photometer in green light (530 mμ). KSCN solutions of known concentration were mixed at 20°C with solns of varying $AgNO_3$ concentrations, and the relative turbidity plotted against time. For a given time the $AgNO_3$ concentration is plotted against the relative turbidity and extrapolated to zero turbidity. The solubility of AgSCN is calculated from the concentration of $AgNO_3$ at which, for a given [KSCN], the turbidity disappears (i.e. the extrapolated value).

SOURCE AND PURITY OF MATERIALS:

Analytical grade chemicals and distilled water were used.

ESTIMATED ERROR:

The authors report an experimental precision of ±2-3% in the solubilities and ±0.1°C.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Potassium nitrate; KNO_3; [7757-79-1] (3) Potassium thiocyanate; KSCN; [333-20-0] (4) Water; H_2O; [7732-18-5]	Stubičan, V.; Težak, B. *Arhiv. Kem.* 1950, *22*, 75-84.

COMMENTS AND/OR ADDITIONAL DATA:

The relative turbidity of the various solutions was determined after 0.5, 1, 2, 4, 5, 10, 20, and 60 minutes. There was a problem of selecting a time for which the extrapolated turbidity would have the value of zero. At larger concentrations (values not specified) of the reacting species, different times tended to give the same extrapolated value. However this was not always the case as different times gave different extrapolated values for the low concentrations. For the cases where extrapolated values for different times did not agree, the authors selected a time at which the particles of the precipitate were fully grown, but had not started to settle.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Silver nitrate; $AgNO_3$; [7761-88-8]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Stubičan, V.; Težak, B. *Arhiv. Kem.* 1950, *22*, 75-84.

VARIABLES:

Concentration of $AgNO_3$ at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[AgNO_3]$/mol dm^{-3}	$[AgSCN]_{satd}$/mol dm^{-3}
1.020	7.0×10^{-4}
0.912	5.0×10^{-4}
0.804	3.5×10^{-4}
0.640	2.5×10^{-4}
0.550	1.5×10^{-4}
0.470	1.0×10^{-4}
0.354	7.5×10^{-5}
0.301	5.0×10^{-5}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubilities were determined turbidimetrically with a Zeiss nephelometer and a Pulfrich photometer in green light (530 mμ). $AgNO_3$ solutions of known concentration were mixed with solutions of varying KSCN concentrations, and the relative turbidity plotted against the KSCN concentration and extrapolated to zero turbidity. The solubility of AgSCN is calculated from the concentration of KSCN at which, for a given $[AgNO_3]$, the turbidity disappears (i.e. the extrapolated value).

SOURCE AND PURITY OF MATERIALS:

Analytical grade chemicals and distilled water were used.

ESTIMATED ERROR:

The authors report an experimental precision of ±2-3% in the solubilities, and ±0.1°C range in temp.

COMMENTS AND/OR ADDITIONAL DATA:

See previous page for comments.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Ammonium thiocyanate; NH_4SCN; [1762-95-4]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Aditya, S.; Prasad, B. *J. Indian Chem. Soc.* 1952, *29*, 293-5.

VARIABLES:

One temperature: 29-30°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The data of Aditya and Prasad were recalculated by the compiler (details are given below):

$$K^{o}_{s0}(\mathrm{AgSCN}) = 1.82 \times 10^{-12}\ \mathrm{mol^2\ dm^{-6}}$$

The original value based on the authors' e.m.f. measurements is

$$K^{o}_{s0}(\mathrm{AgSCN}) = 1.94 \times 10^{-12}\ \mathrm{mol^2\ dm^{-6}}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

E.m.f. measurements were made on the following cell at room temp:

$$\mathrm{Hg,Hg_2Cl_2/KCl(sat)//KCl(sat)//\text{-}NH_4SCN(xM)/AgI,Ag}$$

Six solns were studied where $[NH_4SCN]$ = 0.1, 0.08, 0.06, 0.04, 0.02, and 0.01 mol/L. The e.m.f. of the half-cell Ag,AgI/NH_4SCN(xM) is given by

$$E = E^{o} - (RT/F)\ln(xy_{\pm})$$

where $y_{\pm}$ is the mean molar activity coefficient of NH_4SCN. The observed e.m.f. of the cell is given by

$$E_{obs} = E_{hcal} - E^{o} + (RT/F)\ln(xy_{\pm}) \quad [1]$$

Using an extrapolation method based on an extended Debye-Hückel relation for $y_{\pm}$, E^{o}_{obs} = 0.1501V. The soly product of AgSCN was calculated from

$$\ln K^{o}_{s0} = (E^{o} - E^{o}_{Ag,Ag^{+}})F/RT \quad [2]$$

The value of T used in eq [2] was 303.2K (30°C).

SOURCE AND PURITY OF MATERIALS:

Ag,AgI electrodes were prepared by the method of Owen (1). NH_4SCN stock solutions were standardized by titration with standard $AgNO_3$ using ferric alum indicator. No other details were given.

ESTIMATED ERROR:

Nothing specified. E.m.f. measurements were made with a Leeds and Northrup K-type potentiometer, and E_{obs} values are reported to 1/100 mV.

REFERENCES:

1. Owen, B.B.; *J. Am. Chem. Soc.* 1935, *57*, 1526.
2. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233 (converted to absolute volts by the compiler).

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Ammonium thiocyanate; NH_4SCN; [1762-95-4]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Aditya, S.; Prasad, B. *J. Indian Chem. Soc.* 1952, *29*, 293-5.

COMMENTS AND/OR ADDITIONAL DATA:

The intercept with its standard deviation was redetermined by the compiler: $E^{o}_{obs} = 0.15005 \pm 0.00006$ V. This value leads to a standard deviation of ± 0.25% in the soly product which is meaningless since the magnitude of other sources of error are unknown (e.g. in temp, liq junction potential, and measured e.m.f.).

Several problems appear to be present in the determination of the E^{o} value: E^{o} is calculated from eq [1] using $E_{hcal} = 0.2378$ V. K^{o}_{s0} is then calculated from eq [2].

However, the calcd K'_{s0} still contains an error since the authors use a value of $E^{o}_{Ag,Ag^+} = 0.7922$V at 30°C whereas the compiler calculates a value of 0.7942V (2) at this temperature. Using the authors' values it is found that $E^{o} = 0.0878$ V and from eq [2], $K_{s0} = 1.94 \times 10^{-12}$. However the authors report $K_{s0} = 1.4 \times 10^{-12}$ (as do teritiary sources such as Seidell (3)). This difference is evidently due to a juxtaposition error since the latter K_{s0} value results from taking $E^{o} = 0.0788$V. Taking $E^{o}_{Ag,Ag^+} = 0.7942$V at 30°C, the compiler computes the following value:

$$K^{o}_{s0}(\text{AgSCN}) = 1.82 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

3. Linke, W.F.; Seidell, A. *Solubilities of Inorganic and Metal-Organic Compounds*. American Chemical Society. Washington, D.C. 1958.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Cave, G.C.B.; Hume, D.N. *J. Am. Chem. Soc.* 1953, *75*, 2893-7.

VARIABLES:

Concentration of KSCN at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

KNO_3 was used to maintain a constant ionic strength of 2.2 mol/kg. The temperature is 25°C.

$[KSCN]/mol\ kg^{-1}$	$c_{Ag}/mol\ kg^{-1}$	$[KSCN]/mol\ kg^{-1}$	$c_{Ag}/mol\ kg^{-1}$
0*	1.1×10^{-6}	0.2744	2.21×10^{-3}
0.00548	1.62×10^{-6}	0.2774	2.28×10^{-3}
0.01033	3.65×10^{-6}	0.3343	3.70×10^{-3}
0.04133	3.00×10^{-5}	0.4443	8.26×10^{-3}
0.04440	3.36×10^{-5}	0.5572	0.0146
0.06662	7.99×10^{-5}	0.5536	0.0146
0.08885	1.39×10^{-4}	0.7783	0.0376
0.1111	2.38×10^{-4}	1.114	0.0981
0.1334	3.56×10^{-4}	1.688	0.2684
0.1779	7.25×10^{-4}	2.252	0.61
0.2224	1.28×10^{-3}		

*Binary $AgSCN/H_2O$ system

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Satd solns were prepared by rotating excess solid AgSCN in KSCN solns in a thermostat at 25°C for 1-2 weeks. The soly bottles were waxed on the inside and painted black on the outside. KNO_3 was used to adjust the ionic strength of all solns to 2.2 mol/kg. Equilibrium was established by duplicate analysis, and was approached from undersaturation except for the 0.005m soln and binary system where equil was approached from both directions. Solid and liquid for analysis was separated by centrifuging. Analysis of total Ag in soln was carried out gravimetrically as AgSCN for the highly concentrated solns, polarographically for intermediate concentrations, and colorimetrically with p-dimethylamino benzalrhodanine at low concentrations. The soly of AgSCN in the binary $AgSCN/H_2O$ system was determined by a nephelometric method.

SOURCE AND PURITY OF MATERIALS:

AgSCN was prepared from AR grade $AgNO_3$ and recrystallized AR grade KSCN: conductivity water was used. For solns where [KSCN] < 0.4m, recrystallized reagents in conductivity water were used. For [KSCN] > 0.04m, solns were prepared from AR grade reagents with distilled water.

ESTIMATED ERROR:

Temperature: ± 0.05°C
Soly of quaternary system, not given
Soly of binary system: ± 3% (precision)

REFERENCES:

1. Pearce, J.N.; Smith, L. *J. Am. Chem. Soc.* 1937, *59*, 2063.
2. Robinson, R.A.; Stokes, R.H. *Trans. Faraday Soc.* 1949, *45*, 612.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Cave, G.C.B.; Hume, D.N. *J. Am. Chem. Soc.* 1953, *75*, 2893-7.

COMMENTS AND/OR ADDITIONAL DATA:

Assuming that only mononuclear complexes form, the authors determined the stability constants for reaction 1 for n = 1-4.

$$Ag^+ + nSCN^- \rightleftarrows Ag(SCN)_n^{1-n} \qquad \beta_n \qquad [1]$$

They also recalculated the standard soly product, K^o_{s0}, from the data of Pearce and Smith (1) as described in the compilation on this paper. Combining this K^o_{s0} value with $\gamma_\pm$ = 0.553 for singly charged anions estimated from the literature (2), and $\gamma_\pm$ calcd from the Debye-Hückel equation for multiply charged anions, the standard β_n values were calcd (the hypothetical 1m reference state). To calc the equilibrium constants uncorrected for activity effects (i.e. the 2.2m KNO_3 reference state), $\gamma_\pm(Ag^+$ was estimated as 0.300 and the stnd values were then used to obtain the values given in the table below.

constant	hypothetical 1m soln ref state	2.2m KNO_3 reference state
$K_{s0}/mol^2/kg^2$	1.13×10^{-12}	6.75×10^{-12}
$\beta_2/kg^2/mol^2$	2.45×10^8	3.7×10^7
$\beta_3/kg^3/mol^3$	4.14×10^9	1.2×10^9
$\beta_4/kg^4/mol^4$	7.86×10^9	1.2×10^{10}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

VARIABLES:

Concentration of KSCN at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN added to the initial $AgNO_3$ solution: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN.

c_{Ag}/mol dm^{-3}	$[KSCN]_{tot}$/mol dm^{-3}	c_{Ag}/mol dm^{-3}	$[KSCN]_{tot}$/mol dm^{-3}
0.1	1.205	0.002	0.276
0.06	0.95	0.001	0.2025
0.04	0.84	0.0006	0.179
0.02	0.648	0.0004	0.1538
0.01	0.485	0.0002	0.108
0.002	0.42	0.0001	0.0795
0.004	0.36		

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Turbidimetric method. Solns of $AgNO_3$ and KSCN were mixed and at equilibrium the turbidity measured (establishment of equil not described, but measurements probably made within 1 h as described previously (1)). The soly of AgSCN was calcd from the concentration of KSCN at which, for a given $[AgNO_3]$, the turbidity disappears. The precipitation reaction is:

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3 \quad [1]$$

The disappearance of turbidity is due to complex ion formation. The authors assume only mononuclear complexes form according to

$$AgSCN(s) + (n-1)SCN^- \rightleftarrows Ag(SCN)_n^{1-n} \quad [2]$$

SOURCE AND PURITY OF MATERIALS:

All chemicals were analytically pure, and presumably used as received. Distilled water with a specific conductance of 2 x 10^{-6} ohm^{-1} cm^{-1} was used.

ESTIMATED ERROR:

Solubility: nothing specified, but probably within ± 2-3%.
Temperature: ±0.1°C.

REFERENCES:

1. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.
2. Kratohvil, J.; Težak, B.; Vouk, V.B. *Arhiv. Kem.* 1954, *26*, 191.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

COMMENTS AND/OR ADDITIONAL DATA:

The equilibrium constants for reaction [2] were calculated from

$$\log K_{sn} = \log(C_{Ag}) - (n-1)\log[SCN^-]_{equil} \qquad [3]$$

where $[SCN^-]_{equil} = [KSCN]_{tot} - C_{Ag}$. Eq [3] was applied to those experimental points in the concentration range where each complex predominates. The overall stability constants were calculated from

$$\beta_n = K_{sn}/K_{s0} \qquad [4]$$

where the solubility product is taken as $K_{s0} = 1 \times 10^{-12}\ mol^2\ dm^{-6}$ (no reference is given). The results of these calculations are given below.

$[KSCN]_{tot}$/mol dm^{-3}	complex	K_{sn}	$10^{-10}\beta_n$
0.08 - 0.15	$Ag(SCN)_3^{2-}$	0.020	2.0
0.15 - 1	$Ag(SCN)_4^{3-}$	0.068	6.8

The value of K_{s0} used in the present work for 20°C is very close to the 25°C value (see the critical evaluation). In a related paper (2) the data obtained in the present paper was reviewed and β_4 is given as 6.0×10^{10}. The value given in the above table is probably the correct one. The units for the equilibrium constants are:

$$K_{sn} = mol^{2-n}\ dm^{3(n-2)}$$

$$\beta_n = mol^{-n}\ dm^{3n}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Sodium thiocyanate; NaSCN; [540-72-7]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Leden, I.; Nilsson, R. *Svensk. Kem. Tidskr.* 1954, *66*, 126-35.

VARIABLES:

Ionic strength at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Experimental temp is reported as 25.00°C. μ is the ionic strength in mol dm^{-3}, and the units of K_{s0} are $mol^2\ dm^{-6}$.

Junction solution	(concentration)	μ	$-\log K_{s0}$
$NaClO_4$	(μ)	0.113	11.803 ± 0.006^a
$NaClO_4$	(μ)	0.0113	11.911 ± 0.007^a
NH_4NO_3	(1,4 mol dm^{-3})	0.0113	
NH_4NO_3	(1,2,4 mol dm^{-3})	0.00113	11.948 ± 0.002^a
------		0.0	11.967 ± 0.01^b
$NaClO_4$	(4.00)	4.00	12.110 ± 0.006^c

a. Mean values.
b. Obtained by extrapolation of mean values to zero ionic strength.
c. This point was not used in the extrapolation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The soly products, K_{s0}, were determined by measuring e.m.f. (mostly in N_2 atmospheres) of the cells:

$$Ag,AgSCN/AgClO_4(M_1)//NaClO_4(\mu)// - NaSCN(M_2)/AgSCN,Ag$$

and

$$Ag,AgSCN \left| \begin{array}{l} AgClO_4(M_1) \\ NaClO_4(\mu-M_1) \end{array} \right\| \begin{array}{c} NH_4NO_3(xM) \\ \text{or} \\ NaClO_4(4M) \end{array} \left\| - \begin{array}{l} NaSCN(M_2) \\ NaClO_4(\mu-M_2) \end{array} \right| AgSCN,Ag$$

The e.m.f. of either cell is given by

$$E = (2.3RT/F)\{\log(M_1M_2) + 2\log(y_\pm) - \log K^o_{s0}\} + E_j$$

The liquid junction potential, E_j, was evaluated from the Henderson equation, and the above e.m.f. corrected for the E_j is denoted as E' and is given by

SOURCE AND PURITY OF MATERIALS:

$NaClO_4$ (G.F. Smith) and NaSCN (Kebo, puriss) were used as received. $AgClO_4$ was prepared by pptn from $AgNO_3$ and NaOH followed by boiling in $HClO_4$. All salts were analysed and presumably found to be reasonably pure. AgSCN was pptd from hot solns and washed. Ag,AgSCN electrodes were prepd from Ag-plated Pt wires which were anodized in acidified NaSCN solns: reproducibility of these electrodes was ±0.2 mV. No other details were given.

ESTIMATED ERROR:

$$\left. \begin{array}{l} K^o_{s0}: \pm 2\% \text{ (authors)} \\ K^o_{s0}: \pm 3\text{-}4\% \text{ (compiler)} \end{array} \right\} \sigma \text{ values}$$

e.m.f.'s: > ±0.2mV

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiocyanate; NaSCN; [540-72-7]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Leden, I.; Nilsson, R. *Svensk. Kem. Tidskr.* 1954, *66*, 126-35.

COMMENTS AND/OR ADDITIONAL DATA:

Each value for K_{s0} in the data table represents a mean of 4 to 13 values. For μ = 0.113 mol dm^{-3} there were 18 independent measurements, but 5 were excluded from the mean because of irreproducible e.m.f. values which apparently occurs for Ag^+ and SCN^- concentrations less than 0.001 mol dm^{-3}. Similarly 6 measurements are reported for μ = 0.00113 mol dm^{-3}, but only 4 are used to calc the mean K_{s0}. Extrapolation of the three mean K_{s0} values to zero ionic strength gives K^o_{s0} and the activity coefficients for each experimental solution can be calculated from eq [1] below. The authors estimate the error in K^o_{s0} by taking the difference intercepts obtained from the experimental plot of $\log K_{s0}$ against $\mu^{1/2}/(1 + \mu^{1/2})$, and the intercept obtained by drawing a straight line from the point $\log K_{s0} = -11.948$ to $\mu = 0$ and a slope given by the Debye-Hückel limiting law. A more accurate estimation of the error in K^o_{s0} from standard methods incorporates the sum of the variances of each experimental point: the error thus calculated by the compiler is 3-4%.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$$E' = (2.3RT/F)\{\log(M_1M_2) - \log K_{s0}\}$$

where

$$K^o_{s0} = K_{s0}\cdot y_\pm^2 \qquad [1]$$

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Sodium thiocyanate; NaSCN; [540-72-7]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Leden, I.; Nilsson, R. *Svensk. Chem. Tidskr.* 1954, *66*, 126-35.

VARIABLES:

Concentration of NaSCN at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Experimental temp reported at 25.00°C. All concentrations are in units of mol dm^{-3}, and K_{s0} is in $mol^2\ dm^{-6}$. Ionic strength is constant at 4 mol dm^{-3}.

$[NaSCN]_{total}$	$10^3 C_{Ag}$	$[SCN]_{free}$	$10^{13} K_{s0}$
0.05	0.044	0.05	7.65
0.05	0.052	0.05	7.4
0.08	0.146	0.0796	7.63
0.08	----	0.0796	7.68
0.10	0.287	0.0993	7.64
0.20	1.52	0.196	7.36
0.30	4.45	0.290	7.65
0.40	10.55	0.371	7.54
0.50	18.36	0.453	7.53
0.5	18.10	0.453	7.57

The average $K_{s0} = (7.57 \pm 0.2) \times 10^{-13}\ mol^2\ dm^{-6}$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$NaSCN + NaClO_4$ solns satd with AgSCN were placed in the cell

$$Hg,Hg_2SO_4/NaClO_4(4M)//NaClO_4(4M)//-NaSCN(bM),\ NaClO_4(4-b)M/AgSCN,Ag$$

The e.m.f. of this cell is given by

$$E = E^o - 0.05916 \log\{[SCN^-]/K_{s0}\} \quad [1]$$

$E^o = -82.2$ mV at 25°C as determined by measurements on the cell

$$Hg,Hg_2SO_4/NaClO_4(4M)//NaClO_4(4M)//-AgClO_4(aM),\ NaClO_4(4-a)M/AgSCN,Ag$$

where "a" varied between 0.002 - 0.1M The free SCN^- concentrations used to calc K_{s0} from eq [1] were computed from the C_{Ag} values taking into account complex ion formation. Details on this method of computation as well as the experimental determination of C_{Ag} are probably the same as described in a later paper (1).

SOURCE AND PURITY OF MATERIALS:

$NaClO_4$ (G.F. Smith) and NaSCN (Kebo, puriss) were used as received. $AgClO_4$ was prepared by pptn from $AgNO_3$ and NaOH followed by boiling in $HClO_4$. All salts were analysed and presumably found to be reasonably pure. AgSCN was pptd from hot solns and washed. The Ag,AgSCN electrodes were prepd from Ag-plated Pt wires which were anodized in acidified NaSCN solns the reproducibility of these electrodes was ±0.2mV. No other details were given.

ESTIMATED ERROR:

Solubility: ±5%, average (compiler)
K_{s0}: ±3.6% (authors' stnd dev)
e.m.f. values: > ±0.2 mV
Temperature: not specified.

REFERENCES:

1. Leden, I.; Nilsson, R. *Z. Naturforsch.* 1955, *A10*, 67.

COMPONENTS:

(1) Sodium dithiocyanoargentate; $NaAg(SCN)_2$; [62928-05-6]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiocyanate; NaSCN; [540-72-7]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Leden, I.; Nilsson, R. *Svensk. Chem. Tidskr.* 1954, *66*, 126-35.

VARIABLES:

Concentration of NaSCN at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The experimental temperature is reported as 25.00°C. C_{Ag} is the solubility defined in terms of the total silver present in the satd solutions.* All concentrations are in units of mol dm^{-3}, and units of K_{s0} are mol^2 dm^{-6}. The ionic strength of all solns is constant at 4 mol dm^{-3}.

[NaSCN]	C^*_{Ag}	$[SCN^-]_{free}$	$10^{13}K_{s0}$ as obtained from cell No. I	II	III
0.50	0.0349	0.536	4.00		
0.50	0.0346	0.536	4.05	4.08	
0.60	0.0374	0.543	3.98	3.98	3.98
0.6	0.0384	0.543	4.22	4.19	
0.80	0.0640	0.705	3.86	3.80	3.88
0.80	0.0637	0.705	4.33		
1.00	0.0927	0.862	4.06	4.05	
1.00	0.0942	0.862	4.20		
1.20	0.131	1.01		4.01	
1.20	0.127	1.91	4.51	4.40	

Mean values:

$$\left.\begin{array}{l} K_{s0}(I) = (4.13 \pm 0.20) \times 10^{-13} \\ K_{s0}(II) = (4.07 \pm 0.19) \times 10^{-13} \\ K_{s0}(III) = (3.93 \pm 0.07) \times 10^{-13} \end{array}\right\} \text{mean} = (4.1 \pm 0.2) \times 10^{-13}$$

*Solid phase is $NaAg(SCN)_2 \cdot 2H_2O$; [66418-41-5]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Satd solns prep by rotating excess $NaAg(SCN)_2 \cdot 2H_2O$ in the solns denoted by Z below for several days. The analysis of these solns are not described but are probably similar to the method discussed in a later paper (2). The soly product in 4M $NaClO_4$ is defined by

$$K_{s0}(d) = [Ag^+][SCN^-]^2 \qquad [1]$$

and was determined from e.m.f. data for the cell

$$Hg,Hg_2SO_4 \left| \underset{X}{NaClO_4(4M)} \right\| \underset{Y}{NaClO_4(4M)} \left\| \underset{Z}{\begin{array}{l} NaSCN(bM) \\ NaClO_4(4-b)M \end{array}} \right| NaAg(SCN)_2 \cdot 2H_2O,Ag \qquad [2]$$

Referring to the data table and the above cell, the cell marked III is given by eq [2]. For cell II the salt bridge Y is exchanged for one containing 4M NaSCN. In cell I the side tube of the reference electrode vessel was

SOURCE AND PURITY OF MATERIALS:

$NaClO_4$(G.F. Smith) and NaSCN (Kebo, puriss) were used as received. $AgClO_4$ was prepared by pptn from $AgNO_3$ and NaOH followed by boiling in $HClO_4$; $NaAg(SCN)_2 \cdot 2H_2O$ crystals were pptd by adding 4M $NaClO_4$ to solns containing 0.5M $AgClO_4$ and 3.5M NaSCN. The crystals were filtered and dried between filter paper. All salts were analysed and presumed to be of acceptable purity. Ag was analysed by electrodeposition, and total SCN^- by

ESTIMATED ERROR:

Solubility: av dev ±1-4% (compiler)

K_{s0}: stnd dev ±5% (compiler)

e.m.f.'s: > ± 0.2 mV

REFERENCES:

1. Occleshaw, V.J. *J. Chem. Soc.* 1932, 2404.
2. Leden, I.; Nilsson, R. *Z. Naturforsch.* 1955, *A10*, 67.

COMPONENTS:

(1) Sodium dithiocyanoargentate; $NaAg(SCN)_2$; [62928-05-6]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiocyanate; NaSCN; [540-72-7]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Leden, I.; Nilsson, R. *Svensk. Chem. Tidskr.* 1954, *66*, 126-35.

