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SOLUBILITY DATA SERIES

Volume 65

COPPER(I) HALIDES AND PSEUDOHALIDES

SOLUBILITY DATA SERIES

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COPPER(I) HALIDES AND PSEUDOHALIDES

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INTRODUCTION TO THE SOLUBILITY DATA SERIES

SOLUBILITY OF SOLIDS IN LIQUIDS

NATURE OF THE PROJECT

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

COMPILATIONS AND EVALUATIONS

The formats for the compilations and critical evaluations have been standardized for all volumes. A description of these formats follows.

Compilations

The format used for the compilations is, for the most part, self-explanatory. Normally, a compilation sheet is divided into boxes, with detailed contents described below.

Components: Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The Chemical Abstracts name is also included if this differs from the IUPAC name, as are trivial names if appropriate. IUPAC and common names are cross-referenced to Chemical Abstracts names in the System Index.

The formula is given either in terms of the IUPAC or Hill (1) 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 on a given compilation sheet according to:

(a) saturating components:
(b) non-saturating components;
(c) solvents.

In each of (a), (b) or (c), the components are arranged in order according to the IUPAC 18-column periodic table with two additional rows:

Columns 1 and 2:	H, alkali elements, ammonium, alkaline earth elements
Columns 3 to 12:	transition elements
Columns 13 to 17:	boron, carbon, nitrogen groups; chalcogenides, halogens
Column 18:	noble gases
Row 1:	Ce to Lu
Row 2:	Th to the end of the known elements, in order of atomic number.

The same order is followed in arranging the compilation sheets within a given volume.

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. In the case of multiple entries (for example, translations) an asterisk indicates the publication used for compilation of the data.

Variables: Ranges of temperature, pressure, etc. are indicated here.

Prepared by: The names of all compilers are given here.

Experimental Values: Components are described as (1), (2), etc., as defined in the "Components" box. 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. 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 1989 atomic weights (2). Temperatures are expressed as t/°C, t/°F or T/K as in the original; if necessary, conversions to T/K are made, sometimes in the compilations and always in the critical evaluation. However, the author's units are expressed according to IUPAC recommendations (3) as far as possible.

Errors in calculations, fitting equations, etc. are noted, and where possible corrected. Material inserted by the compiler is identified by the word "compiler" or by the compiler's name in parentheses or in a footnote. In addition, compiler-calculated values of mole or mass fractions are included if the original data do not use these units. If densities are reported in the original paper, conversions from concentrations to mole fractions are included, but otherwise this is done in the evaluation, with the values and sources of the densities being quoted and referenced.

Details of smoothing equations (with limits) are included if they are present in the original publication and if the temperature or pressure ranges are wide enough to justify this procedure and if the compiler finds that the equations are consistent with the data.

The precision of the original data is preserved when derived quantities are calculated, if necessary by the inclusion of one additional significant figure. In some cases, compilers note that numerical data have been obtained from published graphs using digitizing techniques. In these cases, the precision of the data can be determined by the quality of the original graph and the limitations of the digitizing technique. In some cases graphs have been included, either to illustrate data more clearly, or if this is the only information in the original. Full grids are not usually inserted as it is not intended that users should read data from the graphs.

Method: The apparatus and procedure are mentioned briefly. Abbreviations used in Chemical Abstracts are often used here to save space, reference being made to sources of further detail if these are cited in the original paper.

Source and Purity of Materials: For each component, referred to as (1), (2), etc., the following information (in this order and in abbreviated form) is provided if available in the original paper: source and specified method of preparation; properties; degree of purity.

Estimated Error: If estimated errors were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors (identified by "compiler" or the compiler's name in parentheses or in a footnote) from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on Ku and Eisenhart (4).

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: The format for these follows the format for the Original Measurements box, except that final page numbers are omitted. References (usually cited in the original paper) are given where relevant to interpretation of the compiled data, or where cross-reference can be made to other compilations.

Evaluations

The evaluator's task is 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. There are only three boxes on a typical evaluation sheet, and these are described below.

Components: The format is the same as on the Compilation sheets.

Evaluator: The name and affiliation of the evaluator(s) and date up to which the literature was checked.

Critical Evaluation:

(a) Critical text. The evaluator checks that the compiled data are correct, assesses their reliability and quality, estimates errors where necessary, and recommends numerical values based on all the published data (including theses, patents and reports) for each given system. Thus, the evaluator reviews the merits or shortcomings of the various data. Only published data are considered. Documented rejection of some published data may occur at this stage, and the corresponding compilations may be removed.

The solubility of comparatively few systems is known with sufficient accuracy to enable a set of recommended values to be presented. Although many systems have been studied by at least two workers, the range of temperatures is often sufficiently different to make meaningful comparison impossible.

Occasionally, it is not clear why two groups of workers obtained very different but internally consistent sets of results at the same temperature, although both sets of results were obtained by reliable methods. In such cases, a definitive assessment may not be possible. In some cases, two or more sets of data have been classified as tentative even though the sets are mutually inconsistent.

(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, stating the limits within which it should be used.

(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 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, including all those publications appearing in the accompanying compilation sheets and those which, by virtue of their poor precision, have been rejected and not compiled.

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in SI units (3) when the data can be accurately converted.

QUANTITIES AND UNITS USED IN COMPILATION AND EVALUATION OF SOLUBILITY DATA

Mixtures, Solutions and Solubilities

A *mixture* (5) describes a gaseous, liquid or solid phase containing more than one substance, where the substances are all treated in the same way.

A *solution* (5) 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 solute 1 (solid, liquid or gas) is the analytical composition of a saturated solution, expressed in terms of the proportion of the designated solute in a designated solvent (6).

"Saturated" implies equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the same substance in stable equilibrium. (Strictly speaking, it is the activity of the substance in metastable equilibrium 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 reference states used for definition of activities, activity coefficients and osmotic coefficients.

Note that the composition of a 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 proportions of anhydrous salt in solution, rather then the relative proportions of hydrated salt and water.

Physicochemical Quantities and Units

Solubilities of solids have been the subject of research for a long time, and have been expressed in a great many ways, as described below. In each case, specification of the temperature and either partial or total pressure of the saturating gaseous component is necessary. The nomenclature and units follow, where possible, ref. (3). A few quantities follow the ISO standards (7) or the German standard (8); see a review by Cvitaš (9) for details.

A note on nomenclature. The nomenclature of the IUPAC *Green Book* (3) calls the solute component B and the solvent component A. In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing equations given here with those in the *Green Book.*

1. *Mole fraction* of substance 1, x_1 or $x(1)$ (condensed phases), y_1 (gases):

$$x_1 = n_1 \Big/ \sum_{s=1}^{c} n_s \qquad [1]$$

where n_s is the amount of substance of s, and c is the number of distinct substances present (often the number of thermodynamic components in the system). *Mole per cent* of substance 1 is 100 x_1.

2. *Ionic mole fractions* of salt *i*, x_{i+}, x_{i-}:
For a mixture of *s* binary salts *i*, each of which ionizes completely into n_{i+} cations and ν_{i-} anions, with $\nu_i = \nu_{i+} + \nu_{i-}$ and a mixture of *p* non-electrolytes k, of which some may be considered as solvent components, a generalization of the definition in (10) gives:

$$x_{+i} = \frac{\nu_{+i}x_{+i}}{1+\sum\limits_{j=1}^{s}(\nu_j-1)x_j}, \qquad x_{-i} = \frac{\nu_{-i}x_{+i}}{\nu_{+i}} \qquad i = 1 \dots s \qquad [2]$$

$$x_{ok} = \frac{x_j}{1+\sum\limits_{j=1}^{s}(\nu_j-1)x_j}, \qquad k = (s+1)\dots c \qquad [3]$$

The sum of these mole fractions is unity, so that, with $c = s + p$,

$$\sum_{i=1}^{s}(x_{+i} + x_{-i}) + \sum_{i=s+1}^{c} x_{oi} = 1 \qquad [4]$$

General conversions to other units in multicomponent systems are complicated. For a three-component system containing non-electrolyte 1, electrolyte 2 and solvent 3,

$$x_1 = \frac{\nu_{+2}x_{o1}}{\nu_{+2}-(\nu_2-1)x_{+2}} \qquad x_2 = \frac{x_{+2}}{\nu_{+2}-(\nu_2-1)x_{+2}} \qquad [5]$$

These relations are used in solubility equations for salts, and for tabulation of salt effects on solubilities of gases.

3. *Mass fraction* of substance 1, w_1 or $w(1)$:

$$w_1 = g_1 \Big/ \sum_{s=1}^{c} g_s \qquad [6]$$

where g_s is the mass of substance *s*. *Mass per cent* of substance 1 is 100 w_1. The equivalent terms *weight fraction*, *weight per cent* and *g (1)/100 g solution* are no longer used.

4. *Solute mole fraction* of substance 1, $x_{v,1}$:

$$x_{s,1} = m_1 \Big/ \sum_{s=1}^{c'} m_s = x_1 \Big/ \sum_{s=1}^{c'} x_s \qquad [7]$$

where *c'* is the number of solutes in the mixture. These quantities are sometimes called Jänecke mole (mass) fractions (11, 12). *Solute mass fraction* of substance 1, $w_{s,1}$, is defined analogously.

5. *Solvent mole fraction* of substance 1, $x_{v,1}$:

$$x_{v,1} = x_1 \Big/ \sum_{s=1}^{p} x_s \qquad [8]$$

Here, *p* is the number of solvent components in the mixture. *Solvent mass fraction* of substance 1, $w_{v,1}$, is defined analogously.

6. *Molality* of solute 1 in a solvent 2, m_1:

$$m_1 = n_1 / n_2 M_2 \tag{9}$$

SI base units: mol kg^{-1}. Here, M_2 is the molar mass of the solvent.

7. *Aquamolality, Solvomolality* of substance 1 in a mixed solvent with components 2, 3 (13), $m_1^{(3)}$:

$$m_1^{(3)} = m_1 \overline{M} / M_3 \tag{10}$$

SI base units: mol kg^{-1}. Here, the average molar mass of the solvent is

$$\overline{M} = x_{v,2} M_2 + (1 - x_{v,2}) M_3 \tag{11}$$

and $x_{v,2}$ is the solvent mole fraction of component 2. This term is used most frequently in discussing comparative solubilities in water (component 2) and heavy water (component 3) and in their mixtures.

8. *Amount concentration* of solute 1 in a solution of volume V, c_1:

$$c_1 = \text{[formula of solute]} = n_1 / V \tag{12}$$

SI base units: mol m^{-3}. The symbol c_1 is preferred to [formula of solute], but both are used. The old terms *molarity, molar* and *moles per unit volume* are no longer used.

9. *Mass concentration* of solute 1 in a solution of volume V, ρ_1:

$$\rho_1 = g_1 / V = c_1 M_1 / V \tag{13}$$

SI base units: kg m^{-3}.

10. *Mole ratio*, $r_{A,B}$ (dimensionless) (9):

$$r_{n,12} = n_1 / n_2 \tag{14}$$

Mass ratio, symbol $\zeta_{A,B}$, may be defined analogously (9).

11. *Ionic strength*, I_m (molality basis), or I_c (concentration basis):

$$I_m = \frac{1}{2} \sum_i m_i z_i^2 , \qquad I_c = \frac{1}{2} \sum_i c_i z_i^2 \tag{15}$$

where z_i is the charge number of ion i. While these quantities are not used generally to express solubilities, they are used to express the compositions of non-saturating components. For a single salt i with ions of charge numbers z_+ and z_-,

$$I_m = |z_+ z_-| \nu m_i , \quad I_c = |z_+ z_-| \nu c_i \tag{16}$$

Mole and mass fractions and mole ratios are appropriate to either the mixture or the solution point of view. The other quantities are appropriate to the solution point of view only. Conversions between pairs of these quantities can be carried out using the equations given in Table 1 at the end of this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

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 noted carefully in the critical evaluation.

Mineralogical names are also quoted, along with their CA Registry Numbers, again usually in the text and CA Registry Numbers (where available) are given usually in the critical evaluation.

In addition to the quantities defined above, the following are useful in conversions between concentrations and other quantities.

12. *Density*, ρ:

$$\rho = g/V = \sum_{s=1}^{c} \rho_s \qquad [17]$$

SI base units: kg m^{-3}. Here g is the total mass of the system.

13. *Relative density*, $d = \rho/\rho°$: the ratio of the density of a mixture at temperature t, pressure p to the density of a reference substance at temperature t', pressure p'. For liquid solutions, the reference substance is often water at 4°C, 1 bar. (In some cases 1 atm is used instead of 1 bar.) The term *specific gravity* is no longer used.

Thermodynamics of Solubility

Thermodynamic analysis of solubility phenomena provides a rational basis for the construction of functions to represent solubility data, and thus aids in evaluation, and sometimes enables thermodynamic quantities to be extracted. Both these aims are often difficult to achieve because of a lack of experimental or theoretical activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve examination of a large body of data that is not directly relevant to solubility. Where possible, procedures for evaluation are based on established thermodynamic methods. Specific procedures used in a particular volume will be described in the Preface to that volume.

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Table 1. Interconversions between Quantities Used as Measures of Solubilities
c-component Systems Containing c-1 Solutes i and Single Solvent c

	x_i	w_i	m_i	c_i
$x_i =$	x_i	$\dfrac{1}{1+\dfrac{M_i}{M_c}\left\{\dfrac{1}{w_i}-1+\sum_{j\neq 1}^{c-1}\left(\dfrac{M_c}{M_j}-1\right)\dfrac{w_j}{w_i}\right\}}$	$\dfrac{1}{1+\dfrac{1}{m_i M_i}\left(1+\sum_{j\neq i}^{c-1} m_j M_j\right)}$	$\dfrac{1}{1+\dfrac{1}{M_c}\left(\dfrac{\rho}{c_i}-M_i\right)+\sum_{j\neq i}^{c-1}\dfrac{c_j}{c_i}\left(1-\dfrac{M_j}{M_c}\right)}$
$w_i =$	$\dfrac{1}{1+\dfrac{M_c}{M_i}\left\{\dfrac{1}{x_i}-1+\sum_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right\}}$	w_i	$\dfrac{1}{1+\dfrac{1}{m_i M_i}\left(1+\sum_{j\neq i}^{c-1} m_j M_j\right)}$	$\dfrac{c_i M_i}{\rho}$
$m_i =$	$\dfrac{1}{M_c\left(\dfrac{1}{x_i}-1-\sum_{j\neq i}^{c-1}\dfrac{x_j}{x_i}\right)}$	$\dfrac{1}{M_i\left(\dfrac{1}{w_i}-1-\sum_{j\neq i}^{c-1}\dfrac{w_j}{w_i}\right)}$	m_i	$\dfrac{1}{\dfrac{1}{c_i}\left(\rho-\sum_{j\neq i}^{c-1} c_j M_j\right)-M_i}$
$c_i =$	$\dfrac{\rho}{M_i+M_c\left\{\dfrac{1}{x_i}-1+\sum_{j\neq i}^{c-1}\left(\dfrac{M_j}{M_c}-1\right)\dfrac{x_j}{x_i}\right\}}$	$\dfrac{\rho w_i}{M_i}$	$\dfrac{\rho}{\dfrac{1}{m_i}\left(1+\sum_{j\neq i}^{c-1} m_j M_j\right)+M_j}$	c_i

ρ - density of solution; M_i - molar masses of i. For relations for 2-component systems, set summations to 0.

PREFACE

Scope of Treatment

This volume describes the solubility properties of the halides and pseudohalides of copper(I) in both aqueous and non-aqueous media. The salts considered are CuCl, CuBr, CuI, CuSCN, CuSeCN, CuCN, Cu_2CN_2 and CuN_3, and in addition the double or other complex salts which can be formed when the simple salts dissolve in suitable media. The information presented is based on a thorough literature search through 1988. Media for which solubility data have been reported include both pure solvents and solutions containing other substances which promote dissolution of the cuprous salt. The properties considered in this book include the solubilities themselves, phase diagrams where observed and such thermodynamic properties as may aid in treatment of the solubility data. Since in a number of systems double salts were produced upon dissolution of a cuprous halide, information is provided on the double salts which have been produced from the various halides. Recommended values of solubility are given where the available data appear reliable enough to make this feasible.

Full reference citations are made to the original sources of all data compiled and/or discussed. Where Soviet publications were available in English translation, reference is made both to the original journal and the translation. Where the only available source was in the original language, only that publication is given as a reference.

General Solubility Properties of Copper(I) Halides and Pseudohalides

Dissolution in Pure Solvents. The halides (Cl^-, Br^-, I^-) and pseudohalides (CN^-, SCN^-, etc.) of copper(I) are, like the corresponding silver salts, quite sparingly soluble in pure water, with solubility products $\leq 10^{-6}$ mol^2 dm^{-6} at 298 K, although they may have substantial solubilities in some organic solvents. (Note: In subsequent discussions, both halides and pseudohalides will be designated as CuX and will frequently be referred to as 'cuprous' salts, for sake of simplicity.)

Dissolution Aided by Complex Formation or Other Chemical Reaction. Cuprous salts can be dissolved, sometimes to large concentrations, in a wide variety of media. In both aqueous and non-aqueous media they can be made to dissolve by formation of complexes with a variety of ligands provided by more soluble materials. The most common case is dissolution of a halide CuX in a solution of a soluble halide having the same anion, to form one or more complexes of general formula $Cu_mX_n^{m-n}$, with both mononuclear and polynuclear complexes possible. They may also be dissolved in a solution of a soluble halide whose anion (Y^-) is different from that of the Cu(I) salt to produce mixed complexes $Cu_mX_nY_p^{m-n-p}$. Solutions of such materials as thiosulfates, unsaturated organic alcohols and unsaturated organic acids can dissolve Cu(I) halides by producing either anionic [*e.g.* $Cu(S_2O_3)^-$] or cationic [*e.g.* $Cu(ROH)^+$] complexes. Of these the thiosulfates are particularly effective, much more so than the soluble halides. Cu(I) salts derived from a weak acid (HCN, HSCN) will dissolve in acid media. There are also indications that cuprous halides can be dissolved in aqueous solutions of ammonia or amines, but no solubility data has been found for such systems.

General Trends in Solubility

Effect of Ions Present. The solubilities of cuprous salts in aqueous media exhibit definite trends. In pure water at a given temperature the order of solubility is CuCl > CuBr > CuI > CuSCN > CuCN. The same trend is evident when one compares their solubilities in aqueous solutions of soluble halides under similar conditions, as for example the system CuCl–KCl–H_2O with CuBr–KBr–H_2O at the same conditions of concentration and temperature. If a given cuprous halide is dissolved in media containing the same monovalent anion but different cations (*e.g.* CuX in aqueous NH_4X, aqueous KX, etc.), the solubility at given conditions follows the order $NH_4^+ > K^+ > Na^+ > H^+$. Divalent cations all give similar, fairly high, solubility at low ligand concentrations; for high ligand concentrations the order is $Fe^{2+} > Cu^{2+} > Ca^{2+}$. Solubility of a cuprous halide CuX in sodium or potassium thiosulfate is much higher than in an aqueous solution of the soluble halide MX at similar conditions.

Effect of Temperature. The solubilities of the cuprous halides, either in pure water or in water containing a complexing agent, invariably increase with temperature, typically doubling for about 25 K increase in temperature.

Characteristics of Solubility Measurements

Systems Investigated. Some measurements are available for the solubilities of the various cuprous halides in pure water or organic solvent. Many more measurements have been made of their solubilities in media, mostly aqueous, containing a complexing ligand provided by a highly soluble substance. In quite a few cases, measurements have been made in a medium maintained at a constant (nominal) ionic strength by use of an indifferent electrolyte in addition to material providing a complexing ligand; in most cases such studies were undertaken primarily to examine the process of complex formation. In a few cases the solubility of a cuprous halide has been measured as part of the determination of a phase diagram involving the halide, a soluble salt and water, for example the system $CuCl–KCl–H_2O$. A few measurements have also been made in complex systems such as $CuCl–NaCl–CuCl_2–FeCl_2–ZnCl_2–H_2O$; these measurements were typically made as an aid to a practical pursuit such as separation of copper from an ore. The largest number of investigations found were for systems involving CuCl, with much smaller numbers for the other halides and the pseudohalides.

Experimental Procedures Used. The most common method of determination of the solubility involved chemical analysis of a presumably saturated solution for copper content by some standard method. A few investigators used spectroscopic techniques and one set used the refractive index of the solutions. Some measurements at high temperature were made by determining the portion of a weighed amount of solid halide which remained after dissolution took place, and one measurement determined the amount of soluble halide (HCl) required to dissolve a measured amount of Cu(I) halide (CuCl). Assessment of the solubility of the halides in pure water has been attempted by determination of their solubility products, usually by cell measurements, but in some cases more indirectly, by combining equilibrium constants for two or more reactions.

Units of Measurement. Solubility measurements in the literature have been reported in a variety of concentration units. The units most commonly given are mol dm^{-3} for amount concentration c_i and mol kg^{-1} for molality m_i. Systems where the solubility was high have frequently been described in terms of the mass percentages (equal to $100w_i$, where w_i is the mass fraction) of cuprous halide, solvent and other materials present. A variety of other quantities [*e.g.* mass concentrations, $\rho_i/g\ dm^{-3}$; mass ratios, $100\zeta_{ij}/g\ (100\ g)^{-1}$; etc.] have also been reported. In the Compilations, original units are always given, and also (if necessary) conversion by the compiler to mol dm^{-3} or mol kg^{-1}. The terms "concentration" and "molality" will be used to designate the quantities corresponding to these units; if, however, more than one type of unit is involved, the term "concentration" may be used in its general sense in situations where no ambiguity will result. Conversion between mass and volume units is possible where the densities of the solutions were measured, and a few investigators provide this information.

Experimental Difficulties. A number of problems arise in the determination of cuprous halide solubilities. In the first place, all solutions of Cu(I) salts tend to undergo the disproportionation reaction $2Cu^+ \rightleftharpoons Cu^{2+} + Cu_{(s)}$. This is a serious problem in regions where the solubility of the salt is low, and it can introduce uncertainty in any measurement. Second, the dissolved cuprous halides are readily oxidized to Cu(II) by the oxygen of air. Third, the salts all hydrolyze readily to produce hydroxides, hydrous oxides or hydroxy salts. All of these possibilities can produce errors (most likely positive) in the solubility unless steps are taken to eliminate or correct for them.

Elimination of Possible Errors. Errors due to disproportionation can be prevented, at least in principle, by adding metallic copper to the reaction mixture, and this procedure has been followed by some investigators; its efficacy could be evaluated by subjecting the saturated solution to a sensitive test for Cu^{2+}. Some investigators allowed the disproportionation to take place, then analyzed their solutions for Cu^{2+} as well as Cu^+; this procedure causes no difficulty in interpretation of results as long as the concentration of dissolved Cu^{2+} is much smaller than that of Cu^+. Complete prevention of oxidation to Cu(II) can be provided only by total exclusion of oxygen from all stages of the experiment, and most investigators reported attempting to do so. Complete exclusion of oxygen is difficult, so that solutions need to be examined for the absence of Cu^{2+}; many, but not all, investigators reported doing so. Hydrolysis of Cu(I) can be prevented by addition of a small concentration of H^+ (*app.* 10^{-3} mol dm^{-3}) to the solutions studied. Although many investigators have recognized the possibility of hydrolysis, only a few have taken steps to eliminate it except where the material used to promote dissolution was itself an acid.

Fortunately for the significance of available measurements, the possible increase in apparent solubility due to either disproportionation or hydrolysis will ordinarily be far less than 0.1 mol dm^{-3}, so that failure to prevent either of them would introduce appreciable error only when the solubility is quite small, as in solutions where ligand concentration is zero or low. Errors due to oxidation can be of any magnitude, but the presence of even a small amount of Cu^{2+} in a solution should be apparent to a trained observer because of the color of its complexes, so that only a very careless procedure would fail to take account of it.

Problems in Pure Water. A special problem arises with the solubility of a cuprous halide in pure water. When a halide CuX dissolves in water, it will produce not only the ions Cu^+ and X^-, but also a dissolved neutral species CuX^0, possibly in as large a concentration. In addition, the halide ion formed by dissociation may react to dissolve additional CuX by a reaction $CuX_{(s)} + X^- \rightleftharpoons CuX_2^-$. Thus calculations based on the solubility product will give only a lower limit to the actual solubility, whereas direct measurements of the solubility will give only an upper limit to the solubility product. Interpretion or prediction of the solubility in pure water can be done properly only if one can take account of equilibrium constants for formation of CuX^0 and CuX_2^- as well as the solubility product of the halide.

The Problem of Ionic Strength. Many measurements have been reported at purportedly constant ionic strength maintained by addition of some "indifferent" electrolyte to the solution. Within such sets of measurements the ionic strength of the solutions is rarely (in fact almost never) strictly constant. In the process of dissolution the cuprous halide will form not only singly but also multiply charged complexes. As soon as a doubly or triply charged complex is produced, the ionic strength will be increased, by a considerable amount if the multiply charged complexes account for a substantial part of the solubility. Throughout the discussions hereafter, the ionic strengths specified by investigators will be designated as "nominal" as a reminder that the actual ionic strengths of the solutions are almost certainly higher than the values given, which were based on the compositions of the solutions before dissolution of the cuprous halide occurred.

Another problem which arises in the interpretation of data is the implication in many tabulations that the solubility of a given cuprous halide is determined only by the (nominal) ionic strength, the concentration of ligand supplied and the temperature. This can be very far from the truth. For example, the solubility of CuCl is quite different in NaCl–$NaClO_4$ mixtures from that in HCl–$HClO_4$ mixtures, even if all conditions are comparable except for the cation involved. In the case of NaCl, substitution of $NaNO_3$ for $NaClO_4$ can result in changes in the dependence of solubility on chloride concentration, even though all other conditions are the same.

Data at a given ionic strength can be used reliably only for solutions at that ionic strength maintained by the particular indifferent salt employed.

Reliability of Data. Although many solubility results for cuprous halides have been reported to three or more significant figures, it is unusual to find measurements internally consistent or in agreement with other results to 1 per cent or less. In fact, most of the data available were consistent internally or in agreement with other measurements to about 5 per cent at best, and some not this good. The difficulty in obtaining high precision is not surprising in view of the difficulties of measurement discussed above. The probable reliability of each set of data presented will be discussed in the Critical Evaluation. In most cases this is presented in terms of the standard deviation of the data from a smooth curve based on all data on the particular system available for analysis. Data sets have been rejected only if they were in violent disagreement with more than one other set of measurements. A number of questionable sets have included, with remarks in the Critical Evaluations about their probable (lack of) reliability.

Procedures in Evaluation of Data

Data for Pure Solvent. The probable reliability of the solubility of a cuprous halide in pure solvent could only be determined by comparison of the various sets of data available for the solubility or the solubility product.

Simple Comparisons Between Data. The fact that dissolution of a copper (I) halide most often takes place primarily through complex formation is helpful in the evaluation of data. The dissolution process requires that the ratio (S/C_L) of solubility (S) to the concentration of ligand supplied (C_L) be a smooth function of C_L as long as the solid phase is the copper(I) halide. The function also varies much less rapidly with C_L than does the solubility itself. The extent to which it is a smooth function of C_L is a measure of the internal consistency of the data. All data considered herein were subjected to this test, and its results are reflected in evaluation of each of the sets of data. (Note that if the solid halide is transformed to a double salt in some region of ligand concentration, this will usually produce a discontinuity in S/C_L separating regions where the function is smooth.) In the main body of the discussion the ratio S/C_L is specified as *e.g.* c_{CuCl}/c_{HCl}, m_{CuCl}/m_{NH_4Cl}, etc.

The use of the function S/C_L permits intercomparison of considerable bodies of data. Where measurements on a particular system are available from a number of sources, the function S/C_L provides a convenient way of comparing data for which the concentrations of ligand or the temperature were not the same. For different concentrations at the same temperature all S/C_L should lie on a single smooth curve. Results at different temperatures or different ionic strengths should form a family of smooth curves. Failure to show either behaviour gives clues to inconsistencies within or between data sets. The same procedure can be used to compare data where a given anion ligand was supplied by different soluble salts. At low ligand concentrations, dissolution occurs mainly through reaction to form a single complex (*e.g.* $CuX_{(s)} + X^- \rightleftharpoons CuX_2^-$). Where this is the predominant reaction, the effects of deviation from ideal solution behaviour will be small, and the ratio S/C_L will be nearly (or completely) independent of the cation present. Thus plots of this function for sets of data at the same temperature differing only in the cation present should have a common origin and a region of strong similarity below ligand concentrations where the effects of particular cations on activity coefficients introduce (sometimes large) differences in solubility.

Use of a Detailed Model for the Solubility. A few systems provide data of sufficient quantity and precision to permit modelling of the solubility in terms of equilibrium constants for formation of various complexes and parameters representing the behaviour of the activity coefficients of the species present. Such models can then be used for more rigorous comparison of various sets of data and as interpolation functions to predict solubilities at ligand concentrations (and sometimes other conditions) where they have not been measured. The model can serves primarily as a template to which large bodies of data can be compared to establish their relative reliability and precision. The use of such models will be discussed in detail for the cases where they could be employed. The equations used for representation of activity coefficents are given in the section dealing with the solubility properties of CuCl.

Subsidiary Data and Results

Formation of Double Salts. A number of investigators reported replacement of solid cuprous halide by one or more double salts during the process of dissolution in particular regions of ligand concentration. These and other double salts have also been reported by investigators not concerned with solubility properties. The various known double salts are discussed for each of the Cu(I) halides and pseudohalides, for two reasons. First, it is always possible that a double salt may be the equilibrium solid phase produced by dissolution of the salt under conditions (temperature, ligand concentration) other than those which have been reported. Second, the existence of a double salt involving a ligand-bearing substance implies that the cuprous halide should be soluble in aqueous or other solutions of that material, whether or not solubility results have been reported for such a medium.

Thermodynamic Properties of Complexes Formed. Complete representation of the solubility properties of a given Cu(I) halide in a particular medium requires knowledge of the complexes produced and the thermodynamic information needed to calculate the concentration of each one at a particular temperature and set of concentrations of other substances present. The typical reactions which occur when a halide CuX dissolves in an aqueous solution of a more soluble halide MX are

$$\begin{aligned}
CuX_{(s)} &\rightleftharpoons Cu^+ + X^- \quad K_{S0} &&= [Cu^+][X^-] \\
CuX_{(s)} &\rightleftharpoons CuX^0 \quad K_{S1} &&= [CuX^0]; \; \beta_1 = [CuX^0]/[Cu^+][X^-] \\
CuX_{(s)} + X^- &\rightleftharpoons CuX_2^- \quad K_{S2} &&= [CuX_2^-]/[X^-]; \; \beta_2 = [CuX_2^-]/[Cu^+][X^-]^2
\end{aligned}$$

or in general

$$m\,\mathrm{CuX}_{(s)} + (n-m)\,\mathrm{X}^- \rightleftharpoons \mathrm{Cu}_m\mathrm{X}_n^{m-n} \qquad K_{\mathrm{S}mn} = [\mathrm{Cu}_m\mathrm{X}_n^{m-n}]/[\mathrm{X}^-]^{(n-m)}$$

$$\beta_{mn} = [\mathrm{Cu}_m\mathrm{X}_n^{m-n}]/[\mathrm{Cu}^+]^m[\mathrm{X}^-]^n$$

where the K's are equilibrium constants for formation of the complexes from solid CuX and the β's are stability constants for production of the complexes from Cu^+ and X^-. Note that the subscript n denotes the number of halide atoms (X) in the complex and the subscript m denotes the number of copper atoms present (omitted when $m = 1$). Note also that in the text the ligand-providing halide will often be referred to, for simplicity, as the "soluble chloride (bromide, iodide)".

A similar set of reactions and equilibrium constants can be written when dissolution comes about by addition of a ligand Y^-. For example,

$$\mathrm{CuX}_{(s)} + \mathrm{Y}^- \rightleftharpoons \mathrm{CuXY}^- \qquad K_{\mathrm{S}11} = [\mathrm{CuXY}^-]/[\mathrm{Y}^-], \quad \text{or in general}$$

$$m\,\mathrm{CuX}_{(s)} + p\,\mathrm{Y}^- \rightleftharpoons \mathrm{Cu}_m\mathrm{X}_m\mathrm{Y}_p^{-p} \qquad K_{\mathrm{S}mmp} = [\mathrm{Cu}_m\mathrm{X}_m\mathrm{Y}_p^{-p}]/[\mathrm{Y}^-]^p,$$

with a corresponding set of β's. The subscript m is omitted if $m = 1$, as before, and the latter two subscripts describe the moles of X and Y as written in the complex. Finally ligands Z of charge other than -1 give rise to equilibrium constants similar except for the charges on the complexes.

In many cases, the literature contains values for the solubility product $K_{\mathrm{S}0}$. Frequently, references fail to state what concentration units are to be employed in using the constants, but all appear to refer to either concentration in mol dm^{-3} or to molality. The distinction is not significant if the solubility product is designed for use at zero ionic strength. For other than zero ionic strength, the type of unit will be identified whenever possible.

The selection of a set of complexes to represent solubility data is to a considerable extent arbitrary, and various investigators have used different sets. Within this book, the simplest set which represents a given set of solubility data will be used, usually $K_{\mathrm{S}2}$, $K_{\mathrm{S}3}$ and $K_{\mathrm{S}36}$, with $K_{\mathrm{S}0}$ and $K_{\mathrm{S}1}$ included in cases where the solubility was low enough for Cu^+ and CuX^0 to make significant contributions. The stability constants β_{mn}, while of theoretical interest, are not nearly so useful in representation of solubilities, as will be discussed later.

Many methods have been used to represent the behaviour of activity coefficients at ionic strengths where deviations from ideal solution are significant. The method used in this book will be that published by Pitzer and Mayorga[1] for binary systems and expanded to cover multicomponent solutions by Pitzer and Kim[2]. It represents the mean activity coefficient for a given ion pair in terms of a series of empirical virial parameters. The first three of these, $\beta^{(0)}$, $\beta^{(1)}$ and C, have been found adequate to represent all solubility measurements considered herein within the apparent precision of the measurements. The equations needed for application of the method are presented in the section on CuCl. Virial parameters are provided in the text for all systems where they could be obtained from the available data.

Representation of data at a variety of temperatures requires knowledge of the temperature dependence of the equilibrium constants and of each of the other parameters. This information is presented whenever and insofar as it has been possible to extract it from the experimental data.

Recommended Values for Solubility. Wherever the available data appeared sufficiently reliable, smoothed tables of recommended values for the solubility of the halides in particular media are given. In most cases this was possible only where the data were sufficiently numerous and precise to permit construction of a model in terms of equilibrium constants and activity parameters, as described above. In addition to values of the solubility itself as a function of ligand concentration at one or more temperatures, values of S/C_{L} are given in both tabular and graphical form, since this function greatly facilitates interpolation both with respect to concentration and with respect to temperature, where values can be recommended at more than one temperature. In each case the basis for preparation of the recommended values and comparisons with observed data are given.

For a few systems the only solubility data available was from experiments in which an indifferent electrolyte was present along with the salt providing a complexing ligand. Where the data for such systems could be fitted with precision by a model, this was then used to predict the solubility in the absence of the added salt, with the understanding that these predictions are probably somewhat less precise than the original measurements.

Order of Presentation

In the text individual halides are considered in their order of prominence, *viz.* Cl^-, Br^-, I^- and then the pseudohalides. In each case aqueous solutions are considered first, followed by the (relatively few) data involving organic or mixed solvents. For a given cuprous compound, the order followed is (as far as pertinent to that compound):

1. The system CuX–solvent, without and with "indifferent" salt present.
2. Ternary systems involving soluble halides.
3. Quaternary or higher order systems, with those containing a soluble halide and an "indifferent" salt first, those involving two soluble halides second, and then more complex systems.
4. Systems involving non-halide ligands.

Where relevant, concluding sections will describe double salt formation, phase diagrams and thermodynamic properties, with recommended values for the solubility given at the end.

The data in the Compilations are arranged in the same general order. In some cases, papers which described complex (*e.g.* quaternary) systems contained also data on simpler systems. Such data are located with other systems of the higher complexity. For a given type of system, the Compilations are arranged in chronological order.

References

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COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

THE BINARY SYSTEM

There have been only a few reports of the solubility of CuCl in pure water. In 1902 Bodländer and Storbeck[1] measured the solubility (at about 293 K) under conditions where Cu^{2+} was produced by disproportionation. They obtained the concentrations of both Cu(I) and Cu(II) present; their data are not compiled because lack of knowledge of the anions present makes interpretation of the data impossible. A few other authors have given values (mostly unreliable) of the solubility at or near 298 K as part of measurements on ternary systems. In 1955 Gavrish and Galinker[2] measured the solubility of CuCl in water under high pressure at 19 temperatures from 433 to 633 K. In 1973 Hikita *et al.*[3] reported the solubility in aqueous $HClO_4$ at several ionic strengths for 288, 298 and 308 K.

There have been numerous reports of the solubility product of CuCl based on solubility measurements in ternary or more complex systems. In addition to these, Sosnitskii and Fofanov[4] (1979) deduced the solubility product of CuCl at 298.15 K, zero ionic strength, from measurement of a concentration cell. Ahrland and Rawsthorne[5] (1970) obtained a value of the solubility product in aqueous $NaClO_4$–$HClO_4$ at 298.15 K and ionic strength 5 mol dm^{-3} from extensive solubility and cell measurements of CuCl in this system.

The solubility of CuCl in pure water is not determined solely by the solubility product, K_{S0}, since there is compelling evidence from Ahrland and Rawsthorne[5] and from analysis[6] by the compiler of the data of Hikita *et al.*[3] that the neutral complex $CuCl^0$ contributes appreciably to the solubility of CuCl in pure water and in aqueous solutions with low chloride concentrations. (In addition, there may be some contribution from $CuCl_2^-$ even in pure water, as discussed in the Preface.) As a consequence, a solubility product calculated from solubility measurements will be high unless preliminary correction has been made for the $CuCl^0$ (and possibly $CuCl_2^-$) present. Conversely, solubilities calculated from an independently derived solubility product will be low unless correction can be made for species present other than Cu^+ and Cl^-. Available data on the solubility at or near 298 K are given in Table 1.