COMMENTS AND/OR ADDITIONAL DATA:

The solid phase in equilibrium with solns where $[SCN^-] > 0.5M$ is $NaAg(SCN)_2 \cdot 2H_2O$: below this concentration $NaAg(SCN)_2 \cdot 2H_2O$ is not stable and the solid phase is AgSCN. While the authors did analyse this solid, they could not analyse for the water of crystallization: they assume the stoichiometry of 2 waters of crystallization based on the work of Occleshaw (1). The soly product defined in eq [1] is valid only for a constant value of $[Na^+] = 4.0$ mol/dm^3. The concentration of SCN^- required for use in eq [3] was calculated from the measured solubility of $NaAg(SCN)_2 \cdot 2H_2O$ and the distribution of thiocyanatoargentate complexes in the saturated solutions (no details are given, but presumably are identical to those discussed in a later paper (2)).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

placed directly into soln Z. K_{s0} was calculated from (E given in mV)

$$E = E^o - 59.16\left\{2\log[SCN^-] - \log K_{s0}\right\} \qquad [3]$$

where $E^o = -82.2$ mV as determined from the cell

$$Hg,Hg_2SO_4 \left|\ NaClO_4(4M) \right\|\ NaClO_4(4M) \left\|\ \begin{matrix} AgClO_4(aM) \\ NaClO_4(4-a)M \end{matrix} \right|\ AgSCN,Ag$$

SOURCE AND PURITY OF MATERIALS:

the Volhard method. The preparations of indicator and reference electrodes were not discussed.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Sodium thiocyanate; NaSCN; [540-72-7]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Leden, I.; Nilsson, R. *Z. Naturforsch* 1955, *A10*, 67-76.

VARIABLES:
Concentration of NaSCN at 25°C and ionic strength.

PREPARED BY:
Mark Salomon

EXPERIMENTAL VALUES: Experimental temp is 25°C. The soly of AgSCN is denoted by c_{Ag}. All concentrations are given in units of mol/dm^3.

	10^6c_{Ag} after t days							
	set 1		set 2					
[NaSCN]	t = 4	t=7	t=1.67	t=3.4	t=5.3	t=11	t=36	10^6c_{Ag}(average)
0		1.14	1.03	0.79	0.55	0.28	0.03	1.33 ± 0.03**
2.26×10^{-6}	0.68							0.68 ± 0.1
5.65×10^{-6}		0.24	0.42	0.38	0.24	0.21*	0.08*	0.32 ± 0.1
1.13×10^{-5}		0.17	0.23	0.26	0.17	0.15*	0.08*	0.21 ± 0.05
2.26×10^{-5}		0.12	0.36	0.27	0.26	0.24		0.25 ± 0.1
5.65×10^{-5}		0.13	0.04*	0.11	0.10	0.08	0.15	0.11 ± 0.03
1.13×10^{-4}	0.085	0.	0.13	0.10	0.08	0.14	0.31*	0.10 ± 0.03
2.26×10^{-4}	0.38*		0.13	0.09	0.10	0.15	0.06	0.11 ± 0.03
5.65×10^{-4}	0.16		0.19	0.13	0.11	0.07*	0.08*	0.15 ± 0.03
1.13×10^{-3}		0.21	0.38	0.14	0.15	0.15*	0.12*	0.22 ± 0.1
2.26×10^{-3}		0.52						0.52 ± 0.1
5.65×10^{-3}		1.35						1.35 ± 0.1
2.26×10^{-2}	7.85							7.9 ± 0.1
5.65×10^{-2}	37.9							37.9 ± 0.5
0.113		133						

TABLE 1. Solubility of AgSCN at Ionic Strength of 0.113 mol/dm^3

* Point not included in calculation of the average c_{Ag}

**Extrapolated value

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Satd solns of AgSCN prepared isothermally at 25°C by rotation from 1-36 days. Solns were adjusted to ionic strengths of 0.113 or 4M with $NaClO_4$. Solns dilute in NaSCN (Tables 1, 2) analysed for Ag radiochemically via ^{110}Ag as described earlier (1). Equil is stated to be reached in 1 day. For higher [NaSCN], c_{Ag} was determined by electrodeposition of Ag (E), potentiometric titration (T), or by radioassay (R) (see Table 3). Details for the first two methods are given elsewhere (2). The authors also evaluated the stability constants for

$$Ag^+ + nSCN^- \rightleftarrows Ag(SCN)_n^{1-n} \qquad \beta_{1,n} \qquad [1]$$

and

$$mAg^+ + nSCN^- \rightleftarrows Ag_m(SCN)_n^{m-n} \qquad \beta_{m,n} \qquad [2]$$

Method of analysis of total SCN^- or free SCN^- concentrations, c_{SCN} and $[SCN^-]_{free}$, not given, but probably similar to method previously described: i.e. Volhard method (2).

SOURCE AND PURITY OF MATERIALS:
Nothing specified, but probably as in earlier papers (1,2).

ESTIMATED ERROR:
Standard deviations in Table 1 are authors' values; in Table 2 are compiler's values. For data in Table 3 compiler calculates stnd deviations varying from ± 1 to 8%

REFERENCES:

1. Berne, E.; Leden, I. *Z. Naturforsch.* 1953, *A8*, 719.
2. Leden, I.; Nilsson, R. *Svensk. Kem. Tidskr.* 1954, *66*, 126.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Sodium thiocyanate; NaSCN; [540-72-7]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Leden, I.; Nilsson, R. Z. *Naturforsch.* 1955, *A10*, 67-76.

EXPERIMENTAL VALUES: (continued)

TABLE 2. Solubility of AgSCN at an ionic strength of 4 mol dm^{-3}

$10^6 C_{Ag}$ after t days

	set 1		set 2					
[NASCN]	t=4	t=5	t=1.67	t=3.4	t=5.3	t=11	t=36	$10^6 C_{Ag}$ (average)
0		0.5	0.69	0.51	0.34	0.13	0.13	0.95**
5×10^{-6}		0.09	0.43	0.26	0.20	0.05	0.20	?
1×10^{-5}	0.06	0.08	0.29	0.23	0.12	0.04	0.16	?
2×10^{-5}	0.03	0.02	0.03	0.04	0.08	0.07	0.29*	0.04 ± 0.02
5×10^{-5}	0.05	0.04	0.02	0.01	0.02	0.01	0.45*	0.03 ± 0.02
1×10^{-4}		0.05						0.05
2×10^{-4}	0.04	0.07	0.10	0.07	0.05	0.08	0.11	0.07 ± 0.03
5×10^{-4}	0.08							0.08
1×10^{-2}	0.19		0.28	0.22	0.15	0.20		0.21 ± 0.05

* Point not included in calculation of the average C_{Ag} (compiler)

**Extrapolated value

TABLE 3. AgSCN solubility at higher [NaSCN] and ionic strength of 4 mol/dm^3

method of analysis	[NaSCN]	C_{Ag}	rotation time, days	$\bar{n}$	$[SCN^-]_{free}$
R	0.002	3.6×10^{-7}	4	2.03	0.002
R	0.005	9.8×10^{-7}	4	2.26	0.005
R	0.01	2.6×10^{-6}	4	2.44	0.010
R	0.02	8.3×10^{-6}	5	2.75	0.020
T	0.03	1.5×10^{-5}	11	2.95	0.030
T	0.03	1.4×10^{-5}	11		
T	0.05	5.2×10^{-5}	8	3.23	0.050
T	0.05	4.4×10^{-5}	8		
R	0.05	4.8×10^{-5}	4		
T	0.08	1.4×10^{-4}	6	3.43	0.080
T	0.1	2.8×10^{-4}	6	3.50	0.099
R	0.1	2.5×10^{-4}	5	3.5	0.099
T	0.2	1.52×10^{-3}	6	3.69	0.196
E	0.227	2.02×10^{-3}	13	3.70	0.222
E	0.300	4.45×10^{-3}	6	3.73	0.290
E	0.316	5.18×10^{-3}	13	3.73	0.301
E	0.364	7.56×10^{-3}	13	3.70	0.344
E	0.400	1.06×10^{-2}	6	3.68	0.371
E	0.409	1.05×10^{-2}	13	3.68	0.379
E	0.455	1.39×10^{-2}	13	3.62	0.417
E	0.500	1.84×10^{-2}	13	3.55	0.453
E	0.500	1.81×10^{-2}	7		
E	0.550	2.35×10^{-2}	0.5	3.43	0.480
E	0.550	2.30×10^{-2}	2.5		

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Sodium perchlorate; $NaClO_4$; [7601-89-0] (3) Sodium thiocyanate; NaSCN; [540-72-7] (4) Water; H_2O; [7732-18-5]	Leden, I.; Nilsson, R. *Z. Naturforsch.* 1955, *A10*, 67-76.

COMMENTS AND/OR ADDITIONAL DATA:

The difficulty in the determination of C_{Ag} in the absence of NaSCN is probably due to the adsorption of ^{110}Ag on the walls of the vessel. The final C_{Ag} values were obtained by extrapolation to zero time from a plot of log C_{Ag} against time. For those cases where only one experimental point is available, the standard deviation was assumed to equal the difference between the experimental value and the value calculated from the equation

$$c_{Ag} = (K_{s0}/[SCN^-]) \sum_{0}^{4} \beta_{1,n}[SCN^-]^n + \beta_{2,6}K_{s0}^2[SCN^-]^4 \left\{ \frac{2 - 9\beta_{1,4}K_{s0}[SCN^-]}{(1 - 9\beta_{1,4}K_{s0}[SCN^-])^2} \right\} \quad [3]$$

where $\beta_{1,0} = 1$. Using the soly products determined previously (2), the stability constants were evaluated graphically (the paper also reports data obtained potentiometrically in unsaturated solns which yield β values slightly different from those obtained from the soly method which are listed in Table 4 below). The concentration of free SCN^- was calculated from the total concentration from

$$[SCN^-]_{free} = c_{SCN} - \bar{n}c_{Ag} \quad [4]$$

where $\bar{n}$ is the average ligand number.

TABLE 4. Stability constants as a function of ionic strength, μ, at 25°C

μ/mol dm^{-3}	$10^{12}K^*_{s0}$	$10^{-4}\beta_{1,1}$	$10^{-8}\beta_{1,2}$	$10^{-9}\beta_{1,3}$	$10^{-10}\beta_{1,4}$	$10^{-22}\beta_{2,6}$
0	1.08±0.02	5.6±2	1.7±0.2	2.8±2	0.46±0.32	
0.133	1.58±0.02	3.8±2	1.1±0.2	3.8±2	2.5 ±2.2	
4.00	0.77±0.02	3.9±2	2.0±0.2	1.2±2	18 ±2	2 ± 1

$^*K_{s0}$ values from reference 2.

Units of K_{s0} are mol^2 dm^{-6} and for the β's are mol^{1-m-n} dm$^{-3(1-m-n)}$

The standard deviations, σ, in C_{Ag} calcd from eq [3] are ±3 x 10^{-8} mol/dm^3 based on the data in Table 1, and ±2 x 10^{-7} mol/dm^3 based on the data in Table 2: calcd C_{Ag} using the data in Table 3 gave an error of ±6-7% (compiler).

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiocyanate; NaSCN; [540-72-7]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Leden, I.; Nilsson, R.

Z. Naturforsch. 1955, *A10*, 67-76.

VARIABLES:

Concentration of NaSCN at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The experimental temp is 25°C, and all solutions were maintained at a constant ionic strength, μ, of 4 mol dm^{-3}. The solubility was reported as the total silver in soln, c_{Ag}. In the table below, t is the time of rotation in days, $\bar{n}$ is the average ligand number, c_{SCN} is the total SCN^- concentration, and $[SCN^-]_{free}$ is the free SCN^- concentration. All concentrations are given in units of mol dm^{-3}.

t	solid phase*	[NaSCN]	c_{Ag}	c_{SCN}	$\bar{n}$	$[SCN^-]_{free}$
6	A**	0.400	0.0173		3.41	0.374
3	B	0.400	0.0120		3.41	
4	A+B	0.500	0.0346		3.43	
4	A+B	0.500	0.0349		3.43	
2.5	A+B	0.500	0.0354	0.666	3.43	0.539
2.5	A+B	0.550	0.0366	0.685	3.43	0.558
3	A	0.600	0.0384		3.43	0.543
7	A	0.600	0.0374		3.43	0.543
3	A	0.800	0.0640		3.44	0.705
6	A	0.800	0.0637		3.44	0.705
3	A	1.00	0.0942		3.45	0.862
6	A	1.00	0.0927		3.45	0.862
3	A	1.20	0.131		3.45	1.01
6	A	1.20	0.127		3.45	1.01
16	A	4.00	0.827		3.46	2.78

* A = $NaAg(SCN)_2 \cdot 2H_2O$; [66418-41-5] : B = AgSCN

** Metastable equilibrium

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was attained isothermally at 25°C by rotation. Satd solns were analysed for Ag by electrodeposition and for total SCN^- by Volhard titrn. Details on analysis of solid phase are not given. For $[SCN^-]$ <0.5M, $NaAg(SCN)_2 \cdot 2H_2O$ is not stable and the solid phase is AgSCN. The authors analysed their data in terms of the existence of mono- and polynuclear complexes: i.e.

$$Ag^+ + nSCN^- \rightleftarrows Ag(SCN)_n^{1-n} \qquad \beta_{1,n}$$

and

$$mAg^+ + nSCN^- \rightleftarrows Ag_m(SCN)_n^{m-n} \qquad \beta_{m,n}$$

The soly product of $NaAg(SCN)_2 \cdot 2H_2O$ in 4M $NaClO_4$ is defined as

$$K_{s0}(d) = [Ag^+][SCN^-]^2$$

and the soly product of AgSCN is defined in the usual manner as

$$K_{s0} = [Ag^+][SCN^-]$$

SOURCE AND PURITY OF MATERIALS:

Details are given in reference 1. and the reader can refer to the compilation of this paper.

ESTIMATED ERROR:

Reproducibility of the soly varies from ±1-2% (compiler). The standard deviations in the equilibrium constants (see below) are the authors' values.

REFERENCES:

1. Leden, I.; Nilsson, R. *Svensk. Chem. Tidskr.* 1954, *66*, 126.
2. Berne, E.; Leden, I. *Z. Naturforsch.* 1953, *A8*, 719.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiocyanate; NaSCN; [540-72-7]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Leden, I.; Nilsson, R.

Z. Naturforsch. 1955, *A10*, 67-76.

COMMENTS AND/OR ADDITIONAL DATA:

At an ionic strength of 4 mol dm^{-3} ($NaClO_4$), previous results (1) were:

$$K_{s0} = (7.7\pm0.2) \times 10^{-13} \quad ; \quad K_{s0}(d) = (4.1\pm0.2) \times 10^{-13}$$

These soly products were used to determine the overall stability and stepwise formation constants by a graphical method (2). At 25°C and an ionic strength of 4 mol dm^{-3}, the results are:

$$\beta_{1,1} = (3.9\pm3) \times 10^{4} \qquad K_{1,0} = (6\pm3) \times 10^{-8}$$

$$\beta_{1,2} = (1.9\pm0.2) \times 10^{8} \qquad K_{1,1} = (1.5\pm0.1) \times 10^{-4}$$

$$\beta_{1,3} = (1.2\pm2) \times 10^{9} \qquad K_{1,2} = (9\pm2) \times 10^{-3}$$

$$\beta_{1,4} = (1.8\pm0.2) \times 10^{11} \qquad K_{1,3} = (1.4\pm0.2) \times 10^{-1}$$

$$\beta_{2,6} = (1.9\pm1) \times 10^{22} \qquad K_{2,4} = (1.1\pm0.2) \times 10^{-2}$$

The units of the above constants are:

$$K_{s0} = \text{mol}^2\ \text{dm}^{-6}$$

$$K_{m,x} = \text{mol}^{1-x-m}\ \text{dm}^{-3(1-x)}$$

$$\beta_{m,n} = \text{mol}^{1-m-n}\ \text{dm}^{-3(1-m-n)}$$

The relation between the β's and K's is

$$\beta_{m,n} = K_{m,n-1}/K^{m}_{s0} = k_{m,x}/K^{m}_{s0}$$

The soly of $NaAg(SCN)_2\cdot 2H_2O$ in SCN^- solutions was given by

$$C_{Ag} = [SCN^-]^2\ K_{s0}(d)/K_{s0} \left\{ \sum_{-1}^{2} K_{1,x}[SCN^-]^{x-3} + K_{1,3} + K_{2,4}(K_{s0}(d)/K_{s0}) \cdot \left[\frac{2-k}{(1-k)^2}\right] \right\}$$

where $k = 9K_{s0}(d)\cdot\beta_{1,4}$. The standard deviation in the calcd C_{Ag} values was determined by the compiler as $\sigma = \pm 0.006$ mol/dm^3. The concentration of free SCN^- is calcd from

$$[SCN^-]_{free} = C_{SCN} - \bar{n}C_{Ag}$$

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Perchloric acid; $HClO_4$; [7601-90-3]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vanderzee, C.E.; Smith, W.E. *J. Am. Chem. Soc.* 1956, *78*, 721-5.

VARIABLES:

Temperature: range 5 to 45°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The authors reported only one value for the solubility at 25°C. The compiler has taken the data as a function of temperature and calculated the solubility product from 5 to 45°C.

$t/^{\circ}C$	$E_m^o(Ag,AgSCN)/V$	$E_m^o(Ag,Ag^+)/V$	$10^{12}K_{s0}^o/mol^2\ kg^{-2}$
5	0.09084	0.8188	0.0645
15	0.09034	0.8090	0.269
20	0.09001	0.8043	0.524
25	0.08951	0.7993	1.004
30	0.08892	0.7944	1.867
35	0.08828	0.7894	3.412
45	0.08687	0.7791	10.815

The least squares method was used to fit the above data to the equation

$$\log(K_{s0}^o/mol^2\ kg^{-2}) = -4915.96/(T/K) + 4.487 \quad (\sigma = \pm 0.003)$$

The correlation coefficient for the least squares fit is 1.0000 and the standard deviation, σ, was computed from the differences between the calcd K_{s0}^o values and the values in the above table. The authors also report

$$E_m^o(Ag,AgSCN)/V(abs) = 0.08949 - 1 \times 10^{-4}(t - 25) - 1.61 \times 10^{-6}(t - 25)^2$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

E.m.f. measurements were made on the cell

$$Pt,\ H_2/HClO_4(m_1),\ KSCN(m_2)/AgSCN,Ag$$

m values varied from 0.0007 to 0.02 mol kg^{-1}. Standard H-type cells were used with replicate electrodes in each side. Presatd H_2 or N_2 was bubbled through each cell prior to the measurements to eliminate dissolved O_2. The std (half-cell) potential for the Ag,AgSCN electrode was detd for each temp by a least squares analysis using the extended Debye-Hückel equation for the mean molal activity coefficients. The std soly products were calcd by the compiler from the equation

$$\ln K_{s0}^o = [E_m^o(Ag,AgSCN) - E_m^o(Ag,Ag^+)]F/RT$$

The std molal potentials for the Ag/Ag^+ electrode were obtained from ref 1 and converted to abs volts by the compiler.

SOURCE AND PURITY OF MATERIALS:

Freshly distilled conductivity water was used throughout. AR grade 70% $HClO_4$ ($[Cl^-]$ <0.001%) was used as received. AR grade KSCN was recrystallized from water and dried at 150°C: analysis gave a purity of 99.97% and the residual impurity is claimed to be water. Individual cell solutions were prepared with a claimed accuracy of 3-5 parts in 10,000. The H_2 was deoxygenated, and thermal-electrolytic Ag,AgSCN electrodes were used.

ESTIMATED ERROR:

K_{s0}^o: ±0.4%, average (compiler)

e.m.f.'s: reproducibility ±0.1 mV

Temperature: ±0.01°C

REFERENCES:

1. Owen, B.B. *J. Am. Chem. Soc.* 1938, *60*, 2233.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN [333-20-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Golub, A.M. *Zh. Obeschei. Khim.* 1956, *26*, 1837-48.

VARIABLES:

KSCN concentration at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

All concentrations in units of mol dm^{-3}, and K_{s4} is in mol^{-2} dm^6. The ionic strength of all solutions is 1.8 mol dm^{-3} (KNO_3).

[KSCN]	c_{Ag}	K_{s4}
1.0	0.0759	0.160
0.7	0.0326	0.150
0.6	0.0213	0.138
0.5	0.0131	0.134
0.3	0.00323	0.132
0.2	0.00113	0.149

The solubility product was determined (see below) to be

$$K_{s0}(AgSCN) = 4.1 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$$

at an ionic strength of 1.8 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were prepared isothermally by placing excess solid in sealed flasks of known [KSCN]. KNO_3 was used to maintain a constant ionic strength of 1.8 mol/dm^3. The reaction mixtures were equilibrated at 20°C for two days with frequent shaking. Solutions were analysed gravimetrically by ppting Ag_2S with CS_2. The ppt was filtered, washed with water, alcohol, ether, CS_2, alcohol, and ether, and dried at 90°C.

SOURCE AND PURITY OF MATERIALS:

C.p. grade KSCN was recrystallized, dried, and melted for 10-15 min. $AgNO_3$ and KNO_3 were c.p. grade and used as received. AgSCN prepared by mixing solns of $AgNO_3$ and KSCN. The AgSCN was filtered, washed, and dried in a desiccator over $CaCl_2$. Treatment of water was not specified.

ESTIMATED ERROR:

Solubility: not specified, but precision probably within ±1-2%.
K_{s0}: σ= ±8% (compiler)
Temperature: not specified.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; $AgSCN$; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; $KSCN$; [333-20-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Golub, A.M. *Zh. Obeschei. Khim.* 1956, *26*, 1837-48.

COMMENTS AND/OR ADDITIONAL DATA:

In the concentration range studied, the only significant complex is claimed to be $Ag(SCN)_4^{3-}$. This stoichiometry was determined from the soly measurements by plotting C_{Ag} against [KSCN]: the slope of this plot = 4 and K_{s4} for the reaction

$$AgSCN(s) + 3SCN^- \rightleftarrows Ag(SCN)_4^{3-}$$

was calcd from

$$K_{s4} = [Ag(SCN)_4^{3-}]/\left\{[KSCN] - 3\,[Ag(SCN)_4^{3-}]\right\}^3$$

In this paper the author uses a potentiometric method to determine the overall stability constant β_4 in unsaturated solutions: i.e.

$$Ag^+ + 4SCN^- \rightleftarrows Ag(SCN)_4^{3-}$$

The soly product was then calculated from

$$K_{s0} = K_{s4}/\beta_4 = (4.1 \pm 0.3) \times 10^{-12}\ mol^2\ dm^{-6}$$

where

$$K_{s4} = 0.15 \pm 0.01\ mol^{-2}\ dm^{6*}$$

$$\beta_4 = (3.6 \pm 0.3) \times 10^{10}\ mol^{-4}\ dm^{12*}$$

*Recalculated from the original data by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Klein, E. *Z. Elektrochem.* 1956, *60*, 1003-7.

VARIABLES:

Temperature: range 12 to 85°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$t/^{\circ}C$	$K_{s0}/mol^2\ dm^{-6}$
12	8×10^{-13}
21	1.8×10^{-12}
25	1.6×10^{-12}
35	6.6×10^{-12}
47	3.16×10^{-11}
57	1.15×10^{-10}
63	1.27×10^{-10}
69	2.82×10^{-10}
85	6.3×10^{-10}

The author has fit his results to the following smoothing equation:

$$K_{s0} = 725 \times 10^{-4290/(T/K)}$$

By taking differences between the K_{s0} values calcd from the smoothing equation and the measured values, the compiler calculates a standard deviation of ±41% in the values obtained from the smoothing equation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The soly products were determined by a potentiomatic titration method. No details were given.

COMMENTS AND/OR ADDITIONAL DATA:

Since the author states that he used a potentiometric titration method to determine the soly products, it is clear that a third electrolyte must be present. There is no way of determining the ionic strength and if the ionic strength was constant during the titration.

From the smoothing equation, the compiler calculates ΔH_{s0} = 82 kJ mol^{-1}.

SOURCE AND PURITY OF MATERIALS:

Nothing specified

ESTIMATED ERROR:

Nothing specified

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium sulfite; Na_2SO_3; [7757-83-7]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Klein, E. *Z. Elektrochem.* 1956, *60,* 1003-7.

VARIABLES:

Concentration of Na_2SO_3 at 42°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The two experimental results at 42°C are:

$[Na_2SO_3]$/mol dm^{-3}	c_{Ag}/mol dm^{-3}
0.107	0.00463
1.40	0.0517

The reaction studied is

$$AgSCN(s) + 2SO_3^{2-} \rightleftarrows Ag(SO_3)_2^{3-} + SCN^-$$

The formation of $Ag(SCN)_2^-$ was not considered by the author, but is probably negligible. The temperature dependence of the solubility is given by

$$c_{Ag} = [Ag(SO_3)_2^{3-}] = \left[2 + 10^{1553/((T/K)-3.58)}\right]^{-1}[SO_3^{2-}]_{total} \qquad [1]$$

This relation was derived from the temperature dependence of the solubility product, K_{s0} (determined in this paper)

$$K_{s0}(AgSCN) = 725 \times 10^{-4290/(T/K)} \qquad [2]$$

and the temperature dependence of the stability constant for $Ag(SO_3)_2^{3-}$ (see equation [3] below). The value of K_{s0}(AgSCN) was not measured at 42°C but was calculated from eq [2] which was previously shown by the compiler to have a standard deviation of ±41% (see the compilation for the AgSCN/H_2O system studied by Klein).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturated solns were prepared isothermally by stirring a mixture of excess AgSCN with varying Na_2SO_3 concentrations. Purified N_2 was bubbled into the solns to prevent the oxidation of the sulfite. Equilibrium was reached after 12-15 h of stirring (no details are given). The total sulfite was determined by iodometric titration and the total silver (present in the form $Ag(SO_3)_2^{3-}$) was determined by titrn with thiourea.

SOURCE AND PURITY OF MATERIALS:

Na_2SO_3 crystals were zone refined. AgSCN was precipitated from aqueous solution, presumably by mixing $AgNO_3$ with an alkali metal thiocyanate. No other details were given.

COMMENTS AND/OR ADDITIONAL DATA:

The stability constant β_2 for the reaction

$$Ag^+ + 2SO_3^{2-} \rightleftarrows Ag(SO_3)_2^{3-} \qquad [3]$$

was found to vary with temp as

$$\beta_2 = 10^{1185/[(T/K) + 4.3]}$$

ESTIMATED ERROR:

Nothing is specified and may be large. The av error in eq [1] is expected to be very large (at least ±40%).

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gyunner, E.A.; Yakhkind, N.D.

Zh. Neorg. Khim. 1968, *13*, 245-52.

VARIABLES:

Concentration of KSCN at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

KNO_3 used to maintain a constant ionic strength of 2 mol dm^{-3} at 20°C.

[KSCN]/mol dm^{-3}	c_{Ag}/mol dm^{-3}	[KSCN]/mol dm^{-3}	c_{Ag}/mol dm^{-3}
0.400	0.015*	1.300	0.186
0.600	0.027	1.400	0.220
0.800	0.053	1.600	0.300
1.000	0.095	1.800	0.372
1.100	0.125	2.00	0.475
1.200	0.156		

*Not used to average the K_{s36} value.

The average formation constant, K_{s36}, for the reaction

$$3AgSCN(s) + 3SCN^- \rightleftarrows Ag_3(SCN)_6^{3-}$$

was given as

$$K_{s36} = (4.5\pm0.2) \times 10^{-2}\ mol^{-2}\ dm^6$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A refractometric method was used. A series of solutions with varying [KSCN] and previously detd refractive indices (n_1) were saturated with AgSCN at 20°C. Equilibrium having been attained (no details given), the new refractive index, n_2, was used to calculate the solubility, S, of AgSCN using the equation:

$$S = K(n_2 - n_1)$$

where K is a constant. KNO_3 was used to maintain a constant ionic strength of 2 mol dm^{-3}.

K_{s36} was calculated from

$$K_{s36} = c_{Ag}/3(c - 4c_{Ag})^3$$

where c =[KSCN].

SOURCE AND PURITY OF MATERIALS:

Not specified.

ESTIMATED ERROR:

Authors state accuracy in refractive index measurement is ±1 x 10^{-4}, and accuracy in soly is therefore ±2-3 x 10^{-3} mol dm^{-3}. The compiler assumes that "accuracy" refers to an error range.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Gyunner, E.A.; Yakhkind, N.D.

Zh. Neorg. Khim. 1968, *13*, 245-52.

COMMENTS AND/OR ADDITIONAL DATA:

Using the data in the above tables, the authors calculated equilibrium constants for the reactions

$$AgSCN(s) + (n-1)SCN^- \rightleftarrows Ag(SCN)_n^{1-n} \qquad K_{sn}$$

for n = 2, 3, and 4. These constants were calculated from

$$K_{sn} = C_{Ag}/\left[c - (n-1)C_{Ag}\right]^{n-1}$$

The authors claim that only K_{s36} values are significant due to its constancy. However the K_{sn} values for n = 3,4 also show some constancy, particularly for $0.4 \leqslant$ KSCN $\leqslant$ 1.2 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Perchloric acid; $HClO_4$; [7601-90-3]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lal, S.C.; Prasad, B. *Indian J. Chem.* 1975, *13*, 372-4.

VARIABLES:

Temperature: range 15 - 55°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES: The solubility product of AgSCN was determined from standard electrode potentials, and were calculated from the equation

$$\log K^\circ_{s0} = (E^\circ_{Ag,AgSCN} - E^\circ_{Ag,Ag^+})F/RT\ln 10 \qquad [1]$$

$t/^\circ C$	$E^\circ_{Ag,AgSCN}/V^*$	$E^\circ_{Ag,Ag^+}/V$	$10^{12}K^\circ_{s0}/mol^2\ kg^{-2}$
15	0.09030	0.8090	0.269
20	0.08992	0.8043	0.523
25	0.08946	0.7993	1.003
30	0.08890	0.7944	1.865
35	0.08822	0.7894	3.406
45	0.08675	0.7791	10.78
55	0.08496	0.7691	31.08 .

The standard electrode potential of the Ag,AgSCN electrode (vs SHE) as a function of temperature was given by

$$E^\circ_{Ag,AgSCN}/V = 0.09091 - 1.75 \times 10^{-5}\ t - 1.65 \times 10^{-6}\ t^2$$

The solubility product data was fit by least squares by the compiler to

$$\log K^\circ_{s0} = -4882/(T/K) + 4.376$$

The standard deviation of the above equation is 0.003 log units and the correlation coefficient is 1.000.

*Authors state reproducibility within ±0.1 mV and report E values to 0.01mV.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

E.m.f. measurements were made on the cell

$$Pt,H_2/KSCN(m_1),HClO_4(m_2)/AgSCN,Ag$$

The e.m.f. of this cell is given by

$$E = E^\circ_{Ag,AgSCN} - RT\ \ln\ \{(m_1 \cdot m_2)\gamma_\pm{}^2\} \qquad [2]$$

E° was evaluated by extrapolation to zero ionic strength using the following relation for the mean molal activity coefficient:

$$\log\gamma_\pm = -A\mu^{1/2}/(1 + \mu^{1/2}) + b\mu \qquad [3]$$

Fourteen values of m_1 and m_2 were used for each temp and the total ionic strength ($m_1 + m_2$) varied from 0.001 to 0.060 mol/dm^3. The cells were placed in an air thermostat (±0.05°C) and the e.m.f. measured hourly for at least 3 h. Duplicate cells were used and agreement was within ±0.1 mV. Corrections for atmospheric pressure were made. E°_{Ag,Ag^+} values were obtained from Owen's work (1) and converted to abs volts by the compiler.

SOURCE AND PURITY OF MATERIALS:

Doubly distilled water was used. A.R. grade KSCN was recrystallized, and A.R. grade $HClO_4$ (60%) was used as received. Solutions were de-oxygenated by bubbling of N_2. Purified H_2 was presaturated at the required temperature. Thermal-electrolytic Ag,AgSCN electrodes were used.

ESTIMATED ERROR:

E° extrapolation at 25°C checked by compiler and reproducibility is within experimental error of ±0.1mV: hence stnd dev in $\log K_{s0}$ is ±0.001 and ±0.4% in K_{s0}.

Temperature: ±0.05°C.

REFERENCES:

1. Owen, B.B.; Brinkley, S.R. *J. Am. Chem. Soc.* 1938, *60*, 2233.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiocyanate; NaSCN; [540-72-7]

(4) Sodium thiosulfate; $Na_2S_2O_3$; [10579-83-6]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Makarewicz, Z. *Roczniki Chem.* 1975, *49*, 879-84.

VARIABLES:

Concentrations of NaSCN and $Na_2S_2O_3$

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Temperature is 25°C; ionic strength is constant at 1.0 mol/dm^3 ($NaClO_4$).

c_{Ag}/mol dm^{-3}	[NaSCN]/mol dm^{-3}	[$Na_2S_2O_3$]/mol dm^{-3}
0.0228	0.4	0.04
0.04467	0.4	0.08
0.05464	0.4	0.10
0.08474	0.4	0.15
0.01873	0.3	0.04
0.04036	0.3	0.08
0.05133	0.3	0.10
0.08014	0.3	0.15
0.01538	0.2	0.04
0.03623	0.2	0.08
0.04988	0.2	0.10
0.07506	0.2	0.15
0.01574	0.1	0.04
0.03535	0.1	0.08
0.04685	0.1	0.10
0.07369	0.1	0.15

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were prepared isothermally at 25°C by shaking with an excess of solid AgSCN. The method of establishing equilibrium is not described. The soly of AgSCN was determined gravimetrically by pptn of Ag_2S with thiourea: 10% NH_4Cl soln was added to coagulate the ppt. $NaClO_4$ was used to maintain the ionic strength of all solns at 1.0 mol/dm^3.

SOURCE AND PURITY OF MATERIALS:

Solutions of $AgNO_3$, NH_4SCN, $Na_2S_2O_3$, NH_4Cl, NaSCN, and $NaClO_4$ were prepared from analytically pure reagents. AgSCN was precipitated from a soln of NH_4SCN and $AgNO_3$. No other details were given.

ESTIMATED ERROR:

Nothing specified: however if the soly is reproducible to ±1 unit in the last significant figure, the reproducibility in the solubility is better than ±1%.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Sodium thiosulfate; $Na_2S_2O_3$; [10579-83-6]

(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Makarewicz, Z. *Roczniki Chem.* 1975, *49*, 879-84.

VARIABLES:

Concentration of $Na_2S_2O_3$ at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Concentrations in units of mol dm^{-3}, β_{111} in mol^{-2} dm^6, and K_r is unitless. The ionic strength is constant at 1.0 mol dm^{-3} ($NaClO_4$).

c_{Ag}	$[Na_2S_2O_3]_{tot}$	$[S_2O_3^{2-}]_{equil}$	K_r	$10^{12}\beta_{111}$
0.02123	0.04	0.01877	1.13	1.03
0.04318	0.08	0.03682	1.17	1.07
0.05530	0.10	0.04470	1.24	1.12
0.08412	0.15	0.06588	1.28	1.16
0.1140	0.20	0.08600	1.33	1.20
0.1466	0.25	0.1034	1.42	1.29
0.1743	0.30	0.1257	1.39	1.26

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were prepared isothermally by shaking with an excess of solid AgSCN. The ascertainment of equilibrium was not described. The solubility of AgSCN was determined gravimetrically by precipitation of Ag_2S with thiourea: 10% NH_4Cl solution was added to coagulate the ppt. $NaClO_4$ was used to maintain a constant ionic strength of 1.0 mol dm^{-3}. No analysis of the solid phase was reported.

SOURCE AND PURITY OF MATERIALS:

Solutions of $NaNO_3$, NH_4SCN, $Na_2S_2O_3$, NH_4Cl, and $NaClO_4$ were prepared from analytically pure reagents. AgSCN was precipitated from a solution of NH_4SCN and $AgNO_3$. No other details were given.

ESTIMATED ERROR:

Nothing specified: however if the soly is reproducible to ±1 unit in the last significant figure, the reproducibility in the soly is better than ±1%.

REFERENCES:

1. Lur'e, Yu. Yu. *Spravo Chnik Po. Analoticheskoi Khimii.* Moskva. page 95.
2. Fridman, A.D.; Sarbeov, D.S. *Zh. Neorg. Khim.* 1960, *5*, 791.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Sodium perchlorate; $NaClO_4$; [7601-89-0] (3) Sodium thiosulfate; $Na_2S_2O_3$; [10579-83-6] (4) Water; H_2O; [7732-18-5]	Makarewicz, Z. *Roczniki Chem.* 1975, *49*, 879-84.

COMMENTS AND/OR ADDITIONAL DATA:

The author states that the complex formed is the mixed species $AgSCN \cdot S_2O_3^{2-}$. The existence of this species is based on the "near constancy" of K_r. The equilibrium constant K_r is defined by

$$K_r = [Ag(SCN)(S_2O_3)^{2-}]/[S_2O_3^{2-}]_{equil} = S/([Na_2S_2O_3]_{tot} - S)$$

where S = solubility = C_{Ag}. The overall stability constant β_{111} for the reaction

$$Ag^+ + SCN^- + S_2O_3^{2-} \rightleftarrows Ag(SCN)(S_2O_3)^{2-}$$

was calculated from

$$\beta_{111} = (S/K_{s0} - \beta_1)/[S_2O_3^{2-}]_{equil}$$

The solubility product, K_{s0}(AgSCN), was taken as 1.1×10^{-12} mol^2 dm^{-6} (1) and β_1 for the formation of $Ag(S_2O_3)^-$ was taken as 5.6×10^4 (2) mol^{-1} dm^3. The "slight" increasing trend in K_r was ascribed to the formation of higher complexes such as $Ag(S_2O_3)_2^{3-}$. The equilibrium constant for disproportionation, K_D,

$$2Ag(SCN)(S_2O_3)^{2-} \rightleftarrows Ag(SCN)_2^- + Ag(S_2O_3)_2^{3-} \quad K_D = 0.06$$

was calcd from

$$pK_D = \log \beta_{111} - 1/2 \log \beta_2(Ag(SCN)_2^-) - 1/2 \log \beta_2(Ag(S_2O_3)_2^{3-})$$

Values of β_2 were taken from ref (2):

$$\log \beta_2(Ag(SCN)_2^-) = 8.23$$

$$\log \beta_2(Ag(S_2O_3)_2^{3-}) = 13.46$$

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Dash, U.N.; Mohanty, J.; Panda, K.N.

Thermochim. Acta 1976, *16*, 55-61.

VARIABLES:

Concentration of $NaClO_4$ and temperature (range 15-35°C)

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Concentrations are given in units of mol dm^{-3}.

$t/^{\circ}C$	$10^2[NaClO_4]$	10^6c_{Ag}	$t/^{\circ}C$	$10^2[NaClO_4]$	10^6c_{Ag}
15	0.250	0.757	25	1.750	3.486
15	0.500	1.035	25	2.250	4.666
15	1.000	1.265	25	0*	0.976
15	1.500	1.749	25	0*	0.976**
15	2.250	2.846	30	0.250	1.513
15	0*	0.661	30	0.750	2.080
15	0*	0.655**	30	1.000	2.661
20	0.250	0.975	30	1.500	3.691
20	0.750	1.393	30	1.750	4.006
20	1.250	1.951	30	2.500	6.594
20	2.000	3.107	30	0*	1.247
20	2.500	4.814	30	0*	1.260**
20	0*	0.769	35	0.500	2.249
20	0*	0.776**	35	0.750	2.758
25	0.250	1.285	35	1.250	3.446
25	0.500	1.368	35	2.000	5.790
25	0.750	1.689	35	2.250	6.853
25	1.000	1.998	35	0*	1.563
25	1.500	3.102	35	0*	1.560**

* AgSCN solubilities at zero ionic strength obtained by extrapolation.
** These values were recalculated by the compiler: see details next page.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturated solutions analysed for Ag by potentiometric titration using 1 x 10^{-6} mol dm^{-3} KCl soln. Other details are said to be essentially similar to that of previous studies (1): it is therefore assumed that solutions of $NaClO_4$ with excess AgSCN were rotated in a thermostat maintained at the required temperature (±0.03°C) for several weeks. Saturation was verified for several samples by duplicate analysis. Titrations in the cited paper (1) quoted to be accurate to within ±0.2%. A microburet was used for the titrations.

SOURCE AND PURITY OF MATERIALS:

AgSCN precipitated from soln of $AgNO_3$ and KSCN (B.D.H., Analar grade). The ppt was washed repeatedly with conductivity water and dried under vacuum over $CaCl_2$ for several weeks. Analysis by "standard" methods gave a purity of 99.7%. $NaClO_4$ was prepared as described previously (2).

ESTIMATED ERROR:

Nothing specified, but error in soly is probably $\geqslant$ ±0.2% as was quoted in related work by the authors (1).

REFERENCES:

1. Dash, U.N.; Mohanty, J. *Thermochim. Acta* 1975, *12*, 18-9.
2. Nayak, B.; Dash, U.N. *Thermochim. Acta* 1973, *6*, 623. 3. Harned, H.S.; Owen, B.B. *Phys. Chem. of Electrolytic Solns.* Reinhold. NY. 1967.
4. Vanderzee, C.E.; Smith, W.E. *J. Am. Chem. Soc.* 1956, *78*, 721.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]

(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Dash, U.N.; Mohanty, J., Panda, K.N.

Thermochim. Acta 1976, *16*, 55-61.

COMMENTS AND/OR ADDITIONAL DATA:

The authors evaluated the solubility, s_o, at zero ionic strength by an extrapolation method using the equation

$$\log s - A\mu^{1/2}/(1 + Ba^o\mu^{1/2}) = \log s_o + b\mu$$

where μ is the ionic strength ($[NaClO_4] + [AgSCN]$), s is the measured soly of AgSCN, A and B are the Debye-Hückel constants whose values were obtained from reference 3 as a function of temp, and a^o is the ion size parameter which was taken as 0.6mm as evaluated from the data of Vanderzee and Smith (4). A plot of the left hand side of this equation against the ionic strength gives log s_o as the intercept. The intercepts obtained by the authors (see table below) differ from their reported s_o values listed in the data table above: the compiler therefore fit the experimental data to the above equation by the least squares method, and the results are given below. The soly product at zero ionic strength, K^o_{s0}, was calculated from s^2_o.

t/°C	log s_o*	log s_o	b/mol^{-1} dm^3 (eq [1])	$10^{12}K^o_{s0}$/mol^{2}dm^{-6}	$10^{12}K^o_{s0}$/mol^{2}kg^{-2}
15	-6.1835	-6.184	25.58	0.429	0.430
20	-6.1183	-6.110	28.49	0.603	0.605
25	-6.0123	-6.011	28.14	0.952	0.958
30	-5.9049	-5.900	26.51	1.588	1.602
35	-5.8068	-5.801	25.57	2.434	2.463

*Author's values. All other data calculated by the compiler. If, as suggested by the authors' reference to their previous work (1), the error in the soly is about ±0.2%, then log s_o should be reported to three significant figures. An error of ±0.2% in s_o leads to an error of ±0.4% in K^o_{s0}. The data for K^o_{s0}/mol^2 kg^{-2} calculated from (K^o_{s0}/mol^2 dm^{-6})/d^2_o where d_o is the density of pure water at the various temperatures.

The compiler has used the least squares method to obtain the following:

$$\log(K^o_{s0}/\text{mol}^2\ \text{dm}^{-6}) = -3419/(T/K) - 0.527 \quad (\sigma = 0.024)$$

$$\log(K^o_{s0}/\text{mol}^2\ \text{kg}^{-2}) = -3439/(T/K) - 0.459 \quad (\sigma = 0.024)$$

where σ is the standard deviation for the precision of the least squares fit: the correlation coefficient for both relations is 0.997.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Acetone; C_3H_6O; [67-64-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

August 1978

CRITICAL EVALUATION:

The soly of AgSCN in $H_2O/(CH_3)_2CO$ mixtures has been reported by Kratohvil and Težak (1), Woolley (2), and Szarvas, Korondán, and Szabó (3). A single study in pure acetone has also been reported (4). Because of differing exptl conditions such as temperature, solvent composition, and ionic strength, comparisons are difficult to make, and tentative or recommended values cannot be given. One can however make qualitative comparisons to determine if any data are grossly inconsistent.

Kratohvil and Težak studied the soly of AgSCN in two mixed solvents containing 48.5% and 82% acetone by weight: their experiments, based on the turbidimetric method, were carried out at 293 K in solns of varying ionic strength. Woolley used a combined radioassay and e.m.f. method to calculate K_{s0}^{o} and stability constants as a function of solvent composition at 298 K. Both studies report the existence of $Ag(SCN)_2^-$, but Woolley's work indicates that $Ag(SCN)_3^{-2}$ becomes insignificant in solvents containing more than 34% acetone by weight. Szarvas et. al. used the potentiometric titrn method to calc K_{s0} in 0.001 mol dm^{-3} at 298 K: however solvent compositions are reported in terms of vol % which are not defined, and hence cannot be converted to a weight basis. In pure acetone, Golub (4) reports a value for K_{s2} obtained from direct measurements of the soly, C_{Ag}. The complex $Ag(SCN)_3^{2-}$ was not detected.

The only K_{s0} data available are from references (2) and (3) at 298 K. Little significance can be given to the attempt (1) to calc K_{s0} at 293 K from the empirical Ricci-Davis equation (5) as discussed in the compilation. By visual observation of the data tables, it is apparent that Woolley's K_{s0}^{o} values differ significantly from those of Szarvas et. al. The fact that the latter K_{s0} values are much lower than Woolley's values may be due to the neglect of complex ion formation, or that the silicone membrane used in construction of the specific ion electrode is attacked by acetone.

K_{s2} can be used to make qualitative comparisons since, to a large extent, it is independent of concn: i.e. $K_{s2} \simeq K_{s2}^{o}$ as seen from the relation

$$K_{s2} = K_{s0}\beta_2 \simeq K_{s2}^{o} \qquad [1]$$

The evaluator found that Woolley's data can be fit by least squares to

$$\log K_{s2}^{o} = 0.035(\text{wt \% acetone}) - 3.92 \qquad (\sigma = \pm 0.08) \qquad [2]$$

The correlation coeff for this fit is 0.992, and σ was calcd from differences in the obsd and calcd log K_{s2}^{o}. Equation [2] was used to calculate log K_{s2} for several solvent compositions as well as for the pure solvents, and the results are given in the table below. Although the temperatures differ for several of the entries to the table, it is apparent that qualitative agreement exists for K_{s2} between the works referenced in 1, 2, and 4.

Calculated and Experimental log K_{s2} Values

wt % acetone	source eq. [2]*	ref. (1)	ref. (4)	recommended value*
0	-3.92			-3.80
48.5	-2.22	-2.22		
82	-1.04	-1.45		
100	-0.41		-0.39	

*Data for 298 K: remaining data are for 293 K. For recommended value, see the critical evaluation for the binary aqueous system.

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Acetone; C_3H_6O; [67-64-1] (3) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. August 1978

CRITICAL EVALUATION: (continued)

REFERENCES:

1. Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243.
2. Woolley, E.M. *PhD Dissertation*. Brigham Young University. Provo, Utah. 1969.
3. Szarvas, P.; Korondan, I.; Szabó, M. *Magy. Kem. Folyoirat.* 1974, *80*, 207.
4. Golub, A.M. *Zh. Obeschei. Khim.* 1956, *26*, 1837.
5. Ricci, J.E.; Davis, T.W. *J. Am. Chem. Soc.* 1940, *62*, 407.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Acetone; C_3H_6O; [67-64-1]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

VARIABLES:

Concentration of KSCN and composition of solvent at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ soln: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN. The composition of the $H_2O/CH_3C(O)CH_3$ mixed solvent is given in weight percent acetone.

	$[KSCN]_{tot}/mol\ dm^{-3}$	
$c_{Ag}/mol\ dm^{-3}$	48.5% acetone	82% acetone
0.01	0.205	0.102
0.006		0.075
0.004	0.125	0.0525
0.002		0.031
0.001	0.058	0.019
0.0006		0.0115
0.0004	0.03125	0.0077
0.0002		0.00365
0.0001	0.0095	0.001675
0.00006		0.000875
0.00004	0.0040	0.000575
0.00002	0.001625	0.00023
0.00001	0.000725	0.0000875

AUXILIARY INFORMATION

METHOD:

Turbidimetric method. Solns of $AgNO_3$ and KSCN were mixed and at equilibrium the turbidity measured (establishment of equil not described, but measurements probably made within 1 h as described earlier (1)). The soly of AgSCN was calcd from the concentration of KSCN at which, for a given $[AgNO_3]$, the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3 \qquad [1]$$

The disappearance of turbidity is due to complex ion formation. The authors assume only mononuclear complexes form according to

$$AgSCN(s) + (n-1)SCN^- \rightleftarrows Ag(SCN)_n^{1-n} \qquad [2$$

SOURCE AND PURITY OF MATERIALS:

All chemicals were analytically pure, and presumably used as received. Distilled water with a specific conductance of 2 x 10^{-6} ohm^{-1} cm^{-1} was used. Commercial acetone was distilled twice from $AgNO_3$.