Table 1. Solubility of CuCl in Water at or near 298 K

Reference	Date	T/K	$\frac{I_c}{\text{mol dm}^{-3}}$	K_{S0} [a]	Solubility [a]	Basis
Bodländer & Storbeck[1]	1902	293	0*	$1.2 \cdot 10^{-6}$	–	solubility
Kremann & Noss[7]	1912	300	0*	–	0.016	thermodynamics
Kolthoff & Furman[8]	1931	298	0*	$1 \cdot 10^{-6}$	–	not stated
Kepner & Andrews[9]	1948	298	0*	–	0.00238	solubility
Latimer[10]	1952	298	0	$3.2 \cdot 10^{-7}$	–	cell EMF
NBS Circular 500[11]	1952	298	0	$2.3 \cdot 10^{-7}$	–	thermodynamics
Zhuk[12]	1954	298	0	$1.8 \cdot 10^{-7}$	–	previous work
Egorov[13]	1957	298	0	$5.84 \cdot 10^{-7}$	–	thermodynamics
Butler[14]	1964	298	–	$1.9 \cdot 10^{-7}$	–	not stated
Chaltykyan[15]	1966	298	0*	$1.85 \cdot 10^{-7}$	$4.3 \cdot 10^{-4}$	not stated
Ahrland & Rawsthorne[5]	1970	298	5.0	$4.2 \cdot 10^{-8}$	$2.3 \cdot 10^{-4}$	See note [b]
Hikita *et al.*[3]	1973	298	0	–	$5.8 \cdot 10^{-4}$	See note [c]
Krestov *et al.*[16]	1977	298	0	$2.1 \cdot 10^{-7}$	–	thermodynamics
Sosnitskii & Fofanov[4]	1979	298	0	$2.5 \cdot 10^{-7}$	–	cell EMF
Kale *et al.*[17]	1979	298	0*	–	$3.8 \cdot 10^{-3}$	solubility

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CRITICAL EVALUATION:

a All solubilities were reported in mol dm^{-3}. Some of the K_{S0} use molality as the reference state; the difference is trivial for zero ionic strength. The ionic strengths shown as 0* are for the small ionic strength produced in the course of dissolution.

b The solubility given was calculated from the solubility product and the equilibrium constant for $CuCl^0$ formation given by the authors.

c The solubility listed was obtained by extrapolation (by the compiler) of the data given for solubility in aqueous $HClO_4$ at ionic strengths from 0.5 to 6.5 mol dm^{-3}.

Data at or near 298 K

The more recent determinations of the solubility product (K_{S0}) of CuCl at 298 K from either cell potentials or thermodynamic data indicate that it is of the order of 10^{-7}, as shown in Table 1; thus the solubility of CuCl in pure water at this temperature must be somewhat less than 10^{-3} mol dm^{-3}. On this basis we can disregard the measurements reported by Kremann and Noss[7], Kepner and Andrews[9] and Kale *et al.*[17], all of which are higher than this.

The value of K_{S0} reported by Kolthoff and Furman[8] was given without attribution, but appears to be based on that of Bodländer and Storbeck[1]. Neither Butler[14] nor Chaltykyan[15] gives a source for his value; the values they selected apparently represented their estimates based on other available values. Zhuk[12] accepted handbook values of the solubility product as a basis for further thermodynamic study of the system (among others). The remaining values in Table 1 are based at least partially on independent work and will be discussed in detail.

The value of K_{S0} given for 293 K by Bodländer and Storbeck[1] appears to be high, probably because they did not take in to account the increase in solubility produced by the $CuCl_2$ present in their solutions. The remaining values apply to 298 K, and all but one of those for zero ionic strength fall into the range $2.3 \cdot 10^{-7}$ to $3.2 \cdot 10^{-7}$, so that this almost certainly represents the range in which the true value is to be found under those conditions. The most direct determination is that of Sosnitskii and Fofanov[4], who report a value of $(2.5 \pm 0.8) \cdot 10^{-7}$ from their cell measurements. The value given by Latimer[10] comes from single-electrode potentials and is somewhat uncertain because of long-standing difficulty in getting a reliable value for the potential of the Cu/Cu^+ electrode. The value given in NBS Circular 500[11] is based on the standard Gibbs energies of formation of Cu^+ and $CuCl_{(s)}$, each derived from multiple sources, and is subject to possible uncertainties in these quantities. The data of Hikita *et al.*[3] on the system $CuCl-HClO_4-H_2O$ and their data on solutions with low concentrations of HCl in the system $CuCl-HCl-HClO_4-H_2O$ are best represented using a value of K_{S0} near the low end of the range given by Sosnitskii and Fofanov[4]. Overall, the other determinations confirm the result of the direct determination of K_{S0} by Sosnitskii and Fofanov[4], and their value is Recommended for use at 298 K, zero ionic strength.

In addition to the data for zero ionic strength, there are the solubility product at ionic strength 5.0 mol dm^{-3} from Ahrland and Rawsthorne[5] and data of Hikita *et al.*[3] on the solubility in aqueous $HClO_4$ (See Compilations). These are consistent with each other after allowing for the differences in the activity coefficient behaviour of the two media[18]. It should be noted that the solubility in aqueous $NaClO_4$ at ionic strength 5.0 mol dm^{-3} is distinctly higher than that in aqueous $HClO_4$ of the same ionic strength because of substantial differences in the effect of the two media on activity coefficients.

It remains to discuss the thermodynamic treatments of Zhuk[12], Egorov[13] and Krestov *et al.*[16]. Each of these includes CuCl as one case in the thermodynamic treatment of a large number of slightly soluble salts. Zhuk[12] combined handbook data for K_{S0} with thermodynamic data from a variety of sources, including NBS Circular 500[11]; his work provides no

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CRITICAL EVALUATION:

information beyond the material available in that publication. Egorov[13] used thermodynamic information from Latimer[10], Kelley[19] and a variety of other authors to produce equations designed to give the solubility product between 273 and 373 K. However, his value for K_{S0} at 298 K is high by at least a factor of two; the usefulness of his equations in predicting the change of K_{S0} with temperature will be considered below. Krestov *et al.*[16] used thermodynamic data from Naumov *et al.*[20] to obtain equations (quite different in form from those of Egorov) to predict K_{S0} from 273 to 373 K. Their value for K_{S0} at 298 K is reasonable; the effectiveness of their equation for prediction of its value at other temperatures is considered below.

Solubility at Other Temperatures

The only measurements reported for the solubility of CuCl in pure water at temperatures far from 298 K are those of Gavrish and Galinker[2], whose measurements extended from 433 K to within 13 K of the critical temperature of water. A plot of the logarithms of their values of solubility (in molality) *vs.* the reciprocal of the temperature (K) gives a straight line except for random deviations. A least squares fit gives a standard deviation from linearity of 9 per cent, with maximum deviation near 20 per cent. In view of the difficulty of their experiments, such deviations are not surprising, and their values are Recommended for temperatures above 373 K, with an uncertainty of ± 10 per cent.

Extrapolation of the data of Hikita *et al.*[3] gives values for the solubility in pure water of $(3.8 \pm 0.3) \cdot 10^{-4}$ and $(8.2 \pm 0.6) \cdot 10^{-4}$ mol dm^{-3} at 288 and 308 K, respectively. These values are Recommended for their temperatures, with the uncertainties indicated.

The equations given by Egorov[13] and by Krestov *et al.*[16] for temperatures between 273 and 373 K are Not Recommended for use. The equations of Egorov[13] not only give much too high a value for the solubility product at 298 K, but also give a temperature dependence much smaller than those given by Hikita *et al.*[3] and by Gavrish and Galinker[2], which are consistent with each other. The equation of Krestov *et al.*[16] predicts a reasonable solubility at 298 K, but also gives much too small a temperature dependence. In view of these facts, it is not possible to recommend values for the solubility of CuCl in pure water in the range between 308 and 433 K.

TERNARY SYSTEMS INVOLVING MONOVALENT CATIONS

Data were found for the solubility of CuCl in aqueous HCl, NaCl, KCl, NH_4Cl and LiCl. Those for HCl are the most satisfactory both in quantity and quality of the data available. The other systems suffer somewhat either from scarcity of data or from disagreement between the sets of data available. The five systems are discussed in turn below.

$CuCl-HCl-H_2O$

Three investigations are mainly of historical interest. In the 1880's, Le Chatelier[21] measured the solubility of CuCl in aqueous HCl at 290 K for six HCl concentrations from 0.9 to 5.7 mol dm^{-3}, and Engel[22] made measurements at about 293 K for four concentrations between 1.8 and 6.9 mol dm^{-3} (See Compilations). The measurements of Le Chatelier[21] are low compared with later more extensive measurements; those of Engel[22] appear satisfactory except that the value for the highest concentration is substantially low. Neither set is sufficiently extensive to be of practical use. In 1895, Engel[23] made a second set of measurements at 289 K for three HCl concentrations between 4.9 and 6.9 mol dm^{-3}. All are distinctly low and at the highest concentration much lower than his previous results. This set is not included in the Compilations. The measurements which appear to be the most reliable are those of Chang and Cha[24] (1934), Hikita *et al.*[3] (1973) and Camacho Rubio *et al.*[25] (1985). They have been used as a basis for evaluation of all available data; they will be discussed

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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individually in succeeding paragraphs, where the available data are examined in chronological order.

The first extensive measurements of the solubility were made by Abel[26] in 1901. He made measurements at 288 K for 14 concentrations of HCl from 0.04 to 2.1 mol dm^{-3}. At the lowest three concentrations (0.04 to 0.063 mol dm^{-3}) his results are low by about a factor of two. The remaining results are reasonable within about 10 per cent, most of them high by 5 to 10 per cent. In 1909 Poma[27] measured the solubility at 298 K for 1, 2 and 4 mol dm^{-3} HCl without and with added $CuCl_2$. His measurements for "pure" aqueous HCl appear to be a few per cent high; measurements in solutions containing $CuCl_2$ will be discussed along with other quaternary systems. In 1918 Noyes and Chow[28] measured the solubility at 298 K for four HCl concentrations between 0.1 and 1.2 mol dm^{-3}. Their results appear good only to about 10 per cent (low at the lower end, high at the upper) but, along with related measurements, were adequate to provide approximate values of the equilibrium constant and enthalpy change for the reaction in which solid CuCl dissolves to form $CuCl_2^-$.

In 1922 Edgar and Cannon[29] measured the concentrations of both cuprous and cupric copper which accompanied the reduction of AgCl by CuCl in HCl solution at 298 and 313 K. They made 15 sets of duplicate measurements with H^+ molalities from 0.0027 to 0.255 mol kg^{-1} and Cu^{2+} molalities from 0.0104 to 0.0004 mol kg^{-1}. The solubilities of CuCl thus determined for solutions in which H^+ was the predominant cation agree well with other measurements; those in which Cu^{2+} was present at appreciable molalities will be discussed later. In 1928 Fedotieff[30] measured the solubility at 292 K in five solutions between 1.36 and 7 mol dm^{-3}. His results are marginal, as much as 11 per cent high compared with the average of other measurements.

Chang and Cha[24] made an extensive set of measurements in 1934. They measured the solubility of CuCl in aqueous HCl of 36 concentrations between 0.73 and 17.1 mol dm^{-3}, half of them above 7 mol dm^{-3}. They used two methods; in one set of experiments they analyzed solutions saturated with excess solid CuCl, while in the other set they measured the amount of gaseous HCl which had to be added to a given amount of water to dissolve a weighed amount of solid CuCl. The first method was used for concentrations of HCl between 6.4 and 17.1 mol dm^{-3}, the second for concentrations between 0.73 and 12 mol dm^{-3}. The reproducibility of measurements by either method and the agreement between the two in the region of overlap is 1 to 2 per cent except at the highest concentrations, where it is about 5 per cent. The results below 7 mol dm^{-3} can be compared directly with other measurements and agree with these within 5 per cent or less. They are rated Acceptable. The results for concentrations above 7 mol dm^{-3} can be compared only with graphical results of Morosov and Ustanishkova[31] and of Glodzińska and Zembura[32], both discussed below; they are Accepted tentatively, with an uncertainty of 5 per cent or less, in view of the high quality of the results at lower concentrations.

The only set of measurements which covered a wide range of temperatures was published by Morosov and Ustanishkova[31] in 1944. They presented 23 solubility measurements at five temperatures between 273 and 373 K, for HCl molalities from 1 to 20, about half of them above 10 mol kg^{-1}. Unfortunately, they presented their results only as graphs of the mass percentages of the components, with an uncertainty of reading individual points of as much as 10 per cent. Their results cannot be compared directly with other results (in mol dm^{-3}) for lack of knowledge of the densities of their solutions. Approximate comparisons were made by plotting the ratio of solubility to chloride molality against the chloride molality used, with both converted to mol kg^{-1}. (This sort of plot is not affected in a major way by differences in concentration units.) Comparing such a plot for their data at 298 K with similar ones for the data of Hikita *et al.*[3] for the lower concentrations and those of Chang and Cha[24] over the full range (both of these for mol dm^{-3}) indicated that the Morosov data follow appropriate trends and are probably reliable within the precision to which their

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

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graphs can be read. Their results at 273 K and at temperatures above 298 K cannot be compared with any other data. They may be used to give an indication of the solubility for temperatures where other data are not available, with the understanding that they may be in error by 10 per cent or more.

In 1948 Chaltykyan[33] published graphical data on the solubility of CuCl in aqueous HCl at 298 K from 1.7 to 9.8 mol dm^{-3} (5 points); to the extent they can be compared with other data, they are distinctly low. Four sets of measurements were published between 1950 and 1970, none of the quality of the previous results. In 1953, Gokhale[34] published a set of measurements at 300 K for seven concentrations of HCl between 0.15 and 4 mol dm^{-3}. These are substantially low below 1 mol $dm^{-3}$and about 10 per cent high at higher concentrations. In 1959 Malik, Rahman and Ali[35] presented data at an unspecified temperature (probably the ambient temperature of their laboratory) for 19 concentrations of HCl between 0.13 and 2.8 mol dm^{-3}. All results are high by at least a factor of two for any reasonable choice of temperature. In 1968 O'Connor, Thomasian and Armington[36] published graphical results for the solubility of CuCl at 295 K at seven concentrations of HCl between 0.9 and 5.6 mol dm^{-3}. Their results at the lowest concentrations are distinctly high; at concentrations of 2 mol dm^{-3} and above, they are erratic, differing by as much as 8 per cent from more reliable data. Also in 1968, Wilke[37] published the solubility of CuCl in a single molality of HCl (16 mol kg^{-1}) at four temperatures between 298 and 328 K, as part of a larger investigation of the solubility of CuCl in aqueous chlorides. His result at 298 K is consistent with the work of Morosov and Ustanishkova[31], but that at 328 K appears low, as may be his results at intermediate temperatures. The results of Malik *et al.*[35] have been Rejected and are not compiled. The numerical results of Gokhale[34] and the graphical results of O'Connor *et al.*[36] are given, but should not be assigned much weight.

In 1973 Hikita, Ishikawa and Esaka[3] published a very extensive set of data for the solubility of CuCl in aqueous HCl and in aqueous HCl–$HClO_4$ mixtures of six nominal ionic strengths from 0.5 to 6.5 mol dm^{-3} at temperatures of 288, 298 and 308 K. Among these data are 11 points at 298 K for "pure" HCl at concentrations from 0.5 to 5 mol dm^{-3} and 3 points each at 0.5, 1.0 and 2.0 mol dm^{-3} for each of the other two temperatures. The quality of these data is excellent; they average 1 per cent or less from the most probable values based on all of the data available. They presented many more measurements for solutions containing $HClO_4$ as well as HCl; these will be discussed later.

In 1974 Glodzińska and Zembura[32] published solubility data at 298 K for eight HCl solutions between 1.9 and 10.1 mol dm^{-3}. Their data are presented in graphical form, with an estimated error of 4 to 8 per cent. When compared with other data, they appear much less accurate than this, with deviations (±) from 3 to nearly 20 per cent. In 1979 Kale, Tamhankar and Chaudhari[17] presented data at 293, 302, 313 and 323 K for six HCl concentrations between 0 and 0.6 mol dm^{-3}. These results are Not Acceptable; they are distinctly high at low HCl concentrations and substantially low at the highest concentration used. In particular, the solubilities given in pure water are much higher than those corresponding to the solubility product of CuCl. Also in 1979, Novikov, Voropaev, Rud'ko and Zharskii[38] published data at 298 K on aqueous solutions containing HCl and $CuCl_2$. These included four points on aqueous HCl without added $CuCl_2$. Unfortunately, these points all appear high by 20 to 40 per cent. Their measurements on solutions containing $CuCl_2$ will be discussed later.

In 1985 Camacho Rubio, Paez Dueñas and Moreno Carretero[25] published an extensive set of data on the solubility of CuCl in aqueous HCl solutions, both without and with added NaCl or $CuCl_2$; for most sets of data, constant ionic strength was maintained by $HClO_4$ and/or $NaClO_4$. Their measurements covered the temperature range from 298 to 328 K, with measurements for which HCl was the only soluble chloride at 298 and 303 K. Unfortunately, all of their results are presented only in graphical form. The results for "pure" HCl

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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at 298 K agree with those of Hikita *et al.*[3] and Chang and Cha[24] within the uncertainty (2 to 5 per cent) of reading data from their graphs. The two results at 303 K are 5 to 10 per cent high compared with the other data.

Summary. Of all the data surveyed, those of Hikita *et al.*[3] appear the most reliable. They can be trusted to 1 or 2 per cent in the range they covered (up to 6.5 mol dm^{-3} HCl at 298 K). The data of Chang and Cha[24] are consistent with these up to 6.5 mol dm^{-3}; their data for higher concentrations (up to 17 mol dm^{-3}) can be relied upon to about 5 per cent, and those of of Edgar and Cannon[29] to about the same extent for solutions with HCl molalities below 0.25 mol kg^{-1}. The only data available for temperatures far removed from 298 K are the graphical results of Morosov and Ustanishkova[31], which cover the range from 273 to 373; they should give values within about 10 per cent where their graphs can be read to that precision. The data of Chaltykyan[33], Malik *et al.*[35], Kale *et al.*[17] and Novikov *et al.*[38] are all unreliable. The other data presented can be trusted to about 10 per cent for the conditions under which the solubility was measured.

$CuCl$–$NaCl$–H_2O

The solubility of CuCl in aqueous NaCl has been measured by quite a few investigators over a wide temperature range (273 to 370 K); the quality of some of the measurements leaves much to be desired. Four substantial sets of measurements are available for systems in which CuCl was dissolved in aqueous NaCl with no other soluble salt present. In 1953 Gokhale[34] reported solubilities at three aqueous NaCl concentrations for each of five temperatures between 281 and 370 K. More extensive results were published in 1964 by Sin, Shokin and Kuznetsova[39] and in 1969 and 1970 by Utkina and coworkers[40,41]. The Sin group reported solubility at a number of NaCl concentrations for five temperatures between 293 and 363 K; the Utkina group reported solubility at either four or five concentrations of NaCl for five temperatures ranging from 273 to 368 K.

A number of investigations have been made of the solubility in aqueous NaCl also containing HCl or an "indifferent" electrolyte. The most detailed of these was made in 1970 by Ahrland and Rawsthorne[5], who examined the solubility at 298.15 K for 33 concentrations of Cl^- in a medium containing H^+ at 0.1 mol dm^{-3} and maintained at a constant nominal ionic strength of 5 mol dm^{-3} by use of $NaClO_4$; they gave only one point, at 5 mol dm^{-3}, for a solution where the only anion present was Cl^-. In 1978 Peters and Johnson[42] gave a set of graphical data in a patent application; their solutions all had HCl concentrations of *app.* 0.26 mol dm^{-3}, with NaCl concentrations from 1.5 to 6.8 mol dm^{-3}, at temperatures of 278, 295, 323 and 348 K. In 1983 Fontana *et al.*[43] gave a graphical set of data at 298 K for solutions containing 1.0 mol dm^{-3} HCl and 0 to 3.6 mol dm^{-3} NaCl. In 1985 Camacho Rubio *et al.*[25] published an extensive set of measurements of the solubility of CuCl in aqueous mixtures of NaCl and HCl, maintained at one of a number of nominal ionic strengths with $NaClO_4$ and $HClO_4$ and with chloride concentration varied over the full range of each ionic strength. They gave no data for solutions which contained no H^+, but did present data for a mol ratio Na/H of 10, where the behaviour of the system would be little different from one containing sodium as the only cation. Their results for solutions containing H^+ as well as Na^+ will be discussed in a later section. However, those where H^+ was a minor constituent were used in evaluating the data for solutions containing only NaCl, since the data for the mixed solutions was of at least as good quality as those for solutions in "pure" aqueous NaCl.

As an aid to evaluation of the measurements in aqueous NaCl, a model was developed to represent the data of Sin *et al.*[39], Utkina *et al.*[40,41] and Gokhale[34], along with data from later investigators for which the concentration of H^+ was less than 10 per cent of the total cation concentration (for such mixtures the changes in solubility produced by substitution of a small part of the Na^+ by H^+ could be calculated from the known properties of CuCl

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in aqueous HCl). The model represented data from 273 to 370 K (156 points in all) with an estimated standard deviation of 9 per cent. The model was then used to evaluate the consistency of data and to compare data sets where there were modest differences in temperatures or concentrations.

The earliest set of measurements reported were those published by Kremann and Noss[7] in 1912. They gave data at 300 K for five solutions (0 to 8.4 mol dm^{-3} NaCl) in equilibrium with solid CuCl alone, three solutions in equilibrium with solid NaCl and one solution in equilibrium with both solid salts. Their value for the solubility of CuCl in pure water is high by at least an order of magnitude. The next point, at 1.85 mol dm^{-3}, is in modest agreement with the most probable value. The remaining points for which the solid phase was CuCl are low by at least 20 per cent. They presented a phase diagram for the ternary system, which will be discussed later. In 1928 Fedotieff[30] measured the solubility at 298 K for seven NaCl concentrations ranging from 0.16 to 6.3 mol dm^{-3}. His results were somewhat erratic, either lower or higher than other measurements by an average (r.m.s.) of 10 per cent. They can probably be trusted to about this precision. In 1948 Chaltykyan[33] published graphical data on the solubility of CuCl in aqueous NaCl at 298 from 1.8 to 9.8 mol dm^{-3}. These data are erratic and generally substantially low.

In 1953 Gokhale[34] presented the first set of measurements covering a range of temperatures. He measured three points at each of five temperatures (282, 299, 323, 345 and 370 K), in each case at 1, 2 and 4 mol dm^{-3} NaCl. His results suffer from lack of precision. Temperatures were given at best to 0.2 K, and to 1 K at the lowest temperature, 282 K; solubilities are given only to 0.01 mol dm^{-3}, leading to uncertainties as great as 10 per cent in regions where the solubility was low. His results vary erratically from high to low, compared with the most probable values, most being high or low by 5 to 30 per cent. While they give a general picture of the change of solubility with concentration and temperature, they cannot be relied upon, although his results at 370 K compare favorably with other measurements.

In 1962 Kosyakina[44] reported 17 points for a phase diagram of the system CuCl–NaCl–H_2O at 298 K, of which seven points were for solutions supposedly at equilbrium with solid CuCl (two of them with both solid salts present). The NaCl content of these solutions ranged from 0 to 8.6 mol kg^{-1}. Her results for the solubility of CuCl were uniformly high by 50 per cent or more, with the value for pure water high by two orders of magnitude. These results cannot be given serious consideration as values of the solubility; they are presented as a contribution to knowledge of the phase diagram of the ternary system, to be discussed in a later section.

In 1964 Sin *et al.*[39] published data at 293, 303, 323, 343 and 363 K, with four points [0.7 to 3.3 mol kg^{-1} NaCl] at 293 and 8 to 12 points (1 to 7 mol kg^{-1} NaCl) at each of the other temperatures. They reported their results in mass per cent (given also in mol kg^{-1} in the Compilations). They gave densities for most of their solutions, so that their results can also be converted to mol dm^{-3} for comparison with other data. In most cases, they presented pairs of results at nearly identical NaCl concentrations. These pairs are somewhat erratic, with members of a pair differing by an average (r.m.s.) of 5 per cent (worst case 23 per cent). With the scatter, their points deviate overall by about 7 per cent (r.m.s.) from the average of all available data. A smoothed set of their data can probably be trusted to about this precision. In 1968 Wilke[37] gave data for three solutions (1.54, 3.08 and 6.54 mol kg^{-1} NaCl) at 298, 308, 318 and 328 K. These data are very erratic, distinctly high at low NaCl concentrations and low at the high concentrations. They cannot be given serious consideration compared with other data available.

The 1969 data of Utkina *et al.*[40] contain five measurements each at 273, 298, 323, 348 and 368 K, for NaCl concentrations ranging from 0.04 to 5.8 mol dm^{-3}. The points at concentrations below 1 mol dm^{-3} are all high by 30 per cent or more; those at other concentrations

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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are generally about 10 per cent high compared with the average of all available data. Their 1970 measurements[41] contain four points each at 298 and 368 K, at concentrations from 1.7 to 5.1 mol dm^{-3}. These are also high with respect to other measurements and do not agree very well with their earlier data, differing from them by as much as 10 per cent, high or low. However, their two sets of data and those of Sin *et al.*[39] are still the best available for a wide range of concentration and temperature. The Sin data appear to be superior at low NaCl concentrations. The Utkina and Sin data are Accepted provisionally, with possible inaccuracies of 10 per cent in individual values.

Summary. None of the investigations of the solubility of CuCl in aqueous NaCl (with no other salt present) provides fully satisfactory information. The only value which can be assigned a precision of a few per cent is that of Ahrland and Rawsthorne[5] at 298 K, 5 mol dm^{-3}. The best sets of data for general use are those of Sin *et al.*[39] and those of Utkina *et al.*[40,41] for NaCl concentrations above 1 mol dm^{-3}. Any of these should be assigned a precision of about 10 per cent, with the first probably somewhat low and the latter two somewhat high. None of the remaining data can be considered reliable. Solubilities at low NaCl concentrations can best be estimated from those in aqueous HCl, from which they should differ by no more that a few per cent. More reliable information is available for aqueous NaCl solutions with HCl and/or a perchlorate added, to be discussed later.

$CuCl–KCl–H_2O$

Six sets of data were found for the solubility of CuCl in aqueous KCl, of which three merit serious consideration. The earliest report was that of Le Chatelier[21] in 1884; he presented six points at 290 K for KCl concentrations of 0.3 to 4.1 mol dm^{-3}. In 1902 Bodländer and Storbeck[1] published measurements in KCl concentrations from 0.001 to 2.0 mol dm^{-3} at temperatures varying from 289 to 293 K. At KCl concentrations below 0.1 mol dm^{-3} they observed Cu^{2+} in their solutions, due to oxidation. Only the four points at 0.1 mol dm^{-3} and above can be considered as part of the ternary system. The most extensive set of measurements is that given by Brönsted[45] in 1912, in a study of the phase diagram of the system $CuCl–KCl–H_2O$ at 293 K. He gave 21 measurements for which the solid phase was CuCl, many more where the solid phase was $CuCl\cdot 2KCl$ and four points with the solid phase KCl.

The data of Brönsted[45] are by far the most comprehensive. Unfortunately, the four points for molalities below 1.5 are much too low, compared with the solubility of CuCl in aqueous solutions of either HCl or NaCl, and must be discarded. The remaining points are reasonable and fall on a smooth curve within about 5 per cent. They agree within this limit with those measurements of Le Chatelier[21] which fall in this concentration range. His results near 2 mol kg^{-1} are about 5 per cent lower than those of Le Chatelier and about 15 per cent lower than those given by Bodländer and Storbeck[1]. The results of Le Chatelier[21] vary by about 10 per cent for nearly identical concentrations of KCl; his results above 0.5 mol dm^{-3} are smooth within about 5 per cent. The results of Bodländer and Storbeck[1] are quite erratic; the points between 0.5 and 1 mol dm^{-3} agree with those of Le Chatelier.

Three presentations of the solubility are highly unsatisfactory. In 1924 Valeton and Frömel[46] studied the phase diagram of the system $CuCl–KCl–H_2O$ at 298 K, purportedly at molalities of KCl below 1 mol kg^{-1}. They reported solutions in equilibrium with double salts $CuCl\cdot 2KCl$ and $CuCl\cdot KCl\cdot H_2O$ as well as some in equilibrium with solid CuCl or solid KCl. However, the solubilities reported for CuCl are enormously higher than those reported by other investigators, in some cases higher than the molality of KCl given! It would appear that some serious errors must have been made either in analysis of solutions or in presentation of the data. They did verify the existence of their double salts by chemical analysis; these results will be discussed later. Chaltykyan's 1948 paper[33] contained graphical data for the solubility of CuCl in aqueous KCl from 2 to 8 mol dm^{-3} at 298 K. His values are

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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quite erratic and are far lower than any other at high concentrations of KCl. Finally, in 1959 Malik *et al.*[35] reported a series of solubility measurements in aqueous KCl from 0.13 to 2.1 mol dm^{-3} at an unspecified temperature (presumably near 300 K). Their 14 measurements are all higher by factors of 2 or 3 than any others, even at concentrations where the nature of the cation should have little influence on the solubility. Their results are not presented in the Compilations.

Other features of the measurements described above will be discussed in later sections, *viz.* the data of Bodländer and Storbeck[1] on the quaternary system $CuCl-CuCl_2-KCl-H_2O$, the phase diagram of Brönsted[45], and the double salts involving CuCl and KCl reported by Valeton and Frömel[46].

Summary. The data of Brönsted[45] above 2 mol kg^{-1} can be Accepted tentatively, with an estimated uncertainty of 5 per cent. Between 0.5 and 2 mol dm^{-3}, estimates of about this precision can be obtained from the combined results of Le Chatelier[21] and of Bodländer and Storbeck[1]. Below 0.5 mol dm^{-3}, estimates can best be obtained from the solubility of CuCl in aqueous HCl at corresponding concentrations. None of the other measurements cited are recommended for use.

$CuCl-NH_4Cl-H_2O$

Three sets of data were found for the solubility of CuCl in aqueous NH_4Cl. In 1941 Iguchi and Nakanishi[47] published a set of data at 343 K for NH_4Cl concentrations from 9 to 29 mass per cent (2 to 33.5 mol kg^{-1} NH_4Cl), eight points in all. At the higher concentrations the mol ratio of dissolved CuCl to NH_4Cl reached unity. In 1944 Morosov and Ustanishkova[31] reported measurements of the solubility in solutions from 7.5 mass per cent NH_4Cl (1.6 mol kg^{-1}) to 43.5 mass per cent NH_4Cl (21 mol kg^{-1}) at five temperatures from 273 to 373 K. For many solutions they reported a double salt as the solid phase; these will be discussed in a later section. Solid CuCl (alone or accompanied by another solid) was reported as the solid phase for 25 of their solutions. Finally, in 1968 Wilke[37] published data for the solubility in each of three molalities of NH_4Cl (1.8 to 7) at 298, 308, 318 and 328 K.

The results of Morosov and Ustanishkova[31] are the most extensive. Unfortunately, their data were presented only as a set of fairly small scale graphs of mass per cent NH_4Cl against mass per cent CuCl, which can be read to no better than ten per cent at best, less well at low concentrations. The data in the compilations are the compiler's best effort to extract numerical data from graphs. They are smooth and internally consistent, and show reasonable variation with temperature. At temperatures of 323 K and higher, the mol ratio of dissolved CuCl to NH_4Cl approaches unity at high NH_4Cl concentrations. They are Accepted tentatively, within the large uncertainty reading the graphs. The data of Iguchi and Nakanishi[47] cover a larger range of NH_4Cl molalities. The two sets are in reasonable agreement at low molalities, however, the Iguchi data show much less rapid increase of solubility with NH_4Cl molalities. They should not be relied upon for intermediate NH_4Cl molalities (4 to 12 mol kg^{-1} NH_4Cl) but can be used for the high solubility of CuCl in solutions with NH_4Cl molalities above 20. The data of Wilke[37] do not agree with either of the other two sets, varying from higher at low molalities of NH_4Cl to much lower at high molalities. They are Not Acceptable.

Summary. Within the limited precision of the data available, the results of Morosov and Ustanishkova[31] are suitable for use for the concentrations and temperatures covered, within the rather poor precision with which their data can be taken from their graphical presentation. The data of Iguchi and Nakanishi[47] are suitable for use at 343 K for molalities from 20 to 33 mol kg^{-1} NH_4Cl. The data of Wilke[37] should not be used.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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$CuCl-LiCl-H_2O$

The only data reported for this system were those of Wilke[37], who gave the solubility of CuCl in aqeous solutions containing 4.9 and 9.8 mol kg^{-1} LiCl at 298, 308, 318 and 328 K. These cannot be compared with any other measurements on the same system, and in view of the problems with Wilke's other measurements, are probably not very accurate. Wilke did find that the solubility in aqueous LiCl was less than that in aqueous HCl (considerably less than in other alkali halides), and this observation can be used as a guide in estimating the solubility of CuCl in aqueous LiCl.

TERNARY SYSTEMS INVOLVING DIVALENT OR TERVALENT CATIONS

The only systems involving divalent cations (only) for which solubility data have been reported are $CuCl-CaCl_2-H_2O$, $CuCl-FeCl_2-H_2O$ and $CuCl-CuCl_2-H_2O$; these are discussed below along with qualitative information on solutions in aqueous $MgCl_2$ and aqueous $AlCl_3$. Data available for quaternary and more complex systems containing divalent cations are discussed in a later section.

$CuCl-CaCl_2-H_2O$

The solubility of CuCl in aqueous solutions of $CaCl_2$ has been reported by Shirokova *et al.*[48], Wilke[37] and Utkina *et al.*[41]. Shirokova *et al.*[48] made measurements at 303, 323, 343 and 363 K, with between 6 and 15 molalities at each temperature (See Compilations). Wilke[37] gave data at 298, 308, 318 and 328 K for each of three $CaCl_2$ molalities (1.7, 3.4 and 6.7). Utkina *et al.*[41] reported solubility for 298 and 368 K with six $CaCl_2$ concentrations (mol dm^{-3}) at each temperature.

The data of Shirokova *et al.*[48] are the most extensive. They cover a range from 0.5 mol kg^{-1} $CaCl_2$ to saturation (11 to 13 mol kg^{-1}) at each of their four temperatures (42 points in all). They reported their data in mass per cent, easily convertible to mol kg^{-1}; see Compilations. Utkina *et al.*[41] gave data for concentrations from 0.90 to 4.50 mol dm^{-3} at each of their temperatures. The two sets of data cannot be compared directly because of the difference in concentrations units employed and temperatures investigated. A rough comparison can be made by plotting the ratio of solubility to $CaCl_2$ concentration against the $CaCl_2$ concentration for each set of data, using quantities in mol kg^{-1} for the Shirokova data and mol dm^{-3} for the data of Utkina *et al.* (Such a plot is insensitive to the choice of concentration unit, completely so at concentrations sufficiently low that the density of solution is near that of pure water.) Comparison made in the fashion indicates that the two sets of data differ by no more than 10 per cent. In addition, the effect of temperature on solubility is the same for both sets to at least this precision.

Of the two sets, the data of Utkina *et al.*[41] are smoother, deviating from a smooth curve by 5 per cent or less. The data set of Shirokova *et al.*[48] contains a number of pairs of points, at nearly identical $CaCl_2$ concentrations, which differ from each other by 10 to 15 per cent, although the majority of the points fall much more closely on a smooth curve. The data of Utkina *et al.*[41] are Recommended for use at the concentrations and temperatures to which they apply, subject to an uncertainty of 5 per cent. The data of Shirokova *et al.*[48] are Accepted tentatively for other temperatures and concentrations, with an uncertainty of 10 per cent. The data of Wilke[37] are Unacceptable. His results are somewhat higher than the other two at his lowest molality but low by as much as a factor of two at the higher molalities. In addition, the increase in solubility with temperature for his data is far less than that given by the other two sets of investigators.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

$CuCl-FeCl_2-H_2O$

The only data available for this system are those of Kremann and Noss[7] for $FeCl_2$ molalities from 0 to 5.2 at 295 K. These data are smooth, and, except for points at 0 and 0.48 mol kg^{-1}, agree with the effects of $FeCl_2$ on the solubility in more complex systems to be discussed below. Their point at zero $FeCl_2$ molality is much too high, as previously noted, and that at 0.48 mol kg^{-1} likewise. The remaining eight points follow a smooth curve with a standard deviation of about 4 per cent and are Recommended for use.

$CuCl-CuCl_2-H_2O$

Data for the solubility of CuCl in aqueous $CuCl_2$ have been reported by Fedotieff[30] and by Utkina *et al.*[41]. Fedotieff[30] measured the solubility at 292 K for five $CuCl_2$ concentrations from 1.0 to 4.9 mol dm^{-3}. Utkina *et al.*[41] obtained data at 298 and 368 K for five concentrations between 1.0 and 4.5 mol dm^{-3}. The data of Fedotieff[30] agree with those of Utkina *et al.*[41] at 298 K within a few per cent after a small adjustment for the difference in temperature. Both sets agree with expectations based on the solubility in more complex solutions containing a second soluble chloride in addition to $CuCl_2$, discussed under quaternary systems. They are Recommended for use at room temperature. The Utkina *et al.*[41] data at 368 K cannot be compared with any other. They are Recommended tentatively in view of the good quality of the data at 298 K.

In addition to the data considered above, information is available from a number of investigators for the solubility in solutions containing a second soluble chloride in addition to $CuCl_2$. Poma[27], Edgar and Cannon[29], Novikov *et al.*[38] Pochtarev *et al.*[49], Pochtarev *et al.*[50] and Camacho Rubio *et al.*[25] all published solubility data for aqueous mixtures of HCl and $CuCl_2$. Sin *et al.*[39] and Pochtarev *et al.*[51] gave data for aqueous $NaCl-CuCl_2$ mixtures. Shirokova *et al.*[48] presented data for aqueous $CaCl_2-CuCl_2$. All of these results are discussed under quaternary systems.

Other Systems

Information on two other systems have been reported in the form of abstracts, without any numerical data. Shutov and coworkers[52] reported making measurements of the solubility of CuCl in aqueous $MgCl_2$ at 298, 323, 348 and 368 K, but do not give numerical information on the concentrations of $MgCl_2$ investigated or the actual solubilities determined. They state that the solubility was greater in $MgCl_2$ solutions than in the corresponding concentrations of NaCl or $CaCl_2$. Later, members of the same group state, in another abstract[53], that they had measured the solubility of CuCl in aqueous $AlCl_3$ from 0.1 mol dm^{-3} to saturation at 273, 298, 323, 348 and 368 K, and found it greater than in aqueous $MgCl_2$ or NaCl. Search of the literature disclosed no detailed publication of the experiments mentioned above.

Recently, Karimova, Ksandrov and Nikandrov[107] presented phase diagrams of the system $CuCl-MgCl_2-H_2O$ at 273, 283 and 313 K.

SYSTEMS INVOLVING A SOLUBLE CHLORIDE WITH AN INDIFFERENT SALT

A number of investigations of solubility have been made using either HCl or NaCl with $HClO_4$ or $NaClO_4$ added to maintain a desired (nominal) ionic strength, primarily to examine the equilibria involved in complex formation by CuCl. [Note: The actual ionic strengths of the solutions cannot be constant, since formation of complexes with charge greater than unity produces an increase in ionic strength. Note also that in the discussion which follows, the chloride concentrations listed are those of the initial solutions, not the (lower) values of free Cl^- present after complex formation.]

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

McConnell and Davidson[54] made five measurements in aqueous $HCl-HClO_4$ at 298 K, ionic strength 1.0 mol dm^{-3}, with chloride concentrations from 0.2 to 0.8 mol dm^{-3}. Vestin *et al.*[55] made a much more extensive set of measurements on the same system at 298 K, ionic strength 4.0 mol kg^{-1}. Hikita *et al.*[3] measured the solubility in aqueous $HCl-HClO_4$ at 288, 298 and 308 K, with six ionic strengths (0.5 to 6.5 mol dm^{-3}) at 298 and three ionic strengths (0.5 to 2.0 mol dm^{-3}) at the other two temperatures. They made six or more measurements with variable chloride for each temperature and ionic strength, with 47 points at 298 K and 23 points at each of the other temperatures. In each case, the concentration of chloride was varied from a small fraction (5 to 17 per cent) to the full ionic strength. Camacho Rubio *et al.*[25] measured the solubility in aqueous $HCl-HClO_4$ at 303 K, ionic strength 2.0 mol dm^{-3}, for [Cl^-] from 0.2 to 2.0 mol dm^{-3}, 15 points in all. In a second paper, Camacho Rubio *et al.*[108] measured the solubility in aqueous $HCl-HClO_4$ at 293, 303, 313 and 323 K, ionic strength 1.0, 1.5 and 2.0 mol dm^{-3}, for [Cl^-] from 0.2 to 2.0 mol dm^{-3}, 44 points in all.

Ahrland and Rawsthorne[5] studied the solubility in aqueous $NaCl-NaClO_4$ at 298 K, ionic strength 5.0 mol dm^{-3}, with 32 points for chloride concentrations from 0.003 to 5.0 mol dm^{-3}. They also measured the potentials of numerous concentration cells involving this system; these provide indirect information about the solubility. All of their solutions contained 0.1 mol dm^{-3} of H^+, presumably to guard against hydrolysis of the dissolved Cu(I); this small (2 per cent) replacement of Na^+ by H^+ has an almost negligible effect on the solubility. Sin *et al.*[39] measured the solubility of CuCl in aqueous $NaCl-Na_2SO_4$ at 293 K for NaCl concentrations of 0.7 to 3.4 mol dm^{-3} and Na_2SO_4 concentrations from 0 to 0.36 mol dm^{-3}.

Of the four sets of measurements on aqueous $HCl-HClO_4$, the data of Hikita *et al.*[3] are the most extensive and appear to have the best precision. All 93 points can be represented, along with their data on $CuCl-HCl-H_2O$, by a common set of parameters with a standard deviation of 2 per cent, with the worst points (at 288 and 308 K) deviating by 7 per cent. Their data at 298 K can be represented to 1.5 per cent (worst points 3 per cent). The data of Camacho Rubio *et al.*[25] at 303 K are uniformly about 5 per cent lower than would be expected from the data of Hikita *et al.*[3] (somewhat worse than would be anticipated from the uncertainty in reading their data from graphs) and scatter somewhat more from a smooth curve. In their second paper, Camacho Rubio *et al.*[108] present a 4-parameter equation (See Compilations) which represents their data as well as those of Hikita *et al.*[3] within 5% and can be used in the ionic strength range of 1.0 to 2.0 mol dm^{-3} and in the temperature range of 20 to 50°C. The data of Vestin *et al.*[55] cannot be compared directly with those of Hikita *et al.*[3] because of the difference in concentration units. A comparison of the ratio of solubility to initial chloride concentration indicates that the Vestin data are somewhat less smooth, but follow closely the course of the Hikita data in concentration regions where they overlap. The data of Hikita *et al.*[3] are Recommended for the concentration and temperature ranges they cover, with estimated precision of 2 per cent. The data of Vestin *et al.*[54] are Recommended for concentration ranges not given by Hikita *et al.*[3], with an estimated precision of 2 to 4 per cent. The data of Camacho Rubio *et al.*[25] appear to be about 5 per cent low, on the average. The data of McConnell and Davidson[54] are distinctly inferior to the previous three sets, being typically 40 to 50 per cent high; they have been Rejected and are not compiled.

The values for the solubility of CuCl in aqueous $NaCl-NaClO_4$ given by Ahrland and Rawsthorne[5] are distinctly higher than those of Hikita *et al.*[3] for given chloride concentrations, typically 40 to 60 per cent. This is due to the difference between Na^+ and H^+ in their effect on the activity coefficients of the ions present in solution. Both sets can be represented to good precision using a common set of equilibrium constants (zero ionic strength), the known activity parameters[18] for the simple salts (HCl, NaCl, etc.) and suitable derived parameters for the ion pairs between the cation and the various complex ions formed. The only significant difference is that the Ahrland and Rawsthorne data are slightly less smooth (standard deviation about 3 per cent). They are Recommended for use with $NaCl-NaClO_4$

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

solutions of CuCl.

The data of Sin *et al.*[39] on aqueous $NaCl$–Na_2SO_4 are Not Recommended for use. They cover only a small range of concentration of Na_2SO_4, are somewhat erratic and show no distinctive effect of the added salt on the solubility. (In addition, their data on solubility in aqueous NaCl alone are somewhat erratic, although on the average comparable to other measurements.)

Comparison of the data of Hikita *et al.*[3] with those of Ahrland and Rawsthorne[5] points to a precaution which must be observed in considering data for solubility involving complex formation. Many data are available in the literature for solubility of materials in solutions of constant nominal ionic strength. It is easy, but erroneous, to draw the inference that such results apply to all solutions of the same initial ligand concentration and ionic strength. The effect of changing a non-complexing cation can be quite serious, as described above. In addition, the effect of changing an "indifferent" anion (for example, replacing $NaClO_4$ by $NaNO_3$) cannot be ignored, since this too may produce changes in the activity coefficients of all ions present. Fortunately, activity coefficient behaviour of most "indifferent" salts is well known; such information is discussed in later sections.

SYSTEMS INVOLVING TWO OR MORE SOLUBLE CHLORIDES

Numerous studies have been made of the solubility of CuCl in aqueous solutions containing more than one soluble chloride, including HCl with NaCl, HCl or NaCl with $CuCl_2$, and a variety of others. Some of these, directed toward practical use, were made on solutions containing as many as four soluble chlorides. Others, directed more toward theoretical ends, contain one or two "indifferent" electrolytes along with the soluble chlorides. The various systems will be discussed in groups of increasing complexity.

Systems Containing HCl and NaCl

Data on the system $CuCl$–HCl–$NaCl$–H_2O were first reported by Gokhale[34] in 1953. He published the solubility at "room temperature" (presumably about 300 K) of CuCl in seven solutions made up by adding various proportions of 12 mol dm^{-3} HCl to a solution originally containing 4 mol dm^{-3} of NaCl. In the solutions as used, HCl concentrations ranged from 0 to 1.79 mol dm^{-3} and NaCl from 3.99 to 3.40 mol dm^{-3}. In 1978 Peters and Johnson[42] gave a set of graphical data at four temperatures from 278 to 348 K for the solubility of CuCl in aqueous solutions containing about 0.26 mol dm^{-3} of HCl and 1.5 to 6.8 mol dm^{-3} of NaCl (25 points in all). In 1982 Winter *et al.*[56] gave graphical data for the solubility of CuCl in each of 7 mixtures of aqueous HCl and NaCl at six temperatures between 293 and 363 K, with some numerical data at 343 K. In 1983 Fontana *et al.*[43] made a spectroscopic study of the complexes present in the system $CuCl$–$NaCl$–HCl–H_2O at 298 K. They dissolved various amounts of CuCl in solutions containing 1 mol dm^{-3} HCl and 0, 1, 3 or 4 mol dm^{-3} NaCl. They then obtained the amount of CuCl dissolved (up to saturation) by summing the concentrations of the various complexes observed. They presented their results only in graphical form. In 1985 Camacho Rubio *et al.*[25] published an extensive set of measurement of the solubility of CuCl in the system $(Na,H)Cl$–$(Na,H)ClO_4$–H_2O. They presented data at 303 K, ionic strength 2.0 mol dm^{-3} for mol ratios Na/H of 0, 0.1, 1.0 and 10, in each case varying the chloride concentration from 0.2 to 2.0 mol dm^{-3}. They also gave data, at this same temperature, for solutions with Na/H of 1.0 at ionic strengths 0.5, 1.0 and 5.0 mol dm^{-3}, again varying chloride concentration over a 5 to 10-fold range. Finally, for ionic strength 2.0 mol dm^{-3}, $Na/H = 1$, they give a similar set of results for temperatures of 293 and 313 K. Their results were presented only in the form of graphs (see Compilations), some of which are on a very small scale. In general their graphs can be read to 2 or 3 per cent, in some cases no better than 5 to 10 per cent.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Because of the abundance of data on the solution of CuCl in aqueous HCl and aqueous NaCl, both with and without an indifferent electrolyte present, it is possible to compare all of the above data with the solubilities which would be expected if H^+ and Na^+ affected the solubility independently (through their effects of the activity coefficients of the species present). This has been done, and the discussion below is based on such treatment as well as on direct comparison of sets of data where similarity in conditions makes this possible. Of the five sets of data cited above, those of Gokhale[34], Winter *et al.*[56] and Camacho Rubio *et al.*[25] give the effect on the solubility of altering the ratio of Na^+ to H^+; they will be considered first. The remaining investigations give the effect of changing chloride concentration for NaCl–HCl mixtures with the H^+ concentration fixed (usually at a small value) and will be taken up second. (Note that the results of Ahrland and Rawsthorne[5], discussed earlier, were for a mol ratio Na/H of 49, and give essentially no information about the effect of mixing the two cations.)

The data of Gokhale[34] cover only a small range (near 4.0 mol dm^{-3}) of NaCl concentrations with H/Na mol ratios from 0 to 0.52 and are of moderately good quality. They have an internal consistency of about 5 per cent and are about that amount higher than would be expected from other measurements. They suffer from the fact that they lack definite information about the temperature; their actual temperature may have been somewhat different from the estimate of 300 K given above. In addition, their rather limited range of concentrations of HCl and NaCl with no concentration (HCl, NaCl or total) held constant, limits their usefulness. They show an increasing trend in solubility for increased H^+, but this is mainly due to increases in the total chloride concentration; it is less than would be expected for similar increases in the concentration of NaCl, as would be expected from the fact that HCl promotes the solubility less than NaCl does. The trend in their data is quite reasonable except that they report a (questionable) small decrease in solubility for the first small addition of HCl.

Winter *et al.*[56] examined the effect of changing the Na/H mol ratio for nominal ionic strengths of 3.0 and 5.0 mol dm^{-3} at temperatures of 293, 303, 313, 323, 333 and 343 K. At ionic strength 3.0 they varied the ratio from 0 to 1 (4 points); at ionic strength 5.0 it was varied from 0.2 to 0.8 (again 4 points). The changes in solubility they report are generally smooth and almost linear in the Na/H ratio, with the solubility increasing 20 to 30 per cent on going from aqueous HCl to aqueous NaCl. Their results at temperatures below 323 K agree with expectations based on other data to about 5 per cent (slightly more than the uncertainty of reading their graphical data), with deviations randomly positive and negative. Their results at and above 323 K agree with other data only to about 9 per cent, mostly on the high side. However, their data as a whole appear reliable to about the percentages cited.

The work of Camacho Rubio *et al.*[25] represents the most systematic attempt to determine the effect of mixtures of aqueous HCl and NaCl on the solubility of CuCl. Most of their measurements were made at 303 K, nominal ionic strength 2.0 mol dm^{-3}, but some of them are at other temperatures and some at other ionic strengths between 0.5 and 5.0 mol dm^{-3}, and in each set of experiments they used a wide range of chloride concentrations. First of all, the effects of changing $[Cl^-]$ at constant ionic strength and other variables are smooth within approximately the uncertainty (2 to 4 per cent) of reading their data from the graphs they present, only rarely deviating from a smooth curve by any larger amount. Within somewhat larger limits (*app.* 10 per cent), the effects of changing temperature and those of changing ionic strength are reasonable, compared with other available data. There are some problems with their results, however. They give a set of results for "pure" HCl solutions from 0.5 to 5.0 mol dm^{-3} at 298 K which agree with the corresponding results of Hikita *et al.*[3] within about 5 per cent on the average, but show deviations of about the same amount from a smooth curve, compared with deviations of about 1 per cent for the Hikita data. They give a set of results for the effect of variation of chloride concentration in aqueous

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

HCl–$HClO_4$ at 303 K, nominal ionic strength 2.0, which are only a few per cent higher than those observed for the same system by Hikita *et al.*[3] at 298 K, compared with the increase of 10 to 15 per cent obtained by interpolation between the Hikita data for 298 and 308 K (the Hikita data follow a trend with temperature consistent with other measurements at higher temperature). The most serious problems are found in their data on the effect of changing the mol ratio Na/H at 303 K, ionic strength 2.0 mol dm^{-3}. Their graphs show a sharp increase in solubility produced by replacement of 10 per cent of the H^+ by Na^+ and in some cases both a maximum and a minimum in the solubility as the mol ratio Na/H is varied; the data vary by up to 7 per cent from linear dependence on the Na/H ratio. This is in marked contrast to the effects given by Winter *et al.*[56], which are much more reasonable and conform to a situation in which the Na^+ and H^+ exert their effects on the solubility more or less independently. Since there are no other data available for direct comparison, one should not trust the data of Camacho Rubio *et al.*[25] with respect to the effect of replacing H^+ by Na^+ to better than about 10 per cent.

Peters and Johnson[42] made measurements in solutions with only a small amount of HCl present in what was primarily aqueous NaCl. Their results are mostly high compared with what would be expected from other data. At 295 K, where duplicate points are given, these differ by 4 to 6 per cent. Their results at 323 and 348 K are 10 per cent or more higher than the corresponding results of Sin *et al.*[39] and of Utkina *et al.*[40] for aqueous solutions of the same chloride concentration with no HCl present. The Peters and Johnson results can probably be trusted to about 10 per cent, with errors generally on the high side.

The results of Fontana *et al.*[43] have the advantage of covering a range of concentrations (and ionic strengths) at 298 K, and their graph permits reading values for chloride concentrations anywhere in the range 0.9 to 4.6 mol dm^{-3}. However, there are only five measured points in this range, and other information must be obtained from their smooth curve. Unfortunately, their results appear to be systematically high, in most cases by 20 per cent or more; for example, their value, at 298 K, for the solubility in a (supposedly) equimolar mixture of HCl and NaCl at a total concentration of 2 mol dm^{-3} is more than 25 per cent higher than that given by Camacho Rubio *et al.*[25] for such a mixture at 303 K, and their point at a total concentration of 4.6 mol dm^{-3} is higher than that given by Ahrland and Rawsthorne[5] for 5.0 mol dm^{-3} NaCl, which should show the higher solubility. The problem may arise from their indirect method of getting the solubility by summing the spectroscopically determined concentrations of the complex species present. In addition there is some ambiguity about the actual proportions of the two soluble chlorides present. They state that all solutions were made up to pH 0, implying a HCl concentration of 1.0 mol dm^{-3}, but the information they provide about the materials used to obtain their solutions implies that the actual solutions contained smaller (and different) concentrations of HCl. Their results for solubility can thus not be given serious consideration for use; the phase diagram they present and their determination of the distributions of complex species in their solutions will be discussed in later sections.

Summary. The data of Gokhale[34] are adequate to about 5 per cent for a limited range of concentrations at a temperature of about 300 K. Winter *et al.*[56] provide the most reliable information on the solubility in mixed solutions of aqueous HCl and NaCl, not only near room temperature, but also up to 343 K. Their data are Recommended for the concentration region (3 to 5 mol dm^{-3}) and temperature range (293 to 343 K) they cover, with an estimated uncertainty of 5 to 10 per cent. The data of Camacho Rubio *et al.*[25] may be used to obtain approximate ideas of the solubility for intermediate ranges of the mol ratio Na/H, particularly for ionic strength 2 mol dm^{-3}, with an estimated precision of about 10 per cent. (In general, results of the same order of reliability can be obtained by linear interpolation between the solubility in aqueous HCl and that in aqueous NaCl.) The data of Peters and Johnson[42] on solutions with only a small amount of HCl present can be used to get approximate values of the solubility in such solutions, but are probably high by as much as

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

10 per cent. The data of Fontana *et al.*[43] appear uniformly high, and should not be relied upon.

Systems Containing HCl and NH_4Cl

Two reports have been found of the solubility of CuCl in aqueous mixtures of HCl and NH_4Cl. In 1941 Iguchi and Nakanishi[47] published values of the solubility at 323 K in mixtures containing from 0 to 3 mol kg^{-1} HCl along with 13 to 14 mol kg^{-1} NH_4Cl. In 1945 Morosov and Ustanishkova[31] presented isotherms for the quaternary system CuCl–HCl–NH_4Cl–H_2O at 323, 343 and 373 K. The Iguchi data illustrate that the addition of HCl increases the solubility less than would be produced by a corresponding increase in NH_4Cl molality, but all solubilities reported are near 1 mol CuCl dissolved for each mol of soluble chloride. The two sets agree in assigning a very high solubility to CuCl in the presence of large molalities of NH_4Cl, but they cannot be compared because of differences in the temperature and the lack of numerical data in the Morosov publication. The data of Iguchi and Nakanishi[47] are Accepted tentatively. Morosov and Ustanishkova[31] discuss the presence of a double salt at 343 K but not at higher temperatures; this will be considered in a later section.

Systems Involving $CuCl_2$ and HCl

A number of investigations have been made in aqueous systems involving copper(II) chloride along with HCl. In 1909 Poma[27] published data on the solubility at 298 K in solutions containing 1, 2 and 4 mol dm^{-3} HCl with from 0 to 0.5 mol dm^{-3} of $CuCl_2$ added (6 to 8 points for each HCl concentration, 30 in all). In 1922 Edgar and Cannon[29] gave data for low molalities of the two electrolytes at 298 and 313 K, with H^+ from 0.003 to 0.25 mol kg^{-1} and Cu^{2+} 0.01 to 0.0004 mol kg^{-1}, 15 points in all (see Compilations). In 1974 Pochtarev *et al.*[49] published isotherms at 293, 313, 333 and 353 for solutions in equilibrium with both solid CuCl and solid $CuCl_2$ (19 points in all). In 1979 Novikov *et al.*[38] published a set of measurements at 283 K for HCl from 0 to 9.2 mol kg^{-1} and $CuCl_2$ from 4.8 to 0 mol kg^{-1}. They gave 30 points in all, among which 14 had CuCl as the solid phase, 12 had $CuCl_2{\cdot}2H_2O$ as the solid phase, and four had a mixture of the two salts; their solutions had mol ratios of Cu^{2+}/H^+ from 0 to 4.0 at low H^+ molalities and from 0 to 0.14 at high H^+ molalities. In 1980 Pochtarev *et al.*[50] published many data for the system CuCl–HCl–$CuCl_2$–H_2O, including the data reported by Pochtarev *et al.*[49] and many others. They reported measurements at 293 K for 29 mixtures in equilibrium with solid CuCl only and additional measurements at 293, 313, 333 and 353 K for solutions in equilibrium with both solid CuCl and solid $CuCl_2$ (9 points at 293 K, 21 in all). The first set covered a range from 0.4 to 9.0 mol dm^{-3} of HCl and 0.6 to 3.1 mol dm^{-3} of $CuCl_2$. The second set covered a range of 0.8 to 9.4 mol dm^{-3} of HCl and 5.0 to 2.3 mol dm^{-3} of $CuCl_2$; it contained 9 points at 293 K, with 5, 4 and 3 points at the other temperatures, respectively. Finally, Camacho Rubio *et al.*[25] made measurements on the system CuCl–HCl–$CuCl_2$–$HClO_4$–H_2O at total nominal ionic strength 2.0 mol dm^{-3}, with H^+ concentrations of 2.0, 1.85, 1.70 and 1.25 mol dm^{-3}, Cu^{2+} concentrations of 0, 0.05, 0.10 and 0.25 mol dm^{-3}; for each set the concentration of Cl^- was varied over the full range of concentration (6 to 9 values for each set, 34 points in all), with $HClO_4$ used to maintain the desired ionic strength. In a second paper, Camacho Rubio *et al.*[108] presented measurements at 40 and 50°C in graphical form.

The solubility behaviour of CuCl in aqueous HCl is very well known and that in aqueous $CuCl_2$ is reasonably well known. It is much smaller in the latter medium at concentrations where the effect of the cation on activity coefficients is significant. It is therefore reasonable to expect the solubility in aqueous HCl–$CuCl_2$ mixtures to be lower than that in an aqueous solution of HCl with the same total chloride concentration, the amount depending on the fraction of the chloride contributed by $CuCl_2$. This criterion can be used to estimate the reliability of data where direct comparison with other data is not possible.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

The data of Poma[27] are generally satisfactory, with internal consistency of a few per cent and average deviation from expectations based on the two ternary systems of less than 5 per cent (generally low). They are considered Acceptable. The data of Edgar and Cannon[29] are satisfactory for the limited range of conditions they cover. All of their measurements are at such low concentrations that the effect of changing the cation is not significant, and they confirm that low concentrations of $CuCl_2$ produce very nearly the same effect on the solubility as does the equivalent amount of Cl^- supplied by HCl. There is some difficulty in knowing the exact composition of their solutions, since in the data they report (their Table I) the positive and negative charges do not balance.

The data of Novikov *et al.*[38], those of Pochtarev *et al.*[49] and those of Pochtarev *et al.*[50] are questionable. The 1980 Pochtarev data cover a wide range of concentrations (listed above) and Cu/H mol ratios from 0.06 to 5.0 (the majority of those for which the solution was in equilibrium with CuCl only had ratios below 0.3). Those points for which the total chloride concentrations was below 7 mol dm^{-3} can be compared directly with the solubilities which would be found if either HCl or $CuCl_2$ provided all of the chloride. Of 14 such points, eight gave solubilities higher than would have been observed in aqueous HCl and all but two of the remainder were decidedly nearer to that in HCl than would be expected from the amount of $CuCl_2$ present; one gave a solubility far lower than that in either aqueous HCl or aqueous $CuCl_2$ with the same chloride concentration. Their remaining 15 points are at too high a chloride concentration to be compared with other data or with expectations based on the behaviour of the ternary systems. While the sort of behaviour they report is not impossible, it does not seem reasonable. In the absence of confirmatory evidence, their results can be taken only to give an approximate idea of the solubility of CuCl in high concentrations of aqueous $HCl-CuCl_2$. The data of Novikov *et al.*[38] were reported in mass per cent (convertible to mol kg^{-1}) and cannot be compared directly with any other data. However, their few data for solutions containing only HCl are erratic (generally much higher than would be expected). In addition, two of their points near 1 mol dm^{-3} total chloride concentration differ by a factor of 3 for a difference in total chloride of 3 per cent. Their results also should be taken as approximate only until additional evidence is available.

The data of Camacho Rubio *et al.*[25] appear generally satisfactory. Their results for the system $CuCl-HCl-HClO_4-H_2O$ for 10 different concentrations of chloride agree with other measurements within approximately the uncertainty (5 to 10 per cent) of reading their graphical presentation of their data. They give two points for the system $CuCl-HCl-CuCl_2-H_2O$ with no $HClO_4$ present; these agree to the same extent with values expected from the ternary systems. The bulk of their data is for the system $CuCl-HCl-CuCl_2-HClO_4-H_2O$. Most of these data are in satisfactory agreement with predictions of a model using parameters based on the behaviour of the systems $CuCl-HCl-H_2O$ and $CuCl-CuCl_2-H_2O$, however, their data for low chloride concentrations in solutions containing 0.1 and 0.25 mol dm^{-3} of $CuCl_2$ are surprisingly low. In their second paper, Camacho Rubio *et al.*[108] present a 6-parameter equation (See Compilations) which represents their results as well as literature data within 10% and can be used for $CuCl_2-HCl-HClO_4$ solutions in the ionic strength range of 1.0 to 2.0 mol dm^{-3} and in the temperature range of 20 to 50°C. In fact, this equation predicts higher CuCl solubilities for the conditions indicated above.

Summary. The data of Poma[27] are Recommended for the temperature and concentration range they cover, as are the limited data of Edgar and Cannon[29]. The data of Camacho Rubio *et al.*[25] are also Recommended, except that their points for large Cu/H ratio and low concentrations of chloride should be subject to further verification. The equation given by Camacho Rubio *et al.*[108] is also Recommended for the ionic strength range of 1.0 to 2.0 mol dm^{-3} and the temperature range of 20 to 50°C. The data of Novikov *et al.*[38], those of Pochtarev *et al.*[49] and those of Pochtarev *et al.*[50] should be taken only to give an approximate idea of the solubility of CuCl at high concentrations of aqueous $HCl-CuCl_2$ mixtures.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Systems Involving $CuCl_2$ and NaCl or KCl

Two sets of measurements were found for the system $CuCl-NaCl-CuCl_2-H_2O$. In 1964 Sin *et al.*[39] published a limited set of data (10 points) on the solubility of CuCl in aqueous solutions containing 0.9 to 5.3 mol dm^{-3} NaCl with 0 to 0.18 mol dm^{-3} $CuCl_2$ at 323 K. In 1978 Pochtarev *et al.*[51] gave data on the solubility at 300 K in aqueous mixtures with NaCl concentrations of 0.2 to 5.8 mol dm^{-3} and $CuCl_2$ from 4.5 to 0.2 mol dm^{-3}. As in their 1980 measurements on $CuCl-HCl-CuCl_2-H_2O$ described above, they presented one set of measurements in which the solid phase was CuCl alone (25 points) and another in which both solid CuCl and solid $CuCl_2$ were at equilibrium with the solution. In 1902 Bodländer and Storbeck[1] reported values of the solubility at temperatures from 289 to 293 K for 15 solutions containing aqueous KCl at concentrations from 0.001 to 2.0 mol dm^{-3} with small concentrations of Cu^{2+} produced by disproportionation during the course of the experiment. These are the only measurements reported for the system $CuCl-KCl-CuCl_2-H_2O$.

The data of Sin *et al.*[39] are erratic. Results for the three solutions in which only NaCl was present agree with other data within a few per cent, but their results for solutions containing $CuCl_2$ as well are both higher and lower than would be expected based on the properties of the two systems. The data as a whole are probably reliable within somewhat less than 10 per cent. The results of Pochtarev *et al.*[51] are definitely more satisfactory. The results reported for solutions in equilibrium with solid CuCl (only) cover a range from 30 to 89 per cent of the chloride supplied by $CuCl_2$, with 3 to 5 points each in five different ranges of Cu/H mol ratio. Except for four points, the solubilities given for 17 solutions with nominal ionic strength less than 7 mol dm^{-3} lie between the value expected for aqueous NaCl and that for aqueous $CuCl_2$ with the same total chloride. All except the four agree within 5 to 10 per cent with predictions based on the properties of the two ternary systems. Although their values cannot be checked directly against any other measurements, they appear generally reasonable. The solubilities given for solutions in equilibrium with both solid CuCl and $CuCl_2$, and eight of those where the solid phase was CuCl only, involve ionic strengths too high for comparison with other results, but appear on the whole satisfactory. These results are Accepted tentatively, subject to possible future verification.

The results of Bodländer and Storbeck[1] are of little utility. They reported the presence of Cu^{2+} only for KCl concentrations below 0.1 mol dm^{-3}. Their solubility data in this range are reported at best to 5 per cent, some to only one significant figure, and all appear to be low.

Summary. Of the two sets of data available for the solubility of CuCl in aqueous $NaCl-CuCl_2$ mixtures, the results of Sin *et al.*[39] at 323 K cover only a very limited range of concentration of $CuCl_2$ and are of doubtful validity. The much more extensive results of Pochtarev *et al.*[51] at 300 K appear valid within 5 to 10 per cent and are Accepted tentatively, subject to possible future verification. The early results of Bodländer and Storbeck[1] are of interest historically and because they give information on the disproportionation of Cu(I) at low chloride concentrations, but have little value as guides to the solubility of CuCl.

Other Systems

The only measurements found for the system $CuCl-CaCl_2-CuCl_2-H_2O$ are those of Shirokova *et al.*[48], who found no significant change in solubility produced by addition of 1 or 2 per cent of $CuCl_2$ to aqueous solutions of $CaCl_2$. Two sets of measurements are available of systems involving up to four soluble chlorides. In 1982 Winter *et al.*[56] published data on the solubility of CuCl at 323 K for systems in which various amounts of $FeCl_2$ were added to aqueous HCl–NaCl (12 points in all, of which two contained $CuCl_2$ as well). In 1984 Berger and Winand [57] studied the effect on the solubility of adding $FeCl_2$ and/or $ZnCl_2$ to aqueous HCl–NaCl solutions at 303 and 363 K (26 points at 303 K and 8 points at 363 K). All of their points at 323 K had CuCl as the solid phase; at 303 K, 10 of their solutions had NaCl

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

as the solid phase and were presumably not saturated with CuCl.

Winter *et al.*[56] carried out their measurements in connection with their extensive study of solubility in aqueous HCl-NaCl mixtures described above. They reported all of their data in mol dm^{-3} and made measurements of solubility at nominal ionic strengths of 5 to 9 mol dm^{-3}, all from the soluble chlorides present. They used solutions with mol ratios Na/H from 0.20 to 1.0 and added to these 1.0 and 2.0 mol dm^{-3} divalent chloride (in the second case either all $FeCl_2$ or 1.0 mol dm^{-3} of each divalent chloride) (see Compilations). With the exception of two points, their data for solutions containing only HCl and/or NaCl agree with their more extensive graphical data described earlier and with other data on this system within about 5 per cent. The solutions with added divalent chloride cannot be compared directly with other measurements and can only be examined for consistency. By combining pairs of their measurements one can examine the effect of adding any of the soluble chlorides (total chloride and ionic strength increased) or that of replacing one by another in such a way as to keep the same total chloride concentration (usually with an increase in ionic strength). These results are consistent with the known effects of each of the separate salts in promoting the solubility of CuCl, which are in the order NaCl > HCl > $FeCl_2$ > $CuCl_2$. These trends are observed consistently in both additions and substitutions, with the increase in solubility produced by adding a given amount of chloride greatest when NaCl was used and least (quite small) when $CuCl_2$ was used for that purpose; similarly replacement of Na^+ by H^+ or Fe^{2+} at constant total chloride reduces the solubility, quite substantially in the case of Fe^{2+}. Where duplicate measurements were available, they agreed within about 5 per cent. The results of Winter *et al.*[56] on the complex system are Accepted to this precision.

Berger and Winand[57]gave their results in mol kg^{-1}, but also reported the densities of their solutions, so that their data can be converted to mol dm^{-3} if desired. They examined the effect of adding chloride in the form of the various salts (NaCl, HCl, $FeCl_2$ and $ZnCl_2$) studied. (Note that theirs are the only results available for the effect of dissolved $ZnCl_2$ on the solubility of CuCl.) They used a slightly different strategy, in which series of solutions contained (approximately) constant concentrations of two of the salts (usually NaCl and HCl) and increasing amounts of one or both of the others. In one such series, at 303 K, the concentrations of NaCl and HCl were held constant, while that of $FeCl_2$ was increased (this series also contained two measurements in which $ZnCl_2$ was added, one with and one without $FeCl_2$ present). In another series at this temperature, the concentration of $ZnCl_2$ was held constant, while those of the other salts were varied. At 363 K the concentrations of NaCl, HCl and $ZnCl_2$ were held constant while that of $FeCl_2$ was increased. (Note that the ionic strength increases upon addition of material within each series.) Additions of chloride in the form of either NaCl or $FeCl_2$ increased the solubility (as would be expected), but addition in the form of $ZnCl_2$ actually decreased the solubility. Unfortunately, the increases they report are not a smooth function of the amount of chloride added; in their first series ($FeCl_2$ added) there are random deviations of up to 8 per cent from a smooth curve when the ratio of solubility to total chloride concentration is plotted against the chloride concentration. Furthermore, their results for solutions without $ZnCl_2$ vary randomly about 10 per cent from expectations based on other measurements in solutions involving only the other three cations, so that their results can only be assigned about this precision.

Summary. The measurements of Shirokova *et al.*[48] on the effect on CuCl solubility of adding $CuCl_2$ to aqueous $CaCl_2$ are too limited in scope to be useful. The results of Winter *et al.*[56] on the system CuCl-NaCl-HCl-$FeCl_2$-H_2O appear to be valid to about 5 per cent. These data describe mainly the effect of $FeCl_2$ and contain only a small indication of the effect of $CuCl_2$ in the mixed system. The data of Berger and Winand[57] for the system CuCl-NaCl-HCl-$FeCl_2$-$ZnCl_2$-H_2O appear to be valid within about 10 per cent. Within this limit, they describe the effects of both $FeCl_2$ and $CuCl_2$ in their complex system and give an indication of the effect of $ZnCl_2$ on the solubility.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

SYSTEMS CONTAINING ORGANIC COMPLEXING AGENTS

Because of the known ability of dienes to complex with CuCl[58,59], L. J. Andrews and coworkers made an extensive set of measurements on the effectiveness of unsaturated alcohols and organic acids in promoting the solubility of CuCl in aqueous solutions. The results of their measurements are discussed below.

Systems Involving Unsaturated Alcohols

In 1948 Kepner and Andrews[9] published a set of data on the solubility of CuCl at 298 K in aqueous allyl alcohol [2-propenol, $CH_2{=}CH{-}CH_2OH$] both in the absence of added HCl and in the presence of 0.0094 mol dm^{-3} HCl. In the series without HCl, the solubility was measured at four concentrations of alcohol from 0 to 0.11 mol dm^{-3}. Their first series with added HCl contains 6 points at alcohol concentrations from 0 to 0.10 mol dm^{-3}. Their last series gives a measurement at zero alcohol concentration and at three others, *app.* 0.4, 0.6 and 0.99 mol dm^{-3}. In 1949 Keefer and Andrews[60] made a new set of measurements on the same general system at 298 K at constant nominal ionic strength of 0.1 mol dm^{-3} and chloride concentrations of 0, 0.00938 and 0.0938 mol dm^{-3} (14 points in all). For 12 of these points the media contained 0.1 mol dm^{-3} of H^+, using $HClO_4$ as needed to maintain the acidity and the desired ionic strength; for the remaining two the acidity was held at 0.01 mol dm^{-3} using $HClO_4$, and $NaClO_4$ was added to bring the ionic strength to 0.10. They used concentrations of allyl alcohol between 0.01 and 0.08 in media containing zero or the lower concentration of chloride and between 0.02 and 0.04 in media with a chloride concentration of 0.0938 mol dm^{-3}. Also in 1949, Keefer, Andrews and Kepner[61] published data for the effect at 298 K of ten additional unsaturated alcohols on the solubility of CuCl in water; all but one of these alcohols were simple derivatives of allyl alcohol. All of these measurements were made at an ionic strength of 0.1 maintained as necessary with $HClO_4$; in each case measurements were made at chloride ion concentrations of zero, 0.01 and 0.1 mol dm^{-3}. In most cases the concentrations of alcohol used were in the same range as used for allyl alcohol; the main exception was for β-chloroallyl alcohol, where a concentration of 0.5 mol dm^{-3} (only) was used. The measurements on individual alcohols were all less extensive than for allyl alcohol, with points at a single alcohol concentration for two of them and for only two concentrations for two more.