ESTIMATED ERROR:

Solubility: nothing specified, but reproducibility probably about ±2-3%.

Temperature: ±0.1°C.

REFERENCES:

1. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.
2. Ricci, J.E.; Davis, T.W. *J. Am. Chem. Soc.* 1940, *62*, 407.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Potassium nitrate; KNO_3; [7757-79-1] (3) Potassium thiocyanate; KSCN; [333-20-0] (4) Acetone; [67-64-1] (5) Water; H_2O; [7732-18-5]	Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

COMMENTS AND/OR ADDITIONAL DATA:

The equilibrium constants for reaction [2] were calculated from

$$\ln K_{sn} = \log C_{Ag} - (n-1)\log[SCN^-]_{equil} \qquad [3]$$

where $[SCN^-]_{equil} = [KSCN]_{tot} - C_{Ag}$. Eq. [3] was applied to those experimental points in the concentration range where each complex predominates. The overall stability constants were calculated from

$$\beta_n = K_{sn}/K_{s0} \qquad [4]$$

The solubility product was calculated from the Ricci-Davis equation (2)

$$\log(K_{s0})_s \quad \log(K_{s0})_w - (484/a)(\varepsilon_s^{-1} - \varepsilon_w^{-1}) \qquad [5]$$

where ε is the dielectric constant, the subscripts s and w refer to the mixed solvent and water, respectively, and "a" is an empirical constant identified with an ionic radius. Taking $(K_{s0})_w = 1 \times 10^{-12}$ $mol^2\ dm^{-6}$ and a = 2.97 and 4.03 for ε_s = 50.4 and 29.0 Debye, respectively (cf. reference 2), the following results were obtained:

weight % acetone	(ε)	$10^{14}K_{s0}$	$[KSCN]_{tot}$ /mol dm^{-3}	complex	K_{sn}	$10^{-13}\beta_n$
48.5	(50.4)	6.0	0.0008 - 0.01	$Ag(SCN)_2^-$	0.0060	0.010
			0.05 - 0.2	$Ag(SCN)_3^{2-}$	0.018	0.30
82	(29.0)	0.22	0.0006 - 0.012	$Ag(SCN)_2^-$	0.035	1.6

Eq. [5] was derived for 25°C and the value of $(K_{s0})_w$ used is the value for 25°C (see the critical evaluation). Although the authors use ε values for 20°C the derived K_{s0} and β_n are, at best, qualitative (compilers comment). The units of the equilibrium constants are:

$$K_{sn} = mol^{2-n}\ dm^{3(n-2)}$$

$$\beta_n = mol^{-2}\ dm^{3n}$$

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Acetone; C_3H_6O; [67-64-1]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.[1]

VARIABLES:

Concentration of KSCN and composition of solvent at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The total solubility of AgSCN, $C_{Ag}/\text{mol dm}^{-3}$, was fit by a relative least squares method (2) to

$$C_{Ag} = K^o_{s0}/([SCN^-]_{free}\,\gamma_\pm^2) + B + C\,[SCN^-]_{free} + D\,[SCN^-]_{free}/\gamma_\pm^2 \qquad [1]$$

where $[SCN^-]_{free}$ is the (uncomplexed) concentration of SCN^- in soln, and B,C,D are constants. These constants are given in the table below along with the solubility product K^o_{s0}(AgSCN). Units of K^o_{s0} are $\text{mol}^2\ \text{dm}^{-6}$; for units of B, C, D see COMMENTS section. The composition of the solvent is given in weight percent acetone.

% $(CH_3)_2CO$	$-\log K^o_{s0}$*	$-\log B$	$-\log C$	$-\log D$
9.64	10.83±0.74	6.69±0.04	3.56±0.03	1.88±0.02
19.80	11.26±0.39	6.55±0.05	3.18±0.04	1.47±0.04
34.43	11.43±0.27	5.81±0.05	2.85±0.04	0.59±0.03
42.08	11.40±0.65	6.16±0.17	2.40±0.07	-----
54.15	11.68±0.09	5.96±0.09	1.98±0.06	-----

*Average values based on equations [3] and [4] below. The errors given in this table are standard deviations.

AUXILIARY INFORMATION

METHOD:

Solns were prepared isothermally at 25.00 ±0.01°C by rotating mixtures of KSCN with $AgClO_4$ containing ^{110}Ag. $[Ag^+]$ determined by e.m.f. measurements using the cell

$$\text{ind/AgSCN(satd), KSCN}(x\text{M})\text{// ref} \qquad [2]$$

where ind is an Orion model 94-16 sulfide ion electrode, // is a salt bridge of 1M KNO_3, and ref is a calomel electrode. The activity of Ag^+ was obtained from

$$\log a_{Ag^+} = mE + b \qquad [3]$$

Since $K^o_{s0} = (a_{Ag^+})(a_{SCN^-})$

$$\log a_{SCN^-} = -mE - (b - \log K^o_{s0}) \qquad [4]$$

The constants m and b were determined from measurements on solns with known a_{Ag^+}. $[SCN^-]$ was determined from mass balance considerations, $\gamma_\pm$ (the mean molar activity coefficient) from the extended Hückel equation,* and

SOURCE AND PURITY OF MATERIALS:

All chemicals were reagent grade. Double dist water of specific conductance < $1.5 \times 10^{-6}\ \text{ohm}^{-1}\ \text{cm}^{-1}$ at 25°C was used. Gas chromatographic analysis of the acetone showed the only impurity to be <0.2% water. Electrodeposited Ag containing ^{110}Ag was dissolved in HNO_3 and fumed to near dryness three times in 72% $HClO_4$.

ESTIMATED ERROR:

C_{Ag}: σ < ±5%

E.m.f.: ±1 mV for $[SCN^-] < 10^{-3}\ \text{mol dm}^{-3}$

±0.3 mV for $[SCN^-] > 10^{-3}\ \text{mol dm}^{-3}$

$\gamma_\pm$: ±2%

REFERENCES:

1. Available as order No. 69-20,136 from University Microfilms, Ann Arbor, Mich., U.S.A. 48106.

2. Anderson, K.P.; Snow, R.L. *J. Chem. Educ.* 1967, *44*, 756.

COMPONENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium perchlorate; $KClO_4$; [7778-74-7]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Acetone; C_3H_6O; [67-64-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.[1]

COMMENTS AND/OR ADDITIONAL DATA:

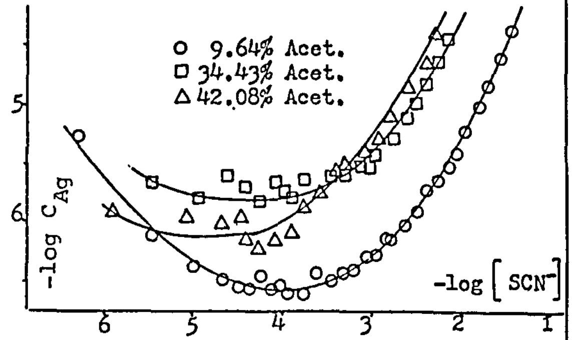
In the figures at the right, the points are the experimental results and the lines were calculated from equation [1]. The overall stability constants can be calculated from the data in the above table using the constants B, C, D and the relations

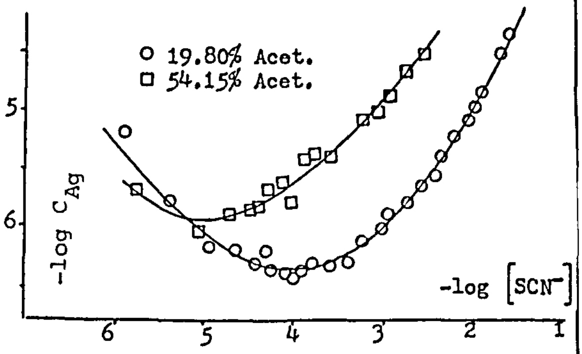
$$B/K^{\circ}_{s0} = \beta^{\circ}_1 \text{ mol}^{-1} \text{ dm}^3$$

$$C/K^{\circ}_{s0} = \beta^{\circ}_2 \text{ mol}^{-2} \text{ dm}^6$$

$$D/K^{\circ}_{s0} = \beta^{\circ}_3 \text{ mol}^{-3} \text{ dm}^9$$

In the least squares fit to eq [1] $[SCN^-]_{free}$ was obtained from mass balance considerations for $[SCN^-] > 10^{-4}$ mol dm^{-3} and from eq [4] for $[SCN^-] <$ mol dm^{-3}.





AUXILIARY INFORMATION

METHOD:

K°_{s0} is obtained as $(a_{Ag^+})(a_{SCN^-})$. K°_{s0} was also determined from the intercept of eq [4]. For the determination of C_{Ag}, the equilibrium mixtures were centrifuged at 25 ±0.4°C and aliquots of soln taken for analysis. Evaporating the aliquots to dryness, C_{Ag} was determined in a thallium activated NaI scintillation detector.

*See the compilation for Woolley's CH_3OH/H_2O study.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium perchlorate; $KClO_4$; [7778-74-7]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Acetone; C_3H_6O; [67-64-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Szarvas, P.; Korondán, I.; Szabó, M.
Magy. Kem. Foly. 1974, *80*, 207-11.

VARIABLES:

Solvent composition at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at approximately 0.001 mol dm^{-3}.

Volume % acetone	$-\log K_{s0}$	$10^{13}K_{s0}/mol^2\ dm^{-6}$
20	12.12	7.59
40	12.20	6.31
60	12.20	6.31
80	12.32	4.79

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$$\mathrm{SCN}_{\text{membrane}}/\mathrm{KSCN}(0.001M)//\mathrm{KNO_3}(1M)//\text{-}$$
$$\mathrm{KCl}(0.001M)/\mathrm{AgCl},\mathrm{Ag}$$

The indicator electrode is a RADELKIS SCN^- specific ion electrode which utilizes a silicone rubber matrix.

SOURCE AND PURITY OF MATERIALS:

All reagents were of analytical purity, and were used as received. The solvents were repeatedly distilled.

ESTIMATED ERROR:

log K_{s0}: ±0.05 log units (authors).
Temperature: ±0.05°C

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium perchlorate; $KClO_4$; [7778-74-7]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Dimethylformamide; C_3H_7NO; [68-12-2]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Szarvas, P.; Korondán, I.; Szabó, M.

Magy. Kem. Foly. 1974, *80*, 207-11.

VARIABLES:

Solvent composition at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at approximately 0.001 mol dm^{-3}.

volume % $HCON(CH_3)_2$	$-\log K_{s0}$	$10^{14}K_{s0}/mol^2\ dm^{-6}$
20	12.76	17.4
40	13.02	9.55
60	13.06	8.71
80	13.16	6.92

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$\overset{\text{SCN}}{\text{membrane}}$/KSCN(0.001M)//$KNO_3$(1M)//-

KCl(0.001M)/AgCl,Ag

The indicator electrode is a RADELKIS SCN^- specific ion electrode which utilizes a silicone rubber matrix.

SOURCE AND PURITY OF MATERIALS:

All reagents were of analytical purity, and were used as received. The solvents were repeatedly distilled.

ESTIMATED ERROR:

log K_{s0}: ±0.05 log units (authors).

Temperature: ±0.05°C.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Dimethyl sulfoxide; C_2H_6OS; [67-68-5] (3) Water; H_2O; [7732-18-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. August 1978

CRITICAL EVALUATION:

The solubility of AgSCN in mixtures of water and dimethyl sulfoxide has been studied at 298 K in two laboratories (1,2). Both studies employed a potentiometric titration method to calculate solubility products (1,2) and stability constants (1). Courtot-Coupez and Madec (1) report both K_{s0} and β_2 values as a function of mole fraction of dimethyl sulfoxide: the ionic strength of all solutions was maintained at about 0.11 mol dm^{-3}. Szarvas, Korondán, and Szabó (2) report only K_{s0} as a function of the volume % of dimethyl sulfoxide: they employed constant ionic strength solutions of about 0.001 mol dm^{-3}.

Visual inspection of both sets of data shows significant disagreement in the log K_{s0} values. Direct comparisons cannot be made since Szarvas et. al. report their solvent composition in the poorly defined units of volume %. If we assume their 80 vol % $(CH_3)_2SO$ mixture was prepared by mixing 20 volumes of water with 80 volumes of $(CH_3)_2SO$, the evaluator calculates a mole fraction of 0.503 for dimethyl sulfoxide at 298 K (density of $(CH_3)_2SO$ at 298.15 K is 1.0958 kg m^{-3}(3)). The value of log K_{s0} for this solvent composition is -11.34 which differs from the corresponding value of about -8.5 which was interpolated from the data of Courtot-Coupez and Madec. This difference is much too large to be attributed to differences in ionic strength, or the neglect of complex ions by Szarvas et. al. The K_{s0} values of Szarvas et. al. for most other water-organic solvent mixtures appear to be too low as seen in the compilations and critical evaluations found elsewhere in this volume. It would appear that these results are effected by some systematic error which is difficult to trace. It has been suggested in another evaluation that it is possible that the silicone rubber membrane used in the specific ion electrode is attacked by the organic solvent.

REFERENCES:

1. Courtot-Coupez, J.; Madec, C. *Bull. Soc. Chim. Fr.* 1971, 4621.
2. Szarvas, P.; Korondán, I.; Szabó, M. *Magy. Kem. Folyoirat.* 1974, *80*, 207.
3. Covington, A.K.; Dickinson, T. *Physical Chemistry of Organic Solvent Systems.* Plenum Press. London. 1973, Ch. 1.

COMPONENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]
(3) Tetraethylammonium thiocyanate; $(C_2H_5)_4NSCN$; [4587-19-3]
(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Courtot-Coupez, J.; Madec, C. *Bull. Soc. Chim. Fr.* 1971, 4621-5.

VARIABLES:
Composition of solvent at 25°C

PREPARED BY:
Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at about 0.11 mol dm^{-3}. The composition of the solvent is given in terms of the mole fraction, χ, of dimethyl sulfoxide. The solubility of AgSCN was described in terms of the soly product and the overall stability constant for the formation of $Ag(SCN)_2^-$.

$(CH_3)_2SO/\chi$	$-\log K_{s0}$	$\log \beta_2$
0	11.6	
0.1	10.7	
0.2	10.3	
0.3	9.7	
0.4	9.05	
0.6	8	7.9
0.7	7.8	7.9
0.8	7.6	8

K_{s0} units are $mol^2\ dm^{-6}$ and β_2 units are $mol^{-2}\ dm^6$.

AUXILIARY INFORMATION

METHOD:
The equilibrium constants were calcd from potentiometric titrn data using the cell

$Ag/Et_4NSCN(0.01M), Et_4NClO_4(0.1M)//ref$

where Et = C_2H_5, and the reference electrode is

$Et_4NClO_4(0.1M)//Et_4NClO_4(0.1M)$, -

$AgClO_4(0.01M)/Ag$

0.1M $AgClO_4$ was titrated into the thiocyanate soln and the equilibrium constants calculated directly from this data using the Nernst equation and material balance requirements.

SOURCE AND PURITY OF MATERIALS:
Doubly distilled water and pharmaceutical grade $(CH_3)_2SO$ were mixed prior to use. Et_4NSCN was prepared by dissolving Et_4NCl and KSCN in hot anhydr alcohol. The resulting KCl was removed by filtration and the Et_4NSCN recryst three times from alcohol and dried under vac at 80°C. $AgClO_4$ (BDH) was used as received, and Et_4NClO_4 was recrystallized.

ESTIMATED ERROR:
Nothing is specified, but precision of ±0.1 log units is assumed by the compiler.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Szarvas, P.; Korondán, I.; Szabó, M.

Magy. Kem. Foly. 1974, *80*, 207-11.

VARIABLES:

Solvent composition at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at approximately 0.001 mol dm^{-3}.

volume % $(CH_3)_2SO$	$-\log K_{s0}$	$10^{12}K_{s0}/mol^2\ dm^{-6}$
20	12.30	0.50
40	11.98	1.05
60	11.62	2.40
80	11.34	4.57

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$$\overset{SCN}{\text{membrane}}/KSCN(0.001M)//KNO_3(1M)//-$$

$$KCl(0.001M)/AgCl,Ag$$

The indicator electrode is a RADELKIS SCN^- specific ion electrode which utilizes a silicone rubber matrix.

SOURCE AND PURITY OF MATERIALS:

All reagents were of analytical purity, and were used as received. The solvents were repeatedly distilled.

ESTIMATED ERROR:

$\log K_{s0}$: ±0.05 log units (authors).

Temperature: ±0.05°C.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) 1,4-Dioxane; $C_4H_8O_2$; [123-91-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

August 1978

CRITICAL EVALUATION:

The three studies available (1-3) are not directly comparable as seen in the following descriptions. Kratohvil and Težak (1) report C_{Ag} as a function of [KSCN] at 293 K in a single mixed solvent containing 57.5 % p-dioxane by weight. Woolley reports K_{s0}°, β_1°, β_2°, and β_3° values at 298.15 K for a series of mixed solvents, and the C_{Ag} dependence on [SCN^-] is shown in graphical form. From Woolley's plot of log C_{Ag} against log [SCN^-], the evaluator interpolated (visually) log C_{Ag} values for a constant [SCN^-] = 1×10^{-3} mol dm^{-3}: the resulting log C_{Ag} values were plotted against the weight % of p-dioxane. Interpolating to a solvent composition of 57.5 % p-dioxane, it is found that $C_{Ag} = 3 \times 10^{-5}$ mol dm^{-3}. Kratohvil and Težak found that $C_{Ag} = 4 \times 10^{-5}$ mol dm^{-3} at 293 K for the same solvent composition and [SCN^-].

Szarvas et. al. (3) reported K_{s0} values as a function of volume % p-dioxane, and precisely how these compositions are defined is not known. In addition to this uncertainty, the calculated values of K_{s0} appear to be much too small. This may represent an error in this work which could be attributed to the neglect of the formation of complex ions. The results of Kratohvil and Težak, and of Woolley, confirm the existence of complex species. An additional source of error in this latter work (3) may be attributed to the attack on the silicone rubber matrix in the specific ion electrode by the p-dioxane.

REFERENCES:

1. Kratohvil, J.; Težak, B. *Croat. Chem. Acta* 1957, *29*, 63.
2. Woolley, E.M. *PhD Dissertation*. Brigham Young University. Provo, Utah. 1969.
3. Szarvas, P.; Korondán, I.; Szabó, M. *Magy. Kem. Folyoirat.* 1974, *80*, 207.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) 1,4-Dioxane; $C_4H_8O_2$; [123-91-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Croat. Chem. Acta* 1957, *29*, 63-6.

VARIABLES:

Concentration of KSCN at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ solution: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN. The composition of the solvent is 42.5% water and 57.5% p-dioxane by weight.

c_{Ag}/mol dm^{-3}	$[KSCN]_{tot}$/mol dm^{-3}
0.01	0.185
0.004	0.1125
0.001	0.037
0.0004	0.015
0.0001	0.0031
0.00004	0.00105
0.00002	0.00045
0.00001	0.00022

AUXILIARY INFORMATION

METHOD:

A turbidimetric method was used as described previously (1,2). KSCN was added to solutions of known $AgNO_3$ concentration, and the solubility of AgSCN obtained as the concentration of KSCN at which the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows Ag(SCN(s) + KNO_3$$

SOURCE AND PURITY OF MATERIALS:

Chemicals of analytical purity were used (presumably as received). p-Dioxane was distilled at least once from $AgNO_3$. The compiler assumes distilled water was used as in previous works (1,2).

ESTIMATED ERROR:

Nothing specified, but reproducibility probably ±2-3% as in previous works (1,2).

REFERENCES:

1. Schulz, K.; Težak, B. *Arhiv. Kem.* 1951, *23*, 200.
2. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) 1,4-Dioxane; $C_4H_8O_2$; [123-91-1]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.[1]

VARIABLES:

Concentration of KSCN and composition of solvent at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The total solubility of AgSCN, $C_{Ag}/\text{mol dm}^{-3}$, was fit by a relative least squares method (2) to

$$C_{Ag} = K^{o}_{s0}/([SCN^{-}]_{free}\gamma_{\pm}^{2}) + B + C\,[SCN^{-}]_{free} + D\,[SCN^{-}]_{free}/\gamma_{\pm}^{2} \qquad [1]$$

where $[SCN^-]_{free}$ is the (uncomplexed) concentration of SCN^- in soln, and B, C, D are constants. These constants are given in the table below along with the solubility product K^o_{s0}(AgSCN). Units of K^o_{s0} are $\text{mol}^2\ \text{dm}^{-6}$; for units of B, C, D see COMMENTS section. The composition of the solvent is given in weight percent p-dioxane.

% dioxane	$-\log K^o_{s0}$*	$-\log B$	$-\log C$	$-\log D$
8.20	11.18±0.44	6.32±0.09	3.16±0.06	2.57±0.30
20.47	10.70±0.70	6.16±0.07	2.98±0.06	1.78±0.06
28.49	10.87±1.10	6.33±0.07	3.03±0.06	0.52±0.05
40.75	11.55±0.35	6.11±0.14	2.21±0.09	----
48.75	11.31±0.41	6.02±0.15	1.78±0.09	----
60.73	11.27±1.00	5.85±0.25	1.40±0.11	----

*Average values based on equations [3] and [4] below. The errors given in this table are standard deviations.

AUXILIARY INFORMATION

METHOD:

Solutions were prepared isothermally at 25.00±0.01°C by rotating mixtures of KSCN with $AgClO_4$ containing ^{110}Ag. $[Ag^+]$ was determined by e.m.f. measurements using the cell

ind/AgSCN(satd), KSCN(xM)/ref [2]

where ind is an Orion model 94-16 sulfide ion electrode, // is a salt bridge of 1M KNO_3, and ref is a calomel electrode. The activity of Ag^+ was obtained from

$$\log a_{Ag^+} = mE + b \qquad [3]$$

Since $K^o_{s0} = (a_{Ag^+})(a_{SCN^-})$

$$\log a_{SCN^-} = -mE - (b - \log K^o_{s0}) \qquad [4]$$

The constants m and b were determined from measurements on solns with known a_{Ag^+}. $[SCN^-]$ was determined from mass balance considerations, $\gamma_\pm$ (the mean molar activity coefficient) from the extended Hückel equation,* and K^o_{s0} is

SOURCE AND PURITY OF MATERIALS:

All chemicals were reagent grade. Double dist water of specific conductance 1.5 x 10^{-6} ohm^{-1} cm^{-1} at 25°C was used. Gas chromatographic analysis of the dioxane showed the only impurity to be < 0.2% water. Electrodeposited Ag containing ^{110}Ag was dissolved in HNO_3 and fumed to near dryness three times in 72% $HClO_4$.

ESTIMATED ERROR:

C_{Ag}: σ < ±5%

E.m.f.: ±1 mV for $[SCN^-]<10^{-3}\text{mol dm}^{-3}$

±0.3 mV for $[SCN^-]>10^{-3}\text{mol dm}^{-3}$

$\gamma_\pm$: ±2%

REFERENCES:

1. Available as order No. 69-20,136 from University Microfilms, Ann Arbor, Mich., U.S.A. 48106.
2. Anderson, K.P.; Snow, R.L; *J. Chem. Educ.* 1967, *44*, 756.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) 1,4-Dioxane; $C_4H_8O_2$; [123-91-1]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. <u>1969</u>.[1]

COMMENTS AND/OR ADDITIONAL DATA:

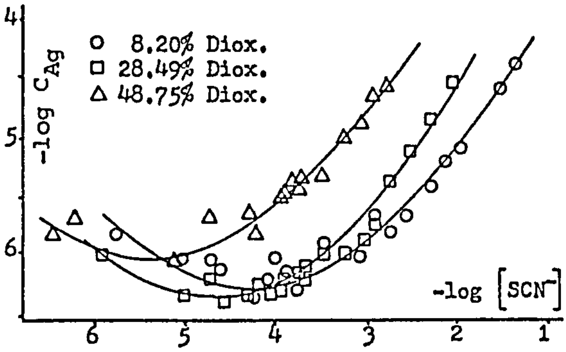
In the figures at the right, the points are the experimental results and the lines were calculated from equation [1]. The overall stability constants can be calculated from the data in the above table using the constants B, C, D and the relations

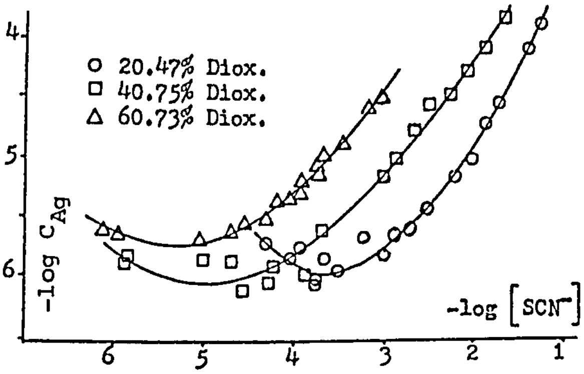
$$B/K^{o}_{s0} = \beta^{o}_{1} \text{ mol}^{-1} \text{ dm}^{3}$$

$$C/K^{o}_{s0} = \beta^{o}_{2} \text{ mol}^{-2} \text{ dm}^{6}$$

$$D/K^{o}_{s0} = \beta^{o}_{3} \text{ mol}^{-3} \text{ dm}^{9}$$

In the least squares fit to eq [1] $[SCN^-]_{free}$ was obtained from mass balance considerations for $[SCN^-] > 10^{-4}$ mol dm^{-3} and from eq [4] for $[SCN^-] < 10^{-4}$ mol dm^{-3}.