The original results of Kepner and Andrews[9] are of somewhat dubious precision. The authors reported visual evidence of hydrolysis in the solutions which contained no HCl, and their result for zero alcohol concentration in these solutions is distinctly high. The results for alcohol concentrations below 0.1 mol dm^{-3} are about 6 per cent lower than the later results of Keefer and Andrews[60] at a higher ionic strength (0.1 compared with 0.0094), and probably have a precision no better than this. Their results for alcohol concentrations above 0.1 have no counterparts; they may be Accepted tentatively, with a precision no better than 5 per cent. The results of Keefer and Andrews[60] are definitely more satisfactory. The points for each chloride concentration (including zero) fall on a family of smooth curves; for a given chloride concentration, the solubility decreased a few per cent upon addition of H^+. The amount of CuCl dissolved ranged from 0.7 mol per mol alcohol (at low alcohol concentrations) to 0.5 mol per mol alcohol (at high alcohol concentrations). The set of results appears to be satisfactory to 1 or 2 per cent. The authors were able to represent their data (except for 3 points) with this sort of precision in terms of formation of $CuCl_2^-$ and two complexes involving the alcohol; this matter will be discussed in a later section on Thermodynamics.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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The series of alcohols studied by Keefer, Andrews and Kepner[61] shows the effect of the structure of the alcohol on its effectiveness in promoting the solubility of CuCl. For all other alcohols, the solubility of CuCl was less than in aqueous allyl alcohol. Two simple substitutions of the carbinol carbon produced a modest reduction in solubility; *viz.* solubilities were about 15 per cent less in aqueous methylvinylcarbinol [3-buten-2-ol, $CH_2=CH-CH(OH)-CH_3$] and in aqueous ethylvinylcarbinol [1-penten-3-ol, $CH_2=CH-CH(OH)-CH_2-CH_3$]. Solubilities were about 25 per cent less for α,α-dimethylallyl alcohol [2-methyl-3-buten-2-ol, $CH_2=CH-C(CH_3)_2OH$], with two methyl groups substituted on the carbinol carbon, and about 1/3 less for 4-methyl-4-penten-2-ol [$CH_2=C(CH_3)-CH_2-CH(OH)-CH_3$], which has an additional carbon between the hydroxyl and the double bond. The remaining six alcohols gave solubilities less than half as great as those in aqueous allyl alcohol. The extreme case was that of β-chloroallyl alcohol [2-chloro-2-propenol, $CH_2=CCl-CH_2OH$] which, at a concentration of 0.5 mol dm^{-3}, gave little solubility beyond what would have been observed in the absence of alcohol, *i.e.*, about $8 \cdot 10^{-4}$ mol dm^{-3} for HCl concentration of zero or 0.01 mol dm^{-3} and about $6 \cdot 10^{-3}$ mol dm^{-3} for HCl conentration of 0.1 mol dm^{-3}. The other alcohols, giving solubilities from 1/3 to 1/2 as large as for allyl alcohol, were γ,γ-dimethylallyl alcohol [3-methyl-2-buten-1-ol, $CH_3-C(CH_3)=CH-CH_2OH$], β-methylallyl alcohol [2-methyl-2-propenol, $CH_2=C(CH_3)-CH_2OH$], crotyl alcohol (2-buten-1-ol, $CH_3-CH=CH-CH_2OH$), 2-methyl-2-buten-1-ol [$CH_3-CH=C(CH_3)-CH_2OH$] and 3-methyl-3-buten-2-ol [$CH_2=C(CH_3)-CH(OH)-CH_3$].

The alcohols which produced solubilities comparable with that in aqueous allyl alcohol all showed a decrease in solubility of CuCl upon addition of HCl to the medium. Those which were less effective in enhancing the solubility of CuCl showed a minimum in solubility at 0.01 mol dm^{-3} chloride followed by an increase for 0.1 mol dm^{-3} chloride. If, however, one considers the *increase* in solubility produced by the alcohol above the values (quoted above) expected in its absence, this increase diminished regularly with addition of chloride for all of the alcohols studied. It appears that in the case of the less effective alcohols the enhancement of solubility produced by addition of chloride in the absence of alcohol overpowers the diminution in alcohol-produced solubility induced by the addition of chloride ion. In any case the authers were able to represent all of their data within a few per cent by suitable choices of equilibrium constants for the formation of alcoholic complexes with CuCl and Cu^+ (to be discussed later).

Summary. There are no other measurements to be compared with those of Andrews and coworkers. However, the results of Keefer and Andrews[60] on aqueous allyl alcohol and those of Keefer, Andrews and Kepner[61] on more complex alcohols are Accepted tentatively in view of their internal consistency and smoothness of data. The early results of Kepner and Andrews[9] for low concentrations of allyl alchohol are about 4 per cent low compared with the later measurements. Their results for alcohol concentrations above 0.1 mol dm^{-3} cannot be compared with any other; they are probably valid within 5 to 10 per cent.

Systems Involving Unsaturated Organic Acids

Andrews and coworkers also published measurements of the solubility of CuCl in aqueous solutions of a variety of unsaturated organic acids, in all cases at 298 K. In 1948 Andrews and Keefer[62] published data on the solubility in media containing maleic acid [*(Z)*-2-butenedioic acid, $HOOC-CH=CH-COOH$] along with (a) sulfuric acid and (b) perchloric acid. In the case of sulfuric acid, the concentration of inorganic acid was varied from 1.19 to 0.06 mol dm^{-3} with the concentrations of maleic acid held at about 0.15 mol dm^{-3}, except for two measurements in which smaller concentrations of maleic acid were used (12 points in all).

In the other set of experiments (7 points) the concentration of maleic acid was maintained at 0.146 mol dm^{-3} while that of perchloric acid was varied from 0.903 to 0.06 mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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In this same paper they reported the solubility (12 points) in aqueous fumaric acid [(*E*)-2-butenedioic acid, HOOC-CH=CH-COOH] solutions containing 0.34 to 0.50 mol dm^{-3} of fumaric acid, with sulfuric acid concentrations varied from 0.48 mol dm^{-3} to zero. In 1949 Andrews and Keefer[63] published a more extensive set of data on the solubility of CuCl in aqueous solutions of maleic acid (27 points in all). Nine of their measurements were made at an ionic strength of 1.0 mol dm^{-3} maintained by $HClO_4$. For three of these experiments no chloride was added; in another three HCl was used to give an initial chloride concentration of about 0.01 mol dm^{-3} and in the remaining three a concentration of 0.1 mol dm^{-3} of HCl was used. In each of the three sets the maleic acid concentration was varied over a 3- to 4-fold range centered on 0.1 mol dm^{-3}. In a second group of nine experiments the ionic strength was set at 0.1 mol dm^{-3} ($HClO_4$), again using HCl concentrations of 0, 0.01 and 0.10 mol dm^{-3}, with maleic acid concentrations varied as before. In a final group of nine experiments ionic strength was maintained at 0.1 mol dm^{-3} using $NaClO_4$, with chloride ion provided by KCl; the same procedure as before was used for varying chloride and maleic acid concentrations. Also in 1949, Keefer, Andrews and Kepner[64] published data on the solubility of CuCl in aqueous solutions of with unsaturated organic acids at an ionic strength of 0.1 mol dm^{-3} ($HClO_4$) using concentrations of 0, 0.01 and 0.20 (or 0.094) mol dm^{-3}. The acids investigated included fumaric acid (again), 3 other dibasic acids and 4 monobasic acids. The number of measurements made for a particular acid ranged from 2 to 9.

The largest number of measurements were made on media containing maleic acid. In the 1948 set[62] at variable ionic strengths, duplicate points agreed within about 2 per cent, and the points were smooth to about this precision with respect to variation of either the concentration of maleic acid or that of the inorganic acid used. The solubility decreased more or less linearly as the concentration of inorganic acid was increased, going from about 0.11 mol of CuCl dissolved per mol of maleic acid at the lowest concentrations of inorganic acid to about 0.07 mol CuCl per mol maleic acid for an inorganic acid concentration of 1.2 mol dm^{-3}. The effects of sulfuric and perchloric acids were essentially the same. The more extensive measurements reported in 1949[63] were made at conditions such that they cannot be compared directly with the earlier set. The various sets of measurements form a regular family of curves with respect to variation of solubility with maleic acid concentration and appear smooth to 1 or 2 per cent. The effect of inorganic acid in decreasing the solubility is again apparent. The solubilities of CuCl in the set where no inorganic acid was present are 2 to 5 times larger (for other conditions the same) as those where 1.0 mol dm^{-3} of inorganic acid was present, with those having 0.1 mol dm^{-3} of inorganic acid in between. Addition of chloride ion as either HCl or KCl reduced the solubility of CuCl materially. The increase in solubility produced by the organic acid, obtained by correcting the observed solubilities for that produced by the chloride ion itself, was reduced by a factor of about 2 for inclusion of 0.1 mol dm^{-3} of chloride ion. Overall, the maleic acid dissolved as much as 0.22 mol CuCl per mol acid if neither inorganic acid nor chloride ion was present, but no more than 0.052 mol per mol when both of these were present at 0.1 mol dm^{-3} and only about 0.026 mol per mol when $[Cl^-]$ was 0.1 mol dm^{-3} and $[H^+]$ was 1.0 mol dm^{-3}. All of these measurements can be Accepted tentatively, with an estimated precision of 1 or 2 per cent.

Measurements of the solubility of CuCl in media containing fumaric acid are given in the 1948 paper[62] and by Keefer, Andrews and Kepner[64] in 1949. The solubilities reported are considerably higher than those reported for maleic acid solutions, but in neither case are the data as consistent as those for that acid. In the earlier work[62], with no chloride present, the acid dissolved from 0.22 to 0.27 mol CuCl per mol fumaric acid, with no consistent effect of sulfuric acid in changing the solubility. With respect to variation of fumaric acid concentration, the points vary from smoothness by 2 to 10 per cent. In the later work[64], at acidity and ionic strength of 0.1 mol dm^{-3}, solubility was reduced by addition of chloride

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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ion, as with maleic acid, but the variation of solubility with fumaric acid concentration was not smooth, varying as much as 10 per cent from a smooth curve. The set of measurements are probably reliable within 5 to 10 per cent.

The other seven acids investigated by Keefer, Andrews and Kepner[64] were, like fumaric acid, all studied in a medium with total acidity and ionic strength of 0.1 mol dm^{-3}. The solubility of CuCl varied widely among the acids studied. Aqueous vinylacetic acid (3-butenoic acid, CH_2=CH-CH_2-COOH) dissolved even more CuCl than aqeous fumaric acid, from 0.38 to as much as 0.63 mol CuCl per mol acid for concentrations of organic acid below 0.1 mol dm^{-3} in the absence of added chloride ion. On the other extreme, citraconic acid [*(Z)*-2-methyl-2-butenedioic acid, HOOC-C(CH_3)=CH-COOH] contributed very little to the solubility of CuCl at concentrations of 0.34 and 0.45 mol dm^{-3}. The remaining five acids ranged in between, with itaconic acid [methylenebutanedioic acid, HOOC-C(=CH_2)-CH_2-COOH] and crotonic acid [*(E)*-2-butenoic acid, CH_3-CH=CH-COOH] giving somewhat less solubility than maleic acid. Mesaconic acid [*(E)*-2-methyl-2-butenedioic acid, HOOC-C(CH_3)=CH-COOH], tiglic acid [*(E)*-2-methyl-2-butenoic acid, CH_3-CH=C(CH_3)-COOH] and β,β-dimethyl acrylic acid [3-methyl-2-butenoic acid, $(CH_3)_2C$=CH-COOH] all produced substantially less solubility than maleic acid, but more than citraconic acid. To the extent that they can be evaluated, the data all appear smooth to 1 or 2 per cent. The solubility contributed by the acid is in all cases reduced substantially by the addition of chloride ion, as much as 50 per cent for 0.1 mol dm^{-3} added. (Note that the total amount of inorganic acid was the same for all measurements, so no effect due to hydrogen ion was observed.) As with the unsaturated alcohols considered above, the authors were able to represent their data within a few per cent by suitable choice of equilibrium constants for formation of complexes between cuprous species and the acids (this matter will be discussed in the section on Thermodynamics). In the absence of other data, the results are Accepted with an estimated precision of 1 or 2 per cent.

Summary. The results of Andrews and coworkers for the solubility of CuCl in aqueous solutions of unsaturated organic acids are Accepted tentatively, with an estimated precision of 1 to 2 per cent, except for the data on aqueous fumaric acid, where a lesser precision of 5 to 10 per cent applies.

Systems Involving Other Organic Ligands

In 1975 Sigal *et al.*[65] published a set of data on the enhancement of solubility at 295 K produced by addition of organic additives to a solution of CuCl in an aqueous solution containing 1.08 mol dm^{-3} of KCl and 0.26 mol dm^{-3} of HCl. The additives used were 2-butene-1,4-diol [$C_4H_8O_2$, $H_2C(OH)$-CH=CH-CH_2OH], acetonitrile (CH_3CN) and urea (CH_4N_2O, H_2NCONH_2). Their data were presented in graphical form. Both their graphs and numerical data read from it are given in the Compilations. The data are consistent and are Accepted tentatively, but cannot be compared with any other. Of the three additives, the diol was considerably the most effective, dissolving approximately 0.6 mol CuCl per mol organic additive. Acetonitrile was also effective, dissolving about 0.25 mol of CuCl per mol of nitrile. Urea was relatively ineffective, dissolving only about 0.05 mol per mol. For the first two additives, the solubility of CuCl was nearly doubled for the highest concentrations used (0.24 mol dm^{-3} for the diol and 0.40 mol dm^{-3} for acetonitrile). The authors also mention solubility increases produced by thiourea and quinoline, but do not give details of their effects on the solubility of CuCl.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

DOUBLE AND COMPLEX SALTS OF CuCl

When CuCl is dissolved in water with the aid of some complexing ligand, there is always the possibility that the material will be transformed into a double salt in the process of dissolution. Such a process has been observed for the dissolution of CuCl in aqueous KCl and in aqueous NH_4Cl, where production of double salts limits the extent to which the solubility of CuCl can be increased by increasing the concentration of the soluble chloride. Double salt formation may well occur in other aqueous systems under conditions where the solubility has not yet been determined. Knowledge of the existence of a given double salt can give clues to two possible features of the solubility of a cuprous halide. First, it suggests that double salt formation may occur in the dissolution process at conditions other than those where the solubility has been determined; second, it can indicate the possibility of dissolving the halide in media where no measurements have been made. For these reasons, information is provided about those double salts of the cuprous halides which have been observed in the past.

Over the past 150 years there have been many reports in the past of double or otherwise complex salts formed from CuCl. The majority of these involve other chlorides, but compounds containing neutral inorganic molecules (*e.g.* ammonia) or unsaturated organic molecules (*e.g.* olefins) have also been prepared. In the discussion below, salts formed with other chlorides will be considered first, followed by those with other types of salts and finally by those formed with neutral organic molecules. Early work on preparation and properties of double salts and coordination compounds of CuCl has been summarized by Mellor[66], whose treatise can be consulted for some details of the investigations.

Double Salts with Monovalent Chlorides

There have been two reports of double salts containing CuCl and **hydrogen chloride**. In 1894 Neumann[67] claimed to have produced a 1 : 1 salt, $CuCl \cdot HCl$, at temperatures below 273 K. In 1959 Malik *et al.*[35] used the Method of Wet Residues in conjunction with their measurements of the solubility of CuCl in aqueous HCl and concluded that the complex salt H_2CuCl_3 ($CuCl \cdot 2HCl$) was formed at the lower ranges of HCl concentration and H_3CuCl_4 ($CuCl \cdot 3HCl$) at the higher ranges, but they did not isolate these salts. No other investigators of the system $CuCl-HCl-H_2O$ have found any double salts, so that the existence of any of the three salts described above is Doubtful.

Chassevant[68] reported obtaining crystals of a double salt with **lithium chloride**, but was unable to isolate them for analysis. There have been no further reports of such a salt.

The earliest report of a double salt with **sodium chloride** was made in 1840 by Mitscherlich[69], who was the first to describe the preparation and properties of CuCl itself. He prepared what he believed to be $CuCl \cdot 2NaCl$. In 1893 Chassevant[68] claimed to have isolated the same compound. Details are lacking, and there have been no reports of this salt occurring in connection with solubility measurements. Its existence is probable, but it is not likely to be found as the solid phase in equilibrium with CuCl dissolved in aqueous NaCl.

There have been numerous reports of double salt formation with **potassium chloride**, the earliest being that of Mitscherlich[69], who isolated a salt believed to be $CuCl \cdot 2KCl$ as colorless octahedra. The same salt was reported by Deherain[70] in 1862, Chassevant[68] in 1893, Brönsted[45] in 1912, Korreng[71] in 1914, Valeton and Frömel[46] in 1924, Brink and MacGillavry[72] in 1949 and Malik *et al.*[35] in 1959. Of all of these the most definitive work was that of Valeton and Frömel[46], who gave a chemical analysis corresponding to this composition, and that of Brink and MacGillavry[72], who determined the structure of the compound by X-ray analysis. The existence of this salt is beyond question. Brönsted[45] found a region of the system $CuCl-KCl-H_2O$ in which the solid phase was a double salt

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

that he believed to be CuCl·2KCl, but he gave no details of the identification. He made cell measurements on this double salt and gave values for the changes in enthalpy and Gibbs energy for the reaction $CuCl_{(s)} + 2KCl \rightleftharpoons CuCl \cdot 2KCl$. Korreng[71] inferred the presence of this salt from investigation of the melting-point diagram of the system CuCl–KCl, but was unable to isolate the salt for examination. Valeton and Frömel[46] prepared a second double salt whose analysis corresponded to $CuCl{\cdot}KCl{\cdot}H_2O$. This salt had been obtained by Schiff[73] in 1858 and by Le Chatelier[21] in 1884, but neither had identified it positively. Malik *et al.*[35] also claimed such a salt from their Method of Wet Residues. However, Brönsted[45] found indications of only one double salt in his solubility measurements.

In 1895 Wells[74] prepared three double salts containing **cesium chloride**, *viz.* 2CuCl·CsCl, 2CuCl·3CsCl and a hydrated salt $2CuCl{\cdot}3CsCl{\cdot}H_2O$. He described the crystalline form of each of his salts. In 1954 Brink *et al.*[75] prepared crystals of the 2 : 1 salt and determined its orthorhombic crystal structure using X-ray diffraction. At least this salt exists, but there have been no solubility data reported for the system $CuCl–CsCl–H_2O$, in which it might be found. There have been no further reports of the other two salts reported by Wells[74].

There have been numerous reports of double salts formed between CuCl and **ammonium chloride**, beginning with the work of Mitscherlich[69], who prepared what he believed to be $CuCl{\cdot}2NH_4Cl$. Deherain[70] prepared a salt which he believed to be a hemi-hydrate of the 1 : 2 salt [his formula $4NH_4Cl \cdot Cu_2Cl_2 \cdot H_2O$] but Wells and Hurlburt[76] were able to prepare it only in anhydrous form. They gave a chemical analysis verifying the composition they claimed. In 1952 Brink and van Arkel[77] prepared this salt and determined its structure by X-ray diffraction. Other possible salts have been reported, with varying amounts of substantiating evidence. In 1895 Wells and Hurlburt[76] prepared a salt whose chemical analysis corresponded to $3CuCl{\cdot}2NH_4Cl$ (their $4NH_4Cl{\cdot}3Cu_2Cl_2$), and assigned this formula to a salt prepared earlier by Ritthausen[78], who gave a slightly different composition. A 1 : 1 salt, $CuCl{\cdot}NH_4Cl$, was claimed by Deherain[68] and by Morosov and Ustanishkova[31], but neither gave definitive evidence of the composition of their materials. Both of these also claimed to have produced material of the composition $2CuCl{\cdot}NH_4Cl$. In the Morosov work, the 2 : 1 salt was believed to be in equilibrium with some solutions of CuCl in aqueous NH_4Cl at 298 K and the 1 : 1 salt at 323 K. Finally, Rosenheim and Steinhauser[79] prepared a salt of the formula $CuCl \cdot NH_4Cl \cdot 4(NH_4)_2S_2O_3$ and verified its composition by chemical analysis. All of the double salts with cesium chloride described by Wells[74] produced this material when treated with aqueous **ammonium thiosulfate**.

Remy and Laves[80] made a thorough investigation of the double salts between CuCl and **methyl-substituted ammonium chlorides**. For methyl ammonium chloride, they obtained 1 : 1 and 1 : 2 salts ($CuCl \cdot CH_3NH_3Cl$ and $CuCl \cdot 2CH_3NH_3Cl$). With dimethyl ammonium chloride, $(CH_3)_2NH_2Cl$, they obtained a 1 : 1 salt for large ratios of the ammonium chloride to CuCl and a 2 : 1 salt for equimolal ratios. Trimethylammonium chloride produced a 2 : 1 salt and an 1 : 2 salt. Tetramethyl ammonium chloride $(CH_3)_4NCl$ gave only a 1 : 1 salt.

Double Salts with Magnesium Chloride and Sodium Thiosulfate

Karimova, Ksandrov and Nikandrov[107] prepared double salts $12\,CuCl \cdot MgCl_2 \cdot 12\,H_2O$ and $CuCl \cdot 5\,MgCl_2 \cdot 12\,H_2O$. Their existence was confirmed by chemical analysis, X-ray difractometry and differential thermal analysis. Canneri and Luchini[81] prepared a double salt $CuCl \cdot Na_2S_2O_3$ and verified its composition by chemical analysis.

Salts with Neutral Molecules Coordinated to Copper

CuCl, like AgCl, will dissolve in solutions of **ammonia** and **amines**, and salts with these molecules coordinated to Copper(I) have been reported. Mellor[66] discusses compounds between CuCl and NH_3. Marykyan[82] prepared a compound between CuCl and **pyridine**

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

to which he assigned the formula $Cu_2(C_5H_5N)_4Cl_2$ - more simply $CuCl \cdot 2C_5H_5N$. He measured its limited solubility in water from 298 to 343 K. Chaltykyan[15] reported preparing $CuCl{\cdot}PH_3$. Harris[83] produced a double salt in which CuCl was combined with **cupric tetrammine chloride** to form $CuCl \cdot Cu(NH_3)_4Cl_2$ and another with **cupric ethylenediamine chloride** of the formula $3CuCl \cdot Cu(en)_2Cl_2$. In later work[84] he and a coworker were able to prepare and identify the hydrated salt $CuCl \cdot Cu(en)_2Cl_2 \cdot 1.5H_2O$. Ritthausen[78] claimed to have produced a monohydrate $CuCl \cdot Cu(NH_3)_4Cl_2 \cdot H_2O$.

Compounds have also been prepared in which CuCl is coordinated to mono- or di-olefins. In 1939 Gilliland, Seabold, Fitzhugh and Morgan[85] reported preparation of 1 : 1 compounds between CuCl and **ethene** (C_2H_4), **propene** (C_3H_6) and **isobutene** (C_4H_8) and measured their (fairly large) vapor pressures as a function of temperature. In 1935 Koblyanskii *et al.*[86] reported production of two compounds with **butadiene**, $2CuCl \cdot C_4H_6$ and its monohydrate $2CuCl \cdot C_4H_6 \cdot H_2O$. In 1941 Gilliland, Bliss and Kip[58] reported preparation of the anhydrous compound with butadiene, along with similar compounds with **isoprene** (2-methyl-1,3-butadiene), of formula $2CuCl \cdot C_5H_8$, and with **ethine**, of formula $2CuCl \cdot C_2H_2$; they gave the vapor pressures of these compounds as a function of temperature. Ward and Makin[59] also prepared the compound with isoprene and in addition a similar compound with **piperylene** (1,3-pentadiene) of formula $2CuCl \cdot C_5H_8$; they measured the vapor pressures for each of these compounds.

In addition to the compounds discussed above, compounds of CuCl with **phosgene**, **carbon monoxide** and other neutral molecules have been reported, but these have little significance with respect to the solubility of CuCl. The reader is referred to Mellor[66] for details and references on these compounds.

Summary. The double salts reported to have been formed between CuCl and other chlorides can be grouped as follows:

1. Existence and identity have been firmly established for $CuCl \cdot 2KCl$, $CuCl \cdot KCl$, $CuCl{\cdot}2NH_4Cl$ and $2CuCl \cdot CsCl$ which have been reported by two or more observers, with their identity confirmed by chemical analysis, X-ray diffraction, or both.
2. Salts whose existence seems reasonable on the basis of reports by one or two observers, but for which there is not strong confirmatory evidence include $CuCl \cdot 2NaCl$, $CuCl \cdot NH_4Cl$, $2CuCl \cdot NH_4Cl$, $CuCl \cdot 2NH_4Cl$, $3CuCl \cdot 2NH_4Cl$, $CuCl \cdot NH_4Cl \cdot 4(NH_4)S_2O_3$, $12\,CuCl \cdot MgCl_2 \cdot 12\,H_2O$ and $CuCl \cdot 5\,MgCl_2 \cdot 12\,H_2O$.
3. Salts reported by one or two observers, but with weak or conflicting evidence, so that their existence is doubtful, include $CuCl{\cdot}HCl$, $CuCl{\cdot}2HCl$, $CuCl{\cdot}3HCl$, $CuCl{\cdot}xLiCl$, and $2CuCl \cdot 4NH_4Cl \cdot H_2O$.
4. The series of salts of CuCl with the various methylammonium chlorides reported by Remy and Laves[80] almost certainly exist, but there is no confirmatory evidence that the formulas they assigned are correct in all cases.

Of the salts listed above, only six have been observed in the course of solubility measurements of CuCl. These are $CuCl{\cdot}2KCl$, $CuCl{\cdot}KCl$, $CuCl{\cdot}NH_4Cl$, $2CuCl{\cdot}NH_4Cl$, $12\,CuCl \cdot MgCl_2 \cdot 12\,H_2O$ and $CuCl \cdot 5\,MgCl_2 \cdot 12\,H_2O$. Other double salts might well be found in solubility measurements at suitable conditions of temperature and concentration. The identification of double salts with CsCl and the methylammonium chlorides indicate that CuCl should have substantial solubility in aqueous solutions of these materials, although no actual solubility measurements have been found for these systems.

The evidence for the various compounds reported between CuCl and unsaturated hydrocarbons is strong, even though most were reported by only a single set of observers, since the experimental work in these cases was quite thorough. It is of interest that the mono-olefins complex with a single molecule of CuCl and the di-olefins with two molecules. The

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

compounds formed were all relatively unstable and not water-soluble; however, water-soluble derivatives of any of the unsaturated compounds should promote solubility of CuCl, as observed with the unsaturated alcohols and organic acids discussed earlier.

PHASE DIAGRAMS OF SYSTEMS INVOLVING CuCl

A number of the investigations of the solubility of CuCl in aqueous chlorides contain either phase diagrams or the information needed to construct a phase diagram for the system studied. For some systems there has been only one such report. For those where phase diagram data are available in more than one publication, the various reports disagree. Because of this situation, no actual phase diagrams are included in this section. The available data (most of which is contained in the Compilations) will be discussed below.

$CuCl-HCl-H_2O$

The only phase diagram data for this system reported in the literature are those of Morosov and Ustanishkova[31], who measured the solubility of CuCl in aqueous HCl up to concentrations obtained when the solution was in equilibrium with gaseous HCl at atmospheric pressure (these are the last entries for each temperature in the Compilations of their data). (Note: Their data were presented in a different graphical form by Chaltykyan[15].) They gave the mass percentages of HCl and CuCl in these solutions; these are given in Table 2, along with the corresponding molalities calculated from them.

Table 2. **Composition of Aqueous Solutions in Equilibrium with Solid CuCl and Gaseous HCl at Atmospheric Pressure**

T/K	$100w_{CuCl}$	$100w_{HCl}$	$\frac{m_{CuCl}}{mol\,kg^{-1}}$	$\frac{m_{HCl}}{mol\,kg^{-1}}$
273	19.02	34.7	4.15	20.6
298	24.9	30.	5.58	18.2
323	26.0	27.5	5.65	16.2
353	29.13	23.25	6.18	13.4
373	30.0	19.27	5.97	10.4

Their graphical data also give the mass percentage of HCl for solutions under atmospheric pressure of HCl in the absence of dissolved CuCl. These data are given in Table 3. At 273 K they give a single point for a solution saturated with HCl under atmospheric pressure but unsaturated in CuCl. This occurs at 10 per cent CuCl, 39 per cent HCl (1.98 and 21.0 mol kg^{-1}, respectively).

Table 3. **Composition of Solutions in Equilibrium with Gaseous HCl at Atmospheric Pressure in the Absence of Dissolved CuCl**

T/K	$100w_{HCl}$	$\frac{m_{HCl}}{mol\,kg^{-1}}$
273	44.2	21.7
298	40.0	18.3
323	36.7	15.9
353	32.4	13.1
373	29.0	11.2

Comparison of the two tables indicates the small extent to which saturation with CuCl decreases the solubility of HCl in water at atmospheric pressure. Abundant data are available illustrating the same sort of effect in other systems involving CuCl with a soluble chloride.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

The results quoted above are Accepted tentatively, since the results given for the solubility of CuCl in aqueous HCl solutions agree with those of other investigators within the precision to which the graphical results can be read.

$CuCl-NaCl-H_2O$

Phase diagram data for this system have been reported in mass units by Kremann and Noss[7] and Kosyakina[44] and in volume units by Fedotieff[30], Utkina *et al.*[40], Peters and Johnson[42] and Fontana *et al.*[43]. Utkina *et al.*[40] gave densities for their solutions, so that their data can be compared with any of the other sets. The most extensive work was that of Peters and Johnson[42], whose graphical data cover the entire range of possible solutions at four different temperatures (278, 295, 343 and 348 K). Their phase diagrams are shown in the Compilation of their data; most of their points are at NaCl concentrations below that where NaCl precipitates out.

Fedotieff[30] gave numerical data for ten points on the phase diagram at 292 K, including one where both CuCl and NaCl were present as solids and three where the solid phase was NaCl alone. His data agree as well as could be expected with the data of Peters and Johnson[42] at 295 K. Both found CuCl and NaCl together as solid phases at a total chloride concentration of about 6.3 mol dm^{-3}, with about 3.0 mol dm^{-3} of CuCl dissolved. Utkina *et al.*[40] measured the solubility of CuCl as a function of NaCl concentration at five different temperatures (273, 298, 323, 348 and 368 K) up to concentrations where they reported a mixture of CuCl and NaCl as solid phases. Their data for the solubility of CuCl itself are in agreement with the works cited above and other data on the system, but they reported finding NaCl as the solid phase at NaCl concentrations about 20 per cent lower than those reported by Peters and Johnson[42] or Fedotieff[30]. Finally, Fontana *et al.*[43] gave a partial phase diagram for solutions at 298 K containing less than 2 mol dm^{-3} of dissolved CuCl, with points on both the CuCl and the NaCl side of the diagram. Their solutions all contained 1.0 mol dm^{-3} of HCl, so that their results cannot be compared directly with the others cited. However, their curves parallel those of Peters and Johnson[42] and of Fedotieff[30] at similar temperatures and indicate that CuCl persists as the solid phase to higher concentrations than those given by Utkina *et al.*[40].

The results reported in mass units are both questionable. Kremann and Noss[7] made measurements over the entire concentration range at 300 K (9 points in all, see Compilations). Their data on the solubility of CuCl are reasonable up to about 5 mol kg^{-1} NaCl, but the molality at which they find both NaCl and CuCl as solid phases (9.8 mol kg^{-1}) seems much too high (it is nearly 60 per cent higher than the solubility given for NaCl in pure water). The data of Kosyakina[44] at 298 K do not agree with any other data. Her solubilities for CuCl are distinctly higher than reported by others, and her data show no sharp discontinuity at the point where NaCl replaces CuCl as the solid phase, although all other data show this.

Summary. The phase diagram data of Fedotieff[30] at 292 K and those of Peters and Johnson[42] at a variety of temperatures are Recommended for use. The other pieces of data cited are Not Recommended, for reasons given above. It is interesting to note that all observers find that the presence of dissolved CuCl increases the solubility of NaCl beyond its value in pure water.

$CuCl-KCl-H_2O$

Three sets of phase diagrams have been reported for solutions of CuCl in aqueous KCl. In 1912 Brönsted[45] gave 44 points for a phase diagram at 295 K (see Compilations). In 1924 Valeton and Frömel[46] gave a phase diagram for 298 K, and in 1966 Chaltykyan[15] gave phase diagrams for 298 and 323 K.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Brönsted[45] found CuCl as the only solid phase for molalities from zero to 6.4 mol kg^{-1} KCl, 4.1 mol kg^{-1} CuCl, at which a double salt identified as $CuCl{\cdot}2KCl$ appeared. The double salt was the solid phase in a range where the molality of CuCl decreased to 0.27 mol kg^{-1} and that of KCl first fell gradually to 4.5 and then rose again to 5.1 mol kg^{-1}, at which point solid KCl appeared. Thereafter solid KCl was the only solid phase until the CuCl molality reached zero with a KCl molality of 4.6 mol kg^{-1}. Brönsted did not state how he identified the chemical composition of the double salt, which he described as snow-white, usually large, crystals.

When Valeton and Frömel[46] investigated the system at 298 K, they found a region where a hydrated salt $CuCl{\cdot}KCl{\cdot}H_2O$ was the solid phase, along with a large region where the solid phase was $CuCl{\cdot}2KCl$ and a very small region where the solid phase was CuCl. They isolated both double salts and determined their compositions by chemical analysis. However, the concentrations of CuCl which they report are unreasonably high compared both with the Brönsted results and with results for other solutions, whereas most of the solubilities reported by Brönsted are satisfactory compared with results for other systems. It is possible that Brönsted failed to observe the double salt or that it does not appear at 295. The phase diagrams of Chaltykyan[15] do not indicate what solid phases appear other than CuCl except to remark that one branch of each curve corresponds to equilibrium with a double salt.

Summary. In view of the discrepancies between the work of Brönsted[45] and that of Valeton and Frömel[46] and the ambiguity in the work of Chaltykyan[15], none of the published phase diagrams for $CuCl{-}KCl{-}H_2O$ can be recommended for use.

$CuCl{-}NH_4Cl{-}H_2O$

Morosov and Ustanishkova[31] studied the systems $CuCl{-}NH_4Cl{-}H_2O$ and $CuCl{-}NH_4Cl{-}HCl{-}H_2O$ over the entire possible molality range at temperatures from 273 to 373 K. (Their phase diagrams for the ternary system are reproduced in somewhat modified form by Chaltykyan[15].) For the ternary system they reported finding $CuCl{\cdot}NH_4Cl$ as the solid phase over a range of CuCl concentrations at 323 K, $2CuCl{\cdot}NH_4Cl$ as the solid phase at 298 and an unspecified double salt (presumably also $2CuCl{\cdot}NH_4Cl$) over a range of concentrations at 273 K. They found no evidence of double salt formation at either 353 or 373 K. The table below lists the concentrations at which one or another double salt was observed. The two extreme sets of data for 323 K were taken from their numerical data; all others were read from their graphs; the molalities given have been calculated by the compiler. Corresponding data for the regions where either CuCl or NH_4Cl was the only solid phase present are listed in the Compilations.

Table 4. **Composition of Solutions in Equilibrium with Double Salts for $CuCl{-}NH_4Cl{-}H_2O$**

T/K	$100w_{NH_4Cl}$	$100w_{CuCl}$	$\frac{m_{NH_4Cl}}{mol\ kg^{-1}}$	$\frac{m_{CuCl}}{mol\ kg^{-1}}$	Solid Phases
273	17.5	13	4.7	1.9	CuCl, $2CuCl{\cdot}NH_4Cl$
	22.	13	6.3	2.0	$2CuCl{\cdot}NH_4Cl$
	26	14	8.1	2.4	$2CuCl{\cdot}NH_4Cl$, NH_4Cl
298	20	26.5	7.0	5.1	CuCl, $2CuCl{\cdot}NH_4Cl$
	23.5	28.5	9.2	6.0	$2CuCl{\cdot}NH_4Cl$
	31	34.5	17.	10.1	$2CuCl{\cdot}NH_4Cl$, NH_4Cl
323	26.7	47.3	19.2	18.4	CuCl, $CuCl{\cdot}NH_4Cl$
	29.	48.	24.	21.	$CuCl{\cdot}NH_4Cl$
	31.95	48.88	31.2	25.7	$CuCl{\cdot}NH_4Cl$, NH_4Cl

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Morosov and Ustanishkova[31] also gave phase diagrams for the quaternary system $CuCl-NH_4Cl-HCl-H_2O$ at 323, 353 and 373 K. It was not found possible to read from these diagrams the concentrations at which the various solid phases were found. They give numerical data for three points at 323 K:

1. CuCl and $CuCl\cdot NH_4Cl$ were present as solids in a solution at equilibrium with one atmosphere of gaseous HCl, containing 5.25 mass per cent NH_4Cl, 22.87 mass per cent HCl and 33.12 mass per cent CuCl (2.52, 16.2 and 8.62 mol kg^{-1}, respectively).
2. $CuCl\cdot NH_4Cl$ and NH_4Cl were present as solids in a solution at equilibrium with one atmosphere of gaseous HCl, containing 8.9 mass per cent NH_4Cl, 28.09 mass per cent HCl and 15.75 mass per cent CuCl (3.51, 16.3 and 3.36 mol kg^{-1}, respectively).
3. The double salt and NH_4Cl were present as solids in a series of solutions with lower HCl concentrations, one of which was specified as containing 12.56 mass per cent NH_4Cl, 16.44 mass per cent HCl and 25.33 mass per cent CuCl (5.14, 9.87 and 5.60 mol kg^{-1}, respectively).

Summary. The data of Morosov and Ustanishkova[31] are Accepted tentatively for systems involving NH_4Cl. Except for the few numerical data cited above, their results are all limited to the precision with which graphs could be read. It is of interest to note that the solubility of NH_4Cl in the presence of dissolved CuCl is distinctly higher than in pure water and that the solubilities of NH_4Cl and CuCl both reach very high values, especially at higher temperatures.

Systems Involving $CuCl_2$

A number of publications give phase diagram data for CuCl in aqueous $CuCl_2$, most with another soluble chloride also present. In 1928 Fedotieff[30] presented data for the solubility of CuCl in aqueous $CuCl_2$ at 292 K up to the point where the solution was saturated with both salts; this solution contained 661.9 g dm^{-3} of $CuCl_2$ and 97.4 g dm^{-3} of CuCl (4.92 and 0.88 mol dm^{-3}, respectively). In 1979 Novikov *et al.*[38] published data at 283 K for the system $CuCl-CuCl_2-HCl-H_2O$, covering the entire diagram for each of four different ranges of HCl mass percentages (from 2.5 to 20 mass per cent; see Compilations). In 1980 Pochtarev *et al.*[50] published data on the same system at four temperatures (293, 313, 353 and 373 K), giving for each temperature a number of solutions saturated with both solid CuCl and solid $CuCl_2$. They had previously published[51] a similar set of data for the system $CuCl-CuCl_2-NaCl-H_2O$ at 299.5 K.

Both the data of Novikov *et al.*[38] and those of Pochtarev *et al.*[50] on the system $CuCl-CuCl_2-HCl-H_2O$ show that increase in mass percentage of HCl decreases that of $CuCl_2$ and increases that of CuCl when the solution is saturated with both salts. However, they disagree about the magnitude of the effects, which are much larger in the Novikov data. In addition the data of Novikov indicate that the solubility of $CuCl_2$ is increased by the addition of CuCl in amounts less than that required for saturation. Although both sets are somewhat erratic, the data of Novikov *et al.*[38] are smooth within a few per cent, while those of Pochtarev *et al.*[50] scatter over 10 per cent or more when the concentrations of the copper salts are plotted against the HCl concentration. The Novikov *et al.*[38] data are also in better agreement with what would be expected from the ternary systems $CuCl-HCl-H_2O$ and $CuCl-CuCl_2-H_2O$; they are probably the more reliable of the two. Neither set should be considered definitive without further confirmation. Finally, there is some question about the form in which $CuCl_2$ appears as a solid phase. Novikov *et al.*[38] identify it as $CuCl_2\cdot 2H_2O$, while Pochtarev *et al.*[50] describe it simply as $CuCl_2$.

The earlier results of Pochtarev *et al.*[51] contain data for solutions with both CuCl and solid NaCl present as well as solutions where CuCl and $CuCl_2$ were present as solids together. These data are somewhat smoother than those for $CuCl-CuCl_2-HCl-H_2O$ but are still

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

somewhat erratic. They indicate a decrease in saturation mass percentage of $CuCl_2$ and an increase in that of CuCl with increasing mass percentage of NaCl, as with the aqueous HCl system. However, they give only selected points on the total phase diagram, and their results are not confirmed by other data. They are also at ionic strengths too large for comparison with data on the ternary systems.

Summary. The single point given by Fedotieff[30] at 292 K for a solution saturated with both CuCl and $CuCl_2$ agrees with what would be expected from extrapolation of the data on the two ternary systems and is considered Satisfactory. For the system $CuCl-CuCl_2-HCl-H_2O$, the data of Novikov *et al.*[38] at 283 K are the only ones which cover the entire concentration range of the two salts. They are smoother than the data of Pochtarev *et al.*[50] and are probable reliable within 3 to 5 per cent. The data of Pochtarev *et al.*[50] are the only data available for temperatures above 300 K. They are probably reliable to about 10 per cent for the range they cover. The data of Pochtarev *et al.*[51] on the system $CuCl-CuCl_2-NaCl-H_2O$ are the only data available for this system and are probably accurate to about 10 per cent. Overall, none of the phase data available on systems involving aqueous $CuCl_2$ should be considered fully reliable without independent verification.

Other Systems

In 1912 Kremann and Noss[7] published data on the system $CuCl-FeCl_2-H_2O$ at 294.5 K including a phase diagram with 10 points where CuCl was the only solid phase, 3 points where the solid phase was $FeCl_2{\cdot}4H_2O$ and one point where the solution was saturated with both salts. They indicate a modest increase in the solubility of $FeCl_2$ with addition of CuCl up to saturation. Their data have not been confirmed by any other work. However, they are quite smooth and are Accepted tentatively, subject to future verification. In 1966 Chaltykyan[15] published phase diagrams for this system at 298 and 323 K, apparently derived from the results of Kremann and Noss[7]; his results are questionable.

In 1965 Shirokova *et al.*[48] measured the solubility of CuCl in aqueous $CaCl_2$ at four temperatures (303, 323, 343 and 363 K) up to molalities where hydrated $CaCl_2$ was also present as solid phase. The compositions they give for solutions saturated with both solid phases are given in Table 5.

Table 5. Composition of Solutions Saturated with CuCl and $CaCl_2$

T/K	$100w_{CaCl_2}$	$100w_{CuCl}$	$\frac{m_{CaCl_2}}{\mathrm{mol\ kg^{-1}}}$	$\frac{m_{CuCl}}{\mathrm{mol\ kg^{-1}}}$	Solid Phases
303	46.8	16.8	11.6	4.7	CuCl, $CaCl_2{\cdot}6H_2O$
323	47.8	17.9	12.6	5.3	CuCl, $CaCl_2{\cdot}2H_2O$
	47.8	16.8	12.2	4.8	CuCl, $CaCl_2{\cdot}2H_2O$
343	48.2	19.0	13.2	4.5	CuCl, $CaCl_2{\cdot}2H_2O$
363	47.0	21.4	13.4	6.8	CuCl, $CaCl_2{\cdot}2H_2O$

Comparison of the duplicate points at 323 K gives some indication of the consistency of their results. It is interesting to note in their solubility data that the solubility of CuCl goes through a maximum at $CaCl_2$ concentrations about 2/3 of that required to saturate the solution with the latter salt. Since their solubility data overall are consistent and agree with other data within 5 or 10 per cent, the results given in the table are Accepted tentatively, subject to possible errors of that magnitude.

Chaltykyan[15] gives graphical phase diagrams for CuCl in aqueous $CaCl_2$ at 298 and 323 K, based on his own previous work (source otherwise unspecified). He indicates that there is a region of double salt formation, but does not specify the salt(s) presumably formed. His results are indicative of the behaviour of the system, but not definitive.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; $CuCl$; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Berger and Winand[57] observed the phase behaviour in the complex system $CuCl-NaCl-HCl-FeCl_2-ZnCl_2-H_2O$ at 298, 303 and 363 K, including regions where the solid phase was CuCl and regions where it was NaCl. They presented phase diagrams for the system at 303 K giving the concentration of dissolved CuCl against the total chloride concentration present, both in mol dm^{-3}, for $ZnCl_2$ concentrations of zero and 0.64 mol dm^{-3}. (The data necessary to construct such diagrams are contained in the Compilations.)

As is the case with other soluble chlorides, the solubility of NaCl is increased by the addition of CuCl to the solution up to the point where the solution becomes saturated with CuCl. For both concentrations of $ZnCl_2$, the curves show breaks at intermediate concentrations of CuCl suggestive of possible double salt formation, but Berger and Winand[57] do not report observing any. The points at which both CuCl and NaCl were found together as solid phases had concentrations as listed in Table 6.

Table 6. **Solutions[a] with Both CuCl and NaCl Present as Solids at 303 K**

c_{NaCl}/mol dm^{-3}	c_{HCl}/mol dm^{-3}	c_{FeCl_2}/mol dm^{-3}	c_{ZnCl_2}/mol dm^{-3}	c_{CuCl}/mol dm^{-3}
4.80±0.0.4	0.11	1.74	0	3.27
5.99	0.15	1.13	0.64	2.64±0.04

[a] In the first case concentrations of NaCl, and in the second case concentrations of CuCl, were given just on either side of the point where both solids appeared rather than at that exact point.

Their results cannot be compared directly with any other. They are in general smooth to about 10 per cent and are Accepted tentatively as good to at least this precision.

Summary. All of the results cited above are Accepted tentatively. The data of Kremann and Noss[7] appear to have a precision of 5 per cent or better. Those of Shirokova *et al.*[48] and those of Berger and Winand[57] can be assigned a precision of about 10 per cent.

THERMODYNAMIC PROPERTIES

Introduction

Since cuprous halides go into solution primarily by formation of one or more complexes, knowledge of the thermodynamic properties of the complexes which may be present makes possible the calculation of solubility under conditions where measurements are not available. Two things are required: (a) a set of equilibrium constants for formation of the various complexes and (b) the information necessary to account for deviations of the solution from ideal solution behaviour. Since most data on the solubility of CuCl involves its dissolution in aqueous solutions of soluble chlorides, this situation will be considered first. In this case complexes are formed by reaction of chloride ions with solid CuCl according to a set of reactions given by Eq. 1, below (braces denote activities):

$$m\,\mathrm{CuCl}_{(s)} + (n-m)\,\mathrm{Cl}^- \rightleftharpoons \mathrm{Cu}_m\mathrm{Cl}_n^{m-n}, \quad \text{with } K_{Smn} = \{\mathrm{Cu}_m\mathrm{Cl}_n^{m-n}\}/\{\mathrm{Cl}^-\}^{(n-m)} \qquad (1)$$

The most useful set of equilibrium constants for calculation of solubility are precisely the K_{Smn} of Eq. 1, in appropriate units. An alternative approach has been to obtain equilibrium constants for the formation of the complexes from Cu^+ and Cl^-. Such *stability constants* correspond to the reactions given by Eq. 2:

$$m\,\mathrm{Cu}^+ + n\,\mathrm{Cl}^- \rightleftharpoons \mathrm{Cu}_m\mathrm{Cl}_n^{m-n}, \quad \text{with } \beta_{mn} = \{\mathrm{Cu}_m\mathrm{Cl}_n^{m-n}\}/\{\mathrm{Cu}^+\}^m\{\mathrm{Cl}^-\}^n \qquad (2)$$

The stability constants are not useful *per se*, since neither the concentration nor the activity

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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of the cuprous ion can be calculated directly. However, they are related to the K_{Smn} through the solubility product of CuCl, K_{S0}, *viz*:

$$K_{Smn} = \beta_{mn}\{Cu^+\}^m\{Cl^-\}^m = \beta_{mn}(K_{S0})^m \qquad (3)$$

Many determinations have been reported of both the K_{Smn} of Eq. 1 and the β_{mn} of Eq. 2, a number of which are discussed below. In most cases the constants given are those appropriate only to solutions of a particular soluble chloride, with a specific ionic strength maintained by an "indifferent" salt, usually a perchlorate or a nitrate. Thus, while satisfactory for these limited conditions, they can give only (often very) approximate ideas of the concentrations of complexes produced (and thus the solubility of CuCl) for any other ionic strength, let alone for solutions with a different soluble chloride. Stability constants determined for specific solutions can be used only if one knows the solubility product of CuCl for that particular solution, and this may be quite different from the solubility product in pure water.

An alternative approach is to use available information to get a set of equilibrium constants K_{Smn} extrapolated to zero ionic strength, and then use a set of parameters to obtain the activity coefficients (for all species present in the solutions) necessary to correct for deviation from ideal solution behaviour for particular media of interest. Knowledge of the enthalpy changes associated with complex formation (*via* Eq. 1) and of the temperature dependence of the activity coefficient parameters will permit calculations to be made at a variety of temperatures. The next section describes the procedures used to get such a set of equilibrium constants and enthalpy changes and gives values of each for a set of complexes believed to be the significant ones in most solutions of CuCl in aqueous solutions of soluble chlorides. Succeeding sections discuss the equilibrium data available in the literature, and a final set of sections discuss procedures for incorporation of activity coefficients in the calculations.

Thermodynamic Properties at Zero Ionic Strength

Given a sufficiently extensive and precise set of data for the solubility of a cuprous halide in a particular soluble halide, it is possible to determine at the same time a set of equilibrium constants K_{Smn} along with the activity coefficient parameters appropriate to that medium. Such a determination was made using the extensive data of Hikita *et al.*[3] on the solubility of CuCl in aqueous HCl–$HClO_4$; it has been reported in the literature[6]. More recently, all these parameters have been refined, using all available data for solubility of cuprous chloride, weighting each point to reflect the consistency and apparent reliability of the data. Activity coefficient parameters have been evaluated for use in the various aqueous media involved. The equilibrium constants obtained by this procedure are tabulated below, along with corresponding enthalpy changes; the activity coefficient parameters for the various media are given later.

Enthalpy changes at zero ionic strength have been derived from the calorimetric measurements made by Vasil'ev and Kunin[87]. They measured heats of solution of CuCl in aqueous HCl–$HClO_4$ at four ionic strengths (1, 2, 4 and 5 mol dm^{-3}) and three temperatures (288, 298 and 308 K), with three or four concentrations of HCl at each ionic strength. Using the equilibrium constants and activity parameters discussed above to obtain the distribution of dissolved CuCl between the various possible complexes, values were obtained for the standard enthalpy change associated with the formation of each of the major complexes from solid CuCl[88]. For the two simplest complexes the data were sufficient to give the change in heat capacity also.

Data for the dissociation of CuCl into aqueous ions was obtained as follows:

1. The enthalpy change for the dissociation was calculated using the standard enthalpy of formation of CuCl given in the 1974 work of Vasil'ev and Kunin[89] (this agreed with the early value given in NBS Circular 500[11] within the precision of the latter), the standard

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(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

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enthalpy of formation of Cl^- given in NBS Circular 500[11] and that for Cu^+ given by Wagman[90].

2. The solubility product at 298.15 K determined by Sosnitskii and Fofanov[4] was taken as a first approximation to the proper value. It was then used along with the thermodynamic data for the various complexes to obtain the best fit to the data of Hikita *et al.*[3] for the solubility of CuCl in aqueous $HClO_4$ and in aqueous $HCl-HClO_4$ mixtures with low concentrations of chloride ion. The final value used, given below, is at the lower end of the range recommended by Sosnitskii and Fofanov[4].
3. The standard Gibbs energy for dissociative dissolution of CuCl was calculated from the value of the solubility product, and the corresponding entropy change obtained by combining this with the enthalpy change for the reaction.

The information listed above was sufficient to give a full set of thermodynamic properties at 298 K, zero ionic strength, for all important species produced when CuCl dissolves in an aqueous solution of a soluble chloride. Table 7 gives the values of the changes in thermodynamic properties associated with the formation of each one from solid CuCl and chloride ion as needed. In addition to the solubility product of CuCl, the table gives the equilibrium constants K_{Smn} of Eq. 1 for the reactions producing each of the complexes from solid CuCl (Note that the data available were sufficient to give thermodynamic properties for the two doubly charged complexes $CuCl_3^{2-}$ and $Cu_2Cl_4^{2-}$, but not adequate to distinguish between the possible triply charged species. The latter were represented in terms of a single complex $Cu_3Cl_6^{3-}$, which gave the best fit to available solubility data.) Table 8 gives a corresponding set of values for the formation of the various complexes from Cu^+ and Cl^-, obtained by combining the results for the complex species with those for the dissociation of $CuCl_{(s)}$ into ions. The β_{mn} are the stability constants of Eq. 2.

Table 7. Thermodynamic Properties for Formation of Species from $CuCl_{(s)}$ at 298.15 K, Zero Ionic Strength[a]

Species	K_{Smn} / $(\text{mol dm}^{-3})^{(1+m-n)}$	$\Delta_r H^\ominus$ / kJ mol^{-1}	$\Delta_r C_p^\ominus$ / J K^{-1} mol^{-1}	$\Delta_r G^\ominus$ / kJ mol^{-1}	$\Delta_r S^\ominus$ / J K^{-1} mol^{-1}
$Cu^+ + Cl^-$	$1.83 \cdot 10^{-7}$	40.33	–	38.46	6.29
$CuCl^0$	$3.74 \cdot 10^{-4}$	23.01	–	19.6	11.57
$CuCl_2^-$	0.0619	27.32	79.5	6.90	68.50
$CuCl_3^{2-}$	0.0126	14.35	109.	10.84	11.77
$Cu_2Cl_4^{2-}$	$8.16 \cdot 10^{-4}$	28.03	–	17.6	34.9
$Cu_3Cl_6^{3-}$	$3.34 \cdot 10^{-5}$	5.94	–	25.56	−65.8

[a] The dashed entries under $\Delta C_p^\ominus$ indicate the fact that the available data were insufficient to permit evaluation of these quantities.

Table 8. Thermodynamic Properties for Formation of Species from Cu^+ and Cl^- at 298.15 K, Zero Ionic Strength

Species	β_{mn} / $(\text{mol dm}^{-3})^{(1-m-n)}$	$\Delta_r H^\ominus$ / kJ mol^{-1}	$\Delta_r G^\ominus$ / kJ mol^{-1}	$\Delta_r S^\ominus$ / J K^{-1} mol^{-1}
$CuCl^0$	2043	−17.32	−18.90	5.3
$CuCl_2^-$	$3.38 \cdot 10^{5}$	−13.01	−31.56	62.2
$CuCl_3^{2-}$	$6.88 \cdot 10^{4}$	−25.98	−27.62	5.48
$Cu_2Cl_4^{2-}$	$2.43 \cdot 10^{10}$	−52.63	−59.28	22.3
$Cu_3Cl_6^{3-}$	$5.43 \cdot 10^{15}$	−115.	−89.8	−84.7

COMPONENTS:	EVALUATOR:
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Literature Data on Enthalpy Changes

Outside of the data of Vasil'ev and Kunin[87] used in obtaining the enthalpy values given above, there is little information in the literature on the enthalpy changes associated with formation of the various complex species at zero ionic strength. Their values and those given by Noyes and Chow[28] and Hikita *et al.*[3] are summarized in Table 9. They are reported in the units originally given (kcal mol^{-1}) and in kJ mol^{-1} (taking 4.1840 J cal^{-1}).

Table 9. Published Values of Enthalpy Changes for Complex Formation from $CuCl_{(s)}$ and Cl^- at Zero Ionic Strength

Complex	T/K	$\Delta_r H^\ominus$ / kcal mol^{-1}	$\Delta_r H^\ominus$ / kJ mol^{-1}	Reference
$CuCl_2^-$	288	7.05	29.5	87
	298	7.25	30.3	87
	308	7.39	30.9	87
	298	5.81	24.3	3[a]
	[b]	6.44	26.9	28
$CuCl_3^{2-}$	288	3.43	14.4	87
	298	3.67	15.4	87
	308	3.88	16.2	87
	298	4.53	19.0	3[a]
$CuCl_4^{3-}$	298	3.58	15.0	3[a]

[a] The values quoted from the results of Hikita *et al.*[3] were derived from their equation for the dependence of equilibrium constants on temperature and ionic strength and give no information about the variation of the enthalpy change with temperature.

[b] The value quoted from Noyes and Chow[28] is an average over the temperature range 273 to 348 K.

The values given by Vasil'ev and Kunin[87] were obtained by them from a large set of measured heats of solution of CuCl in aqueous HCl–$HClO_4$, using what they described as 'most probable stability constants' for $CuCl_2^-$ and $CuCl_3^{2-}$ obtained from previous publications; they did not consider the uncharged complex $CuCl^0$ or any polynuclear or triply charged complexes. They assigned uncertainties of 0.3 to 0.4 kcal mol^{-1} (1.2 to 1.7 kJ mol^{-1}) to the values given for $CuCl_2^-$ and 0.1 to 0.15 kcal mol^{-1} (0.4 to 0.6 kJ mol^{-1}) to those for $CuCl_3^{2-}$. Their values for enthalpy change differ from the corresponding entries in Table 7 by somewhat more than their assigned uncertainties; they are higher in the case of $CuCl_2^-$ and lower in the case of $CuCl_3^{2-}$. The differences can be attributed (a) to the fact that they used a set of stability constants derived mainly from solubility data for CuCl in aqueous NaCl rather than HCl and (b) to the fact that they ignored the presence of any but the two simplest complexes. The values quoted for Hikita *et al.*[3] come from equations which represent the observed solubility of CuCl in aqueous HCl–$HClO_4$ over only a 20°C temperature range and only to about 10 per cent; it is not surprising that they differ substantially from values derived from actual measurements of enthalpy changes. The single value of Noyes and Chow[28] was calculated using measurements spanning 75 K and is surprisingly close to the value given in Table 7.

In addition to the values listed in Table 9, Ahrland, Tagesson and Tuhtar[91] used titration calorimetry to obtain the enthalpy change for the reaction $CuCl_2^- + Cl^- \rightleftharpoons CuCl_3^{2-}$ at ionic strength 5.0 mol dm^{-3} (4.9 mol dm^{-3} $NaClO_4$, 0.1 mol dm^{-3} HCl) at 298 K. Their value for this is 19.9±0.7 kJ mol^{-1}, about 6 kJ mol^{-1} higher than that derivable for zero ionic

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strength from Table 7. This difference is not surprising considering the possible effects of the high concentrations of soluble salts present in their measurements. Sukhova *et al.*[92] give a set of values of enthalpy changes and entropy changes for formation from $\mathrm{Cu^+}$ and $\mathrm{Cl^-}$ of 12(!) complexes, mostly polynuclear, which they believed were present in solutions of CuCl in aqueous $\mathrm{NH_4Cl}$ at 10 mol dm^{-3} ionic strength maintained by use of $\mathrm{NH_4NO_3}$. Their values cannot be compared with any others and may be artifacts of the manner in which they interpreted their solubility and potentiometric data.

Summary. The values given in Table 7 for the enthalpy changes at 298 K, zero ionic strength, for formation of the various chlorocomplexes of CuCl are Recommended as the best values available at the present time. The values given by Vasil'ev and Kunin[87] using a less thorough analysis of their heat of solution data appear to be uncertain by somewhat more than their estimates; their values for ionic strengths other than zero should be usable but again somewhat less precise than the authors claim. The values derived from the equations of Hikita *et al.*[3] are not useful as enthalpy changes. The single values given by Noyes and Chow[28] and by Ahrland *et al.*[91] are reasonable for the conditions used. It should be noted that derivation of enthalpy effects in solutions at other than zero ionic strength requires knowledge of the distribution of complex species in these solutions and also the temperature dependence of the activity coefficients of these species.

Literature Data on Equilibrium Constants

There have been many reports of equilibrium constants for complex formation. These have been summarized in various publications, particularly in the compilations of Sillén and Martell[93], of Smith and Martell[94] and most recently by Fontana *et al.*[43]. Of the many values in the literature, the majority refer to formation of the complexes from $\mathrm{Cu^+}$ and $\mathrm{Cl^-}$ (stability constants, as in Table 8), some to the $K_{\mathrm{S}mn}$ of Eq. 1, and the remainder to equilibrium constants related to one or the other of these. Most of the values given apply to solutions in a particular soluble chloride, at a specific ionic strength maintained by an "indifferent" electrolyte such as a perchlorate or nitrate of the same element as the soluble chloride. The more significant of the reports are discussed below.

Values for the $K_{\mathrm{S}mn}$ of Eq. 1 have been obtained from a variety of measurements, including spectra and polarography as well as solubility. The significant publications, with the species for which constants are given and the aqueous media employed, are Chaltykyan[95] ($\mathrm{CuCl_2^-}$, KCl), Carlson and Wettermark[96] ($\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{2-}}$, 1.0 mol dm^{-3} $\mathrm{HCl{-}HClO_4}$), Braun and Nobe[97] ($\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{2-}}$, HCl-KCl), Hikita *et al.*[3] ($\mathrm{CuCl_2^-}$,$\mathrm{CuCl_3^{2-}}$, $\mathrm{CuCl_4^{3-}}$, $\mathrm{HCl{-}HClO_4}$), Noyes and Chow[28] ($\mathrm{CuCl_2^-}$, dilute HCl), Chang and Cha[24] ($\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{2-}}$, HCl), Bodländer and Storbeck[98] ($\mathrm{CuCl_2^-}$, dilute KCl), Ahrland and Rawsthorne[5] ($\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{2-}}$, $\mathrm{Cu_2Cl_4^{2-}}$, $\mathrm{CuCl_4^{3-}}$, 5.0 mol dm^{-3} $\mathrm{NaCl{-}NaClO_4}$), McConnell and Davidson[54] ($\mathrm{CuCl_2^-}$, $\mathrm{CuCl_3^{2-}}$, 1.0 mol dm^{-3} $\mathrm{HCl{-}HClO_4}$), Latimer[10] ($\mathrm{CuCl_2^-}$, zero ionic strength) and Butler[14] ($\mathrm{CuCl_2^-}$, 1.0 mol dm^{-3} ionic strength). Sugasaka and Fujii[99] give a value of $K_{\mathrm{S}13}/K_{\mathrm{S}12}$ at 298 K (5.0 mol dm^{-3} $\mathrm{NaCl{-}NaClO_4{-}HClO_4}$) obtained in the course of a spectroscopic study. (Note that Noyes and Chow[28] give values for 5 temperatures from 273 to 323 K and that Hikita *et al.*[3] give values for 288, 298 and 308 K.) Of all of the sets of constants reported, only the constants of Hikita *et al.*[3], Chang and Cha[24] and Ahrland and Rawsthorne[5] are adequate for prediction of solubilities in the particular media which they studied (and only those). The other values given can be used to predict concentrations of particular complexes, but must be combined with other results to get prediction of the solubility. All of the constants suffer from the fact they they were derived assuming that activity coefficients for the various species depend only on the ionic strength of the solution, whereas they actually depend also on the nature of the ions present, quite significantly in the case of multiply charged species.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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Sugasaka and Fujii[99] also observed the spectra of CuCl in a medium in which NaOH was used to maintain hydroxide concentrations from 10^{-5} to 1 mol dm^{-3} along with chloride concentrations of either 2 or 4 mol dm^{-3}. They concluded that in the alkaline solutions complexes containing OH^- were formed, specifically $CuClOH^-$, $CuCl_2OH^{2-}$, $CuCl(OH)_2^{2-}$, and give values (all greater than 10^3) for equilibrium constants for formation of these species from $CuCl_2^-$. The merit of their values cannot be assessed, but it is clear that in alkaline solutions species containing hydroxide substantially displace simple chlorocomplexes.

Stability constants for formation of various complex species have been measured for a variety of media, almost all by means of cell measurements and most at or near 298 K. They have been reported by Bodländer and Storbeck[98] ($CuCl_2^-$, dilute KCl), Chang and Cha[24] ($CuCl_2^-$, HCl), Náray-Szabó and Szabó[100] ($CuCl_2^-$, $CuCl_3^{2-}$, $CuCl_4^{3-}$, concentrated KCl), Chaltykyan[95] ($CuCl_2^-$, $CuCl_3^{2-}$, KCl), Sukhova *et al.*[92,101] (13 complexes, concentrated NH_4Cl-NH_4NO_3), Ahrland and Rawsthorne[5] ($CuCl_2^-$, $CuCl_3^{2-}$, $Cu_2Cl_4^{2-}$, $CuCl_4^{3-}$, 5.0 mol dm^{-3} NaCl-$NaClO_4$), Pestrikov and Kranilov[102] ($CuCl_2^-$, 4.0 mol dm^{-3} $NaClO_4$), Braun and Nobe[97] ($CuCl_2^-$, $CuCl_3^{2-}$, HCl-KCl). Vasil'ev and Kunin[87] give a set of values for the stability constants of $CuCl_2^-$ and $CuCl_3^{2-}$ as a function of ionic strength, which they state was derived from a variety of other investigations in the literature, without giving details of their method of selection. The most reliable stability constants are those of Ahrland and Rawsthorne[5]. Any of the values given are useful only if the solubility product of CuCl is known for the particular medium studied and should be used only for that particular medium. Even if this information is available, the constants can give only approximate values for the solubility.

CALCULATION OF UNKNOWN SOLUBILITIES

The solubility of CuCl in a particular medium can be calculated using the equilibrium constants of Table 7, provided that it is possible to calculate the activity coefficients of all species present in the solution. A fairly sophisticated model is required for this purpose, since the activity coefficients of doubly and triply charged species may vary quite substantially from unity. The virial model of Pitzer and Mayorga[18], as applied to mixtures of electrolytes by Pitzer and Kim[103], fulfills the requirements. Adequate representation of solubilities in media up to 7 mol dm^{-3} can be achieved using only three parameters $\beta^{(0)}$, $\beta^{(1)}$ and C for each ion pair present in the solution. Table 10 gives the equations for calculation of the activity coefficients for an ion pair NX. For convenience in calculation, these are put in terms of individual ion activity coefficients, equivalent to the measurable mean ion activity coefficients for the pair[104].

With knowledge of K_{Smn} for the various complexes and the values of the virial parameters for all ion pairs present in solution, an iterative computer program will calculate the solubility of CuCl in aqueous solutions of a soluble chlorides, with or without any "indifferent" electrolyte present. A simple program does so by using an arbitrary initial choice for the concentration of free chloride ion to calculate preliminary concentrations of all complexes present, then adjusts the chloride concentration until the calculated total chloride present corresponds to that provided by the medium and dissolved CuCl. (Note that the ionic strength of the solution will generally be different from that in the absence of dissolved CuCl, since production of multiply charged complex ions will increase the ionic strength of the solution; this effect must be taken care of in the calculation.) The necessary virial parameters have been obtained for solutions of CuCl in a number of aqueous media and are given below. The parameters for ion pairs formed from many soluble salts, whether chlorides or "indifferent" electrolytes are available in the literature[18] and in many cases their temperature derivatives[105]. For cases where more than one soluble salt is present, these can be treated as affecting the solubility independently. [In principle, where two or more

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cations (anions) are present, the treatment should contain allowance for interactions such as 2 cations – 1 anion or 2 anions – 1 cation; in practice this is needed only for quite high ionic strengths or for precision beyond that usually available or required for solubilities.] Also, the virial parameters given in the literature are for concentrations in mol kg^{-1}, whereas the majority of solubility measurements for cuprous halides have been given in mol dm^{-3} or equivalent. The virial coefficients given hereafter are for the concentration units where data was available, adjusted so that they can be used with other parameters in mol kg^{-1}; they should be used only for the concentration units specified in each case.

Table 10. Equations for Calculation of Activity Coefficients[a]

$$\ln \gamma_{\mathrm{N}} = z_{\mathrm{N}}^2 f^{\gamma} + 2\sum_{\mathrm{a}} M_{\mathrm{a}}[B_{\mathrm{Na}} + (\sum_{\mathrm{c}} M_{\mathrm{c}} z_{\mathrm{c}})C_{\mathrm{Na}}] + \sum_{\mathrm{c}}\sum_{\mathrm{a}} M_{\mathrm{c}} M_{\mathrm{a}}[z_{\mathrm{N}}^2 B'_{\mathrm{ca}} + z_{\mathrm{N}} C_{\mathrm{ca}}]$$

$$\ln \gamma_{\mathrm{X}} = z_{\mathrm{X}}^2 f^{\gamma} + 2\sum_{\mathrm{c}} M_{\mathrm{c}}[B_{\mathrm{cX}} + (\sum_{\mathrm{a}} M_{\mathrm{a}}|z_{\mathrm{a}}|)C_{\mathrm{cX}}] + \sum_{\mathrm{c}}\sum_{\mathrm{a}} M_{\mathrm{c}} M_{\mathrm{a}}[z_{\mathrm{X}}^2 B'_{\mathrm{ca}} + |z_{\mathrm{X}}| C_{\mathrm{ca}}]$$

with

$$f^{\gamma} = -A_{\phi}[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2})],$$

$$B_{\mathrm{NX}} = \beta_{\mathrm{NX}}^{(0)} + (2\beta_{\mathrm{NX}}^{(1)}/\alpha^2 I)\{1 - [1 + \alpha I^{1/2}]\exp(-\alpha I^{1/2})\},$$

$$B'_{\mathrm{NX}} = (2\beta_{\mathrm{NX}}^{(1)}/\alpha^2 I^2)\{-1 + [1 + \alpha I^{1/2} + 0.5\alpha^2 I]\exp(-\alpha I^{1/2})\}, \text{ where } \alpha = 2.0,$$

$$C_{\mathrm{NX}} = C_{\mathrm{NX}}^{\phi}/(2|z_{\mathrm{N}} z_{\mathrm{X}}|^{1/2}).$$

[a] Note that for 2–2 and higher valence type electrolytes an additional parameter $\beta^{(2)}$ must be added; see Pitzer and Kim[103].

In Table 10, subscripts c and a stand for all cations present in the solution; M is the concentration of the species indicated, z is its charge, and I is the ionic strength of the solution. A_{ϕ} is the Debye-Hückel coefficient for the osmotic function[18].

Virial Parameters for Aqueous HCl Solutions

Virial parameters for use with solutions of CuCl in aqueous HCl, with or without $HClO_4$ present, are given in Table 11. They are valid for use with concentrations in mol dm^{-3} up to about 7 mol dm^{-3}. This set of parameters, along with the $K_{s_{mn}}$ of Table 7, represented the solubility data of Hikita *et al.*[3] and those of Chang and Cha[24] below 7 mol dm^{-3} with an estimated standard deviation of 2 per cent, the graphical data of Camacho Rubio *et al.*[25] within 5 per cent and other, less precise, data generally within their apparent reliability. The parameters of Table 11 can be relied on to give good values of solubility for ionic strengths up to about 7 mol dm^{-3} and temperatures between 288 and 308 K (the temperature range of reliable data for this system). With use of the temperature derivatives they should give reasonable estimates of solubility over a somewhat wider temperature range.

Virial Parameters for Aqueous NaCl Solutions

A set of virial parameters for complexes formed in aqueous NaCl solutions is given in Table 12. They were derived using all available data for solutions in aqueous NaCl and in aqueous NaCl–HCl mixtures with H^+/Na^+ mol ratios of 0.1 or less. They are not as reliable as the ones given for aqueous HCl, since agreements among the data and the internal consistency of particular sets of data were much less satisfactory. However, the data extend over a much wider temperature range (273 to 368 K), so that the parameters can be used over a similarly wide range. Because of the relatively low quality of most of the data at temperatures much different from 298 K, the temperature derivatives for ion pairs involving complexes are uncertain; they are the best set derivable from available solubility data.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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Table 11. Virial Parameters and Their Temperature Coefficients at 298 K for Ion Pairs with Hydrogen Ion[a,b,c] (for Concentrations in mol dm^{-3})

Ion Pair	$\beta^{(0)}$	$\beta^{(1)}$	C	$d\beta^{(0)}/dT \cdot 10^4$	$d\beta^{(1)}/dT \cdot 10^4$	$dC/dT \cdot 10^5$
H^+-ClO_4^-	0.1747	0.2931	0.0410	4.908	19.31	−5.98
H^+-Cl^-	0.1775	0.2945	0.0004	−3.08	1.42	−3.11
H^+-$CuCl_2^-$	0.2052	0.3115	0.0103	8.75	21.19	−13.66
H^+-$CuCl_3^{2-}$	0.2706	1.6251	0.0238	3.14	6.50	−8.37
H^+-$Cu_2Cl_4^{2-}$	0.3686	1.794	0.0064	–	–	–
H^+-$Cu_3Cl_6^{3-}$	0.4538	4.559	0.0195	–	–	–
$CuCl^0$	0.216	0.232	−0.0228	−20.0	–	–

[a] The values given for the parameters for H^+-Cl^- and H^+-ClO_4^- are from Pitzer and Mayorga[18] and their temperature derivatives from Silvester and Pitzer[105]. Although these were obtained from data in mol kg^{-1}, there is no difficulty in using them, since the procedure used in getting the other parameters allowed for this.

[b] The lack of temperature derivatives for some of the parameters comes from the fact that the available data were not sufficient to permit their evaluation.

[c] The information needed to calculate the activity coefficients of the neutral species $CuCl^0$ has been put in the same form as for ion pairs to simplify calculations.

Table 12. Virial Parameters and Their Temperature Coefficients at 298 K for Ion Pairs with Sodium Ion[a] (for Concentrations in mol dm^{-3})

Ion Pair	$\beta^{(0)}$	$\beta^{(1)}$	C	$d\beta^{(0)}/dT \cdot 10^4$	$d\beta^{(1)}/dT \cdot 10^4$	$dC/dT \cdot 10^5$
Na^+-ClO_4^-	0.0554	0.2755	−0.00059	12.96	23.0	−8.11
Na^+-Cl^-	0.0765	0.2664	0.00064	7.16	7.01	−5.27
Na^+-$CuCl_2^-$	0.2212	0.0495	−0.01276	− 2.70	5.0	−40.3
Na^+-$CuCl_3^{2-}$	0.0197	2.1278	0.02938	9.20	95.0	−33.5
Na^+-$Cu_2Cl_4^{2-}$	−0.0159	0.6372	0.01188	24.7	135.0	−12.
Na^+-$Cu_3Cl_6^{3-}$	0.1467	3.4014	0.02112	11.3	115.0	−18.
$CuCl^0$	0.233	0.372	−0.294	–	–	–

[a] The values given for the parameters for Na^+-Cl^- and Na^+-ClO_4^- are from Pitzer and Mayorga[18] and their temperature derivatives from Silvester and Pitzer[105]. Those for pairs involving complexes were obtained by fitting the solubility data.

The best data available for media which are primarily aqueous NaCl are those of Ahrland and Rawsthorne[5], who worked with media where the mol ratio Na^+/H^+ was 49 at 298.15 K. Calculations using the parameters of Table 12 and including those of Table 11 to account for the (quite small) effect of replacing 2 per cent of the Na^+ with H^+ fitted their data with an estimated standard deviation of 2.6 per cent. The best data at elevated temperatures are those of Sin *et al.*[39] at 343 and 363 K and the 1970 data of Utkina *et al.*[41], in both cases in "pure" aqueous NaCl (no other added salts). The parameters of Table 12 fitted the Sin data to 7 per cent (r.m.s.) and the Utkina data to 6 per cent. The other available data are fitted with less precision, but generally within their own internal consistency and their agreement

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

with the bulk of data for the system. The parameters of Tables 11 and 12 can be used together to calculate the solubility of CuCl in solutions containing both sodium ion and hydrogen ion. They predict the graphical results of Camacho Rubio *et al.*[25] to about 8 per cent and those of Winter *et al.*[56] to 6 per cent. The conditions used by these investigators spanned nearly the entire possible range of the Na^+/H^+ mol ratio and covered temperature ranges of 40 and 50 K, respectively.

Virial Parameters for Aqueous KCl Solutions

A set of virial parameters for solutions of CuCl in aqueous KCl are given in Table 13. They are derived mainly from the extensive solubility data of Brönsted[45] at 295 K, for molalities. Since his results were unreasonably low below 1.2 mol kg^{-1}, the solubility at concentrations lower than this was estimated based on that in aqueous HCl and aqueous NaCl, which are quite similar in this region of molality. Temperature derivatives of the virial parameters are not included, since reliable data was available for only a single temperature. The parameters are suitable for use with molalities, since the data used to obtain them was based on such units.

Table 13. **Virial Parameters at 298 K for Ion Pairs with Potassium Ion**[a] **(for Molalities)**

Ion Pair	$\beta^{(0)}$	$\beta^{(1)}$	C
K^+-Cl^-	0.0484	0.2122	−0.00042
K^+-$CuCl_2^-$	−0.0262	0.67	0.00702
K^+-$CuCl_3^{2-}$	0.066	1.309	−0.01176
K^+-$Cu_2Cl_4^{2-}$	0.0161	0.500	0.00964
K^+-$Cu_3Cl_6^{3-}$	0.0396	1.633	−0.00364
$CuCl^0$	0.275	0.722	−0.0290

[a] The values given for the parameters for K^+-Cl^- are from Pitzer and Mayorga[18]. Those for pairs involving complexes were obtained by fitting the solubility data.

The parameters of Table 13 represent the data of Brönsted[45] above 1.0 mol kg^{-1} within an estimated standard deviation of 7 per cent, which is about the consistency of the data. They represent the data of Le Chatelier[21] at 290 K and below 1.0 mol dm^{-3} to about the same precision. (Note that the latter data were given in different concentration units, but the difference is not significant below unit concentration).