AUXILIARY INFORMATION

METHOD:

obtained as $(a_{Ag^+})(a_{SCN^-})$. K^{o}_{s0} was also determined from the intercept of eq [4]. For the determination of C_{Ag}, the equilibrium mixtures were centrifuged at 25.0±0.4°C and aliquots of soln taken for analysis. Evaporating the aliquots to dryness, C_{Ag} was determined in a thallium activated NaI scintillation detector.

*See compilation for Woolley's CH_3OH/H_2O study.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium perchlorate; $KClO_4$; [7778-74-7]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) 1,4-Dioxane; $C_4H_8O_2$; [123-91-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Szarvas, P.; Korondán, I.; Szabó, M.
Magy. Kem. Foly. 1974, *80*, 207-11.

VARIABLES:

Solvent composition at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at approximately 0.001 mol dm^{-3}.

volume % p-dioxane	$-\log K_{s0}$	$10^{14}K_{s0}/mol^2\ dm^{-6}$
20	12.30	50.1
40	12.69	20.4
60	13.24	5.75
80	14.09	0.81

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$$\overset{SCN}{\text{membrane}}/KSCN(0.001M)//KNO_3(1M)//-$$
$$KCl(0.001M)/AgCl,Ag$$

the indicator electrode is a RADELKIS SCN^- specific ion electrode which utilizes a silicone rubber matrix.

SOURCE AND PURITY OF MATERIALS:

All reagents were of analytical purity, and were used as received. The solvents were repeatedly distilled.

ESTIMATED ERROR:

log K_{s0}: ±0.05 log units (authors).

Temperature: ±0.05°C.

REFERENCES:

COMPONENTS: (1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Ethanol; C_2H_6O; [64-17-5] (3) Water; H_2O; [7732-18-5]	EVALUATOR: Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. September 1978

CRITICAL EVALUATION:
The solubility of AgSCN in excess SCN^- solns has been studied by direct measurements over a wide range of H_2O/C_2H_5OH compositions by Kratohvil and Težak at 293 K (1), and by Woolley at 298 K (2). Golub (3) reports a single point for c_{Ag} in pure ethanol containing 0.5326 mol dm^{-3} KSCN at 293 K. Szarvas et. al. (4) used an e.m.f. method to evaluate K_{s0} values at 298 K in a series of H_2O/C_2H_5OH mixtures, and at a constant ionic strength of ∿ 0.001 mol dm^{-3}. Macfarlane and Hartley (5) are the only investigators to report a value of K°_{s0} in pure ethanol: this value was obtained for 298.2 K from standard half-cell potentials.

Kratohvil and Težak used a turbidimetric method to determine c_{Ag} at 293 K in solutions containing $0.001 \leqslant$ KSCN $\leqslant 0.9$ mol dm^{-3}. Solvent compositions ranged from 30-90 wt % ethanol. These authors calcd K_{s2} and K_{s3} as averages based on their data for c_{Ag} in solutions of varying ionic strength. Woolley's K_{sn} values at 298 K are considerably smaller for equivalent solvent compositions: this tends to indicate some inconsistancy in one of the studies. Kratohvil and Težak's results for β_n (calcd from $\beta_n = K_{s0}/K_{sn}$) are subject to an error of unknown magnitude since the K_{s0} values were calcd from an empirical relation (6) which was concluded by this evaluator to be in error (see the evaluations and compilations for the $AgSCN/CH_3OH$ system). The c_{Ag} data were reproducible to within ±3%, and can be assumed to be accurate within this stated precision.

Woolley reports graphical c_{Ag} data as a function of the free $[SCN^-]$: the data have also been fit to a power series by a least squares method, and K_{sn} values for n = 0-3 were evaluated. It appears that Woolley's K_{s0} data are much too large based on comparisons with the values in H_2O/C_2H_5OH mixtures obtained in (1) and (3), and the value of log K°_{s0} = -14.33 in pure C_2H_5OH (5).

The K_{s0} values of Szarvas et. al. appear to be decreasing in a satisfactory manner as the ethanol content is increased, but the data are of little utility since the compositions of the solvent mixtures were reported in vague units of volume %.

In spite of the large exptl error estimated by the compiler for the K°_{s0} value obtained by Macfarlane and Hartley, their value of 4.7×10^{-3} mol^2 kg^{-2} in pure ethanol at 298.2 K appears to be reasonable. The large exptl error is understandable since pure ethanol has traditionally been a difficult solvent to work with. In addition, the Ag,AgSCN electrode has a history of poor reproducibility (e.g. see the critical evaluation and compilations for the aqueous systems).

REFERENCES:
1. Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243.
2. Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah, 1969.
3. Golub, A.M. *Zh. Obeschei. Khim.* 1956, *26*, 1837.
4. Szarvas, P.; Korondán, I.; Szabó, M. *Magy. Kem. Folyoirat.* 1974, *80*, 207.
5. Macfarlane, A.; Hartley, H. *Phil. Mag.* 1932, *13*, 425.
6. Ricci, J.E.; Davis, T.W. *J. Am. Chem. Soc.* 1940, *62*, 407.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Ethanol; C_2H_6O; [64-17-5]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

VARIABLES:

Concentration of KSCN and composition of solvent at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ solutions: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN. The composition of the H_2O/CH_3CH_2OH mixed solvents is given in weight percent alcohol

		$[KSCN]_{tot}$/mol dm^{-3}		
c_{Ag}/mol dm^{-3}	30% ethanol	50% ethanol	70% ethanol	90% ethanol
0.06		0.84		
0.04		0.68		
0.02		0.49		
0.01	0.43	0.35	0.285	
0.006		0.285		
0.004	0.29	0.28	0.19	
0.002		0.165		
0.001	0.145	0.11	0.0825	0.058
0.0006		0.082		0.04
0.0004	0.0925	0.0615	0.0455	0.029
0.0002		0.037		0.0165
0.0001	0.0425	0.022	0.01375	0.0091
0.00006		0.0135		0.005
0.00004	0.021	0.00875	0.0048	0.00345
0.00002	0.0115	0.00385	0.0021	0.00145
0.00001	0.00575	0.001375	0.0009	0.00062

AUXILIARY INFORMATION

METHOD:

Tubidimetric method. Solns of $AgNO_3$ and KSCN were mixed and at equilibrium the turbidity measured (establishment of equil not described, but measurements probably made within 1 h as described earlier (1)). The soly of AgSCN was calcd from the concentration of KSCN at which, for a given $[AgNO_3]$, the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3 \quad [1]$$

The disappearance of turbidity is due to complex ion formation. The authors assume only mononuclear complexes form according to

$$AgSCN(s) + (n-1)SCN^- \rightleftarrows Ag(SCN)_n^{1-n} \quad [2]$$

SOURCE AND PURITY OF MATERIALS:

All chemicals were analytically pure, and presumably used as received. Distilled water with a specific conductance of 2 x 10^{-6} ohm^{-1} was used. Commercial ethanol was distilled twice from $AgNO_3$.

ESTIMATED ERROR:

Solubility: nothing specified, but probably within ±2-3%.

Temperature: ±0.1°C.

REFERENCES:

1. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.
2. Ricci, J.E.; Davis, T.W. *J. Am. Chem. Soc.* 1940, *62*, 407.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-2]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Ethanol; C_2H_6O; [64-17-5]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

COMMENTS AND/OR ADDITIONAL DATA:

The equilibrium constants for reaction [2] were calculated from

$$\log K_{sn} = \log c_{Ag} - (n-1)[SCN^-]_{equil} \qquad [3]$$

where $[SCN^-]_{equil} = [KSCN]_{tot} - c_{Ag}$. Eq. [3] was applied to those experimental points in the concentration range where each complex predominates. The overall stability constants were calculated from

$$\beta_n = K_{sn}/K_{s0} \qquad [4]$$

The solubility product was calculated from the Ricci-Davis equation (2)

$$\log(K_{s0})_s \quad \log(K_{s0})_w - (484/a)(\varepsilon_s^{-1} - \varepsilon_w^{-1}) \qquad [5]$$

where ε is the dielectric constant, s and w refer to the mixed solvent and water, respectively, and "a" is an empirical constant identified as an ionic radius. Taking $(K_{s0})_w = 1 \times 10^{-12}$ $mol^2\ dm^{-6}$ and $\underline{a} = 2.7, 2.97, 3.41,$ and 4.03 for $\varepsilon_s = 62.6, 50.4, 39.1,$ and 29.0 respectively (cf. ref. 2), the following results were obtained:

wt %	ethanol (ε)	$10^{14}K_{s0}$	$[KSCN]_{tot}/mol\ dm^{-3}$	complex	K_{sn}	$10^{-11}\beta_n$
30	(62.6)	23	0.006 - 0.09	$Ag(SCN)_2^-$	0.0040	0.17
			0.1 - 0.4	$Ag(SCN)_3^{2-}$	0.060	2.6
50	(50.4)	6.0	0.004 - 0.04	$Ag(SCN)_2^-$	0.0060	1.0
			0.16 - 0.8	$Ag(SCN)_3^{2-}$	0.090	15
70	(39.1)	1.3	0.002 - 0.05	$Ag(SCN)_2^-$	0.0080	6.1
			0.08 - 0.3	$Ag(SCN)_3^{2-}$	0.11	85
90	(29.0)	0.22	0.003 - 0.016	$Ag(SCN)_2^-$	0.014	64

Equation [5] was derived for 25°C and the value of $(K_{s0})_w = 1.0 \times 10^{-12}$ is the K_{s0}^o value for 25°C (see the critical evaluation). Although the authors use ε values corresponding to 20°C, the derived K_{s0} and β_n are, at best, qualitative (compiler's comment). The units of the equilibrium constants are

$$K_{sn} = mol^{2-n}\ dm^{3(n-2)}$$

$$\beta_n = mol^{-n}\ dm^{3n}$$

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium perchlorate; $KClO_4$; [7778-74-7]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Ethanol; C_2H_6O; [64-17-5]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.[1]

VARIABLES:

Concentration of KSCN and composition of solvent at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The total solubility of AgSCN, C_{Ag}/mol dm^{-3}, was fit by a relative least squares method (2) to

$$C_{Ag} = K^o_{s0}/([SCN^-]_{free}\gamma_\pm^2) + B + C[SCN^-]_{free} + D[SCN^-]^2_{free}/\gamma_\pm^2 \qquad [1]$$

where $[SCN^-]_{free}$ is the (uncomplexed) concentration of SCN^- in soln, and B, C, D are constants. These constants are given in the table below along with the soly product, K^o_{s0}. Units of K_{s0} are $mol^2\ dm^{-6}$; for units of B, C, and D, see below. The composition of the solvent is given in weight percent ethanol.

% C_2H_5OH	$-\log K^o_{s0}$*	$-\log B$	$-\log C$	$-\log D$
0.00	11.17 ± 0.31	1.76 ± 0.06	3.83 ± 0.02	2.28 ± 0.03
9.67	11.74 ± 0.41	6.46 ± 0.06	3.64 ± 0.05	2.20 ± 0.04
19.86	11.18 ± 0.41	6.48 ± 0.12	3.40 ± 0.05	2.01 ± 0.04
34.47	11.45 ± 0.37	6.53 ± 0.06	3.14 ± 0.07	1.58 ± 0.12
42.15	11.23 ± 0.58	6.54 ± 0.13	2.93 ± 0.06	1.30 ± 0.08
54.20	10.86 ± 0.86	6.31 ± 0.29	2.56 ± 0.05	-----

*Average values based on equations [3] and [4] below. The errors in the table are standard deviations.

AUXILIARY INFORMATION

METHOD:

Solns were prepared isothermally at 25.00 ± 0.01°C by rotating mixtures of KSCN with $AgClO_4$ containing ^{110}Ag. Ag^+ concentrations were determined by e.m.f. measurements using the cell

ind/AgSCN(satd),KSCN(xM)//ref

where ind is an Orion model 94-16 sulfide ion electrode, // is a salt bridge of 1M KNO_3, and ref is a calomel electrode. The activity of Ag^+ is given by

$$\log a_{Ag^+} = mE + b \qquad [3]$$

or, since $K^o_{s0} = (a_{Ag^+})(a_{SCN^-})$,

$$\log a_{SCN^-} = -mE - (b - \log K^o_{s0}) \qquad [4]$$

The constants m and b were determined from measurements on solns with known a_{Ag^+}. $[SCN^-]$ was determined from mass balance considerations, $\gamma_\pm$ (the mean molar activity coefficient) from the extended Hückel equation,* and K^o_{s0} is obtained as $(a_{Ag^+})(a_{SCN^-})$. K^o_{s0} was also determined from the intercept

SOURCE AND PURITY OF MATERIALS:

All chemicals were reagent grade. Double dist water of specific conductivity < 1.5×10^{-6} $ohm^{-1}\ cm^{-1}$ at 25°C was used. Gas chromatographic analysis of the alcohol showed the only impurity to be <0.2% water. Electrodeposited Ag containing ^{110}Ag was dissolved in HNO_3 and fumed to near dryness three times in 72% $HClO_4$.

ESTIMATED ERROR:

C_{Ag}: $\sigma < \pm 5\%$
e.m.f.: ±1mV for $[SCN^-] < 10^{-3} mol/dm^3$
±0.3mV for $[SCN^-] > 10^{-3} mol/dm^3$
$\gamma_\pm$: ± 2 %

REFERENCES:

1. Available as order No. 69-20,136 from University Microfilms, Ann Arbor, Mich., U.S.A. 48106.
2. Anderson, K.P.; Snow, R.L. *J. Chem. Ed.* 1967, *44*, 756.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Ethanol; C_2H_6O; [64-17-5]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.

COMMENTS AND/OR ADDITIONAL DATA:

In the figures at the right, the points are the experimental results and the lines were calculated from equation [1].

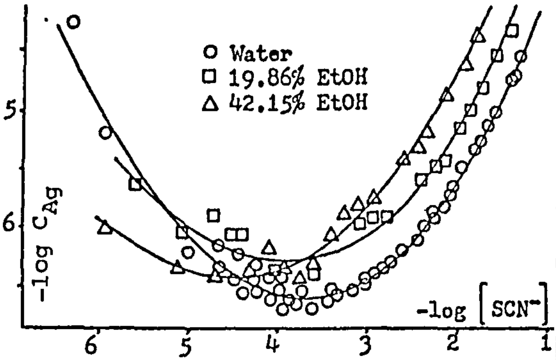
The stability constants can be calculated from the data in the above table using the constants B, C, and D, from:

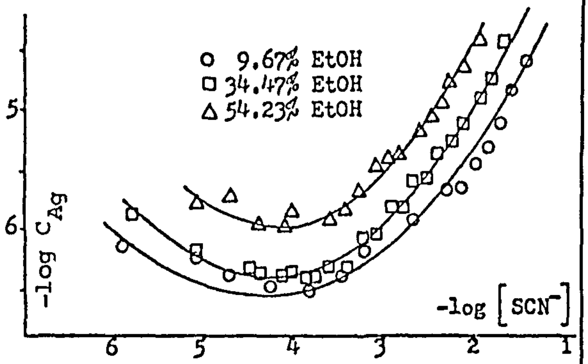
$$B/K_{s0}^{o} = \beta_1^{o}\ \mathrm{mol^{-1}\ dm^{3}}$$

$$C/K_{s0}^{o} = \beta_2^{o}\ \mathrm{mol^{-2}\ dm^{6}}$$

$$D/K_{s0}^{o} = \beta_3^{o}\ \mathrm{mol^{-3}\ dm^{9}}$$

In the least squares fit to Eq.[1] $[SCN^-]_{free}$ was obtained from mass balance considerations for $[SCN^-] > 10^{-4}\ \mathrm{mol\ dm^{-3}}$ and from Eq. [4] for $[SCN^-] < 10^{-4}\ \mathrm{mol\ dm^{-3}}$.





AUXILIARY INFORMATION

METHOD:

of equation [4]. For the determination of C_{Ag}, the equilibrium mixtures were centrifuged at 25.0 ±0.4°C, and aliquots of soln taken for analysis. Evaporating the aliquots to dryness, C_{Ag} was determined in a thallium activated NaI scintillation detector.

*See the compilation for the CH_3OH/H_2O system.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Potassium perchlorate; $KClO_4$; [7778-74-7] (3) Potassium thiocyanate; KSCN; [333-20-0] (4) Ethanol; C_2H_6O; [64-17-5] (5) Water; H_2O; [7732-18-5]	Szarvas, P.; Korondán, I.; Szabó, M. *Magy. Kem. Folyoirat.* 1974, *80*, 207-11.
VARIABLES:	PREPARED BY:
Solvent composition at 25°C	Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at ∿ 0.001 mol dm^{-3}.

Volume % CH_3CH_2OH	$-\log K_{s0}$	$10^{13}K_{s0}/mol^2\ dm^{-6}$
0	12.08	8.3
20	12.20	6.3
40	12.41	3.9
60	12.88	1.3
80	13.62	0.24

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$$\text{SCN}_{\text{membrane}}/\text{KSCN}(0.001\text{M})//\text{KNO}_3(1\text{M})//\text{-KCl}(0.001\text{M})/\text{AgCl,Ag}$$

The indicator electrode is a RADELKIS SCN^- specific ion electrode which utilizes a silicone rubber matrix.

SOURCE AND PURITY OF MATERIALS:

All reagents were of analytical purity, and were used without further purification. The solvents were repeatedly distilled.

ESTIMATED ERROR:

log K_{s0}: ±0.05 log units (authors)

Temperature: ±0.05°C

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Glycerol; $C_3H_8O_3$; [56-81-5]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Croat. Chem. Acta* 1957, *29*, 63-6.

VARIABLES:

Concentration of KSCN at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ solution: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN. The composition of the solvent is 43.0% H_2O and 57.0% glycerol by weight.

c_{Ag}/mol dm^{-3}	$[KSCN]_{tot}$/mol dm^{-3}
0.01	0.425
0.001	0.155
0.0001	0.0425
0.00004	0.023
0.00002	0.013
0.00001	0.007

AUXILIARY INFORMATION

METHOD:

A turbidimetric method was used as described previously (1,2). KSCN was added to solutions of known $AgNO_3$ concentration, and the solubility of AgSCN obtained as the concentration of KSCN at which the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3$$

SOURCE AND PURITY OF MATERIALS:

Chemicals of analytical purity were used (presumably as received). Glycerol was distilled at least once from $AgNO_3$. The compiler assumes distilled water was used as in previous works (1,2).

ESTIMATED ERROR:

Nothing specified, but reproducibility probably ±2-3% as in previous works (1,2).

REFERENCES:

1. Schulz, K.; Težak, B. *Arhiv. Kem.* 1951, *25*, 200.
2. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Methanol; CH_4O; [67-56-1]

(3) Water; H_2O; [7732-18-5]

EVALUATOR:

Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A.

August 1978

CRITICAL EVALUATION:

The two experimental studies available (1,2) are not readily comparable since they involve different temperatures, different solvent compositions, and different ionic media. Under these conditions, neither tentative or recommended values can be given.

Kratohvil and Težak (1) carefully measured the solubility of AgSCN in a 62% CH_3OH soln (by wt) at 293 K: the solubility was measured in excess KSCN solutions with varying ionic strength. They used a turbidimetric method, and their results are probably reproducible to within ±3%. The solubility data was used to calculate a value of $K_{s2} = 6 \times 10^{-3}$ which appears acceptable, but may be too high when compared to the value of 2×10^{-3} obtained by extrapolation of Woolley's 298 K data. The values for β_2 and β_3 are not considered reliable since they were calculated using a K_{s0} value which in turn was calculated from the Ricci-Davis equation (3): as discussed in the compilation, several significant errors were involved in the use of this empirical equation.

Woolley calculated K_{s0}^o and β_n^o values at 298 K in solutions of varying methanol content. Ionic concentrations were obtained from e.m.f. measurements, and the solubility of AgSCN obtained by radiochemical analysis. The data were fit by least squares to an equation yielding K_{s0}^o and standard formation constants for the mononuclear complexes AgSCN, $Ag(SCN)_2^-$, and $Ag(SCN)_3^{2-}$.

The stability constants calculated by Kratohvil and Težak are averages obtained from data points of varying ionic strength. The assumption that the formation constants are independent of ionic strength is probably valid for K_{s2}, but not for K_{s3}.

REFERENCES:

1. Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243.

2. Woolley, E.M. *PhD Dissertation*. Brigham Young University. Provo, Utah. 1969.

3. Ricci, J.E.; Davis, T.W. *J. Am. Chem. Soc.* 1940, *62*, 407.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Methanol; CH_4O; [67-56-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1954, *26*, 243-56.

VARIABLES: Concentration of KSCN at 20°C in a mixed water-methanol solvent containing 62% CH_3OH by weight

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ solution: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN.

c_{Ag}/mol dm^{-3}	$[KSCN]_{tot}$/mol dm^{-3}
0.01	0.36
0.001	0.115
0.0004	0.0625
0.0001	0.023
0.00004	0.0095
0.00002	0.0044
0.00001	0.00175

AUXILIARY INFORMATION

METHOD:

Turbidimetric method. Solns of $AgNO_3$ and KSCN were mixed and at equilibrium the turbidity measured (establishment of equil not described, but measurements probably made within 1 h as described earlier (1)). The soly of AgSCN was calcd from the concentration of KSCN at which, for a given $[AgNO_3]$, the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3 \quad [1]$$

The disappearance of turbidity is due to complex ion formation. The authors assume only mononuclear complexes form according to

$$AgSCN(s) + (n-1)SCN^- \rightleftarrows Ag(SCN)_n^{1-n} \quad [2]$$

SOURCE AND PURITY OF MATERIALS:

All chemicals were analytically pure, and presumably used as received. Distilled water with a specific conductance of 2 x 10^{-6} ohm^{-1} cm^{-1} was used. Commercial methanol (Merck, puriss) was distilled twice from $AgNO_3$.

ESTIMATED ERROR:

Solubility: nothing specified, but probably within ±2-3%.
Temperature: ±0.1°C.

REFERENCES:

1. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.
2. Ricci, J.E.; Davis, T.W. *J. Am. Chem. Soc.* 1940, *62*, 407.

COMPONENTS:	ORIGINAL MEASUREMENTS (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Potassium nitrate; KNO_3; [7757-79-1] (3) Potassium thiocyanate; KSCN; [333-20-0] (4) Methanol; CH_4O; [67-56-1] (5) Water; H_2O; [7732-18-5]	Kratohvil, J.; Težak, B. *Arhiv. Kem.* <u>1954</u>, *26*, 243-56.

COMMENTS AND/OR ADDITIONAL DATA:

The equilibrium constants for reaction [2] were calculated from

$$\log K_{sn} = \log c_{Ag} - (n-1)\log[SCN^-]_{equil} \qquad [3]$$

where

$[SCN^-]_{equil} = [KSCN]_{tot} - c_{Ag}$. Eq. [3] was applied to those experimental points in the concentration range where each complex predominates. The overall stability constants were calculated from

$$\beta_n = K_{sn}/K_{s0} \qquad [4]$$

The solubility product was calculated from the Ricci-Davis equation (2)

$$\log(K_{s0})_s = \log(K_{s0})_w - (484/a)\ (\varepsilon_s^{-1} - \varepsilon_w^{-1}) \qquad [5]$$

where ε_w and ε_s are the dielectric constants of water and the mixed solvent (80.4D and 50.4D, respectively), and "a" is an empirical constant identified with an ionic radius. Taking $(K_{s0})_w = 1 \times 10^{-12}$ mol^2 dm^{-6} and "a" = 2.97, the soly product in the mixed solvent, $(K_{s0})_s$, was found to equal 6.0×10^{-14} mol^2 dm^{-6}. With this estimated value and the values of K_{sn} calculated from eq [3], values of β_n were estimated using eq [4]. The results are given in the table below.