Virial Parameters for Aqueous NH_4Cl Solutions

A set of parameters for use in calculating the solubility of CuCl in aqueous NH_4Cl solutions (molalities) are given in Table 14. They were derived from the graphical data of Morosov and Ustanishkova[31]. No parameters are given for $CuCl^0$, since the data were inadequate for evaluating any; this species would be expected to contribute only about 0.0001 mol kg^{-1} to the solubility.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; $CuCl$; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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Table 14. Virial Parameters and Their Temperature Coefficients at 298 K for Ion Pairs with Ammonium Ion[a] (for Molalities)

Ion Pair	$\beta^{(0)}$	$\beta^{(1)}$	C	$d\beta^{(0)}/dT \cdot 10^4$	$d\beta^{(1)}/dT \cdot 10^4$	$dC/dT \cdot 10^4$
NH_4^+-Cl^-	0.0522	0.1918	−0.0015	0.78	12.6	2.1
NH_4^+-$CuCl_2^-$	−0.0722	0.5845	0.0127	−17.9	4.6	−25.8
NH_4^+-$CuCl_3^{2-}$	0.0153	0.991	0.013	−5.4	21.4	−6.9
NH_4^+-$Cu_2Cl_4^{2-}$	−0.0277	0.891	0.0004	−0.4	41.4	−12.9
NH_4^+-$Cu_3Cl_6^{3-}$	−0.0825	2.133	0.012	1.4	67.1	−15.2

[a] The values given for the parameters for NH_4^+-Cl^- are from Pitzer and Mayorga[18]. Those for pairs involving complexes were obtained by fitting the solubility data.

Because of the scarcity of data, the set of parameters given in Table 14 cannot be claimed unique. However, they will represent the data of Morosov and Ustanishkova[31] with an estimated standard deviation of 5 per cent for NH_4Cl molalities up to 8.5 in regions where double salt formation was not observed; this is about the precision of reading solubilities from their graphs. The regions where the solid phase was CuCl were: at 273 K, up to 4.7 mol kg^{-1}, at 298 K, up to 7 mol kg^{-1}, at 323 K, up to 8.2 mol kg^{-1} and at temperatures above 323 K up to 8.5 mol kg^{-1}. Calculation of solubilities where a double salt is formed requires knowledge of the thermodynamic properties of the double salt, which are not available.

Virial Parameters for Aqueous $CaCl_2$ Solutions.

A set of parameters suitable for calculating the solubility of CuCl in aqueous solutions of $CaCl_2$ is given in Table 15A and their temperature derivatives in Table 15B. These were derived from the measurements of Shirokova *et al.*[48]. These measurements extended from 303 to 323 K and from $CaCl_2$ molalities from 0.5 mol kg^{-1} to saturation with $CaCl_2$ (about 7.5 mol kg^{-1} $CaCl_2$). The data consisted of 40 points in all at four different temperatures; they were presented in graphical form, from which values of the solubility can be read to about 5 per cent.

Of the 40 data points reported by Shirokova *et al.*[48], 5 were seriously inconsistent with the rest. Omitting these points, the remainder could be fitted to an estimated standard deviation of 8 per cent using the parameters of Tables 15A and 15B. (Note that the data covered a 90-fold range of solubility and a 60 K span in temperature.) The parameters reproduce the maxima in solubility observed near 5.0 mol kg^{-1} at all temperatures. The only other data on solubility of CuCl in aqueous $CaCl_2$, those of Utkina *et al.*[41], contain only 6 points each at 298 and 368 K and are reported for concentrations in volume units. They cannot be compared directly with the Shirokova data and are insufficient in number to permit evaluation of a separate set of parameters in their units. However, they show the same trends with both concentration and temperature.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Table 15A. Virial Parameters at 298 K for Ion Pairs with Calcium Ion[a,b] (for Molalities)

Ion Pair	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C
Ca^{2+}-Cl^-	0.3159	1.614	0.0	−0.00012
Ca^{2+}-$CuCl_2^-$	−0.1161	3.271	0.0	0.0269
Ca^{2+}-$CuCl_3^{2-}$	0.288	5.454	0.0	0.0327
Ca^{2+}-$Cu_2Cl_4^{2-}$	0.520	4.30	−5.6	0.0174
Ca^{2+}-$Cu_3Cl_6^{3-}$	0.973	9.208	−1.2	0.01755

[a] The values given for the parameters for Ca^{2+}-Cl^- are from Pitzer and Mayorga[18]. Those for pairs involving complexes were obtained by fitting the solubility data. No parameters are given for the neutral complex $CuCl^0$, since the measurements did not extend into $CaCl_2$ concentrations low enough for this species to contribute significantly to the solubility.

[b] Ion pairs with both ions doubly or triply charged require the additional parameter $\beta^{(2)}$; for its inclusion in equations for activity coefficients, see Pitzer and Kim[103].

Table 15B. Temperature Coefficients at 298 K for $CaCl_2$ Parameters[a,b] (for Molalities)

Ion Pair	$d\beta^{(0)}/dT \cdot 10^4$	$d\beta^{(1)}/dT \cdot 10^4$	$dC/dT \cdot 10^4$
Ca^{2+}-Cl^-	−1.73	39.	0.0
Ca^{2+}-$CuCl_2^-$	6.3	180.	37.
Ca^{2+}-$CuCl_3^{2-}$	0.6	79.	5.
Ca^{2+}-$Cu_2Cl_4^{2-}$	−1.4	59.	3.
Ca^{2+}-$Cu_3Cl_6^{3-}$	−5.1	110.	2.

[a] The coefficients for Ca^{2+}-Cl^- were take from Silvester and Pitzer[105]. The others were derived from fitting the solubility data.

[b] No temperature derivatives are given for the $\beta^{(2)}$'s, since the calculated solubilities were insensitive to values chosen for these parameters.

Other Systems

It was not possible to determine virial parameters to use in calculating solubilities of CuCl in aqueous solutions containing other divalent cations (Cu^{2+}, Fe^{2+}, Zn^{2+}) for lack of sufficient suitable data. Most of the measurements involving these cations were made on solutions with substantial amounts of one or more other cations. A few measurements are available for solutions containing either Cu^{2+} or Fe^{2+} without other cations present, but they are not sufficient to permit evaluation of reliable parameters. A simplified set of parameters which reproduces the data for the $CuCl_2$ and $FeCl_2$ solutions is available in the literature[104].

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

THERMODYNAMICS OF SYSTEMS INVOLVING ORGANIC COMPOUNDS

Systems Involving Unsaturated Alcohols

Andrews and coworkers[9,60,61] interpreted their data on the solubility of CuCl in aqueous solutions of unsaturated alcohols, in the presence and absence of added chloride ion, in terms of stability constants for formation of complexes of the alcohol with neutral CuCl and with Cu^+. They considered in addition the dissociation of CuCl and the formation of $CuCl_2^-$, but assumed ideal solution behaviour and neglected the formation of additional chlorocomplexes of CuCl. Equilibrium constants for this system have been reevaluated on a more general basis, as follows:

1. Activity coefficients have been used for all ions. These were calculated using the f^γ function of Table 10, but without inclusion of virial parameters. (This procedure should be adequate up to ionic strengths of 0.1 mol dm^{-3} and somewhat higher.)
2. The species $CuCl_3^{2-}$ was included in the calculation along with the $CuCl_2^-$ considered by Andrews and coworkers.
3. Equilibrium constants for dissociation of CuCl and the formation of the two chlorocomplexes were taken from Table 7.

The equilibria considered in the calculation were then:

$$\begin{array}{rcll}
CuCl_{(s)} & \rightleftharpoons & Cu^+ + Cl^- & K_{S0} = 1.83 \cdot 10^{-7}\ \mathrm{mol^2\ dm^{-6}} \\
CuCl_{(s)} + Cl^- & \rightleftharpoons & CuCl_2^- & K_{S2} = 0.0619 \\
CuCl_{(s)} + 2Cl^- & \rightleftharpoons & CuCl_3^{2-} & K_{S3} = 0.0126\ \mathrm{mol^{-1}\ dm^3} \\
CuCl_{(s)} + Alc & \rightleftharpoons & Alc \cdot CuCl & K_1 = \{Alc \cdot CuCl\}/\{Alc\} \\
CuCl_{(s)} + Alc & \rightleftharpoons & Alc \cdot Cu^+ + Cl^- & K_2 = \{Alc \cdot Cu^+\}\{Cl^-\}/\{Alc\}
\end{array}$$

where Alc represents the alcohol considered, and the equilibrium constants are for the activities corresponding to concentrations in mol dm^{-3}. A non-linear least squres program was then used to obtain the unkown constants K_1 and K_2 which gave the least (root-mean-square) percentage deviation between calculated and observed solubility of CuCl in the medium considered. The results of these calculations are given for the various alcohols in Table 16.

Table 16. Equilibrium Constants for Complexes of CuCl with Alcohols[a,b]

Alcohol	K_1	$\frac{K_2}{\mathrm{mol\ dm^{-3}}}$	Average (r.m.s.) deviation (%)	Number of Points
Allyl	0.4217	0.00513	2.1	14
Ethylvinylcarbinol	0.2727	0.00394	3.5	9
Methylvinylcarbinol	0.3114	0.00337	1.4	8
α,α-Dimethylallyl	0.2217	0.00247	1.2	9
4-Methyl-4-penten-2-ol	0.1868	0.00151	3.4	7
γ,γ-Dimethylallyl	0.1153	0.00144	6.4	5
3-Methyl-3-buten-2-ol	0.0791	0.00039	1.4	6
2-Methyl-2-buten-1-ol	0.1213	0.00031	0.5	3
β-Chloroallyl	0.0067	0.000022	0.3	3
β-Methylallyl	0.1411	0.00092	2.0	8
Crotyl	0.1022	0.00097	2.4	8

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

[a] The alcohols have been given the names as reported by Andrews and coworkers[60,61]. For formulas and registry numbers, see Compilations.

[b] The very close fits for 2-methyl-2-buten-1-ol and β-chloroallyl alcohol resulted from scarcity of experimental points; the constants for these two must be of the proper order of magnitude, but by no means precise.

The procedure described above gave somewhat better fits to the data than those obtained by the previous workers. It has the advantage that the constants are not restricted to use at 0.1 mol dm^{-3} ionic strength, but can be used at any lower ionic strength and could be used at higher ionic strengths if virial coefficients for ion pairs involving Alc·Cu^+ could be obtained. The stability constants given by Andrews and coworkers are of little utility, for two reasons: first, they neglected the effects of ionic strength, so that any constants they derived are applicable only to an ionic strength of 0.1 mol dm^{-3}. Second, they used the solubility product of CuCl at infinite dilution, which is not appropriate for this ionic strength. If desired, stability constants at zero ionic strength can be obtained from the results of Table 16 by dividing each of the constants by the value of K_{S0} for CuCl listed above. Such constants are nearly the same as those reported by Andrews and coworkers[60,61] for the uncharged species Alc·CuCl, but about half as large as their values for the charged species Alc·Cu^+ because of the effect of ionic strength on the latter.

In most cases, the primary source of solubility was found to be the formation of the complexes with alcohol. However, cuprous ion and chlorocuprous complexes contributed substantially to the solubility in the presence of the largest concentrations of chloride ion used (at or about 0.1 mol dm^{-3}) and for those alcohols in whose solutions CuCl was least soluble. The inclusion of the species $CuCl_3^{2-}$ in the calculations produced only minor differences in the quality of fit or in the values of K_1 and K_2, although it contributed more to solubility than did cuprous ion. The relatively poor fit obtained for γ,γ-dimethylallyl alcohol resulted from two inconsistent points, one high and the other low with respect to the rest. The presence of chloride ion depressed the solubility in aqueous allyl alcohol and in other alcohols with high affinity for CuCl, but enhanced it for those alcohols with poor complexing ability. This occurred because of two opposing effects: Increase in chloride ion concentration increases the amounts of chlorocuprous complexes, but decreases the amount of the charge complex Alc·Cu^+. For alcohols which complex readily with CuCl the latter effect dominates and solubility is decreased; the reverse is true for poorly complexing agents, such as β-chloroallyl, and the (low) solubility of CuCl is increased.

The effects of alcohol structure on the solubility of CuCl are not surprising in view of the fact that complexation apparently occurs at the C=C double bond. All of the alcohols studied except 4-methyl-4-penten-2-ol are related to allyl alcohol by simple substitutions. Substitution of a methyl or ethyl group on the α-carbon (where the OH is located) lowers the solubility only slightly, possibly by obstructing the space available near the double bond, and a second methyl group on the α-carbon reduces solubility somewhat more. However, substitution of even one methyl on the β- or γ-carbon (each part of the double bond) reduces the solubility by a factor of 3 or more, presumably by blocking access of CuCl to the double bond. The lowest solubility is observed with β-chloroallyl alcohol, where the blocking effect is enhanced by the negativity of the chlorine atom. Finally, the solubility in solutions of 4-methyl-4-penten-2-ol, which has an extra carbon atom between the OH and the double bond, is reduced less by γ-methyl substitution than occurs with the other cases of substitution at the γ-carbon, probably because the extra length of the carbon chain reduces the crowding at the double bond.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Systems Involving Unsaturated Organic Acids

Andrews and coworkers[62–64] determined the solubility of CuCl at 298 K in aqueous solutions of 9 unsaturated mono- and di-carboxylic acids. Their most extensive work was done on maleic acid [(*Z*)-2-butenedioic acid][62,63] with fewer observations on other acids, including fumaric acid [(*E*)-2-butenedioic acid] and the remaining seven. The other acids for which measurements were made were vinylacetic (3-butenoic acid, $CH_2{=}CH{-}CH_2{-}COOH$), itaconic [methylenebutanedioic acid, $HOOC{-}C({=}CH_2){-}CH_2{-}COOH$], crotonic [(*E*)-2-butenoic acid, $CH_3{-}CH{=}CH{-}COOH$], tiglic [(*E*)-2-methyl-2-butenoic acid, $CH_3{-}CH{=}C(CH_3){-}COOH$], β,β-dimethylacrylic acid [3-methyl-2-butenoic acid, $(CH_3)_2C{=}CH{-}COOH$], mesaconic [(*E*)-2-methyl-2-butenedioic acid, $HOOC{-}C(CH_3){=}CH{-}COOH$] and citraconic [(*Z*)-2-methyl-2-butenedioic acid, $HOOC{-}C(CH_3){=}CH{-}COOH$].

A considerable variety of measurements were made in the case of maleic acid. In preliminary work, Andrews and Keefer[62] measured the solubility of CuCl in solutions containing, with two exceptions, maleic acid concentrations of about 0.15 mol dm^{-3} and either sulfuric acid or perchloric acid at a variety of concentrations ranging from 0.06 to 1.2 mol dm^{-3}. In a second paper[62] they reported a series of measurements at constant nominal ionic strengths (either 0.1 or 1.0 mol dm^{-3}). In 18 of these, nine at each ionic strength, HCl was included in amounts from zero to 0.1 mol dm^{-3}, and ionic strength was maintained by use of $HClO_4$; in the remaining nine, KCl was used to provide chloride ion, and ionic strength of 0.1 mol dm^{-3} was maintained by use of $NaClO_4$. In all cases the maleic acid concentration was varied from 0.05 to 0.2 mol dm^{-3}.

In the case of fumaric acid, their first paper[62] contained a set of measurements using fumaric acid at 0.034 to 0.050 mol dm^{-3} and sulfuric acid from zero to 0.48 mol dm^{-3}. In a later paper, Keefer, Andrews and Kepner[64] measured the solubility at constant ionic strength of 0.1 mol dm^{-3} maintained by $HClO_4$, with chloride ion of 0, 0.01 and 0.094 mol dm^{-3} supplied by HCl and fumaric acid concentration varied from 0.018 to 0.047 mol dm^{-3}. Except for minor variations, this same procedure was followed for the remaining 7 acids[64].

In the process of dissolution, complexes analogous to those for unsaturated alcohols can be formed, *viz.* $H_2A{\cdot}CuCl$ and $H_2A{\cdot}Cu^+$, where H_2A represents the organic acid. Complexes $HA{\cdot}CuCl^-$ and $HA{\cdot}Cu$ formed by loss of H^+ from the first two are also possible. In some cases, a measurable contribution to the solubility may arise from the dissociation of CuCl and production of $CuCl_2^-$. Andrews and coworkers considered all four complexes in the case of maleic acid, which is relatively strong, and neglected (apparently correctly) the latter two for the remaining acids, all of which are quite weak. They then interpreted their measurements in terms of these species, neglecting the effects of variations in ionic strength on the equilibria.

The results for the various acids have been reinterpreted using the following set of equilibria, written for the dibasic acids; the corresponding equilibria for the monobasic acids are obtained by replacing H_2A by HA and HA^- by A^- in the last five equations and equilibrium expressions. For simplicity in the ensuing discussion, the processes involved will be described as for the dibasic acids. All of the equilibrium constants are expressed in terms of activities with standard state 1.0 mol dm^{-3}.

$$\begin{array}{rcll}
CuCl_{(s)} & \rightleftharpoons & Cu^+ + Cl^- & K_{S0} = 1.83\cdot 10^{-7}\ mol^2\ dm^{-6} \\
CuCl_{(s)} + Cl^- & \rightleftharpoons & CuCl_2^- & K_{S2} = 0.0619 \\
H_2A & \rightleftharpoons & H^+ + HA^- & K_A = \{H^+\}\{HA^-\}/\{H_2A\} \\
H_2A + CuCl_{(s)} & \rightleftharpoons & H_2A\cdot CuCl & K_4 = \{H_2A\cdot CuCl\}/\{H_2A\} \\
H_2A + CuCl_{(s)} & \rightleftharpoons & H_2A\cdot Cu^+ + Cl^- & K_5 = \{H_2A\cdot Cu^+\}\{Cl^-\}/\{H_2A\} \\
HA^- + CuCl_{(s)} & \rightleftharpoons & HA\cdot CuCl^- & K_6 = \{HA\cdot CuCl^-\}/\{HA^-\} \\
HA^- + CuCl_{(s)} & \rightleftharpoons & HA\cdot Cu + Cl^- & K_7 = \{HA\cdot Cu\}\{Cl^-\}/\{HA^-\}
\end{array}$$

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

For evaluation of the best set of complexation constants for each acid, the dissociation constants for the acids, KA, were taken from the compilation of Kortüm, Vogel and Andrussow[106]. The activity coefficients of uncharged species were taken as unity, and those of the singly charged species from the f^{γ} of Table 10, as with the alcohols. For lack of sufficient data, no attempt was made to evaluate virial parameters for the various species considered to be present. This should cause no difficulty for the solutions with ionic strengths of 0.1 mol dm^{-3} but may introduce some inaccuracy for those solutions of maleic acid where an ionic strength of 1.0 was used. For the data on maleic acid, all of the constants were used. For the other acids K_6 and K_7 were omitted, after preliminary calculations indicated the these did not contribute appreciably to the solubility in solutions containing the weak acids. The species $CuCl_3^{2-}$ was omitted in view of the small amount of chloride ions present in all solutions. A non-linear least squares program was used to select the set of equilibrium constants which gave the best fit to the data (K_4 through K_7 for maleic acid, K_4 and K_5 only for the remaining acids). The results obtained are given in Table 17, with the acids arranging in decreasing order of affinity for CuCl.

Table 17. Equilibrium Constants for Complexes of CuCl with Organic Acids

Acid	$10^2 \cdot K_4$	$\frac{10^4 \cdot K_5}{\text{mol dm}^{-3}}$	Average (r.m.s.) Deviation (%)	Number of Points
Vinylacetic	25.7	33.0	2.0	8
Fumaric	9.03	9.79	4.9	9
Itaconic	3.43	2.12	3.7	8
Maleic[a]	2.01	0.10	4.0	27[b]
Crotonic	1.93	1.34	2.9	7
Tiglic	1.38	0.13	3.6	5
Mesaconic	0.86	0.34	3.0	5
Citraconic	0.47	0.014	1.0	2
β-β-Dimethylacrylic	0.84	0.10	0.8	4

[a] For maleic acid the constants K_6 and K_7/mol dm^{-3} are 0.1154 and 0.00515, respectively.

[b] These are the 27 data points of Ref. 63; the seven perchloric acid points of Ref. 62 were fitted to 7 per cent by the same constants.

The constants given for the last four acids are approximate only, in view of the small number of data points available, with those for citraconic acid probably order of magnitude only. The relatively poor fit to the data for fumaric acid arises from the presence of two poor data points, one high and the other low with repect to the remainder.

Andrews and coworkers[63,64] reported their results in terms of stability constants (β's) for formation of the complexes from the organic acid, Cu^+ and Cl^-. These suffer from the same difficulties as those for the alcohols (described above) and in addition are ambiguous for the case of maleic acid, where measurements were made at two quite different ionic strengths, 0.1 and 1.0 mol dm^{-3}. Stability constants at zero ionic strength obtained from the results of Table 17 are not much different from those of Keefer *et al.*[64] for the neutral species $H_2A{\cdot}CuCl$ (or $HA{\cdot}CuCl$), but are about half as large as the Andrews values for the charged species $H_2A{\cdot}Cu^+$, again due to the effect of ionic strength. The constants for maleic acid are substantially different, due to the fact that the Andrews work apparently treated results at different ionic strengths as though they were all at the same ionic strength.

The interpretation of the solubilities in terms of the various equilibria explains the effect of adding other ions to the solution. For all acids except those least effective in complex

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

formation, the addition of chloride ion reduces the solubility of CuCl. This occurs because chloride ion depresses the formation of $H_2A\cdot Cu^+$ (K_4) (in the case of maleic acid, $HA\cdot Cu$ (K_7) also), which is the major contributor to the solubility in the absence of chloride. At the same time the concentration of $CuCl_2^-$ is increased substantially, but only in the case of the least effective acids (the last four in Table 17) is this enough to overcome the decrease in the concentration of complex(es) with the acid. Measurements made at a variety of concentrations of H^+ in the case of maleic acid indicate that this ion also can decrease the solubility; it does so by depressing the formation of both $HA\cdot CuCl^-$ (K_6) and $HA\cdot Cu$ (K_7). The representation also indicates the probable contributions to solubility made under various conditions by the species present. For acids other than maleic, the main complex formed in the absence of chloride is $H_2A\cdot Cu^+$, with a smaller contribution from $H_2A\cdot CuCl$ and very little from $CuCl_2^-$. When the principal anion present is Cl^-, the main contributors are $H_2A\cdot CuCl$ (little affected by the addition of chloride) and $CuCl_2^-$. Maleic acid, being much stronger than the others, has major contributions from $HA\cdot CuCl^-$ and $HA\cdot Cu$. When the only hydrogen ion present is that produced by dissociation of the acid and there is no chloride ion, these are the major contributors, with $HA\cdot Cu$ dominant and a minor contribution from $H_2A\cdot Cu^+$. Addition of hydrogen ions decreases the contributions of the first two ions without materially affecting the others. Addition of chloride ion decreases the contributions of $HA\cdot Cu$ and $H_2A\cdot Cu^+$ while increasing that of $CuCl_2^-$, the new major contributor.

The main effect of structure on the ability of the acids to form complexes with CuCl appears to be related to the locations of the COOH and CH_3 groups with respect to the double bond. The most effective in forming complexes is vinylacetic acid, with neither of these attached to the double bond. Next are fumaric, with two COOH groups *trans* to each other, itaconic with both COOH groups on the same side of the bond and crotonic, with a methyl group and a COOH *trans* to each other. Maleic acid, with two COOH groups *cis* to each other, is somewhat poorer. All of the remaining acids have three groups attached to the double bond and are poor complexing agents.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

RECOMMENDED VALUES FOR SOLUBILITY OF CuCl

General

The available data are extensive and reliable enough to permit tables of recommended values of solubility for aqueous solutions of only five chlorides, *viz.* HCl, NaCl, KCl, NH_4Cl and $CaCl_2$. The tables, given hereafter, contain smoothed values of solubility calculated using the thermodynamic and virial properties of the previous section for those concentration and temperature ranges where reliable data were available. The reliability expected in the several cases varies from 2 (best) to 10 (worst) per cent and is given with each of the tables. In all cases the data are given well beyond the expected precision to facilitate interpolation.

The values of the solubility can be represented compactly by giving the ratio c_{CuCl}/c_{MCl} of CuCl solubility to the initial concentration of the aqueous chloride used or, equivalently, the ratio c_{CuCl}/c_{Cl^-} of CuCl solubility to the initial chloride concentration supplied by the aqueous chlorides. (Typically these functions vary by only a factor of 2 or 3 for 100-fold variation of the solubility.) At any given temperature, these ratios can usually be interpolated linearly. Since the solubility varies exponentially with temperature at a given concentration of aqueous chloride, this sort of procedure must be used to interpolate between the temperatures given. This can be accomplished by using a linear interpolation of the logarithm of c_{CuCl}/c_{MCl} at given concentration, then obtaining the desired value of c_{CuCl}/c_{MCl} by exponentiation.

The general behaviour of c_{CuCl}/c_{MCl} is illustrated by Figs. 1–3. Fig. 1 shows the variation of this function for aqueous HCl and NaCl with concentrations from 0.1 to 6 mol dm^{-3} at 298.15 K. Note that the two curves merge at the lowest concentrations, where the effect of differences between the two media is relatively insignificant, but become quite different (NaCl higher) at the higher concentrations, where the effect of NaCl on activity coefficients differs substantially from that of HCl. The figure also illustrates the nearly linear variation of c_{CuCl}/c_{MCl} with concentration over much of the range. Fig. 2 gives the same sort of comparison at 298.15 K for the other three soluble chlorides, in mol kg^{-1}. In order to compare the two monovalent chlorides with $CaCl_2$, the ratio plotted is m_{CuCl}/m_{Cl^-}, where m_{Cl^-} is the molality of chloride ion provided by the media (twice the molality of the salt in the case of $CaCl_2$). The effects of NH_4Cl and KCl in dissolving CuCl are quite similar, and are much greater than those of HCl and NaCl at high concentrations. $CaCl_2$, on the other hand, is much less effective (on the basis of the amount of chloride ion it supplies) and is more like NaCl or HCl. Fig. 3 give values of c_{CuCl}/c_{MCl} versus concentration for aqueous NaCl at 273, 298, 323 and 348 K. The curves are similar at all four temperatures. The exponential increase of solubility with temperature is quite evident at low concentration of the mediums, becoming less pronounced at high concentrations.

In many practical situations CuCl is dissolved in an aqueous mixture of soluble chlorides. Examination of available data indicates that the solubility of CuCl in a mixture can be calculated reliably using the procedures of the previous section and including the virial parameters for all cation-anion pairs present, when available. A simpler method, almost as precise, is to average the c_{CuCl}/c_{MCl} values for the soluble salts present, weighted by the mole fractions of each cation present. If one of the soluble salts is by far the major contributor, this procedure will give results as precise as the tabulated values for this soluble chloride by itself.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

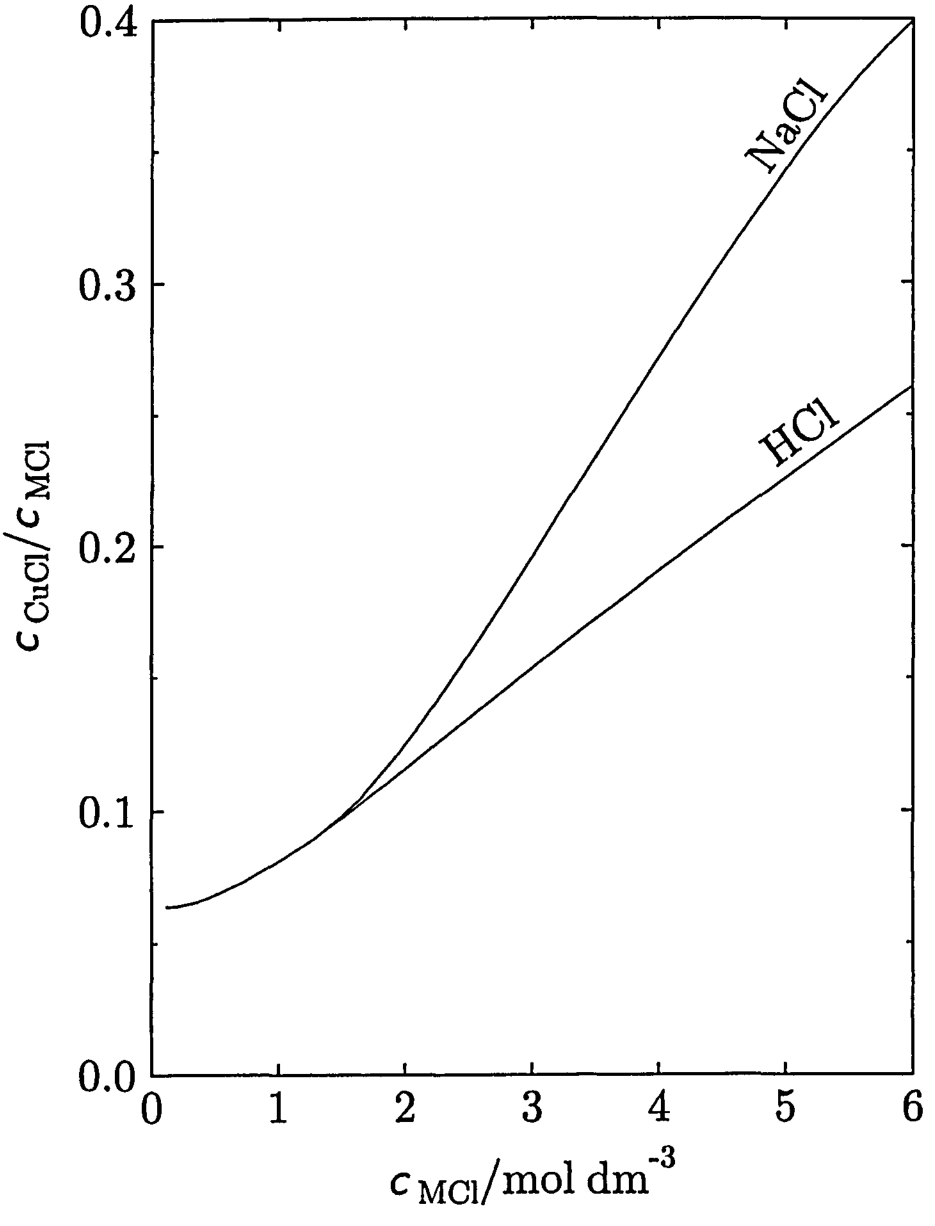

Fig. 1. Ratio of CuCl Solubility to Initial Concentration of Aqueous Chloride Plotted Against Concentration for NaCl and HCl at 298.15 K

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

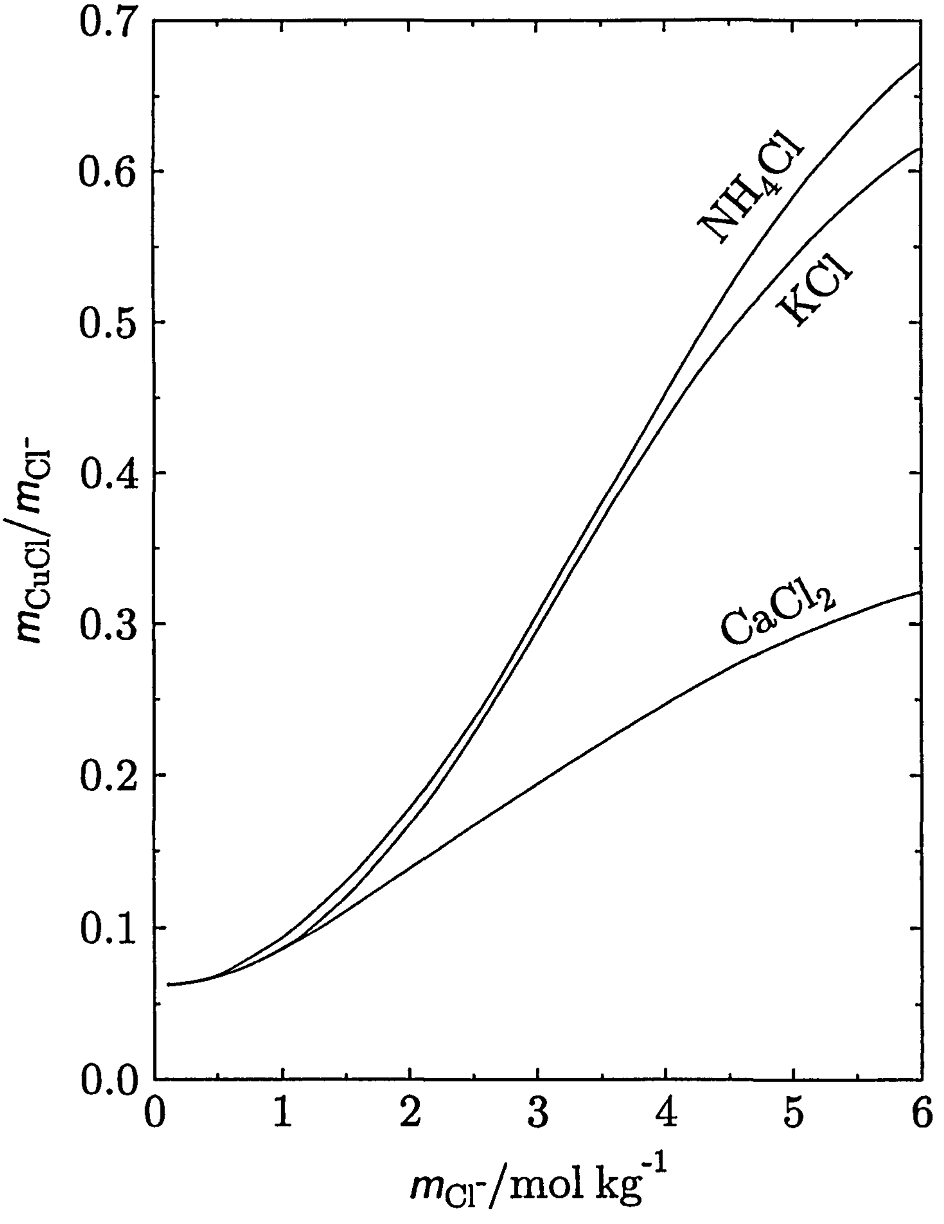

Fig. 2. Ratio of CuCl Solubility to Molality of Chloride Ion Supplied by the Aqueous Chloride, Plotted Against the Chloride Ion Molality for NH_4Cl, KCl and $CaCl_2$ at 298 K

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

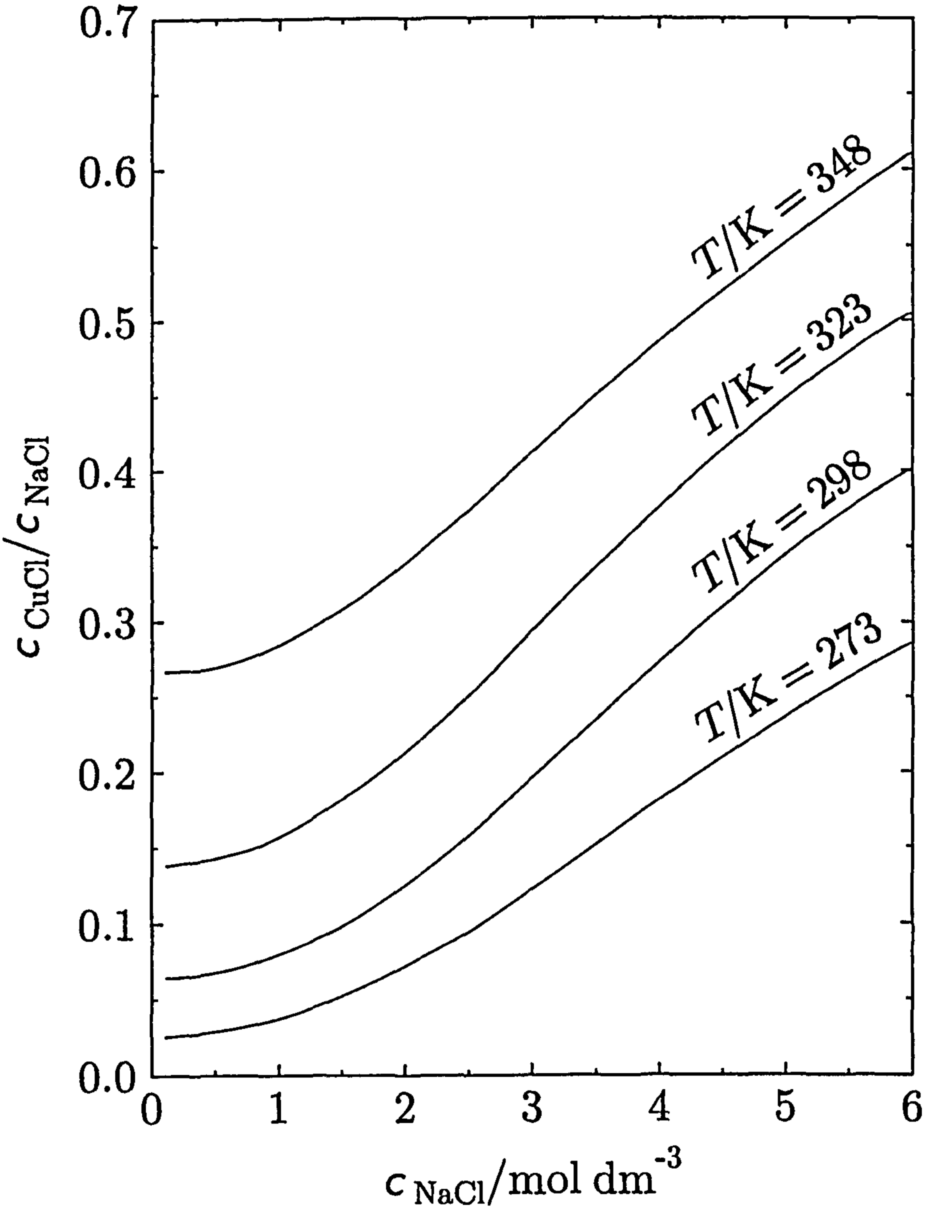

Fig. 3. Ratio of CuCl Solubility to NaCl Concentration Plotted Against Concentration of NaCl at 273, 298, 323 and 348 K

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. Fritz

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Solubility of CuCl in Aqueous HCl

Table 18A gives recommended values of the solubility of CuCl in aqueous HCl at 273, 288, 298, 308 and 323 K for HCl concentrations from 0.1 to 6.0 mol dm^{-3}. The tabulated values at the three intermediate temperatures agree with those of Chang and Cha[24] and those of Hikita *et al.*[3] within an average of 2 per cent, and should be correct to this precision. The values at 273 and 323 K were obtained by extrapolation using known enthalpies of reaction and temperature coefficients of virial parameters. They should be valid within about 5 per cent.