$[KSCN]_{tot}$/mol dm^{-3}	complex	K_{sn}	$10^{-12}\beta_n$
0.004 - 0.04	$Ag(SCN)_2^-$	0.0060	0.10
0.16	$Ag(SCN)_3^{2-}$	0.090	1.5

Eq [5] was derived for 25°C and the value of $(K_{s0})_w$ used was that for 25°C (see the critical evaluation). Although the values for ε are those for 20°C, the derived K_{s0} and β's are, at best, qualitative (compilers comment). The units for the equilibrium constants are:

$$K_{sn} = \text{mol}^{2-n}\ \text{dm}^{3(n-2)}$$

$$\beta_2 = \text{mol}^{-n}\ \text{dm}^{3n}$$

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Methanol; CH_4O; [67-56-1]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Woolley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.[1]

VARIABLES:

Concentration of KSCN and composition of solvent at 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The total solubility of AgSCN, C_{Ag}/mol dm^{-3}, was fit by a relative least squares method (2) to

$$C_{Ag} = K_{s0}^{o}/([SCN^-]_{free}\,\gamma_\pm^2) + B + C\,[SCN^-]_{free} + D\,[SCN^-]_{free}^2/\gamma_\pm^2 \qquad [1]$$

where $[SCN^-]_{free}$ is the (uncomplexed) concentration of SCN^- in soln, and B, C,D are constants. These constants are given in the table below along with the solubility product K_{s0}^{o}(AgSCN). Units of K_{s0}^{o} are $mol^2\ dm^{-6}$; for units of B,C,D see COMMENTS Section. The composition of the solvent is given in weight percent methanol.

% CH_3OH	$-\log K_{s0}^{o}$*	-log B	-log C	-log D
0.00	11.17±0.31	6.76±0.06	3.83±0.02	2.28±0.03
9.47	11.73±0.20	6.78±0.07	3.70±0.05	2.18±0.03
19.84	11.57±0.39	6.59±0.05	3.64±0.04	1.95±0.04
34.48	11.50±0.30	6.53±0.07	3.19±0.06	2.27±0.05
42.10	11.13±0.46	6.11±0.08	3.07±0.07	1.77±0.07
54.20	11.34±0.45	6.47±0.09	2.81±0.06	2.23±0.05

*Average values based on equations [3] and [4] below. The errors quoted in this table are standard deviations.

AUXILIARY INFORMATION

METHOD:

Solns were prepared isothermally at 25.00±0.01°C by rotating mixtures of KSCN with $AgClO_4$ containing ^{110}Ag. $[Ag^+]$ determined by e.m.f. measurements using the cell

$$\text{ind/AgSCN(satd), KSCN(xM)//ref} \qquad [2]$$

where ind is an Orion model 94-16 sulfide ion electrode, // is a salt bridge of 1M KNO_3, and ref is a calomel electrode. The activity of Ag^+ is given by

$$\log a_{Ag^+} = m\,E + b \qquad [3]$$

or, since $K_{s0}^{o} = a_{Ag}a_{SCN}$,

$$\log a_{SCN^-} = -mE - (b - \log K_{s0}^{o}) \qquad [4]$$

The constants m and b were determined from measurements on solns with known a_{Ag^+}. $[SCN^-]$ was determined from mass balance considerations, $\gamma_\pm$ (the mean molar activity coefficient) from the extended Hückel equation,* and K_{s0}^{o}

SOURCE AND PURITY OF MATERIALS:

All chemicals were reagent grade. Double dist water of specific conductance < 1.5 x 10^{-6} ohm^{-1} cm^{-1} at 25°C was used. Gas chromatographic analysis of the methanol showed the only impurity to be < 0.2% water. Electrodeposited Ag containing ^{110}Ag was dissolved in HNO_3 and fumed to near dryness three times in 72% $HClO_4$.

ESTIMATED ERROR:

C_{Ag}: σ<±5% (author)

E.m.f.: ±1 mV for $[SCN^-]<10^{-3}$mol dm^{-3}

±0.3 mV for $[SCN^-] > 10^{-3}$mol dm^{-3}

$\gamma_\pm$: ±2%.

REFERENCES:

1. Available as order No. 69-20,136 from University Microfilms, Ann Arbor, Mich., U.S.A. 48106.
2. Anderson, K.P.; Snow, R.L. *J. Chem. Educ.* 1967, *44*, 756.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium perchlorate; $KClO_4$; [7778-74-7]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Methanol; CH_4O; [67-56-1]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS: (continued)

Wooley, E.M. *PhD Dissertation.* Brigham Young University. Provo, Utah. 1969.

COMMENTS AND/OR ADDITIONAL DATA:

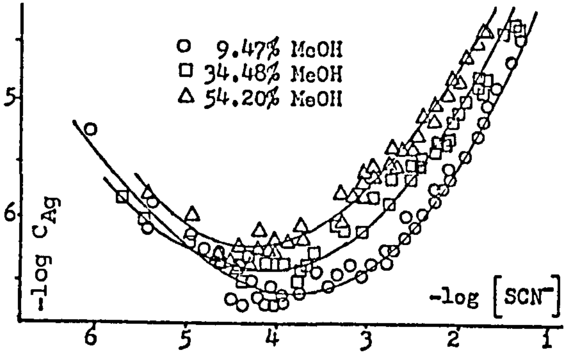
In the figure at the right, the points are the experimental results and the lines were calculated from equation 1. The overall stability constants can be calculated from the data in the above table using the constants B, C, D and the relations

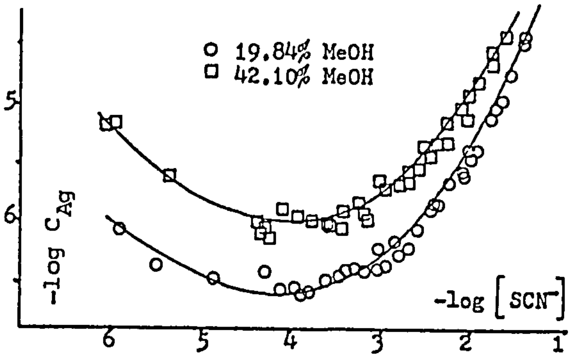
$B/K^o_{s0} = \beta^o_1 \text{ mol}^{-1} \text{ dm}^3$

$C/K^o_{s0} = \beta^o_2 \text{ mol}^{-2} \text{ dm}^6$

$D/K^o_{s0} = \beta^o_3 \text{ mol}^{-3} \text{ dm}^9$

In the least squares fit to eq [1] $[SCN^-]_{free}$ was obtained from mass balance considerations for $[SCN^-] > 10^{-4}$ mol dm^{-3} and from eq [4] for $[SCN^-] < 10^{-4}$ mol dm^{-3}.





AUXILIARY INFORMATION

METHOD:

is obtained as $(a_{Ag^+})(a_{SCN^-})$. K^o_{s0} was also determined from the intercept of eq [4]. For the determination of C_{Ag}, the equilibrium mixtures were centrifuged at 25.0±0.4°C and aliquots of soln taken for analysis. Evaporating the aliquots to dryness, C_{Ag} was determined in a thallium activated NaI scintillation detector.

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*The equation used was

$$\log y_{\pm} = -R\mu^{1/2}/(1 + Sd\mu^{1/2})$$

where $R = 354.5\ (\rho/\varepsilon^3)^{1/2}$; $S = 2.913 \times 10^8 (\rho/\varepsilon)^{1/2}$; $\mu = (1/2\rho)\sum c_i z_i$; $\underline{d}$ is the ion diameter taken as 0.305 nm; ρ is the density; and ε is the dielectric constant.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [1757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) 1-Propanol; C_3H_8O; [71-23-8]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Croat. Chem. Acta* 1957, *29*, 63-6.

VARIABLES:

Concentration of KSCN and solvent composition at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ solutions: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN. The composition of the H_2O/1-propanol mixed solvent is tabulated in terms of weight percent alcohol.

	$[KSCN]_{tot}$/mol dm^{-3}	
c_{Ag}/mol dm^{-3}	42.0% 1-propanol	75.0% 1-propanol
0.01	0.35	0.265
0.004	0.24	0.150
0.001	0.115	0.0675
0.0004	0.0615*	0.0325
0.0001	0.0215	0.00875
0.00004	0.009	0.00315
0.00001	0.00145	0.00055

*The original paper gives a value of 0.615 for this point which is obviously a typographical error.

AUXILIARY INFORMATION

METHOD:

A turbidimetric method was used as described previously (1,2). KSCN was added to solutions of known $AgNO_3$ concentration, and the solubility of AgSCN obtained as the concentration of KSCN at which the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3$$

SOURCE AND PURITY OF MATERIALS:

Chemicals of analytical purity were used (presumably as received). 1-Propanol was distilled at least once from $AgNO_3$. The compiler assumes distilled water was used as in previous works (1,2).

ESTIMATED ERROR:

Nothing specified, but reproducibility probably ±2-3% as in previous works (1,2).

REFERENCES:

1. Schulz, K.; Težak, B. *Arhiv. Kem.* 1951, *23*, 200.
2. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* 1953, *25*, 219.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) 2-Propanol; C_3H_8O; [67-63-0]

(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kratohvil, J.; Težak, B. *Croat. Chem. Acta* <u>1957</u>, *29*, 63-6.

VARIABLES:

Concentration of KSCN and solvent composition at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

$[KSCN]_{tot}$ is the total KSCN concn in the initial $AgNO_3$ solutions: therefore each solution contains KNO_3 in a concentration equal to that of AgSCN. The composition of the water/2-propanol mixed solvents is tabulated in terms of weight percent alcohol.

	$[KSCN]_{tot}$/mol dm^{-3}	
c_{Ag}/mol dm^{-3}	40.5% 2-propanol	71.0% 2-propanol
0.01	0.365	0.285
0.004	0.235	0.175
0.002	---	0.115
0.001	0.115	0.0725
0.0004	0.0625	0.035
0.0002	----	0.019
0.0001	0.02125	0.0085
0.00004	0.0095	0.00285
0.00002	-----	0.00105
0.00001	0.00155	0.0004

AUXILIARY INFORMATION

METHOD:

A turbidimetric method was used as described previously (1,2). KSCN was added to solutions of known $AgNO_3$ concentration, and the solubility of AgSCN obtained as the concentration of KSCN at which the turbidity disappears. The precipitation reaction is

$$AgNO_3 + KSCN \rightleftarrows AgSCN(s) + KNO_3$$

SOURCE AND PURITY OF MATERIALS:

Chemicals of analytical purity were used (presumably as received). 2-Propanol was distilled at least once from $AgNO_3$. The compiler assumes distilled water was used as previous works (1,2).

ESTIMATED ERROR:

Nothing specified, but reproducibility probably ±2-3% as in previous works (1,2).

REFERENCES:

1. Schulz, K.; Težak, B. *Arhiv. Kem.* <u>1951</u>, *23*, 200.
2. Vouk, V.B.; Kratohvil, J.; Težak, B. *Arhiv. Kem.* <u>1953</u>, *25*, 219.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium thiocyanate; KSCN; [333-20-0]
(3) Acetone; C_3H_6O; [67-64-1]

ORIGINAL MEASUREMENTS:

Golub, A.M. *Zh. Obeschei. Khim.* 1956, *26*, 1837-48.

VARIABLES:

Concentration of KSCN at 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Concentration units are mol dm^{-3}.

[KSCN]	c_{Ag}	K_{s2}
1	0.2931	0.4147
0.8	0.2420	0.4235
0.6	0.1658	0.3820
0.4	0.1141	0.3987
0.2	0.0577	0.4018

K_{s2} is the equilibrium constant for the reaction

$$AgSCN(s) + SCN^- \rightleftarrows Ag(SCN)_2^-$$

and the average value, calculated by the compiler, is

$$K_{s2} = 0.404 \pm 0.016$$

AUXILIARY INFORMATION

METHOD:

Excess AgSCN added to KSCN solns were equilibrated isothermally in sealed flasks with frequent shaking at 20°C. Solns were analysed gravimetrically for Ag by pptn of Ag_2S with CS_2. The ppt was filtered, washed with water, alcohol, ether, CS_2, alcohol, and ether, and dried at 90°C. The 0.8M satd soln was evaporated in a desiccator over $CaCl_2$ for 3 days: the solid phase analysed as $KSCN \cdot AgSCN \cdot 3C_3H_6O$. The equilibrium constant K_{s2} was calculated from

$$K_{s2} = [Ag(SCN)_2^-/]\{[KSCN]-[Ag(SCN)_2^-]\}$$

Plots of log $[AgSCN]_{sat}$ against log $[SCN^-]$ were linear with unit slope thereby indicating the only significant soluble species to be $Ag(SCN)_2^-$.

SOURCE AND PURITY OF MATERIALS:

C.p. grade KSCN was recrystallized, dried, and melted for 10-15 min. Solns of c.p. grade $AgNO_3$ and KSCN were mixed to ppt AgSCN which was filtered, washed, and dried in a desiccator over $CaCl_2$. Acetone was "distilled and dehydrated."

ESTIMATED ERROR:

Solubility: precision probably ±1-2% (compiler).
K_{s2}: $\sigma = \pm 0.02$ (compiler).
Temperature: not specified

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Potassium nitrate; KNO_3; [7757-79-1] (3) Potassium thiocyanate; KSCN; [333-20-0] (4) Acetonitrile; C_2H_3N; [75-05-8]	Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.05 mol dm^{-3}.

$$K_{s0} = 1.0 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

AUXILIARY INFORMATION

METHOD:	SOURCE AND PURITY OF MATERIALS:
A potentiometric titrn method was used which employed the cell Ag/KSCN(0.05M)//$AgNO_3$(0.014M)/Ag where // is a salt bridge containing a satd soln of tetraethylammonium picrate. 0.05M $AgNO_3$ was titrd into the KSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titrn.	Acetonitrile was purified by a conventional method (1). Analar grade $AgNO_3$ and KSCN were used as received.
COMMENTS AND/OR ADDITIONAL DATA:	ESTIMATED ERROR:
The titrn curve was not sharply defined. Precipitates appeared after 10-20% of the theoretical amount of 0.05M $AgNO_3$ was added. A well-defined inflection point was obtained at the end point, but very small inflections were observed around 10-25% of the titrn. The curve were treated as though $Ag(SCN)_2^-$ was not present.	Nothing specified, but precision probably $\leq \pm 10\%$ (compiler). REFERENCES: 1. Coetzee, J.F.; Cunningham, G.P.; McGuire, D.K.; Padmanabhan, G.R. *Anal. Chem.* 1962, *34*, 1139.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Tetrabutylammonium perchlorate; $(C_4H_9)_4NClO_4$; [1923-70-2]
(3) Tetrabutylammonium thiocyanate; $(C_4H_9)_4NSCN$; [3674-54-2]
(4) 1,2-Dimethoxyethane (diglyme); $C_4H_{10}O_2$; [110-71-4]

ORIGINAL MEASUREMENTS:

Caillet, A.; Demange-Guerin, G.;
J. Electroanal. Chem. Interfacial Electrochem. 1972, *40*, 187-96.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at ∿ 0.1 mol dm^{-3}. The data were reported in terms of the following equilibria occuring in the presence of ion-pairing:

$$AgSCN(s) + (C_4H_9)_4NClO_4 = AgClO_4 + (C_4H_9)_4NSCN$$

$$K'_{s0} = 1.6 \times 10^{-16} mol^2\ dm^{-6}$$

$$AgClO_4 + 2(C_4H_9)_4NSCN \rightleftarrows (C_4H_9)_4NAg(SCN)_2 + (C_4H_9)_4NClO_4$$

$$\beta'_2 = 1.0 \times 10^{16}\ mol^{-2}\ dm^6$$

In the absence of ion-pairing, the approximate results are:

$$AgSCN(s) = Ag^+ + SCN^- \qquad K_{s0} = 7.9 \times 10^{-19}\ mol^2\ dm^{-6}$$

$$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^- \qquad \beta_2 = 1.3 \times 10^{19}\ mol^{-2}\ dm^6$$

AUXILIARY INFORMATION

METHOD:

A potentiometric titrn method was used. The titration cell is given by

$$Ag/Bu_4NSCN(xM),Bu_4NClO_4(0.1M)//ref$$

where Bu = C_4H_9, and the reference electrode is assumed by the compiler to be identical to one described in a previous paper (1): i.e.

$$ref = AgClO_4(0.01M),Bu_4NClO_4(0.1M)/Ag$$

The concentration for x for Bu_4NSCN is not given, but is assumed to = 0.005 mol/L which is the value employed for the halides which are described in this paper. The equilibrium constants were calculated from the data corresponding to the various parts of the titrn curve where the different ionic species predominate.

SOURCE AND PURITY OF MATERIALS:

Nothing specified, but probably similar to that described earlier (1). Commercial Bu_4NClO_4 and anhydrous $AgClO_4$ were used. The solvent was refluxed in N_2 over Na for 4 h, and fractionated. Karl Fischer titration gave $[H_2O] = 0.005\ mol/dm^3$.

ESTIMATED ERROR:

Nothing specified. A precision ⩽ ±10% is assumed by the compiler.

REFERENCES:

1. Caillet, A.; Demange-Guerin, G. *J. Electroanal. Chem. Interfacial Electrochem.* 1972, *40*, 69.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Tetrabutylammonium perchlorate; $(C_4H_9)_4NClO_4$; [1923-70-2]

(3) Tetrabutylammonium thiocyanate; $(C_4H_9)_4NSCN$; [3674-54-2]

(4) 1,2-Dimethoxyethane (diglyme); $C_4H_{10}O_2$; [110-71-4]

ORIGINAL MEASUREMENTS: (continued)

Caillet, A.; Demange-Guerin, G.

J. Electroanal. Chem. Interfacial Electrochem. 1972, *40*, 187-96.

COMMENTS AND/OR ADDITIONAL DATA:

Since the dielectric constant of 1,2-dimethoxyethane is small (ε = 7.2 D at 25°C), ion-pairing effects are expected to be large. From the equilibrium constants given above, the authors derive the following relationships:

$$pK_{s0} = pK'_{s0} + pK_G(AgClO_4) + pK_G(Bu_4NSCN) - pK_G(Bu_4NClO_4)$$

$$\log\beta_2 = \log\beta'_2 + pK_G(AgClO_4) + 2pK_G(Bu_4NSCN) - pK_G(Bu_4NClO_4) - pK_G(Bu_4NAg(SCN)_2)$$

where K_G is the dissociation constant of the indicated ion-pair. The pK values for $AgClO_4$ and Bu_4NClO_4 (3.8 and 5.1, respectively) were obtained from a previous study (1). pK_G values for Bu_4NSCN and $Bu_4NAg(SCN)_2$ were both assumed to equal 3.5 (note: a typographical error in the paper incorrectly lists pK_G = 4.5).

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Dimethylacetamide; C_4H_9NO; [127-19-5]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.01 mol dm^{-3}. The data are reported in terms of the following equilibrium constants:

$$\log K_{s0}(AgSCN) = -10.5$$

$$\log K_{s0}(AgAg(SCN)_2) = -9.5$$

$$\log \beta_2 = 11.4$$

These constants correspond to the following equilibria:

$AgSCN(s) \rightleftarrows Ag^+ + SCN^-$ $K_{s0}(AgSCN)/mol^2\ dm^6$

$2AgSCN(s) \rightleftarrows Ag^+ + Ag(SCN)_2^-$ $K_{s0}(AgAg(SCN)_2)/mol^2\ dm^{-6}$

$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^-$ $\beta_2/mol^{-2}\ dm^6$

AUXILIARY INFORMATION

METHOD:

The equilibrium constants were determined by potentiometric titration using the cell

$$Ag/KSCN(0.01M)//AgNO_3(0.02M)/Ag$$

where // is a salt bridge containing a satd soln of tetraethylammonium picrate. 0.01M $AgNO_3$ was titrated into the KSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titration. The titration curve showed two well defined plateaus from which the equil constants β_2 and $K_{s0}(AgAg(SCN)_2)$ were calculated. The solubility product for AgSCN was calculated from

$$\log K_{s0} = 1/2 \log[K_{s0}(AgAg(SCN)_2)/\beta_2]$$

SOURCE AND PURITY OF MATERIALS:

Dimethylacetamide was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and KSCN were used as received.

ESTIMATED ERROR:

Nothing specified. A precision of ±0.1 log units is assumed by the compiler.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Dimethylformamide; C_3H_7NO; [68-12-2]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at 0.01 mol dm^{-3}.

$$K_{s0} = 3.2 \times 10^{-12}\ mol^2\ dm^{-6}$$

The titration curve showed two well defined plateaus corresponding to the reactions

$$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^- \qquad \beta_2$$

$$Ag^+ + Ag(SCN)_2^- \rightleftarrows 2AgSCN(s) \qquad \{K_{s0}(AgAg(SCN)_2)\}^{-1}$$

The experimental values for these two equilibria are

$$\beta_2 = 7.9 \times 10^{11}\ mol^{-2}\ dm^6$$

$$K_{s0}(AgAg(SCN)_2) = 1.0 \times 10^{-11}\ mol^2\ dm^{-6}$$

AUXILIARY INFORMATION

METHOD:

A potentiometric titrn method was used which employed the cell

$$Ag/KSCN(0.01M)//AgNO_3(0.024M)/Ag$$

where // is a salt bridge containing satd tetraethylammonium picrate. 0.01M $AgNO_3$ was titrd into the KSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titrn. The equilibrium constants β_2 and $K_{s0}(AgAg(SCN)_2)$ were calco from the titrn curve data corresponding to the regions between the two inflection points. The solubility product was calcd from

$$K_{s0} = \left[K_{s0}(AgAg(SCN)_2)/\beta_2\right]^{1/2}$$

SOURCE AND PURITY OF MATERIALS:

Dimethyl formamide was dried with type 4A molecular sieves and fractionally distilled twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and KSCN were used as received.

ESTIMATED ERROR:

Nothing specified. A precision $\leqslant \pm 10\%$ is assumed by the compiler.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. August 1978

CRITICAL EVALUATION:

Parker and co-workers (1) used potentiometric titration data to evaluate K_{s0} and β_2 in a constant ionic strength medium of 0.05 mol dm^{-3} at 298.15 K. Le Démézet et. al. (2) used a similar experimental technique to determine K_{s0}, β_2, β_3, β_{23}, and β_{34} under the following experimental conditions: the ionic strength was constant at about 0.11 mol dm^{-3}, and the temperature, which was not specified in the paper, was probably around 293 to 295 K. Parker's value of log K_{s0} = 7.1 at 298 K cannot be compared to the value of log K_{s0} = 7.6 obtained by Le Démézet et. al. due to the uncertainty in the temperature of this latter work.

Luehrs and Abate (3) determined the solubility of AgSCN in $AgNO_3$ solutions and find evidence for the presence of a single polynuclear species: Ag_2SCN^+. The stability constant for this species, β_{21},was calculated from the experimental solubility data and a value of log K_{s0} = -7.3: the authors did not evaluate this K_{s0} value, nor did they give a numerical value or quote a source. This value was calculated by the compiler using the solubility data and the reported values for β_{21}. The experimental temperature was about 297 K and a constant ionic strength medium of 1 mol dm^{-3} was employed. In the absence of molar activity coefficient data for 1 mol dm^{-3} solutions, the significance of this value for K_{s0} is not clear.

REFERENCES:

1. Alexander, R.; Ko, E.C.F.; Mac, Y.D.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703.
2. Le Démézet, M.; Madec, C.; L'Her, M. *Bull. Soc. Chim. Fr.* 1970, 365.
3. Luehrs, D.C.; Abate, K. *J. Inorg. Nucl. Chem.* 1968, *30*, 549.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.05 mol dm^{-3}. The data are reported in terms of the following equilibrium constants.

$$\log K_{s0}(\mathrm{AgSCN}) = -7.1$$

$$\log K_{s0}(\mathrm{AgAg(SCN)_2}) = -6.6$$

$$\log\beta_2 = 7.4$$

These constants correspond to the following equilibria:

$$\mathrm{AgSCN(s)} \rightleftarrows \mathrm{Ag^+ + SCN^-} \qquad K_{s0}(\mathrm{AgSCN})/\mathrm{mol^2\ dm^{-6}}$$

$$\mathrm{2AgSCN(s)} \rightleftarrows \mathrm{Ag^+ + Ag(SCN)_2^-} \qquad K_{s0}(\mathrm{AgAg(SCN)_2})/\mathrm{mol^2\ dm^{-6}}$$

$$\mathrm{Ag^+ + 2SCN^-} \rightleftarrows \mathrm{Ag(SCN)_2^-} \qquad \beta_2/\mathrm{mol^{-2}\ dm^6}$$

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$$\mathrm{Ag/KSCN(0.05M)//AgNO_3(0.01M)/Ag}$$

where // is a salt bridge consisting of a satd soln of tetraethylammonium picrate. 0.05M $AgNO_3$ was titrated into the KSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titrn.