Table 18A. Solubility of CuCl in Aqueous HCl from 273 to 323 K

c_{HCl}/mol dm^{-3}	c_{CuCl}/mol dm^{-3} at T/K of				
	273.15	288.15	298.15	308.15	323.15
0.100	0.00258	0.00447	0.00631	0.00864	0.01346
0.200	0.00509	0.00904	0.01266	0.01733	0.02683
0.300	0.00837	0.01397	0.01936	0.02635	0.0404
0.400	0.01186	0.01940	0.02659	0.0358	0.0542
0.500	0.01577	0.02535	0.03435	0.0458	0.0686
0.600	0.02013	0.03181	0.0427	0.0458	0.0686
0.700	0.02496	0.0388	0.0516	0.0676	0.0989
0.800	0.03031	0.0464	0.0611	0.0794	0.1149
0.900	0.0361	0.0545	0.0713	0.0919	0.1315
1.000	0.0426	0.0633	0.0821	0.1051	0.1488
1.100	0.0487	0.0728	0.0936	0.1190	0.1668
1.200	0.0574	0.0830	0.1058	0.1336	0.1854
1.300	0.0656	0.0939	0.1188	0.1490	0.2048
1.400	0.0746	0.1056	0.1326	0.1651	0.2250
1.500	0.0842	0.1180	0.1471	0.1820	0.2458
1.600	0.0945	0.1311	0.1623	0.1996	0.2674
1.700	0.1056	0.1450	0.1784	0.2181	0.2897
1.800	0.1174	0.1584	0.1952	0.2373	0.3127
1.900	0.1299	0.1751	0.2128	0.2573	0.336
2.000	0.1432	0.1912	0.2312	0.2781	0.361
2.200	0.1720	0.2248	0.2704	0.322	0.412
2.400	0.2040	0.2640	0.313	0.369	0.466
2.600	0.2392	0.3051	0.358	0.419	0.522
2.800	0.2779	0.3495	0.407	0.471	0.581
3.000	0.3191	0.397	0.458	0.526	0.642
3.200	0.365	0.448	0.512	0.585	0.705
3.400	0.414	0.502	0.570	0.645	0.771
3.600	0.467	0.559	0.630	0.708	0.838
3.800	0.523	0.619	0.693	0.774	0.907
4.000	0.583	0.683	0.758	0.842	0.978
4.200	0.647	0.750	0.827	0.912	1.050
4.400	0.716	0.820	0.898	0.984	1.124
4.600	0.789	0.893	0.973	1.059	1.199
4.800	0.867	0.971	1.049	1.135	1.276
5.000	0.950	1.051	1.129	1.214	1.353
5.200	1.037	1.136	1.211	1.294	1.431
5.400	1.131	1.223	1.296	1.376	1.510
5.600	1.229	1.314	1.383	1.459	1.589
5.800	1.333	1.409	1.472	1.544	1.668
6.000	1.442	1.507	1.563	1.629	1.747

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. FRITZ

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Table 18B gives the values of the ratio c_{CuCl}/c_{HCl} corresponding to the CuCl solubilities of Table 18A.

Table 18B. **Ratio of CuCl Solubility to HCl Concentration in Aqueous HCl from 273 to 323 K**

c_{HCl}/mol dm^{-3}	c_{CuCl}/c_{HCl} at T/K of				
	273.15	288.15	298.15	308.15	323.15
0.100	0.0258	0.0447	0.0631	0.0864	0.1342
0.200	0.0265	0.0452	0.0633	0.0866	0.1344
0.300	0.0279	0.0466	0.0645	0.0878	0.1346
0.400	0.0297	0.0485	0.0665	0.0895	0.1356
0.500	0.0315	0.0507	0.0687	0.0917	0.1372
0.600	0.0336	0.0530	0.0711	0.0941	0.1391
0.700	0.0357	0.0555	0.0737	0.0966	0.1412
0.800	0.0379	0.0580	0.0764	0.0993	0.1436
0.900	0.0402	0.0606	0.0792	0.1021	0.1461
1.000	0.0426	0.0633	0.0821	0.1051	0.1488
1.100	0.0451	0.0662	0.0851	0.1082	0.1516
1.200	0.0478	0.0692	0.0882	0.1113	0.1545
1.300	0.0505	0.0722	0.0914	0.1146	0.1576
1.400	0.0533	0.0755	0.0947	0.1178	0.1607
1.500	0.0561	0.0787	0.0980	0.1213	0.1639
1.600	0.0591	0.0820	0.1014	0.1248	0.1671
1.700	0.0621	0.0853	0.1049	0.1283	0.1704
1.800	0.0652	0.0887	0.1084	0.1318	0.1737
1.900	0.0682	0.0922	0.1120	0.1354	0.1771
2.000	0.0716	0.0956	0.1156	0.1390	0.1805
2.200	0.0782	0.1027	0.1229	0.1463	0.1873
2.400	0.0850	0.1100	0.1303	0.1536	0.1940
2.600	0.0920	0.1174	0.1378	0.1610	0.2008
2.800	0.0992	0.1248	0.1452	0.1683	0.2074
3.000	0.1066	0.1324	0.1527	0.1755	0.2140
3.200	0.1141	0.1399	0.1601	0.1827	0.2204
3.400	0.1218	0.1475	0.1676	0.1897	0.2266
3.600	0.1296	0.1552	0.1750	0.1967	0.2327
3.800	0.1376	0.1629	0.1823	0.2036	0.2387
4.000	0.1458	0.1707	0.1896	0.2103	0.2444
4.200	0.1541	0.1784	0.1969	0.2171	0.2501
4.400	0.1627	0.1863	0.2042	0.2237	0.2555
4.600	0.1715	0.1942	0.2114	0.2301	0.2607
4.800	0.1806	0.2022	0.2186	0.2365	0.2658
5.000	0.1899	0.2103	0.2258	0.2428	0.2706
5.200	0.1995	0.2184	0.2329	0.2489	0.2753
5.400	0.2094	0.2265	0.2399	0.2548	0.2797
5.600	0.2194	0.2347	0.2469	0.2606	0.2838
5.800	0.2298	0.2429	0.2538	0.2662	0.2876
6.000	0.2403	0.2511	0.2605	0.2716	0.2911

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. Fritz

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Solubility in Aqueous NaCl

Tables 19A and 19B give recommended values of the solubility and of c_{CuCl}/c_{NaCl} for CuCl in aqueous NaCl at temperatures of 273, 298, 323, 348 and 368 K and NaCl concentrations from 0.1 and 6.0 mol dm^{-3}. The values are given over a larger range of temperature than for HCl because of the availability of data. However, the results are somewhat less reliable because the literature data are less so. The values given should be reliable to about 2 per cent at 298 K, but only to about 5 per cent elsewhere.

Table 19A. Solubility of CuCl in Aqueous NaCl from 273 to 368 K

c_{NaCl}/mol dm^{-3}	c_{CuCl}/mol dm^{-3} at T/K of				
	273.15	298.15	323.15	348.15	368.15
0.100	0.00254	0.00635	0.01385	0.02659	0.0402
0.200	0.00515	0.01272	0.02773	0.0530	0.0796
0.300	0.00797	0.01933	0.0429	0.0796	0.1193
0.400	0.01112	0.02633	0.0565	0.1067	0.1594
0.500	0.01460	0.0338	0.0717	0.1344	0.2000
0.600	0.01843	0.0417	0.0874	0.1626	0.2412
0.700	0.02267	0.0502	0.1038	0.1915	0.2831
0.800	0.02733	0.0593	0.1209	0.2212	0.3256
0.900	0.0325	0.0691	0.1389	0.2517	0.369
1.000	0.0382	0.0797	0.1579	0.2832	0.413
1.100	0.0446	0.0991	0.1779	0.3158	0.458
1.200	0.0517	0.1035	0.1991	0.350	0.505
1.300	0.0594	0.1170	0.2215	0.385	0.552
1.400	0.0681	0.1317	0.2454	0.421	0.600
1.500	0.0775	0.1475	0.2707	0.459	0.650
1.600	0.0878	0.1646	0.2976	0.498	0.701
1.700	0.0992	0.1831	0.3261	0.539	0.754
1.800	0.1115	0.2031	0.356	0.582	0.808
1.900	0.1249	0.2246	0.388	0.626	0.863
2.000	0.1395	0.2477	0.422	0.672	0.920
2.200	0.1722	0.2988	0.496	0.769	1.039
2.400	0.2101	0.357	0.577	0.874	1.164
2.600	0.2532	0.422	0.667	0.985	1.294
2.800	0.3016	0.495	0.764	1.104	1.432
3.000	0.356	0.576	0.869	1.228	1.575
3.200	0.416	0.663	0.981	1.359	1.724
3.400	0.482	0.758	1.100	1.496	1.880
3.600	0.553	0.859	1.225	1.638	2.042
3.800	0.630	0.967	1.356	1.784	2.210
4.000	0.712	1.080	1.491	1.935	2.385
4.200	0.798	1.199	1.631	2.090	2.568
4.400	0.889	1.322	1.775	2.249	2.760
4.600	0.984	1.449	1.922	2.412	2.961
4.800	1.082	1.580	2.073	2.578	3.173
5.000	1.183	1.713	2.226	2.749	3.40
5.200	1.286	1.850	2.381	2.924	3.64
5.400	1.391	1.988	2.537	3.103	3.89
5.600	1.497	2.127	2.696	3.288	4.16
5.800	1.604	2.267	2.856	3.48	4.45
6.000	1.711	2.407	3.017	3.68	4.75

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Table 19B. Ratio of CuCl Solubility to NaCl Concentration in Aqueous NaCl from 273 to 368 K

c_{NaCl}/mol dm^{-3}	c_{CuCl}/c_{NaCl} at T/K of				
	273.15	298.15	323.15	348.15	368.15
0.100	0.0254	0.0635	0.1385	0.2659	0.402
0.200	0.0258	0.0636	0.1387	0.2649	0.398
0.300	0.0267	0.0644	0.1397	0.2653	0.398
0.400	0.0278	0.0658	0.1413	0.2668	0.398
0.500	0.0293	0.0675	0.1433	0.2687	0.400
0.600	0.0307	0.0695	0.1457	0.2710	0.402
0.700	0.0324	0.0717	0.1483	0.2736	0.400
0.800	0.0342	0.0741	0.1511	0.2765	0.407
0.900	0.0361	0.0768	0.1543	0.2797	0.410
1.000	0.0382	0.0797	0.1579	0.2832	0.413
1.100	0.0405	0.0828	0.1617	0.2871	0.417
1.200	0.0437	0.0862	0.1659	0.2913	0.420
1.300	0.0457	0.0900	0.1704	0.2958	0.424
1.400	0.0486	0.0941	0.1753	0.3007	0.429
1.500	0.0517	0.0984	0.1805	0.3058	0.433
1.600	0.0549	0.1029	0.1860	0.3113	0.438
1.700	0.0583	0.1077	0.1918	0.3170	0.443
1.800	0.0619	0.1128	0.1980	0.3231	0.449
1.900	0.0658	0.1182	0.2044	0.3294	0.454
2.000	0.0697	0.1238	0.2112	0.336	0.460
2.200	0.0783	0.1358	0.2254	0.350	0.472
2.400	0.0876	0.1486	0.2406	0.364	0.485
2.600	0.0974	0.1625	0.2565	0.379	0.498
2.800	0.1077	0.1769	0.2729	0.394	0.511
3.000	0.1187	0.1919	0.2897	0.409	0.525
3.200	0.1300	0.2072	0.3066	0.425	0.539
3.400	0.1417	0.2229	0.3236	0.440	0.553
3.600	0.1516	0.2386	0.340	0.455	0.567
3.800	0.1658	0.2544	0.357	0.470	0.582
4.000	0.1779	0.2700	0.373	0.484	0.596
4.200	0.1901	0.2854	0.388	0.498	0.612
4.400	0.2021	0.3004	0.403	0.511	0.627
4.600	0.2139	0.3150	0.418	0.524	0.644
4.800	0.2254	0.3291	0.432	0.537	0.661
5.000	0.2366	0.343	0.445	0.550	0.680
5.200	0.2474	0.356	0.458	0.562	0.700
5.400	0.2576	0.368	0.470	0.575	0.721
5.600	0.2674	0.380	0.481	0.587	0.744
5.800	0.2765	0.391	0.492	0.600	0.768
6.000	0.2851	0.401	0.503	0.613	0.792

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. FRITZ

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Solubility of CuCl in Aqueous KCl

Table 20 gives values of the solubility and m_{CuCl}/m_{KCl} for solutions of CuCl in aqueous KCl for temperatures of 293, 298 and 303 K between 1.0 and 5.0 mol kg^{-1}. The temperature range is limited because the only reliable data were near 298 K. Values are not given below 1.0 mol kg^{-1} because no reliable data at lower molalities were available. The reliability of the values given is estimated as 5 to 6 per cent.

Table 20. **Solubility of CuCl and Ratio of CuCl Solubility to KCl Molality in Aqueous KCl from 293 to 303 K**

m_{KCl}/mol kg^{-1}	m_{CuCl}/mol kg^{-1} at T/K of			m_{CuCl}/m_{KCl} at T/K of		
	293.15	298.15	303.15	293.15	298.15	303.15
1.000	0.0759	0.0868	0.0989	0.0759	0.0868	0.0989
1.100	0.0891	0.1014	0.1150	0.0810	0.0922	0.1045
1.200	0.1038	0.1176	0.1328	0.0865	0.0981	0.1107
1.300	0.1204	0.1357	0.1526	0.0926	0.1044	0.1174
1.400	0.1389	0.1559	0.1745	0.0992	0.1114	0.1247
1.500	0.1597	0.1782	0.1907	0.1065	0.1189	0.1325
1.600	0.1828	0.2032	0.2255	0.1142	0.1270	0.1409
1.700	0.2085	0.2307	0.2549	0.1226	0.1357	0.1499
1.800	0.2370	0.2611	0.2872	0.1316	0.1451	0.1595
1.900	0.2684	0.2945	0.3225	0.1413	0.1550	0.1697
2.000	0.3030	0.3310	0.361	0.1515	0.1655	0.1805
2.200	0.382	0.414	0.448	0.1738	0.1883	0.2036
2.400	0.476	0.511	0.549	0.1982	0.2130	0.2286
2.600	0.584	0.622	0.663	0.2245	0.2394	0.2550
2.800	0.706	0.747	0.790	0.2520	0.2670	0.2821
3.000	0.841	0.885	0.931	0.2804	0.2951	0.3102
3.200	0.989	1.035	1.082	0.3091	0.3235	0.338
3.400	1.148	1.195	1.243	0.338	0.352	0.366
3.600	1.317	1.364	1.413	0.366	0.379	0.392
3.800	1.493	1.541	1.589	0.393	0.406	0.418
4.000	1.676	1.724	1.772	0.419	0.431	0.443
4.200	1.864	1.912	1.959	0.444	0.455	0.466
4.400	2.057	2.103	2.150	0.467	0.478	0.489
4.600	2.252	2.298	2.343	0.490	0.500	0.509
4.800	2.450	2.495	2.539	0.510	0.520	0.529
5.000	2.650	2.693	2.736	0.530	0.539	0.547
5.200	2.851	2.893	2.934	0.548	0.556	0.564
5.400	3.052	3.093	3.132	0.565	0.573	0.580
5.600	3.253	3.292	3.330	0.581	0.588	0.595
5.800	3.45	3.49	3.53	0.596	0.602	0.608
6.000	3.65	3.69	3.72	0.609	0.615	0.621

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. FRITZ

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Solubility of CuCl in Aqueous NH_4Cl

Tables 21A and 21B give values of the solubility and of m_{CuCl}/m_{NH_4Cl} for solutions of CuCl in aqueous NH_4Cl at temperatures of 273, 298, 323, 353 and 373 K, between 0.1 and 6.0 mol kg^{-1} for the lower temperatures. For temperatures of 323 K and above, the tables are terminated at a molality where the ratio of solubility to NH_4Cl molality reached 0.95, since it was felt that the model was not reliable to predict higher solubilities than this. The values given should be reliable to about 5 per cent.

Table 21A. Solubility of CuCl in Aqueous NH_4Cl from 273 to 373 K

m_{NH_4Cl}/mol kg^{-1}	m_{CuCl}/mol kg^{-1} at T/K of				
	273.15	298.15	323.15	353.15	373.15
0.100	0.00247	0.00619	0.01356	0.0295	0.0435
0.200	0.00501	0.01243	0.02755	0.0595	0.0876
0.300	0.00788	0.01927	0.0426	0.0915	0.1341
0.400	0.01118	0.02690	0.0591	0.1264	0.1843
0.500	0.01497	0.0355	0.0774	0.1605	0.2386
0.600	0.01928	0.0451	0.0978	0.2064	0.298
0.700	0.02423	0.0559	0.1203	0.2522	0.362
0.800	0.0299	0.0679	0.1451	0.302	0.431
0.900	0.0363	0.0813	0.1715	0.357	0.506
1.000	0.0475	0.0961	0.2026	0.417	0.587
1.100	0.0517	0.1125	0.2354	0.482	0.634
1.200	0.0610	0.1307	0.271	0.552	0.768
1.300	0.0716	0.1506	0.310	0.628	0.868
1.400	0.0835	0.1725	0.352	0.709	0.974
1.500	0.0967	0.1965	0.397	0.797	1.086
1.600	0.1119	0.2228	0.474	0.892	1.208
1.700	0.1287	0.252	0.498	0.992	1.327
1.800	0.1477	0.283	0.553	1.100	1.453
1.900	0.1690	0.317	0.613	1.214	1.585
2.000	0.1928	0.354	0.676	1.334	1.717
2.200	0.2491	0.437	0.814	1.593	1.982
2.400	0.318	0.534	0.967	1.917	2.242
2.600	0.402	0.645	1.137	2.162	
2.800	0.503	0.771	1.323	2.54	
3.000	0.620	0.912	1.426	2.74	
3.200	0.754	1.068	1.745	3.01	
3.400	0.905	1.237	1.981		
3.600	1.070	1.419	2.234		
3.800	1.248	1.611	2.50		
4.000	1.437	1.812	2.79		
4.200	1.633	2.020	3.09		
4.400	1.836	2.235	3.40		
4.600	2.044	2.453	3.72		
4.800	2.155	2.68	4.04		
5.000	2.467	2.90	4.37		
5.200	2.68	3.13	4.68		
5.400	2.79	3.35	4.99		
5.600	3.11	3.58	5.27		
5.800	3.32	3.81	5.55		
6.000	3.53	4.03			

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. FRITZ

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Table 21B. Ratio of CuCl Solubility to NH_4Cl Molality in Aqueous NH_4Cl from 273 to 373 K

m_{NH_4Cl}/mol kg^{-1}	m_{CuCl}/m_{NH_4Cl} at T/K of				
	273.15	298.15	323.15	353.15	373.15
0.100	0.02465	0.0619	0.1356	0.2945	0.435
0.200	0.02504	0.0622	0.1377	0.2975	0.438
0.300	0.02627	0.0642	0.1418	0.3050	0.447
0.400	0.02796	0.0674	0.1477	0.3159	0.461
0.500	0.02993	0.0711	0.1549	0.329	0.477
0.600	0.0321	0.0752	0.1629	0.344	0.496
0.700	0.0346	0.0798	0.1718	0.360	0.516
0.800	0.0373	0.0849	0.1814	0.378	0.539
0.900	0.0403	0.0903	0.1917	0.397	0.562
1.000	0.0435	0.0961	0.2026	0.417	0.587
1.100	0.0470	0.1023	0.2140	0.438	0.613
1.200	0.0509	0.1089	0.2259	0.460	0.640
1.300	0.0550	0.1159	0.2384	0.483	0.667
1.400	0.0596	0.1232	0.2513	0.507	0.696
1.500	0.0646	0.1310	0.2647	0.532	0.734
1.600	0.0699	0.1393	0.2785	0.557	0.753
1.700	0.0757	0.1440	0.2928	0.584	0.781
1.800	0.0821	0.1571	0.307	0.611	0.808
1.900	0.0889	0.1668	0.323	0.639	0.834
2.000	0.0964	0.1769	0.338	0.667	0.858
2.200	0.1132	0.1986	0.370	0.724	0.901
2.400	0.1326	0.2224	0.403	0.780	0.934
2.600	0.1547	0.2480	0.437	0.832	
2.800	0.1795	0.2754	0.473	0.877	
3.000	0.2066	0.304	0.509	0.913	
3.200	0.2356	0.334	0.545	0.941	
3.400	0.2661	0.364	0.583		
3.600	0.2972	0.394	0.620		
3.800	0.328	0.424	0.659		
4.000	0.359	0.453	0.697		
4.200	0.380	0.481	0.735		
4.400	0.417	0.508	0.772		
4.600	0.444	0.533	0.809		
4.800	0.470	0.557	0.852		
5.000	0.493	0.580	0.873		
5.200	0.515	0.601	0.900		
5.400	0.536	0.621	0.923		
5.600	0.555	0.639	0.941		
5.800	0.572	0.656			
6.000	0.588	0.672			

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Solubility of CuCl in Aqueous $CaCl_2$

Tables 22A and 22B give values of the solubility and of m_{CuCl}/m_{CaCl_2} for solutions of CuCl in aqueous $CaCl_2$ at temperatures of 298, 323, 348 and 368 K and $CaCl_2$ molalities between 0.1 and 5.0 mol kg^{-1}. No values are given for temperatures below 298 K, since there were no data available for this region, and the tables for the two higher temperatures are terminated somewhat below 4.0 mol kg^{-1} because of doubts about the reliability of the calculations at the highest ionic strengths and temperatures. In any case, the values given are probably good to no better than 10 per cent because the experimental data on this system were erratic or inconsistent to about this extent. Note that the values of m_{CuCl}/m_{CaCl_2} differ markedly from corresponding values for the other soluble chlorides, since each mole of $CaCl_2$ supplies two moles of chloride.

Table 22A. Solubility of CuCl in Aqueous $CaCl_2$ from 298 to 368 K

m_{CaCl_2}/mol kg^{-1}	m_{CuCl}/mol kg^{-1} at T/K of			
	298.15	323.15	348.15	368.15
0.100	0.01202	0.02521	0.0467	0.0696
0.200	0.02600	0.0520	0.0931	0.1357
0.300	0.0430	0.0829	0.1434	0.2044
0.400	0.0636	0.1185	0.1991	0.2680
0.500	0.0881	0.1594	0.2605	0.357
0.600	0.1168	0.2054	0.327	0.441
0.700	0.1498	0.2567	0.400	0.529
0.800	0.1871	0.3133	0.469	0.622
0.900	0.2381	0.375	0.559	0.718
1.000	0.2757	0.442	0.645	0.817
1.100	0.327	0.513	0.735	0.919
1.200	0.383	0.589	0.823	1.024
1.300	0.443	0.668	0.996	1.130
1.400	0.508	0.752	1.024	1.237
1.500	0.578	0.839	1.125	1.345
1.600	0.651	0.930	1.228	1.454
1.700	0.728	1.023	1.332	1.563
1.800	0.808	1.118	1.437	1.673
1.900	0.808	1.215	1.543	1.782
2.000	0.892	1.215	1.649	1.891
2.200	1.159	1.517	1.859	2.107
2.400	1.347	1.722	2.075	2.321
2.600	1.540	1.928	2.286	2.532
2.800	1.736	2.133	2.494	2.742
3.000	1.932	2.335	2.699	2.950
3.200	2.128	2.536	2.902	3.156
3.400	2.320	2.729	3.101	3.37
3.600	2.507	2.918	3.298	3.57
3.800	2.688	3.101	3.49	3.78
4.000	2.861	3.278	3.68	3.99
4.200	3.025	3.45	3.88	
4.400	3.178	3.61	4.06	
4.600	3.319	3.76	4.25	
4.800	3.45	3.90	4.43	
5.000	3.56	4.03		

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]

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

EVALUATOR:

J. J. FRITZ

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Table 22B. Ratio of CuCl Solubility to $CaCl_2$ Molality in Aqueous $CaCl_2$ from 298 to 368 K

m_{CaCl_2}/mol kg^{-1}	m_{CuCl}/m_{CaCl_2} at T/K of			
	298.15	323.15	348.15	368.15
0.100	0.1202	0.2521	0.467	0.696
0.200	0.1300	0.2602	0.466	0.678
0.300	0.1433	0.2762	0.478	0.681
0.400	0.1589	0.2964	0.498	0.695
0.500	0.1763	0.3187	0.521	0.713
0.600	0.1947	0.342	0.546	0.734
0.700	0.2140	0.367	0.571	0.756
0.800	0.2339	0.392	0.596	0.777
0.900	0.2546	0.417	0.621	0.798
1.000	0.2757	0.441	0.645	0.817
1.100	0.2973	0.466	0.668	0.836
1.200	0.3191	0.490	0.691	0.853
1.300	0.341	0.514	0.712	0.869
1.400	0.363	0.537	0.731	0.884
1.500	0.385	0.560	0.750	0.897
1.600	0.407	0.581	0.767	0.909
1.700	0.428	0.602	0.783	0.920
1.800	0.449	0.621	0.798	0.929
1.900	0.469	0.640	0.812	0.938
2.000	0.489	0.657	0.825	0.945
2.200	0.527	0.689	0.847	0.958
2.400	0.561	0.717	0.865	0.967
2.600	0.592	0.741	0.879	0.974
2.800	0.620	0.762	0.891	0.979
3.000	0.644	0.792	0.900	0.983
3.200	0.665	0.792	0.907	0.986
3.400	0.682	0.803	0.912	0.989
3.600	0.696	0.811	0.916	0.992
3.800	0.707	0.816	0.919	0.995
4.000	0.715	0.819	0.921	0.998
4.200	0.720	0.821	0.923	
4.400	0.722	0.820	0.923	
4.600	0.722	0.817	0.924	
4.800	0.718	0.813	0.923	
5.000	0.711	0.806	0.914	

Other Systems.

Recommended values are not given for any of the other systems because the data were not sufficient for production of tables such as those above. For systems where tables are not given, the reader is referred to previous discussions concerning the best choices available for solubility data.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

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COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	EVALUATOR: J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

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COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

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COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Copper(II) Sulfate; $CuSO_4$; [7758-98-7]
(3) Sodium Chloride; $NaCl$; [7647-14-5]
(4) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sosnitskii, V. N.; Fofanov, G. M.
Zh. Neorg. Khim. 1979, *24*, 1708-1710;
Russ. J. Inorg. Chem. (Engl. Transl.) 1979, *24 (6)*, 947-949.

VARIABLES:

Concentration of NaCl at 298 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Potentiometric Determination of the Solubility Product of Copper(I) Chloride

ΔE at 25.0 ± 0.3°C of cell

Pt | $CuCl_{(s)}$ | $CuSO_4$ (0.1 mol dm^{-3}), $HClO_4$ (0.1 mol dm^{-3}), NaCl (x mol dm^{-3}) | salt bridge | $CuSO_4$ (0.1 mol dm^{-3}), $HClO_4$ (0.1 mol dm^{-3}), NaCl (x mol dm^{-3}) | $AgCl_{(s)}$ | Ag

as function of NaCl concentration from 0.1 to 10.4 mol dm^{-3}.

Slope of $\Delta E/\mathrm{mV}$ *vs.* $\log c_{\mathrm{NaCl}}/\mathrm{mol\ dm^{-3}}$ interpreted to give $K_{S0} = (2.5 \pm 0.77) \cdot 10^{-7}$ $\mathrm{mol^2\ dm^{-6}}$ at zero ionic strength.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potential ($E_{\mathrm{Cu^{2+}/Cu^{+}}}$) of platinum electrode taken to be

$$E_{\mathrm{Cu^{2+}/Cu^{+}}}/\mathrm{V} = 0.153 + 0.059 \log \frac{[\mathrm{Cl^-}][\mathrm{Cu^{2+}}] f_1 f_2}{K_{S0}}\ ^{a}$$

with $[\mathrm{Cl^-}]$ taken as

$[\mathrm{Cl^-}] = [\mathrm{NaCl}]/(1 + \beta_2 K_{S0})$, giving

$$E_{\mathrm{Cu^{2+}/Cu^{+}}}/\mathrm{V} = 0.153 + 0.059 \log \frac{[\mathrm{Cu^{2+}}][\mathrm{NaCl}] f_1 f_2}{K_{S0}(1+\beta_2 K_{S0})}$$

Calculated f_1 and f_2 from Davies equation (Ref. 1).

Does not give standard potential used for Ag/AgCl electrode, nor its use. Salt bridge not specified.

Used values of β_2 from Ref. 2.

[a] Equation corrected by compiler.

SOURCE AND PURITY OF MATERIALS:

Used "chemically pure" materials, source not given.

CuCl purified according to Ref. 3.

ESTIMATED ERROR:

From uncertainty in standard potential of Ag/AgCl electrode (± 3 mV) and estimated uncertainty of 8% in activity coefficients, estimate $\pm\ 0.77 \cdot 10^{-7}$ in K_{S0}.

REFERENCES:

1. Butler, J. N. *Ionic Equilibrium*, Addison Wesley, Massachusetts, 1964.
2. Vasil'ev, V. P.; Kunin, B. T. *Zh. Anal. Khim.* 1975, *20*, 1881.
3. Karyakin, Yu. V.; Angelov, I. I. *Pure Chemical Substances*, Moscow, 1974, p. 240.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H_2O; [7732-18-5]	Gavrish, M. L.; Galinker, I. S. *Dokl. Akad. Nauk SSSR* 1955, *102*, 89–91.
VARIABLES:	PREPARED BY:
$T/K = 433$ to 633	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Water

$t/°C$	$\frac{m_1}{mol\ kg^{-1}}$	$t/°C$	$\frac{m_1}{mol\ kg^{-1}}$	$t/°C$	$\frac{m_1}{mol\ kg^{-1}}$
160	0.431	230	1.55	290	3.36
170	0.44	240	1.6	300	3.55
180	0.61	250	1.73	320	4.7
190	0.67	260	2.3	330	5.4
200	0.96	270	2.7	350	6.32
210	1.27	280	2.99	360	6.93
220	1.43				

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Solutions prepared in 140 cm^3 quartz bomb inside autoclave maintained at desired temperatures. Samples of salt pressed into pellets under 2000 atm, then weighed carefully. Samples put into equilibrium with known mass of water over 2-hour period at selected temperature. Solubility determined by loss of mass of pellet.	Not stated. ESTIMATED ERROR: Not stated. REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Le Chatelier, H.
C. R. Hebd. Seances Acad. Sci. 1884, *98*, 813-816.

VARIABLES:

Concentration of HCl at 290 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 17°C

ρ / g cm^{-3}	$[\mathrm{Cl}]^-_{\mathrm{total}}$ / equiv. dm^{-3}	$[\mathrm{Cu}^+]$ / equiv. dm^{-3}	c_2[a] / mol dm^{-3}	c_1[a] / mol dm^{-3}
–	0.945	0.095	0.898	0.047
1.050	1.71	0.280	1.57	0.140
–	1.97	0.315	1.81	0.157
1.080	3.90	0.900	3.45	0.450
1.35	5.60	1.65	4.78	0.82
–	6.85	2.31	5.70	1.15

[a] Calculated by compiler, following method of Ref. 1; note that Le Chatelier's "equivalent" of Cu^+ was 0.5 mol.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Sealed CuCl and metallic copper in tubes containing HCl solutions, analyzed after decolorization of solution complete (methods not given).

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Engel, R. *Ann. Chim. Phys.* 1889, *17*, 347.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Engel, R. *Ann. Chim. Phys.* 1889, 342–384.
VARIABLES:	**PREPARED BY:**
Concentration of HCl at undefined temperature (probably about 293 K)	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 20°C[a]

ρ / g cm^{-3}	c_2 / mol dm^{-3}	c_1 / mol dm^{-3}
1.049	1.75	0.15
1.065	2.6	0.29
1.132	4.475	0.825
1.261	6.85	1.55
1.345	10.40	3.3

[a] Temperature estimated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Titrated solutions for free acid after 10-fold dilution; obtained c_{CuCl} by titration for acid liberated when Cu^+ precipitated as sulfate by H_2SO_4.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-6]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Engel, R.
C. R. Hebd. Seances Acad. Sci. 1895, *121*, 528–530.

VARIABLES:

Concentration of HCl at 288 to 289 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 15 – 16°C

ρ / g cm^{-3}	c_2 / mol dm^{-3}	c_1 / mol dm^{-3}
–	4.88	0.61
1.19	5.44	0.74
1.27	6.89	1.08
1.29	7.50	1.28
1.38	9.20	1.60

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Kept HCl solutions in contact with metallic copper for up to a year; then analyzed for HCl and CuCl (methods not given).

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Abel, E. *Z. Anorg. Chem.* 1901, *26*, 361–437.
VARIABLES:	**PREPARED BY:**
Concentration of HCl at 288 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 15°C

c_2 / mol dm^{-3}	c_1 / mol dm^{-3}
0.0422	0.0011
0.052	0.00134
0.063	0.00155
0.0928	0.00455
0.173	0.0077
0.204	0.0103
0.300	0.0162
0.438	0.0221
0.500	0.0270
0.530	0.0275
0.610	0.0337
0.988	0.0671
1.27	0.0937
1.33	0.0963
2.07	0.181

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook solid CuCl with HCl solution of 2 mol dm^{-3} at 288 K for 4 to 5 hours under nitrogen, then transferred predetermined aliquots to pure water, precipitating CuCl. The mixture was allowed to settle in a stream of hydrogen, after which the clear solution was analyzed for Cu^+ with permanganate.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Noyes, A. A.; Chow, M.
J. Am. Chem. Soc. 1918, *40*, 739-763.

VARIABLES:

Concentration of HCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 25°C

$[Cl]^-_{total}$ / mol dm^{-3}	c_2 / mol dm^{-3}	c_1 / mol dm^{-3}
1.2815	1.1650	0.1165
0.3364	1.3165	0.01988
0.2290	0.2156	0.01340
0.1038	0.0978	0.00596

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook CuCl plus metallic copper in HCl solutions at 25°C for 10 days. Measured chloride concentration as precipitated AgCl; obtained copper concentration electrolytically after evaporation with HNO_3.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Fedotieff, P. P. *Z. Anorg. Allg. Chem.* <u>1928</u>, *173*, 81–91.
VARIABLES:	**PREPARED BY:**
Concentration of HCl at 292 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 19°C

ρ_2 / g dm^{-3}	ρ_1 / g dm^{-3}	c_2[a] / mol dm^{-3}	c_1[a] / mol dm^{-3}
49.6	11.1	1.36	0.112
141.2	74.6	3.87	0.753
182.9	121.9	5.02	1.231
229.8	187.4	6.30	1.892
256.0	217.7	7.02	2.198

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Produced saturated solutions in sealed glass ampoules with carbon dioxide atmosphere.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Chang, K. S.; Cha, Y.-T.
J. Chin. Chem. Soc. 1934, *2*, 293-306.

VARIABLES:

Concentration of HCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 25°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.7278	0.05605	6.633	1.834	9.069	2.952
0.9742	0.08132	6.781	1.915	9.903	3.299
1.110	0.09961	6.823	2.005	10.06	3.410
1.780	0.1978	6.847	1.938	10.69	3.616
2.755	0.3983	6.995	1.986	11.00	3.623
3.990	0.7471	7.055	2.015	11.20	3.784
5.206	1.212	7.122	2.097	11.26	3.800
6.098	1.607	7.172	2.038	11.31	3.655
6.360	1.722	7.546	2.245	11.66	3.737
6.360	1.739	8.128	2.545	11.66	3.944
6.405	1.754	8.584	2.767	12.04	4.007
6.539	1.800	8.876	2.852	17.08	4.756

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Prepared saturated solutions in two ways: (1) by adding solid CuCl to specified concentration of aqueous HCl; or (2) by adding sufficient gaseous HCl to dissolve a known amount of solid CuCl in contact with a dilute solution of aqueous HCl.

In method (1), concentration of Cu^+ in solution was determined iodometrically.
In method (2), CuCl and HCl were determined by weight.

SOURCE AND PURITY OF MATERIALS:

Merck reagent grade CuCl. Source of HCl not given; no purities stated.

ESTIMATED ERROR:

Not stated; reproducibility apparently about 5%.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Morosov, I. C.; Ustanishkova, G. V. *Izv. Akad. Nauk. SSSR* 1944, 451–456.
VARIABLES:	**PREPARED BY:**
Molality of HCl at 293 to 373 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl

(Note: All data presented graphically, numerical values below obtained from graphs by compiler.)

t/°C	$100w_2$	$100w_1$	$100w_3$	$\frac{m_2{}^a}{\text{mol kg}^{-1}}$	$\frac{m_1{}^a}{\text{mol kg}^{-1}}$
0	16	9.5	75.5	5.8	1.3
	29	16.5	55.5	14.3	3.0
	34	19	47	19.8	4.1
25	8	3.5	89.5	2.5	0.4
	17	15	68	6.9	2.2
	21.5	20	58.5	10.0	3.5
	23	22	55	11.5	4.0
	29	24	47	16.9	5.2
50	4	1.5	94.5	1.1	0.2
	5	2	93	1.5	0.2
	9.5	8	82.5	3.2	1.0
	13	11	76	4.7	1.5
	20	21.5	58.5	9.4	3.7
	22	23	55	11.0	4.2
	26	26	48	14.9	5.5
80	10	11	79	3.5	1.4
	13	15	72	5.0	2.1
	20	26	54	10.2	4.9
	23	30	47	13.4	6.4

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Not given.	Sources not given. CuCl 99.9%
	ESTIMATED ERROR:
	Not given; uncertainty in reading graphs app. 0.5 mass %.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Morosov, I. C.; Ustanishkova, G. V. *Izv. Akad. Nauk. SSSR* 1944, 451–456.