The titrn curve showed two well defined plateaus from which the constants β_2 and $K_{s0}(\mathrm{AgAg(SCN)_2})$ were calcd. The soly product for AgSCN was calcd from

$$\log K_{s0}(\mathrm{AgSCN}) = 1/2 \log\{K_{s0}(\mathrm{AgAg(SCN)_2})/\beta_2\}$$

SOURCE AND PURITY OF MATERIALS:

Dimethyl sulfoxide was dried with type 4A molecular sieves and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and KSCN were used as received.

ESTIMATED ERROR:

Nothing specified. A precision of ±0.1 log units is assumed by the compiler.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Silver nitrate; $AgNO_3$ [7761-88-8]

(3) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]

(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Luehrs, D.C.; Abate, K. *J. Inorg. Nucl. Chem.* 1968, *30*, 549-53.

VARIABLES:

Concentration of $AgNO_3$ at about 24°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Concentration units are mol dm^{-3}. Total ionic strength is constant at 1.0 mol/dm^3.

$[AgNO_3]$	$[AgSCN]_{satd}$	K_{s21}
0.460	0.0394	0.094
0.238	0.0223	0.103
0.0977	0.0114	0.132
0.0677	0.00895	0.152
0.0463	0.00686	0.174

K_{s21} is the equilibrium constant for the reaction

$$AgSCN(s) + Ag^+ \rightleftarrows Ag_2SCN^+$$

and was calculated by the compiler from

$$K_{s21} = [Ag_2SCN^+]/([AgNO_3] - [Ag_2SCN^+])$$

The overall stability constant for the reaction

$$2Ag^+ + SCN^- \rightleftarrows Ag_2SCN^+$$

is given by the authors as

$$\beta_{21} = 2.51 \times 10^6 \text{ mol}^{-2} \text{ dm}^6$$

AUXILIARY INFORMATION

METHOD:

A turbidimetric method was used. $AgNO_3$ solns were titrated with dilute KSCN solns until a faint turbidity was observed. At least 0.00003M AgSCN was required to give a satisfactory end-point. $(C_2H_5)_4NClO_4$ was used to maintain the ionic strength of all solns at 1.0M. The authors find that the only complex present is Ag_2SCN^+ so that the overall stability constant was calcd from a least squares fit to

$$[SCN^-] = K_{s0}\{[Ag^+]^{-1} + [Ag^+]\beta_{21}\}$$

The source of K_{s0}(AgSCN) is not given. However an estimated value can be obtained using the relation

$$K_{s0} = K_{s21}/\beta_{21}$$

Using this relation the compiler calculates

$$K_{s0}(AgSCN) = (5.2\pm1.3) \times 10^8 \text{mol}^2 \text{ dm}^{-6}$$

SOURCE AND PURITY OF MATERIALS:

Anhyd commercial $(CH_3)_2SO$ was passed through a column of activated alumina. $AgNO_3$ dried at 110°C, and N.F. grade KSCN dried under vac at 80°C. KSCN was found to melt at 175°C (uncor). Tetraethylammonium perchlorate was pptd from $HClO_4$ and tetraethylammonium bromide: it was recrystallized from water until free of Br^-.

ESTIMATED ERROR:

Solubility: precision probably ±1% (compiler)

β_{21}: ±20% (authors); ±25% (compiler)

Temperature: ±1°C

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]

(3) Tetraethylammonium thiocyanate; $(C_2H_5)_4NSCN$; [4587-19-3]

(4) Dimethyl sulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Le Démézet, M.; Madec, C.; L'Her, M.

Bull. Soc. Chim. Fr. 1970, 365-9.

VARIABLES:

One temperature: probably 22°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is constant at ∿ 0.11 mol dm^{-3}. The solubility of AgSCN in $(CH_3)_2SO$ is governed by the following equilibria:

$AgSCN(s) \rightleftarrows Ag^+ + SCN^-$	$K_{s0} = 2.5 \times 10^{-8}$ $mol^2\ dm^{-6}$
$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^-$	$\beta_2 = 2.5 \times 10^8$ $mol^{-2}\ dm^6$
$Ag^+ + 3SCN^- \rightleftarrows Ag(SCN)_3^{2-}$	$\beta_3 = 4.0 \times 10^7$ $mol^{-3}\ dm^9$
$2Ag^+ + 3SCN^- \rightleftarrows Ag_2(SCN)_3^-$	$\beta_{23} = 7.9 \times 10^{15}$ $mol^{-4}\ dm^{12}$
$3Ag^+ + 4SCN^- \rightleftarrows Ag_3(SCN)_4^-$	$\beta_{34} = 3.2 \times 10^{23}$ $mol^{-6}\ dm^{18}$

Nowhere in the paper do the authors state the experimental temperature. Since they use the factor 0.058 in the Nernst equation, the compiler assumes that this corresponds to room temperature (22°C) as described in a previous paper (1). The factor 2.3RT/F = 0.0586 at 22°C whereas the authors use their experimental value (1) of the Nernst slope. The ionic strength is about 0.11M and the uncertainty is due to the uncertainty in the concentration of the $AgClO_4$ titrant (a 0.05M soln was used in ref. 1).

AUXILIARY INFORMATION

METHOD:

The solubility product and stability constants were determined from potentiometric titrn data using the cell

$$Ag/Et_4NSCN(0.01M), Et_4NClO_4(0.1M)//-$$
$$LiCl(0.1M),\ AgCl_2^-(0.001M)/Ag$$

where Et = C_2H_5. The thiocyanate solution was titrated with $AgClO_4$ solution (probably 0.05M). The various equilibrium constants were determined from data corresponding to those parts of the titrn curve where each species predominates.

SOURCE AND PURITY OF MATERIALS:

Commercial Et_4NClO_4, KSCN, Et_4NCl, and $(CH_3)_2SO$ were used, but no details on purification are given. Et_4NSCN was prepared by dissolving KSCN and Et_4NCl in alcohol and separating the soln from the insoluble KCl. It is likely that all reagents were purified as described in reference 1.

ESTIMATED ERROR:

Nothing specified, but a precision ⩽ ±10% for all equilibrium constants is assumed by the compiler.

REFERENCES:

1. Courtot-Coupez, J.; L'Her, M. *Bull. Soc. Chim. Fr.* 1969, 675.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Lithium thiocyanate; LiSCN; [556-65-0]

(3) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Macfarlane, A.; Hartley, H. *Phil. Mag.* <u>1932</u>, *13*, 425-43.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

E.m.f. measurements were carried out for the cell

$$\underset{c_1}{\mathrm{Ag,AgCl/LiCl}}\ //\ \underset{c_1}{\mathrm{LiClO_4}}//\underset{c_2}{\mathrm{AgClO_4}}\mathrm{/Ag} \qquad [1]$$

The following results were obtained:

c_1 $(=c_2)$/mol kg^{-1}	E_j	E_1/V electrolytic	granular I	granular II
0.01	-0.0101	0.5622	---	0.5638*
0.01	-0.0101	0.5626	0.5626	-----
0.005	-0.0065	0.5311	---	0.5328*

*See COMMENTS section

Combining the e.m.f. data from cell [1] with that of cell [2] (E_2 = 0.0157 V, E_j = +0.0075 V), the authors were able to calculate the thermodynamic value for the solubility product of AgSCN.

$$\mathrm{Ag,AgSCN}\ /\ \underset{0.01m}{\mathrm{LiSCN}}\ //\ \underset{0.01m}{\mathrm{LiCl}}\ /\ \mathrm{AgCl,Ag} \qquad [2]$$

The authors reported

$$K^{\circ}_{s0}(\mathrm{AgSCN}) = 4.7 \times 10^{-15}\ \mathrm{mol^2\ kg^{-2}}$$

AUXILIARY INFORMATION

METHOD:

Details on measuring apparatus are referred to a previous paper (1). A single measurement was reported on cell [3]: E_3 = 0.1930 V which was said to

$$\mathrm{Pt,H_2/HCl(0.01m)/AgCl,Ag} \qquad [3]$$

agree with previous av value of 0.1940 V(2). Liquid junction potentials were calcd from eq. [4] where Λ is the equiv

$$E_j = (RT/F)\ln(\Lambda_1/\Lambda_2) \qquad [4]$$

conductivity in ohm^{-1} cm^2 mol^{-1}. The results at 25°C are: in 0.01m soln, $\Lambda(LiCl)$ = 27.6, Λ (LiSCN) = 37.0, $\Lambda(LiClO_4)$ = 38.9, $\Lambda(AgClO_4)$ = 37.0; in 0.005m soln, $\Lambda(LiCl)$ = 29.4, Λ $(LiClO_4)$ = 38.3, Λ $(AgClO_4$ = 38.4. All activities were calcd assuming $\gamma_{\pm}$ is the same as that for 0.01m HCl (i.e. $\gamma_{\pm}$ = 0.518) as determined previously (2). The soly product was calcd from

$$\ln K^{\circ}_{s0} = (E^{\circ}_{Ag,AgSCN} - E^{\circ}_{Ag,Ag^+})/(RT/F) \qquad [5]$$

SOURCE AND PURITY OF MATERIALS:

Ethanol was prepd by the method of McKelvy (3). Two types of Ag electrodes were used: one is a Pt grid onto which Ag was deposited electrolytically, and a granular Ag electrode described as granular I prepd by reduction of $AgNO_3$ with ammonium formate, and granular II prepd by reduction of $AgNO_3$ with ferrous sulfate. No description of the prep of Ag,AgCl electrode is given, and presumably this information is given in (2).

ESTIMATED ERROR:

K_{s0}: σ = ±1.3 x 10^{-15} mol^2 kg^{-2} (compiler)

Temperature: ±0.01°C

REFERENCES:

1. Nonhebel, G.; Hartley, H. *Phil. Mag.* <u>1925</u>, *1*, 729.
2. Woolcock, J.W.; Hartley, H. *Phil. Mag.* <u>1928</u>, *5*, 1133.
3. McKelvy, *Bull. Bur. Stnds.* <u>1913</u>, *9*, 327.

COMPONENTS:	ORIGINAL MEASUREMENTS: (continued)
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Lithium thiocyanate; LiSCN; [556-65-0] (3) Ethanol; C_2H_6O; [64-17-5]	Macfarlane, A.; Hartley, H. *Phil. Mag.* 1932, *13*, 424-43.

COMMENTS AND/OR ADDITIONAL DATA:

The value of the standard half-cell potentials required for use in eq [5] probably contain a fairly large exptl error. The stnd potentials required are those corresponding to the following cells:

$$\mathrm{Pt,H_2(1\ atm)/H^+(a = 1),\ Ag^+(a = 1)/Ag} \qquad [6]$$

and

$$\mathrm{Pt,H_2(1\ atm)/H^+(a = 1),\ SCN^-(a = 1)/AgSCN,Ag} \qquad [7]$$

E^o_6 and E^o_7 are denoted by E^o_{Ag,Ag^+} and $E^o_{Ag,AgSCN}$, respectively. The standard potential for cell [1] was calcd by the authors from

$$E^o_1 = E_1 - (2RT/F)\ \ln(m\gamma_\pm) + E_j \qquad [8]$$

and

$$E^o_{Ag,Ag^+} = E^o_1 - 0.0759 \qquad [9]$$

where 0.0759 V is the value of E^o_3 (2). The authors claim that the e.m.f.'s resulting from the use of granular II type electrodes (marked with an asterisk in the above table) are to be preferred due to the absence of surface strain: they report a value of $E^o_{Ag,Ag^+} = 0.749$ V. Using the two E_1 values obtained with the granular II electrode, the compiler obtains, from eqs [8] and [9] $E^o_{Ag,Ag^+} = 0.752 \pm 0.006$ V.

For cell [2], the authors used

$$E^o_2 = E_2 - (2RT/F)\ \ln(m\gamma_\pm) \qquad [10]$$

and

$$E^o_{Ag,AgSCN} = 0.1940 - E^o_2 \qquad [11]$$

where 0.1940 V is the value found previously (2) for cell [3], and the value of 0.1930 V found in the present work is ignored. The authors do not report any value for $E^o_{Ag,AgSCN}$, but instead report only K_{s0}. From eqs [10] and [11], the compiler calculates $E^o_{Ag,AgSCN} = 0.996$ V which, when used with $E^o_{Ag,Ag^+} = 0.7522$ V in eq [5], gives $K^o_{s0} = 4.0 \times 10^{-15}\ \mathrm{mol^2\ kg^{-2}}$ The uncertainties due to the choice of E_1 values for use in eq [8], the use of the E_3 value from previous work which differed by +1mV from the present value, and the uncertainties due to $\gamma_\pm$ and E_j all indicate a fairly large exptl error. Taking the standard deviation of ±6 mV computed by the compiler for E^o_{Ag,Ag^+}, and assuming a similar error in $E^o_{Ag,AgSCN}$, the compiler computes a total standard deviation of $\sigma = [2(0.006)^2]^{1/2} = \pm 0.0084$ V. This total error was applied to the E^o's in eq [5] to compute the standard deviation in K_{s0} which is given in the ESTIMATED ERROR section.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium thiocyanate; KSCN; [333-20-0]
(3) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Golub, A.M. *Zh. Obeschei. Khim.* 1956, *26*, 1837-48.

VARIABLES:

One temperature: 20°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

In 0.5326 mol dm^{-3} KSCN solution the solubility of AgSCN is

$$c_{Ag} = 0.00166 \text{ mol dm}^{-3}$$

AUXILIARY INFORMATION

METHOD:

The satd soln was prepared isothermally at 20°C by placing excess AgSCN in a soln of KSCN which was equilibrated with frequent shaking. The soln was analysed gravimetrically for Ag by precipitating Ag_2S with CS_2. The ppt was filtered, washed with water, alcohol, ether, CS_2, alcohol, and ether and dried at 90°C.

SOURCE AND PURITY OF MATERIALS:

C.p. grade KSCN was recrystallized, dried and melted for 10-15 min. Solns of c.p. grade $AgNO_3$ and KSCN mixed to ppt AgSCN which was filtered, washed, and dried in a desiccator over $CaCl_2$. The ethanol was "distilled and dehydrated."

ESTIMATED ERROR:

Nothing is specified, but the precision in the soly is probably around ±2-3%.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium perchlorate; $KClO_4$; [7778-74-7]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Ethylene glycol; $C_2H_6O_2$; [107-21-1]

ORIGINAL MEASUREMENTS:

Breant, M.; Georges, J. *Bull. Soc. Chim. Fr.* 1972, 382-6.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The ionic strength is probably close to 0.1 mol dm^{-3}

$$\log K_{s0}(\text{AgSCN}) = -13.0 \pm 0.3$$

AUXILIARY INFORMATION

METHOD:

The solubility product was determined from potentiometric titrn data using the cell

Ag/KSCN(xM)//KCl(satd), AgCl(satd)/Ag

The initial [KSCN] is presumed by the compiler to equal 0.01 and titrant is assumed to be 0.1M $AgClO_4$.

COMMENTS AND/OR ADDITIONAL DATA

The authors do not state the initial concentrations of KSCN or $AgClO_4$, or if a constant ionic strength was maintained. In addition to the values assumed above, it is probable that 0.1 $LiClO_4$ was used to maintain a const ionic strength as was reported for the Hg^{2+} studies which are also described in this paper. Although the experimental temp was 25°C, a value of 0.058 V was used for the Nernst slope since this was the slope obtained in standardization experiments.

SOURCE AND PURITY OF MATERIALS:

Ethylene glycol (Erba, R.P. grade) was distilled under vacuum. The following salts were used (presumably as received): KSCN (R.P., Prolabo); $AgClO_4$ (Schuchardt); $LiClO_4$ (G.F. Smith). No other details were given.

ESTIMATED ERROR:

Standard deviation in K_{s0} calculated by the authors is given above. No other information given.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KSCN; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0]
(5) Tetraethylammonium thiocyanate; $(C_2H_5)_4NSCN$; [4587-14-3]
(6) Formamide; CH_3NO; [75-12-7]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One Temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.01 mol dm^{-3}.

$$\log K_{s0}(AgSCN) = -9.9$$

AUXILIARY INFORMATION

METHOD:

The solubility product was determined from potentiometric titration data using the cell

$$Ag/MSCN(0.01M)//AgNO_3(0.01M)/Ag$$

where // is a salt bridge containing a satd soln of tetraethylammonium picrate, and MSCN is either KSCN or $(C_2H_5)_4NSCN$. 0.01M $AgNO_3$ was titrd into the MSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titration.
The titration curves showed only one inflection point indicating that the formation of $Ag(SCN)_2^-$ is negligible under the given experimental conditions.

SOURCE AND PURITY OF MATERIALS:

Formamide was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and KSCN were used as received. Tetraethylammonium thiocyanate was prepared from the bromide and KSCN, recrystallized from an organic solvent, washed with ether, and dried in vacuum at 20-80°C.

ESTIMATED ERROR:

Nothing specified, but a precision of ±0.1 log units is assumed by the compiler.

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Potassium nitrate; KNO_3; [7757-79-1]

(3) Potassium thiocyanate; KSCN; [333-20-0]

(4) Hexamethylphosphorotriamide; $C_6H_{18}N_3OP$; [680-31-9]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.1 mol dm^{-3}. The data are reported in terms of the following equilibrium constants

$$\log K_{s0}(AgSCN) = -7.4$$

$$\log K_{s0}(AgAg(SCN)_2) = -5.1$$

$$\log\beta_2 = 9.7$$

These constants correspond to the following equilibria:

$AgSCN(s) \rightleftarrows Ag^+ + SCN^-$ $K_{s0}(AgSCN)/mol^2\ dm^{-6}$

$2AgSCN(s) \rightleftarrows Ag^+ + Ag(SCN)_2^-$ $K_{s0}(AgAg(SCN)_2)/mol^2\ dm^{-6}$

$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^-$ $\beta_2/mol^{-2}\ dm^6$

AUXILIARY INFORMATION

METHOD:

The equil constants were determined from potentiometric titrn data using the cell

$Ag/KSCN(0.10M)//AgNO_3(0.01M)/Ag$

where // is a salt bridge consisting of a satd soln of tetrethylammonium picrate. 0.10M $AgNO_3$ was titrated into the KSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titrns.

The titration curve showed two well defined plateaus from which the constants β_2 and $K_{s0}(AgAg(SCN)_2)$ were calculated. The solubility product for AgSCN was calculated from

$$\log K_{s0}(AgSCN) = \tfrac{1}{2}\log\left\{K_{s0}(AgAg(SCN)_2)/\beta_2\right\}$$

SOURCE AND PURITY OF MATERIALS:

The solvent was dried with type 4A molecular sieves, and fractionated twice under a reduced pressure of dry N_2. Analar grade $AgNO_3$ and KSCN were used as received.

ESTIMATED ERROR:

Nothing specified. A precision of ±0.1 log units in the equilibrium constants is assumed by the compiler.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Methanol; CH_4O; [67-56-1]	Mark Salomon, U.S. Army Electronics Command, Fort Monmouth, NJ, U.S.A. August 1978

CRITICAL EVALUATION:

Buckley and Hartley (1) were the first to evaluate K_{s0}^{o}(AgSCN) using an e.m.f. method in which the standard electrode potential for the Ag,AgSCN half-cell was evaluated. The resulting value at 298.15 K is

$$K_{s0}^{o}(\text{AgSCN}) = 1.8 \times 10^{-14}\ \text{mol}^2\ \text{kg}^{-2}\quad\text{, or}\ \log K_{s0}^{o}(\text{AgSCN}) = -13.7$$

There are a number of sources of error in the evaluation of this K_{s0}^{o}: unpublished data for ion mobilities were used to evaluate liq junction potentials; e.m.f. values were reported to an accuracy of 0.1 mV when it is apparent that the reproducibility is no better than ±1 mV; the mean molal activity coeff, $\gamma_\pm$, for 0.01 m $AgNO_3$ is assumed to be identical to that for 0.01 m HCl; similarly $\gamma_\pm$ for NaCl solns are assumed to be identical to those for equal concns of HCl. The std deviation in K_{s0}^{o} based solely on a reproducibility of ±1mV is $\geqslant$ ±4%, and the total error due to the remaining sources of uncertainty is probably at least ±10%.

Parker and co-workers (2) determined K_{s0} at 298.15 K in a constant ionic strength medium of 0.01 mol dm^{-3}. Their result is

$$K_{s0}(\text{AgSCN}) = 1.3 \times 10^{-4}\ \text{mol}^2\ \text{dm}^{-6},\quad\text{or}\quad \log K_{s0}(\text{AgSCN}) = -13.9$$

Correcting for activity effects using the Davies equation (3)

$$\log y_\pm = -A\mu^{1/2}/(1 + \mu^{1/2}) + 0.3A\mu = -0.167$$

The evaluator obtains the following result for the stnd equil constant:

$$\log K_{s0}^{o} = \log K_{s0} + 2\log y_\pm = -14.2$$

Converting this stnd value from a volume to a weight basis,

$$\log(K_{s0}^{o}/\text{mol}^2\text{kg}^{-2}) = \log(K_{s0}^{o}/\text{mol}^2\text{dm}^{-6}) - 2\log d_o = -14.0$$

In these calculations, the Debye-Hückel A factor (1.895 $\text{mol}^{-1/2}\text{dm}^{1.5}$) and the density of methanol (d_o = 0.7866 kg m^{-3}) were taken from reference 4.

Tentative Value of K_{s0}^{o}(AgSCN) at 298.15 K

Due to the large experimental errors associated with the two K_{s0}^{o} values, a tentative value appears more appropriate than a recommended one. Taking the mean K_{s0}'s and combining the probable experimental error of ±10% with the deviation from the mean, we have

$$\log(K_{s0}^{o}/\text{mol}^2\ \text{kg}^{-2}) = -13.9 \pm 0.3$$

$$\log(K_{s0}^{o}/\text{mol}^2\ \text{dm}^{-6}) = -14.1 \pm 0.3$$

REFERENCES:

1. Buckley, P.S.; Hartley, H. *Phil. Mag.* 1928, *8*, 320.
2. Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703.
3. Davies, C.W. *Ion Association*. Butterworths. London. 1962.
4. Covington, A.K.; Dickinson, T. *Physical Chemistry of Organic Solvent Systems*. Plenum Press. London. 1973, ch. 1.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium thiocyanate; NaSCN; [540-72-7]

(3) Methanol; CH_4O; [67-56-1]

ORIGINAL MEASUREMENTS:

Buckley, P.S.; Hartley, H.

Phil. Mag. 1928, *8*, 320-41.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The solubility product was determined from standard electrode potentials of the following cells:

$$\mathrm{Pt,H_2/HCl(a=1)\ //\ NaSCN(a=1)/AgSCN,Ag} \qquad E^{o}_{\mathrm{AgSCN,Ag}} \qquad [1]$$

$$\mathrm{Pt,H_2/HCl(a=1)\ //\ AgClO_4(a=1)/Ag} \qquad E^{o}_{\mathrm{Ag,Ag^+}} \qquad [2]$$

where a = 1 represents the hypotehtical 1 molal reference state. The solubility product was calculated from the relation

$$\log K^{o}_{s0} = (E^{o}_{\mathrm{AgSCN,Ag}} - E^{o}_{\mathrm{Ag,Ag^+}})F/2.3RT$$

The results of the measurements (see below) are:

$$K^{o}_{s0}(\mathrm{AgSCN}) = 1.8 \times 10^{-14}\ \mathrm{mol^2\ kg^{-2}}$$

$$c_{\mathrm{Ag}} = (K^{o}_{s0})^{1/2} = 1.3 \times 10^{-7}\ \mathrm{mol\ kg^{-1}}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

To evaluate the E^{o}'s of cells [1] and [2] the authors made e.m.f. measurements on the following cells:

$\mathrm{Ag,AgCl/NaCl(0.01m)//NaClO_4(0.01m)//}$ -
4.4mV 1.1mV
$\mathrm{AgClO_4(0.01m)/Ag}$ [3]

$\mathrm{Ag,AgSCN/NaSCN(0.02m)//NaCl(0.02m)//}$ -
2.6mV 1.9mV
$\mathrm{NaCl(0.1m)/Hg_2Cl_2,Hg}$ [4]

and

$\mathrm{Ag,AgCl/NaCl(0.1m)/Hg_2Cl_2,Hg}$ [5]

The liq junction potentials are listed below the symbols //. To relate the e.m.f.'s of cells [3] and [4] to the standard hydrogen electrode, the authors used the data of Nonhebel and Hartley (1) to evaluate the e.m.f. of the cell

$\mathrm{H_2/HCl(a=1)//HCl(0.1m)/AgCl,Ag}$ [6]

SOURCE AND PURITY OF MATERIALS:

Methanol was purified by the method of Hartley and Raikes (2) which involved drying with aluminum amalgam followed by distillation. The salts were "pure specimens" prepared previously for conductivity studies (no details given, but this is probably reference 3 in which "pure" commercial salts were recrystallized). The AgSCN,Ag electrode was prepared from granular Ag and pptd AgSCN.

ESTIMATED ERROR:

The authors report e.m.f.'s to 0.1mV although their measurements on cell [4] are good to probably ±1mV: this leads to a stnd deviation in K_{s0} of $\geqslant \pm 4\%$.

REFERENCES:

1. Nonhebel, G.; Hartley, H. *Phil. Mag.* 1925, *1*, 729.
2. Hartley, H.; Raikes, *J. Chem. Soc.* 1925, *127*, 524.
3. Frazer, J.E.; Hartley, H. *Proc. Roy. Soc. (London)* 1925, *109*, 351.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sodium thiocyanate; NaSCN; [540-72-7]

(3) Methanol; CH_4O; [67-56-1]

ORIGINAL MEASUREMENTS: (continued)

Buckley, P.S.; Hartley, H.

Phil. Mag. 1928, *8*, 320-41.

COMMENTS AND/OR ADDITIONAL DATA:

Since a number of assumptions are involved in the calcn of the E^o's, a detailed description seems worthwhile. The liq junction potentials, E_j, were calcd from

$$E_j = (RT/F)\ln(\lambda/\lambda') \quad \text{or} \quad E_j = \{(u-v)/(u+v)\}(RT/F)\ln(m_1/m_2)$$

The former equation was used for two monovalent salts having one ion in common, and possessing equivalent conductivities λ and λ'. The latter eqn was used for solns of the same monovalent salt whose concentrations are m_1 and m_2 and whose cations and anions have mobilities u and v, respectively. The data for these calculations were obtained from earlier work (3), and from unpublished data: some of these data are given in the present paper. Assuming $\gamma_\pm$ for 0.01m $AgClO_4$ = 0.745 (i.e. the experimental value (1) for HCl), we have

$$E^o_{Ag,Ag^+} = E_3 + E_7 + (RT/F)\ln(0.01 \times 0.745) = 0.7646V$$

Similarly taking $\gamma_\pm$= 0.664 for 0.02 m NaSCN,

$$E^o_{Ag,AgSCN} = E_5 + E_6 - E_4 + (RT/F)\ln(0.02 \times 0.664) = -0.0489V$$

The authors attempted to use $AgNO_3$ solns in cell [3] but obtained lower E^o_{Ag,Ag^+} values which was attributed to incomplete dissociation of this salt in methanol. Electrolytically prepared Ag,AgSCN electrodes were neither reproducible or constant.

AUXILIARY INFORMATION

METHOD:

For cell [6] E_6 = 0.0711V. Finally the e.m.f. of cell [7] can be calculated

$$H_2/HCl(a=1)//HCl(0.01m)/AgCl,Ag \qquad [7]$$

assuming the mean molal activity coeff for NaCl solns are identical to HCl (1). For 0.01m and 0.1m solns, E_7 was given as

$$E_7 = E_6 + (RT/F)\ln\{(0.1 \times 0.461)/(0.01 \times 0.745)\} = 0.1181V$$

After correcting for the liquid junction potentials, the authors report the experimental values

$$E_3 = 0.5210V \quad ; \quad E_4 = 0.055V$$

$$E_5 = 0.046V$$

In the measurements on cell [4], the initial e.m.f. was 0.023V which rose to a constant value of 0.055V after 4 days.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

Temperature: ±0.02°C

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN ; [333-20-0]
(4) Tetraethylammonium nitrate; $(C_2H_5)_4NNO_3$; [1941-26-0]
(5) Tetraethylammonium thiocyanate; $(C_2H_5)_4NSCN$; [4587-19-3]
(6) Methanol; CH_4O; [67-56-1]

ORIGINAL MEASUREMENTS:

Alexander, R.; Ko, E.C.F.; Mac, Y.C.; Parker, A.J. *J. Am. Chem. Soc.* 1967, *89*, 3703-12.

VARIABLES: One temperature: 25°C

PREPARED BY: Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.01 mol dm^{-3}

$$\log K_{s0}(\text{AgSCN}) = -13.9$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility product was determined from potentiometric titrn data using the cell

$Ag/MSCN(0.01M)//AgNO_3(0.01M)/Ag$

where // is a salt bridge containing a satd soln of tetraethylammonium picrate, and MSCN is either KSCN or tetraethylammonium thiocyanate. 0.01M $AgNO_3$ was titrated into the MSCN soln which was exposed to the atmosphere. The cell was thermostated at 25°C and magnetically stirred during the titration. In calculating the $[Ag^+]$ on the left hand side, the $[Ag^+]$ in the right compartment was corrected for incomplete dissociation: i.e. from reference 1, the dissociation constant of $AgNO_3$ in methanol is

$$K_{diss} = 1.3 \times 10^{-2} \text{ mol dm}^{-3}.$$

SOURCE AND PURITY OF MATERIALS:

Methanol was purified as described elsewhere (2). Analar grade KSCN and $AgNO_3$ were used as received. Tetraethylammonium thiocyanate was prepared from the bromide and KSCN, recrystallized from an organic solvent, washed with ether, and dried in vacuum at 20-80°C.

ESTIMATED ERROR:

Nothing is specified, but the reproducibility in K_{s0} is probably about ±0.1 log units

REFERENCES:

1. Drago, R.S.; Purcell, K.F. *Non-Aqueous Solvent Systems*. ed. T.C. Waddington. Academic Press. London. 1965.
2. Clare, B.W.; Cook, D.; Ko, E.C.F.; Parker, A.J. *J. Am. Chem. Soc.* 1966, *88*, 1911.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]

(3) Tetraethylammonium thiocyanate; $(C_2H_5)_4NSCN$; [4587-19-3]

(4) Nitromethane; CH_3NO_2; [75-52-5]

ORIGINAL MEASUREMENTS:

Bardin, J.-C. *J. Electroanal. Chem. Interfacial Electrochem.* 1970, *28*, 157-66.[1,2]

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is varying and $\leq$ 0.01 mol dm^{-3}. The data are reported in terms of the following equilibria:

$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^-$ $\beta_2 = 2.5 \times 10^{16}\ mol^{-2}\ dm^6$

$2AgSCN(s) \rightleftarrows Ag^+ + Ag(SCN)_2^-$ $K_{s0}(AgAg(SCN)_2) = 4.0 \times 10^{-18}\ mol^2\ dm^{-6}$

$AgSCN(s) \rightleftarrows Ag^+ + SCN^-$ $K_{s0}(AgSCN) = 1.3 \times 10^{-17}\ mol^2\ dm^{-6}$

$AgSCN(s) + SCN^- \rightleftarrows Ag(SCN)_2^-$ $K_{s2} = 0.3$

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out using the cell

$Ag/(C_2H_5)_4NSCN(0.01M)//ref$

where ref is an Ag/AgCl reference electrode as described elsewhere (3). $AgClO_4$ was titrated into the cell which was enveloped with a water jacket. $[Ag^+]$ was determined from the Nernst equation and $[SCN^-]$ from mass balance considerations.

COMMENTS AND/OR ADDITIONAL DATA:

In an earlier paper (2), Badoz-Lambling and Bardin report the same K_{s0} data for the same solvent and supporting electrolytes but indicate the temperature to be 20°C.

SOURCE AND PURITY OF MATERIALS:

$(C_2H_5)_4NSCN$ prep by passing a soln of $(C_2H_5)_4NClO_4$ through a column of the SCN-form of Dowex 1X4 ion-exchange resin. Effluent evap under vac, recryst from methanol, dried under vac at 80°C and stored under vac. Practical CH_3NO_3 washed with aq $NaHCO_3$, $NaHSO_3$, and 5% H_2SO_4, dried with anhyd $CaSO_4$ and fractionally distilled under vac collecting the 110° fraction which was dried over $CaSO_4$ under N_2 for 3 wks. $[H_2O] \leq 0.05M$, $C_2H_5NO_2$ and $C_3H_7NO_3$ were detected.

ESTIMATED ERROR:

Nothing specified, but the precision in the equilibrium constants is probably ±10%.

REFERENCES:

1. Bardin, J.-C. *Thèse*. Paris. 31 Mai 1972. enregistrée au C.N.R.S. sous le No. AO 7142.
2. Badoz-Lambling, J.; Bardin, J.-C. *C.R. Acad. Sci.* 1968, *C266*, 95.
3. Cauquis, G.; Serve, D. *Bull. Soc. Chim. Fr.* 1966, 302.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]

(3) Tetraethylammonium thiocyanate; $(C_2H_5)_4NSCN$; [4587-19-3]

(4) Propandediol-1, 2-carbonate (propylene carbonate); $C_4H_6O_3$; [108-32-7]

ORIGINAL MEASUREMENTS:

Courtot-Coupez, J.; L'Her, M.

Bull. Soc. Chim. Fr. 1969, 675-80.

VARIABLES:

One temperature: 22°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Based on molar units at a temperature of 22°C and a constant ionic strength of 0.11 mol/dm^3, the data are reported in terms of the following equilibrium constants.

$\log K_{s0}(AgSCN) = -16.9 \pm 0.1$

$\log K_{s0}(AgAg(SCN)_2) = -16.4 \pm 0.1$

$\log K_2 = 10.6 \pm 0.1$

$\log \beta_2 = 16.0 \pm 0.1$

$\log \beta_3 = 18.7 \pm 0.1$

These equilibrium constants correspond to the following reactions:

$AgSCN(s) \rightleftarrows Ag^+ + SCN^-$	$K_{s0}(AgSCN)/mol^2\ dm^{-6}$
$2AgSCN(s) \rightleftarrows Ag^+ + Ag(SCN)_2^-$	$K_{s0}(AgAg(SCN)_2)/mol^2\ dm^{-6}$
$2Ag(SCN)_3^{2-} + Ag^+ \rightleftarrows 3Ag(SCN)_2^-$	K_2
$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^-$	$\beta_2/mol^{-2}\ dm^6$
$Ag^+ + 3SCN^- \rightleftarrows Ag(SCN)_3^{2-}$	$\beta_3/mol^{-3}\ dm^9$

AUXILIARY INFORMATION

METHOD:

Potentiometric titrations were carried out on the cell

$$Ag/Et_4NSCN(0.01M),\ Et_4NClO_4(0.1M)//$$

$$AgClO_4(0.01M),\ Et_4NClO_4(0.1M)/Ag$$

where Et = C_2H_5 and the junction which is a porous glass frit, is represented as //. The thiocyanate soln was titrd with 0.5M $AgClO_4$ at room temperature. The various equilibrium constants were calculated from various parts of the titration curve.

SOURCE AND PURITY OF MATERIALS:

The solvent was vacuum distilled and the fraction distilling at 72°C passed through 4A molecular sieves: water content < 20 ppm. $AgClO_4$ (BDH) dried under vacuum at 40°C for 24 h, and stored in vacuum: Et_4NClO_4 treated identically but at room temp. Et_4SCN prep from KSCN and Et_4NCl in hot abs alcohol: the insol KCl separated by filtration and Et_4NSCN pptd and recryst three times from abs ethanol, dried in vacuum at 80°C.

ESTIMATED ERROR:

The standard deviations in the equilibrium constants are given above.

REFERENCES:

COMPONENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) N-methyl-2-pyrrolidinone; C_5H_9NO; [872-50-4]

ORIGINAL MEASUREMENTS:

Virtanen, P.O.I.; Kerkela, R.

Suomen. Kem. 1969, *B42*, 29-33.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at 0.01 mol dm^{-3}.

$$\log K_{s0}(AgSCN) = -10.26$$

$$\log \beta_2 = 11.30$$

AUXILIARY INFORMATION

METHOD:
The soly product and stability const were calcd from potentiometric titrn data obtained from the cell

$$Ag/AgNO_3(0.01M)//KCl(1M)//AgNO_3(0.01M)/Ag$$

One side of this cell was titrd with 0.01M KSCN. The titrn curve showed two equivalence points, and the equil constants calcd by a graphical method.

SOURCE AND PURITY OF MATERIALS:
Technical grade solvent was distilled through a Vigreux column under vacuo, and 80% was retained for use. Water content was < 0.002M (Karl Fischer titrn), and a conductometric titrn of the acidified solvent with stnd NaOH confirmed the absence of amino acid impurities. Commercial salts were dried in vacuum at an "appropriate" temperature. Polished silver wire electrodes were used.

COMMENTS AND/OR ADDITIONAL DATA:

In calculating K_{s0} and β_2, it was assumed that $AgNO_3$ was completely ionized. If $AgNO_3$ is not completely ionized, the authors point out that log K_{s0} may be more negative by as much as 0.2 to 0.3 log units.

ESTIMATED ERROR:
K_{s0}: Nothing specified. Precision of ~ ±0.05 log units can be assumed (compiler).
Temperature: ±0.02°C.

REFERENCES:

COMPONENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Tetrabutylammonium perchlorate; $(C_4H_9)_4NClO_4$; [1923-70-2]
(3) Tetrabutylammonium thiocyanate; $(C_4H_9)_4NSCN$; [3674-54-2]
(4) Tetrahydrofuran; C_4H_8O; [109-99-9]

ORIGINAL MEASUREMENTS:

Caillet, A.; Demange-Guerin, G.

J. Electroanal. Chem. Interfacial Electrochem. 1972, *40,* 187-96.

VARIABLES:

One temperature: 25°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is constant at ∿ 0.1 mol dm^{-3}. The data were reported in terms of the following equilibria occuring in the presence of ion-pairing:

$$AgSCN(s) + (C_4H_9)_4NClO_4 \rightleftarrows AgClO_4 + (C_4H_9)_4NSCN$$

$$K'_{s0} = 4.0 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}$$

$$AgClO_4 + 2(C_4H_9)_4NSCN \rightleftarrows (C_4H_9)_4N{\cdot}Ag(SCN)_2 + (C_4H_9)_4NClO_4$$

$$\beta'_2 = 2.5 \times 10^{18} \text{ mol}^{-2} \text{ dm}^6$$

In the absence of ion-pairing, the approximate results are:

$$AgSCN(s) \rightleftarrows Ag^+ + SCN^- \qquad K_{s0} = 7.9 \times 10^{-19} \text{ mol}^2 \text{ dm}^{-6}$$

$$Ag^+ + 2SCN^- \rightleftarrows Ag(SCN)_2^- \qquad \beta_2 = 1.3 \times 10^{19} \text{ mol}^{-2} \text{ dm}^6$$

AUXILIARY INFORMATION

METHOD:

A potentiometric titrn method was used. The titration cell is represented by

$Ag/Bu_4NSCN(xM), Bu_4NClO_4(0.1M)//ref$

where Bu = C_4H_9 and the reference electrode is assumed by the compiler to be identical to one described in a previous paper (1): i.e.

ref = $AgClO_4(0.01M), Bu_4NClO_4(0.1M)/Ag$

The concentration x for Bu_4NSCN is not given, but is assumed to equal 0.005 mol/L which is the value employed for the halides which are also described in this paper. The equilibrium constants were calculated from the data corresponding to the various parts of the titrn curve where the different ionic species predominate.

SOURCE AND PURITY OF MATERIALS:

Nothing specified, but probably similar to that described earlier (1). Commercial Bu_4NClO_4 and anhydrous $AgClO_4$ were used. The solvent was stored over potassium for 15 days, refluxed over sodium in N_2 for 4 h, and fractionated. Karl Fischer titration gave $[H_2O] = 0.005$ mol dm^{-3}.

ESTIMATED ERROR:

Nothing specified. A precision $\leqslant \pm 10\%$ for exptl equilibrium constants is assumed by the compiler.

REFERENCES:

1. Caillet, A.; Demange-Guerin, G. *J. Electroanalyt. Chem. Interfacial Electrochem.* 1972, *40,* 69.
2. Treiner, C.; Justice, J.C. *C. R. Acad. Sci.* 1969, *C269,* 1364.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Tetrabutylammonium perchlorate; $(C_4H_9)_4NClO_4$; [1923-70-2]

(3) Tetrabutylammonium thiocyanate; $(C_4H_9)_4NSCN$; [3674-54-2]

(4) Tetrahydrofuran; C_4H_8O; [109-99-9]

ORIGINAL MEASUREMENTS: (continued)

Caillet, A.; Demange-Guerin, G.

J. Electroanal. Chem. Interfacial Electrochem. 1972, *40*, 187-96.

COMMENTS AND/OR ADDITIONAL DATA:

Since the dielectric constant of tetrahydrofuran is small ($\varepsilon = 7.4$ D at 25°C) ion-pairing effects are expected to be large. From the equilibrium equations given above, the authors derive the following relationships:

$$pK_{s0} = pK'_{s0} + pK_G(AgClO_4) + pK_G(Bu_4NSCN) - pK_G(Bu_4NClO_4)$$

$$\log \beta_2 = \log \beta'_2 + pK_G(AgClO_4) + 2pK_G(Bu_4NSCN)$$

$$-pK_G(Bu_4NClO_4) - pK_G(Bu_4N{\cdot}Ag(SCN)_2)$$

where K_G is the dissociation constant of the indicated ion-pair. The pK_G values for $AgClO_4$ (unpublished results) and Bu_4NClO_4 (2) are respectively, 3.4 and 6.2. The pK_G values for Bu_4NSCN and $Bu_4N{\cdot}Ag(SCN)_2$ were assumed to equal 3.5 (note: a typographical error in the paper incorrectly lists a value of 4.5).

AUXILIARY INFORMATION

METHOD:

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]
(2) Tetraethylammonium perchlorate; $(C_2H_5)_4NClO_4$; [2567-83-1]
(3) Potassium thiocyanate; KSCN; [333-20-0]
(4) Tetrahydrothiophene-1, 1-dioxide (tetramethylene sulfone); $C_4H_8O_2S$; [126-33-0]

ORIGINAL MEASUREMENTS:

Della Monica, M.; Lamanna, U.; Senatore, L. *Inorg. Chim. Acta* 1968, *2*, 363-6.

VARIABLES:

One temperature: 30°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

Ionic strength is 0.1 mol dm^{-3}.

$$K_{s0} = (5.4\pm0.2) \times 10^{-17}\ mol^2\ dm^{-6}$$

The overall stability constant for the reaction

$$Ag^+ + 2SCN^- \rightleftharpoons Ag(SCN)_2^-$$

was determined as

$$\beta_2 = (1.1\pm0.04) \times 10^{16}\ mol^2\ dm^6$$

AUXILIARY INFORMATION

METHOD:

Potentiometric titrn method used: the cell is represented as

$Ag/AgClO_4(0.003673M)//satd\ calomel$

where // is an NH_4NO_3-agar salt bridge. 5.245×10^{-2}M KSCN was titrd into the cell (±0.01 ml) in an air thermostat. $(C_2H_5)_4NClO_4$ used to maintain ionic strength constant at 0.1M. A conductometric titrn using smooth Pt electrodes is also reported. This latter titrn shows one inflection at the equivalence point indicating the formation constant of $Ag(SCN)_2^-$ to be small. The soly product was calcd from the data in the satd region of the titrn curve, and the overall stability constant, β_2, was calcd from the data in unsaturated solns.

SOURCE AND PURITY OF MATERIALS:

Solvent (shell Italiana) was distilled from NaOH at 10^{-4} torr until its conductivity was 2×10^{-8} $ohm^{-1}cm^{-1}$. $AgClO_4$ recryst from conductivity H_2O and dried under reduced pressure at 110°C. KSCN (Fisher, ACS) recryst from conductivity H_2O and dried under reduced pressure for 40 h at 60°C. $(C_2H_5)_4NClO_4$ prepared from aqueous soln of $AgClO_4$ and removed by filtration and the soln evaporated: $(C_2H_5)_4NClO_4$ filtered, recryst from conductivity H_2O, and dried in vacuum at 50°C.

ESTIMATED ERROR:

The standard deviations given above were calcd from the mean experimental values by the authors. Only one titrn was carried out so that the reproducibility in K_{s0} is not given.

Temperature control was ±0.2°C.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver thiocyanate; AgSCN; [1701-93-5] (2) Ammonia; NH_3; [7664-41-7]	Blytas, G.C.; Kertesz, D.J.; Daniels, F. *J. Am. Chem. Soc.* 1962, *84*, 1083-5.
VARIABLES:	PREPARED BY:
One temperature: -12°C	Mark Salomon

EXPERIMENTAL VALUES:

The solubility of AgSCN is liquid ammonia at -12°C is

61.75 wt % or 9.73 mol/kg

AUXILIARY INFORMATION

METHOD:

The soly was determined by the synthetic method (1) using glass tubes. The tubes were weighed, AgSCN added and heated under vacuum for 2 h and reweighed. NH_3 was distilled into the tube which was then sealed and weighed. The liquidus temperatures were measured during slow heating, and the soly determined at the temp at which the last crystals disappeared. Additional description of the apparatus and method is given in reference 2.

SOURCE AND PURITY OF MATERIALS:

Ammonia was purified by distilling first from a trap containing sodium, and then directly into the solubility tubes. (2) No other information is given.

ESTIMATED ERROR:

Solubility: ±0.1% (as determined from the original "synthesis").

Temperature: not specified.

COMMENTS AND/OR ADDITIONAL DATA:

The authors do not state whether corrections were made for the vapor pressure of NH_3 above the saturated soln. If the vapor pressure is large, then the weight of NH_3 in the gas phase must be subtracted from the total weight of NH_3 initially placed into the solubility tube.

REFERENCES:

1. Menzies, A.W.C. *J. Am. Chem. Soc.* 1936, *58*, 934.
2. Blytas, G.C.; Daniels, F. *J. Am. Chem. Soc.* 1962, *84*, 1075.

COMPONENTS:

(1) Silver thiocyanate; AgSCN; [1701-93-5]

(2) Sulfur dioxide; SO_2; [7446-09-5]

ORIGINAL MEASUREMENTS:

Jander, G.; Ruppolt, W. *Z. Physik. Chem.* 1937, *179A*, 43-50.

Jander, G.; Wickert, K. *Z. Physik. Chem.* 1936, *178A*, 57-73.

VARIABLES:

One temperature: 0°C

PREPARED BY:

Mark Salomon

EXPERIMENTAL VALUES:

The solubility of AgSCN in liquid SO_2 at 0°C is

$$0.14 \text{ g kg}^{-1}$$

$$0.00085 \text{ mol kg}^{-1} \text{ (compilers calcn)}$$

AUXILIARY INFORMATION

METHOD:

The soly was determined isothermally in an ice bath. Liq SO_2 was satd with AgSCN in a sealed tube and rotated in the bath until equil was attained (no details were given). A wad of glass wool in the center of the tube served to filter the satd soln by rotating the tube lengthwise through 180°. Upon rotation the lower half, while still in the bath, was separated by melting the tube just below the glass wool. Analysis was performed by evaporating the SO_2 and dissolving the residue in water followed by quantitative analysis by "known" methods. Details on how the residue was dissolved and on the method of analysis were not given.

COMMENTS AND/OR ADDITIONAL DATA:

Two original sources are cited since they both contain similar information. Source 1 describes the purity of the salts and details on the experimental method whereas source 2 gives details on the preparation of the solvent.

SOURCE AND PURITY OF MATERIALS:

Commercial SO_2 of high purity was passed through con H_2SO_4, asbestos wool to remove dust and non-gaseous impurities, P_2O_5, and asbestos wool. It was collected in a vessel cooled with an ether/CO_2 mixture. Its final specific conductivity was 4.7×10^{-7} $\text{ohm}^{-1}\ \text{cm}^{-1}$ (temp not specified). The AgSCN was either prepared by the authors or was a high purity commercial product. The salt was dried before use.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

SYSTEMS INDEX

Underlined page numbers refer to specific citations in the evaluation text and those not underlined to the compiled data for that system. Salts are listed according to the solvent: i.e. aqueous systems are listed first followed, respectively, by aqueous-organic mixed solvent systems, organic solvent systems, and inorganic solvent systems.

REGISTRY NUMBER INDEX

Underlined page numbers refer to evaluation text and those not underlined to compiled tables.

Compounds not assigned Registry Numbers at the time of this writing are, in order as they appear in the text:

* Existence of this compound is highly speculative.