EXPERIMENTAL VALUES:

(continued)

$t/°C$	$100w_2$	$100w_1$	$100w_3$	$\frac{m_2{}^a}{\text{mol kg}^{-1}}$	$\frac{m_1{}^a}{\text{mol kg}^{-1}}$
100	8.5	11.5	80	2.9	1.5
	13.5	20	66.5	5.6	3.0
	18	28	54	9.1	5.2
	20	30.5	49.5	11.1	6.2

[a] Calculated by compiler.

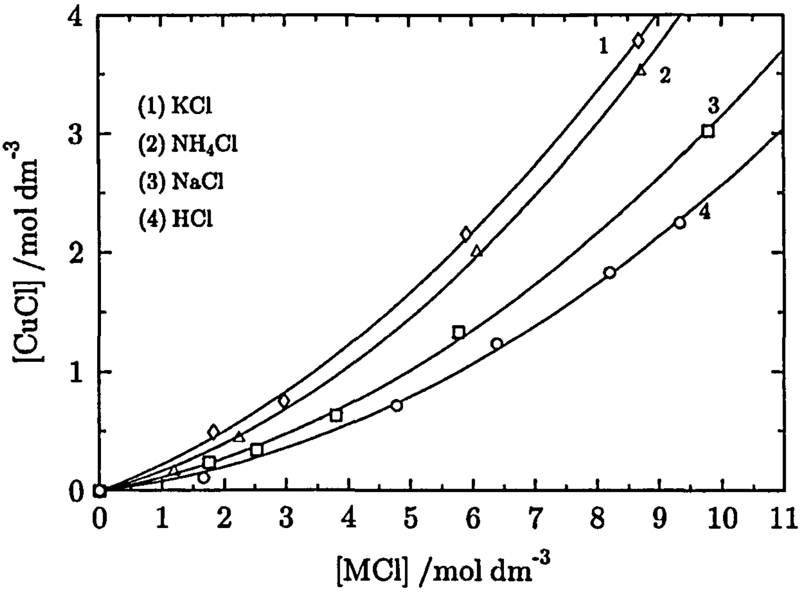
COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Chaltykyan O. A. *Zh. Obsch. Khim.* 1948, *18*, 1626–1638.
VARIABLES: Concentration of HCl at 298 K	PREPARED BY: J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 25°C

c_2[a] / mol dm^{-3}	c_1[a] / mol dm^{-3}
1.67	0.11
4.78	0.72
6.40	1.24
8.20	1.83
9.33	2.24

[a] The numerical results were digitized from the author's Fig. 3, reproduced below, which compares solubility of CuCl in several aqueous chlorides. This figure gives results for three systems measured by this author and one (NH_4Cl) quoted from the literature.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Not given.	Not given.
	ESTIMATED ERROR: Not given; graph can be read to precision indicated.
	REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Malik, W. U.; Rahman, S. M. F.; Ali, S. A.
Z. Anorg. Chem. 1959, *299*, 322–327.

VARIABLES:

Concentration of HCl at unspecified temperature (probably about 300 K)

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl

ρ_2 / g dm^{-3}	c_2[a] / mol dm^{-3}	ρ_1 / g dm^{-3}	c_1[a] / mol dm^{-3}
4.68	0.128	3.9	0.039
9.15	0.251	5.92	0.060
14.05	0.385	8.92	0.090
19.25	0.528	13.87	0.140
23.36	0.641	16.85	0.170
28.3	0.776	19.82	0.200
33.81	0.927	27.75	0.280
38.8	1.064	31.7	0.320
45.3	1.242	35.7	0.360
50.5	1.385	43.6	0.440
55.3	1.517	51.53	0.520
60.9	1.670	56.5	0.571
65.0	1.783	63.0	0.636
70.2	1.925	71.4	0.721
75.4	2.068	77.5	0.783
80.9	2.219	88.2	0.891
84.9	2.329	98.1	0.991
90.0	2.468	101.4	1.024
100.4	2.754	107.0	1.080
(109.00)[b]	(2.990)[b]	(132.80)[b]	(1.341)[b]

[a] Calculated by compiler.

[b] Original (slightly unsaturated) solution.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Prepared nearly saturated solution of CuCl in aqueous HCl of about 3 mol dm^{-3}, which was then diluted up to 20-fold. Analyzed liquid phase of resulting mixtures for Cu^+ by titration with NH_4SCN after addition of ferric alum. Analyzed for HCl — method not stated.

Calculated composition of solid phase by difference between original and final concentrations of solution.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared by reduction of $CuCl_2$ with metallic copper. Source of materials other than CuCl not stated.

Purity not stated.

ESTIMATED ERROR:

Not given.

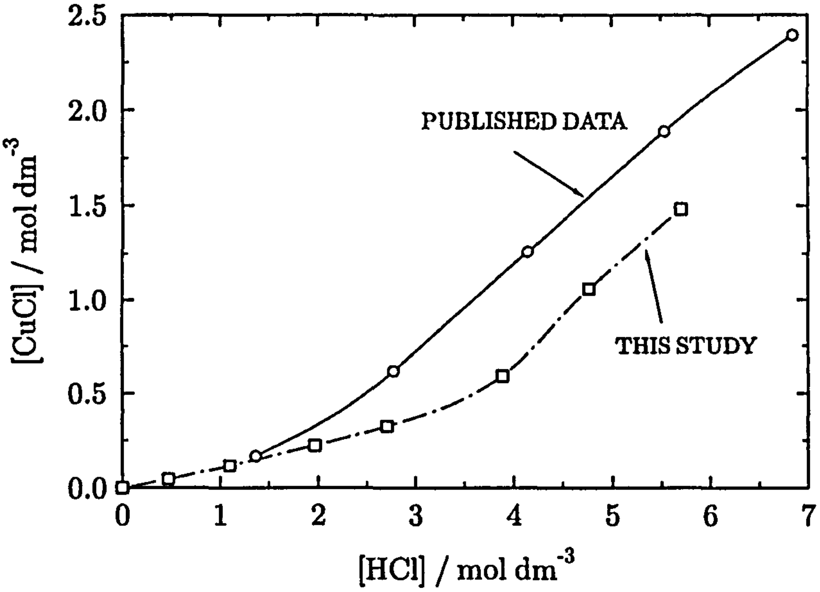
REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	O'Connor, J. J.; Thomasian, A.; Armington, A. F. *J. Electrochem. Soc.* 1968, *115*, 931-932.
VARIABLES:	**PREPARED BY:**
Concentration of HCl at 295 K	J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl at 22°C

Presents graphical display of solubility of CuCl in aqueous HCl from 0.9 to 6.4 mol dm^{-3} at 22°C. In the figure, which is reproduced below, the results of this study are compared with data published previously (Ref. 1). No numerical solubility data given.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Prepared saturated solutions by dilution of a saturated solution of CuCl in 6M HCl. Analyzed for H^+ and Cu^+ after 3 days in closed vials with copper turnings added. Oxidized solutions with gaseous oxygen, then titrated with NaOH (for H^+) and determined copper content iodometrically.	Not stated. ESTIMATED ERROR: Not given. REFERENCES: 1. Linke, W. F. *Solubility of Inorganic and Metal Organic Compounds*, Vol. 1, 4rd ed., Van Norstrand Co., Princeton, 1958, p. 925.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Wilke, K.-Th. *Krist. Tech.* 1968, *3*, K53-K55.
VARIABLES:	**PREPARED BY:**
T/K = 298 to 328	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl

t/°C	HCl in Solution[a]		Solubility of CuCl[a]	
	g/100 ml H_2O	m_2/mol kg^{-1}	g/100 ml H_2O	m_1/mol kg^{-1}
25	22.0	6.0	17.2	1.74
35	22.0	6.0	17.7	1.79
45	22.0	6.0	18.6	1.88
55	22.0	6.0	19.8	2.00

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thermostated solutions with excess CuCl and metallic Cu held under nitrogen atmosphere. After 24 hours, Cu^+ was determined iodometrically after oxidation to Cu^{2+} with H_2O_2.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Glodzińska, W.; Zembura, Z. *Roczniki Chem.* 1974, *48*, 341–343.
VARIABLES:	**PREPARED BY:**
Concentration of HCl at 298 K	J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

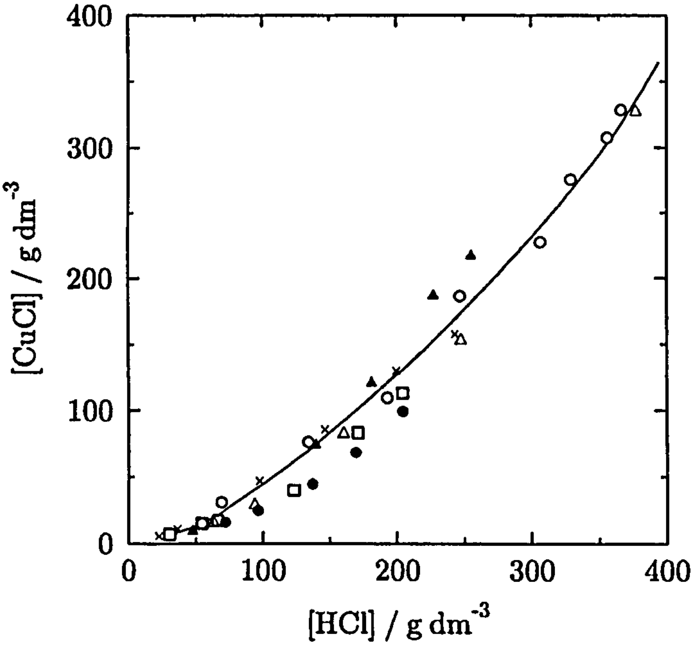
Solubility of CuCl in Aqueous HCl at 25°C

Give graphical presentation of solubility of CuCl (ρ_1/g dm^{-3}) as a function of HCl mass concentration (ρ_2/g dm^{-3} = 50 to 370), with earlier results shown for comparison.

Give equation for solubility of CuCl at 25 ± 0.1°C

$$\rho_1/\text{g dm}^{-3} = -22.2605 + 7.362 \cdot 10^{-1}(\rho_2/\text{g dm}^{-3}) - 7 \cdot 10^{-4}(\rho_2/\text{g dm}^{-3})^2 + 3.35 \cdot 10^{-6}(\rho_2/\text{g dm}^{-3})^3$$

Claimed validity from 55 to 370 g dm^{-3} HCl.



○ This study; △ Engel (1889) at 0°C; □ Le Chatelier (1884) at 17°C; ▲ Fedotieff (1928) at 19°C; × Linke (1958) at 22°C; ● O'Connor *et al.* (1968) at 22°C. Curve calculated from equation given above.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Copper(II) chloride in aqueous HCl reduced with excess metallic copper at 25±0.1°C. Copper oxidized to $CuSO_4$, then determined iodometrically. Chloride determined argentometrically.	Not stated. ESTIMATED ERROR: 4 to 8% REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Kale, S. S.; Tamhankar, S. S., and Chaudhari, R. V. *J. Chem. Eng. Data* 1979, *24 (2)*, 110–111.
VARIABLES:	PREPARED BY:
Concentration of HCl at 293 to 323 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl

c_2 / mol dm^{-3}	$10^2\ c_1$/mol dm^{-3} at t/°C of 20	30	40	50
0.0	0.295	0.380	0.519	0.668
0.129	0.944	1.175	1.603	1.927
0.158	1.122	1.380	1.884	2.238
0.266	1.698	2.113	2.985	3.467
0.398	2.398	2.985	4.121	4.897
0.603	3.388	4.168	5.888	6.839

Give equation $\ln c_1/\text{mol dm}^{-3} = A + B\text{K}/T + C\ln(1 + Dc_2/\text{mol dm}^{-3})$, where c_1 is solubility of CuCl and c_2 is concentration of HCl, and $A = 2.2265$, $B = -2.3480 \cdot 10^3$, $C = 1.0486$, $D = 15.0$.

Quote $\sigma = 1.1513 \cdot 10^{-3}$

Derive $\Delta H = 4.696$ kcal mol^{-1}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of solution and solid CuCl were stirred under nitrogen until saturation attained at a temperature constant within 0.1°C.

Cuprous chloride determined by method of Vogel (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

AR grade reagents used.

ESTIMATED ERROR:

2 to 5%

REFERENCES:

1. Vogel, A. I. *Quantitative Inorganic Analysis*, 3rd ed., The ELBS and Longman, London, 1975, p. 358.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kremann, R.; Noss, F.
Monatsh. Chem. 1912, *33*, 1205–1215.

VARIABLES:

Composition at 299.7 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System CuCl–NaCl–H_2O at 26.5°C

$100\zeta_{2,3}$	$100\zeta_{1,3}$	Solid Phase	m_2/mol kg^{-1} [a]	m_1/mol kg^{-1} [a]
0	1.55	CuCl	0	0.016
10.80	3.15	CuCl	1.85	0.318
20.70	7.30	CuCl	3.54	0.737
40.60	27.00	CuCl	6.95	2.73
49.10	36.48	CuCl	8.40	3.68
57.21	44.14	CuCl+NaCl	9.79	4.46
55.10	41.10	NaCl	9.43	4.15
56.80	41.70	NaCl	8.71	4.21
50.90	18.70	NaCl	8.71	1.89
(35.9) [b]	0	NaCl	6.14	0

[a] Calculated by compiler.

[b] Quoted from Landolt-Börnstein by authors.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook mixtures in thermostat, analyzed solutions — methods not given.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared by reducing solution of $CuSO_4$ and NaCl with SO_2. Source of NaCl not stated.

Purities not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fedotieff, P. P.
Z. Anorg. Allg. Chem. 1928, *173*, 81–91.

VARIABLES:

Composition at 292 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System CuCl–NaCl–H_2O at 19°C

ρ_2/g dm^{-3}	ρ_1/g dm^{-3}	Solid Phase	c_2/mol dm^{-3} [a]	c_1/mol dm^{-3} [a]
9.3	1.2	CuCl	0.159	0.012
47.2	5.4	CuCl	0.808	0.055
80.2	12.3	CuCl	1.37	0.124
123.1	29.2	CuCl	2.11	0.295
170.7	54.4	CuCl	2.92	0.549
243.2	129.0	CuCl	4.16	1.303
369.8	298.3	CuCl+NaCl	6.33	3.012
361.5	245.8	NaCl	6.18	2.482
329.0	50.4	NaCl	5.63	0.509
317.0	0	NaCl	5.42	0

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experiments carried out in sealed ampoules under CO_2 atmosphere; one drop of hydrochloric acid added to solutions.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Water; H_2O; [7732-18-5]	Chaltykyan O. A. *Zh. Obshch. Khim.* 1948, *18*, 1626-1638.
VARIABLES: Concentration of NaCl at 298 K	PREPARED BY: J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NaCl at 25°C

c_2[a] mol dm^{-3}	c_1[a] mol dm^{-3}
1.76	0.24
2.52	0.34
3.81	0.63
5.77	1.33
9.79	3.02

[a] The numerical results given above were digitized from author's Fig. 3, which compares solubility of CuCl in several aqueous chlorides. This figure is shown in the compilation of his data for aqueous HCl.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Not given.	Not given.
	ESTIMATED ERROR: Not given; graph can be read to precision indicated.
	REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kosyakina, O. A.
Dokl. Nauchn. Konf. Jaroslavsk. Gos. Ped. Inst. 1962, *1 (4)*, 21–25.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System CuCl–NaCl–H_2O at 25°C

$100w_2$	$100w_1$	$100w_3$	Solid Phase	m_2/mol kg^{-1} [a]	m_1/mol kg^{-1} [a]
26.45	–	73.55	NaCl	6.15	–
26.78	1.65	71.57	NaCl	6.40	0.233
28.40	4.66	67.54	NaCl	7.19	0.607
29.75	8.36	61.89	NaCl	8.22	1.364
30.03	10.90	59.07	NaCl	8.70	1.863
29.88	14.20	55.92	NaCl	9.14	2.564
29.62	18.40	51.98	NaCl	9.75	3.574
28.90	21.70	49.40	NaCl	10.01	4.436
27.10	24.80	48.10	NaCl	9.64	5.206
24.15	28.60	47.25	NaCl	8.74	6.112
23.90	28.75	47.35	NaCl+CuCl [b]	8.64	6.131
23.85	28.73	47.42	NaCl+CuCl [b]	8.60	6.118
20.15	25.24	54.61	CuCl	6.31	4.667
15.20	10.40	74.40	CuCl	3.50	1.412
10.05	4.10	85.85	CuCl	2.00	0.482
4.11	2.05	93.84	CuCl	0.819	0.241
–	1.63	98.37	CuCl	–	0.167

[a] Calculated by compiler.

[b] Double Salt definitely not produced in region of two solid phases.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions and solid kept in dark bottle for 3 days at 25±0.1°C. Analysis of liquid phase was

1. for Cl — mercurometric titration
2. for Na — weighed as sodium zinc uranyl acetate
3. for Cu — titration with $KMnO_4$, using Reiniger method

Constitution of third phase from analysis of wet residues.

SOURCE AND PURITY OF MATERIALS:

CuCl — "C.P." CuCl, with analysis 95.8% CuCl, 0.2% sulfate, 0.14% alkalies.

Other materials — not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Wilke, K.-Th.
Krist. Tech. 1968, *3*, K53–K55.

VARIABLES:

Molality of NaCl at 298 to 328 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NaCl

t/°C	NaCl in Solution[a] g/100 ml H_2O	NaCl in Solution[a] m_2/mol kg^{-1}	Solubility of CuCl[a] g/100 ml H_2O	Solubility of CuCl[a] m_1/mol kg^{-1}
25	35.9	6.14	19.9	2.01
	18.0	3.08	5.8	0.59
	9.0	1.54	3.6	0.36
35	35.9	6.14	20.5	2.07
	18.0	3.08	7.2	0.73
	9.0	1.54	4.0	0.40
45	35.9	6.14	21.4	2.16
	18.0	3.08	8.0	0.81
	9.0	1.54	4.0	0.40
55	35.9	6.14	21.9	2.21
	18.0	3.08	8.4	0.85
	9.0	1.54	4.2	0.42

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thermostated solutions with excess CuCl and metallic Cu held under nitrogen atmosphere. After 24 hours, Cu^+ was determined iodometrically after oxidation to Cu^{2+} with H_2O_2.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vysh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1969, *12*, 706–708.

VARIABLES:

Concentration of NaCl at 273 to 368 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NaCl

t/°C	c_2/mol dm^{-3}	c_1/mol dm^{-3}	ρ/g cm^{-3}	Solid Phase
0±0.5	0.76	0.04	1.016	CuCl
	1.64	0.12	1.058	CuCl
	2.57	0.31	1.120	CuCl
	3.70	0.75	1.242	CuCl
	5.05	1.60	1.262	CuCl+NaCl
25.0±0.1	0.047	0.0056	1.008	CuCl
	0.83	0.07	1.038	CuCl
	2.22	0.43	1.135	CuCl
	4.05	1.18	1.235	CuCl
	4.77	1.92	1.335	CuCl+NaCl
50.0±0.1	0.043	0.01	1.008	CuCl
	0.81	0.14	1.036	CuCl
	2.26	0.64	1.136	CuCl
	3.85	1.50	1.274	CuCl
	4.83	2.16	1.348	CuCl+NaCl
75.0±0.1	0.049	0.019	1.004	CuCl
	0.78	0.21	1.057	CuCl
	2.54	0.89	1.139	CuCl
	3.02	1.29	1.221	CuCl
	5.04	2.55	1.367	CuCl+NaCl

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Kept solutions in contact with solid under a stream of nitrogen at constant temperature until equilibrium attained.
Analyzed solutions for Cu^+ with permanganate; analyzed for Cl^- using Volhard method.
Method of determining composition of solid phase not stated.
Interpret results qualitatively in terms of formation of $CuCl_2^-$ and $CuCl_3^{2-}$.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Temperature as shown.
No estimate given for concentrations.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vysh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1969, *12*, 706–708.

EXPERIMENTAL VALUES:

(continued)

$t/°C$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$	Solid Phase
95.0±0.5	0.08	0.05	0.986	CuCl
	0.77	0.33	1.020	CuCl
	2.41	1.23	1.150	CuCl
	4.07	2.54	1.310	CuCl
	5.77	3.53	1.425	CuCl+NaCl

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1970, *13*, 437–439.

VARIABLES:

Concentration of NaCl at 298 and 368 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NaCl

ρ_2 / g dm^{-3}	c_2[a] / mol dm^{-3}	$t/°C = 25$		$t/°C = 95$	
		ρ_1/g dm^{-3}	c_1/mol dm^{-3} [a]	ρ_1/g dm^{-3}	c_1/mol dm^{-3} [a]
100	1.71	25	0.25	70	0.71
200	3.42	85	0.86	200	2.02
250	4.28	140	1.41	265	2.68
300	5.13	225	2.27	350	3.53

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1969, *12*, 706.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Chloride; KCl; [7447-40-7] (3) Water; H_2O; [7732-18-5]	Le Chatelier, H. *C. R. Hebd. Seances Acad. Sci.* 1884, *98*, 813-816.
VARIABLES:	PREPARED BY:
Concentration of KCl at 290 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous KCl at 17°C

ρ / g cm^{-3}	$[Cl]^-_{total}$ / equiv. dm^{-3}	$[Cu^+]$ / equiv. dm^{-3}	c_2[a] / mol dm^{-3}	c_1[a] / mol dm^{-3}
1.016	0.295	0.025	0.283	0.0125
1.020	0.320	0.030	0.305	0.015
1.029	0.600	0.064	0.568	0.032
1.056	1.300	0.223	1.188	0.112
1.135	2.920	1.100	2.370	0.550
1.310	6.000	3.90	4.050	1.950

[a] Calculated by compiler, following procedure of Ref. 1.; note that Le Chatelier's "equivalent" of Cu^+ was 0.5 mol.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Sealed CuCl and metallic copper in tubes containing KCl solutions, analyzed after decoloration of solution (complete methods not given).

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Engel, R. *Ann. Chim. Phys.* 1889, *17*, 347.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Potassium Chloride; KCl; [7447-40-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Brönsted, J. N.
Z. Phys. Chem. 1912, *80*, 206–234.

VARIABLES:

Composition at 295 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System $CuCl–KCl–H_2O$ at 22°C

m_2 / mol kg^{-1}	m_1 / mol kg^{-1}	Solid Phase	m_2 / mol kg^{-1}	m_1 / mol kg^{-1}	Solid Phase
0.540	0.012	CuCl	5.139	2.411	A
0.945	0.044	CuCl	5.061	2.261	A
1.215	0.096	CuCl	5.189	2.353	A
1.486	0.156	CuCl	5.122	2.367	A
1.756	0.256	CuCl	4.767	1.786	A
2.298	0.480	CuCl	4.838	1.765	A
2.569	0.612	CuCl	4.728	1.438	A
2.837	0.795	CuCl	4.553	1.072	A
3.109	0.963	CuCl	4.539	0.794	A
3.378	1.193	CuCl	4.511	0.640	A
3.919	1.519	CuCl	4.529	0.513	A
3.927	1.585	CuCl	4.671	0.441	A
3.918	1.483	CuCl	4.643	0.399	A
4.191	1.813	CuCl	4.689	0.371	A
4.460	2.067	CuCl	4.926	0.310	A
5.165	2.705	CuCl	5.059	0.274	A
5.424	2.950	CuCl	5.075	0.249	A
5.565	3.365	CuCl	5.101	0.274	A+KCl
6.321	4.062	CuCl	5.085	0.226	KCl
6.281	4.046	CuCl	4.963	0.174	KCl
6.446	4.090	CuCl+A	4.827	0.080	KCl
5.276	2.575	A	4.639	0.000	KCl

Solid phase: (A) $CuCl{\cdot}2KCl$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not stated.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Potassium Chloride; KCl; [7447-40-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Valeton, J. J. P.; Frömel, W.
Z. Anorg. Allg. Chem. 1924, *137*, 91–100.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System CuCl–KCl–H_2O

$100x_2$	$100x_1$	$100x_3$	Solid Phase	m_2/mol kg^{-1} [a]	m_1/mol kg^{-1} [a]
8.0	0	92.0	KCl	4.8	0
1.49	0.20	98.31	KCl	0.84	0.11
0.90	0.23	98.87	KCl	0.51	0.13
0.85	0.25	98.90	KCl	0.48	0.14
0.75	0.25	99.00	KCl+A	0.42	0.14
0.75	0.30	98.95	A	0.42	0.17
0.80	0.40	98.80	A	0.45	0.22
0.85	0.52	98.63	A	0.48	0.29
1.05	0.80	98.15	A	0.59	0.45
1.15	0.90	97.95	A	0.65	0.51
1.22	1.00	97.78	A	0.69	0.57
1.35	1.10	97.55	A	0.77	0.63
1.50	1.25	97.25	A	0.86	0.71
1.55	1.25	97.20	A	0.89	0.71
1.62	1.32	97.06	A+B	0.93	0.75
1.45	1.44	97.11	B	0.83	0.82
1.25	1.55	97.20	B	0.71	0.89
1.24	1.65	97.11	B	0.71	0.94
1.20	1.66	97.14	B	0.69	0.95
1.15	1.75	97.10	B	0.66	1.00

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solids and solution at 25°C inside sealed glass vessels for up to 48 hours, with 5 cm^3 specimens removed for analysis every 10 hours. Analyzed for copper electrolytically after oxidation to Cu(II) with concentrated HNO_3 and conversion to $CuSO_4$ with H_2SO_4. Analyzed for potassium as K_2SO_4 and for chloride using the Volhard method.

Confirmed nature of double salts by analysis for KCl and CuCl (results given).

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Mitscherlich, E. *Berl. Akad. Ber.* 1840, 8.
2. Schiff, A. *Lieb. Ann.* 1858, *107*, 90.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Potassium Chloride; KCl; [7447-40-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Valeton, J. J. P.; Frömel, W.
Z. Anorg. Allg. Chem. 1924, *137*, 91–100.

EXPERIMENTAL VALUES:

(continued)

$100x_2$	$100x_1$	$100x_3$	Solid Phase	m_2/mol kg^{-1} [a]	m_1/mol kg^{-1} [a]
1.10	1.80	97.10	B	0.63	1.03
1.05	1.85	97.10	B	0.60	1.06
1.00	1.90	97.10	B	0.57	1.09
0.95	1.97	97.08	B	0.54	1.13
0.90	2.05	97.05	B+CuCl	0.51	1.17
0.62	2.10	97.28	CuCl	0.35	1.20
0.54	1.91	97.55	CuCl	0.31	1.09
0.25	0.96	98.79	CuCl	0.10	0.54
0.18	0.68	99.14	CuCl	0.10	0.38
0.09	0.27	99.64	CuCl	0.05	0.15

Solid phases: (A) $2KCl{\cdot}CuCl$; (B) $KCl{\cdot}CuCl{\cdot}H_2O$.

[a] Calculated by compiler.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Potassium Chloride; KCl; [7447-40-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Chaltykyan O. A.
Zh. Obshch. Khim. 1948, *18*, 1626–1638.

VARIABLES:

Concentration of KCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous KCl at 25°C

c_2[a] / mol dm^{-3}	c_1[a] / mol dm^{-3}
1.83	0.49
2.97	0.75
5.90	2.15
8.68	3.78
9.0	3.95

[a] The numerical results given above were digitized from the author's Fig. 3, which compares solubility of CuCl in several aqueous chlorides. This figure is shown in the compilation of his data for aqueous HCl.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given; graph can be read to precision indicated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Potassium Chloride; KCl; [7447-40-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Malik, W. U.; Rahman, S. M. F.; Ali, S. A.
Z. Anorg. Chem. 1959, *299*, 322–327.

VARIABLES:

Concentration of KCl at unspecified temperature (probably about 300 K)

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous KCl

ρ_2 / g dm^{-3}	c_2[a] / mol dm^{-3}	ρ_1 / g dm^{-3}	c_1[a] / mol dm^{-3}
10.0	0.134	1.4	0.0141
19.0	0.255	3.0	0.0303
30.0	0.402	5.0	0.0504
49.0	0.657	11.2	0.150
60.0	0.804	18.2	0.184
71.0	0.952	26.8	0.271
80.0	1.073	35.7	0.360
89.2	1.196	41.2	0.416
100.0	1.341	50.6	0.511
110.9	1.487	54.4	0.549
124.0	1.663	73.4	0.741
134.0	1.797	82.3	0.831
146.6	1.966	99.1	1.001
158.6	2.127	109.0	1.101
(223.8)[b]	(3.002)[b]	(186.0)[b]	(1.878)[b]

[a] Calculated by compiler.

[b] Original unsaturated solutions.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Prepared unsaturated solution of CuCl in KCl of 3.0 mol dm^{-3}. Prepared mixture of solution and solid by dilutions up to 20 fold. Analyzed liquid phase for Cu^+ by titration with NH_4SCN after addition of ferric alum, analyzed for potassium by precipitating and weighing dipotassium sodium cobaltinitrite. Calculated composition of solid phase by difference between original and final composition of solution.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared by reduction of $CuCl_2$ with metallic copper. Source of materials other than CuCl not given.
Purity not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Ammonium Chloride; NH_4Cl; [12125-02-9]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Morosov, I. C.; Ustaniskova, G. V.
Isv. Akad. Nauk SSSR 1944, 451-456.

VARIABLES:

Composition at 273 to 373 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System $CuCl-NH_4Cl-H_2O$

(Note: All data presented graphically, numerical values below obtained from graphs by compiler.)

$t/°C$	$100w_2$	$100w_1$	$100w_3$	Solid Phase	m_2^a/mol kg^{-1}	m_1^a/mol kg^{-1}
0	10	3	87	CuCl	2.1	0.3
	17.5	13	69.5	CuCl+A	4.7	1.9
	22	13	65	A	6.3	2.0
	26	14	60	A+NH_4Cl	8.1	2.4
	26	11.5	62	NH_4Cl	7.8	2.3
	26	9	65	NH_4Cl	7.5	1.4
	22.5	0	67.5	NH_4Cl	6.2	0
25	10	3	87	CuCl	2.1	0.3
	14	9	77	CuCl	3.4	1.2
	17	16	67	CuCl	4.7	2.4
	20	26.5	53.5	CuCl+A	7.0	5.1
	23.5	28.5	48	A	9.2	6.0
	31	34.5	34.5	A+NH_4Cl	17	10.1
	31	26.5	41.5	NH_4Cl	14	6.4
	30	15.5	54.5	NH_4Cl	10	2.9
	29	11	60	NH_4Cl	9.0	1.9
	28.5	5.5	66	NH_4Cl	8.1	0.8
	27	0	73	NH_4Cl	6.9	0

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Sources not given
CuCl 99.9%
NH_4Cl 98.6%

ESTIMATED ERROR:

Not given; uncertainty in reading graphs *app.* 0.5 mass %.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; $CuCl$; [7758-89-6] (2) Ammonium Chloride; NH_4Cl; [12125-02-9] (3) Water; H_2O; [7732-18-5]	Morosov, I. C.; Ustaniskova, G. V. *Isv. Akad. Nauk SSSR* <u>1944</u>, 451–456.

EXPERIMENTAL VALUES:

(continued)

t/°C	$100w_2$	$100w_1$	$100w_3$	Solid Phase	m_2[a] / mol kg^{-1}	m_1[a] / mol kg^{-1}
50	10.5	7	82.5	$CuCl$	2.4	0.9
	14.5	14	71.5	$CuCl$	3.8	2.0
	17.5	23	59.5	$CuCl$	5.5	3.9
	21	23	46	$CuCl$	8.5	7.2
	22.5	37	40.5	$CuCl$	10.4	9.2
	24	41	35	$CuCl$	13	12
	26	47	27	$CuCl$+B	18	18
	29	48	23	B	24	21
	31	48.5	20.5	B+NH_4Cl	28	24
	32.5	46	21.5	NH_4Cl	28	22
	34	40	26	NH_4Cl	24	16
	35	35.5	29.8	NH_4Cl	22	12
	35.5	29.5	35	NH_4Cl	19	8.5
	35.5	20	44.5	NH_4Cl	15	4.5
	35	16	49	NH_4Cl	13	3.3
	35	10	55	NH_4Cl	12	1.8
	34.5	5	60.5	NH_4Cl	11	0.8
	34	0	66	NH_4Cl	9.6	0
80	11.5	11.5	77	$CuCl$	2.8	1.5
	20	35.5	44.5	$CuCl$	8.2	7.9
	24.5	50	25.5	$CuCl$	18	20
	27.5	61.5	11	$CuCl$+NH_4Cl	[b]	[b]
	32	57	10.5	NH_4Cl	[b]	[b]
	38	43	19	NH_4Cl	37	22
	40	26.5	23.5	NH_4Cl	32	11
	39	14.5	46.5	NH_4Cl	16	3
	38.5	3.5	58	NH_4Cl	12	0.6
	38	0	62	NH_4Cl	11.5	0
100	7.5	7.5	85	$CuCl$	1.6	0.9
	14	21	65	$CuCl$	4.0	3.3
	16	27	57	$CuCl$	5.2	4.8
	22.5	52	25.5	$CuCl$	16	21
	23.5	59.5	17.0	$CuCl$	26	35
	24.5	65	10.5	$CuCl$	[b]	[b]
	25	70	5	$CuCl$	[b]	[b]
	26	72.5	1.5	$CuCl$+NH_4Cl	[b]	[b]
	40	46.5	13.5	NH_4Cl	[b]	[b]
	42	34.5	23.5	NH_4Cl	33	15
	42	31.5	26.5	NH_4Cl	30	12
	43.5	17	39.5	NH_4Cl	21	4
	42	0	58	NH_4Cl	13.5	0

Solid phases: (A) $2NH_4Cl{\cdot}CuCl$; (B) $NH_4Cl{\cdot}CuCl$.

[a] Calculated by compiler.

[b] Salt content too high for reasonable calculation of molality.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Ammonium Chloride; NH_4Cl; [12125-02-9] (3) Water; H_2O; [7732-18-5]	Wilke, K.-Th. *Krist. Tech.* 1968, *3*, K53–K55.
VARIABLES:	**PREPARED BY:**
Molality of NH_4Cl at 298 to 318 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NH_4Cl

t/°C	NH_4Cl in Solution[a] g/100 ml H_2O	NH_4Cl in Solution[a] m_2/mol kg^{-1}	Solubility of CuCl[a] g/100 ml H_2O	Solubility of CuCl[a] m_1/mol kg^{-1}
25	37.4	7.00	34.2	3.45
	18.7	3.50	11.0	1.11
	9.4	1.76	4.6	0.46
35	37.4	7.00	34.9	3.53
	18.7	3.50	12.3	1.24
	9.4	1.76	5.5	0.56
45	37.4	7.00	35.4	3.58
	18.7	3.50	13.7	1.38
	9.4	1.76	6.4	0.65
55	37.4	7.00	35.8	3.62
	18.7	3.50	14.5	1.46
	9.4	1.76	6.9	0.70

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Thermostated solutions with excess CuCl and metallic Cu held under nitrogen atmosphere. After 24 hours, Cu^+ was determined iodometrically after oxidation to Cu^{2+} with H_2O_2.	Not stated. **ESTIMATED ERROR:** Not given. **REFERENCES:**

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Lithium Chloride; LiCl; [7447-41-8] (3) Water; H_2O; [7732-18-5]	Wilke, K.-Th. *Krist. Tech.* 1968, *3*, K53–K55.
VARIABLES:	**PREPARED BY:**
Molality of LiCl at 298 to 328 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous LiCl

t/°C	LiCl in Solution[a] g/100 ml H_2O	LiCl in Solution[a] m_2/mol kg^{-1}	Solubility of CuCl[a] g/100 ml H_2O	Solubility of CuCl[a] m_1/mol kg^{-1}
25	82.8	19.5	38.6	3.90
	41.4	9.8	24.4	2.46
	20.7	4.9	10.4	1.05
35	82.8	19.5	40.5	4.09
	41.4	9.8	25.6	2.59
	20.7	4.9	11.3	1.14
45	82.8	19.5	42.4	4.28
	41.4	9.8	26.9	2.72
	20.7	4.9	11.8	1.19
55	82.8	19.5	44.1	4.45
	41.4	9.8	28.1	2.92
	20.7	4.9	12.7	1.28

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Thermostated solutions with excess CuCl and metallic Cu held under nitrogen atmosphere. After 24 hours, Cu^+ was determined iodometrically after oxidation to Cu^{2+} with H_2O_2.	Not stated. ESTIMATED ERROR: Not given. REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Calcium Chloride; $CaCl_2$; [10043-52-4]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Shirokova, G. N.; Shokin, I. N.; Kuznetsova, A. G.
Tr. Mosk. Inst. Khim.-Tekh. Inst. Mendeleeva 1965, *49*, 73–77.

VARIABLES:

Molality of $CaCl_2$ at 303 to 363 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous $CaCl_2$[a]

T/K	$100w_2$	$100w_1$	$100w_3$	m_2/mol kg^{-1}	m_1/mol kg^{-1}
303	5.2	0.9	93.9	0.5	0.1
	10.8	3.2	86.0	1.1	0.4
	23.6	14.6	61.8	3.4	0.4
	24.8	14.6	60.6	3.7	2.4
	28.0	18.6	53.4	4.7	3.5
	28.3	19.6	52.1	4.9	3.8
	30.6	22.4	47.0	5.9	4.8
	32.0	22.4	47.6	6.1	4.8
	33.7	22.5	39.8	7.6	5.7
	37.1	22.0	40.9	8.2	5.4
	37.9	21.4	40.7	8.4	5.3
	38.6	21.4	40.0	8.7	5.4
	39.4	19.6	41.0	8.7	4.8
	39.6	18.7	41.7	8.6	4.5
	46.8[b]	16.8[b]	36.4[b]	11.6[b]	4.7[b]

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Placed $CaCl_2$ solutions and solid salt in sealed wide mouth test tubes under oxygen-free nitrogen. Mixtures were kept in a thermostat at the desired temperatures for 3–4 hours; observed that equilibrium was reached in this amount of time, as indicated by successive analyses.

Analyzed for Ca^{2+}, Cu^+ and Cl^- by standard methods.

Measured densities of saturated solutions, but did not report results.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared by "literature method" (reference not given). Sources and purities of materials not given.

ESTIMATED ERROR:

Not given; data appear consistent to about 0.5 mass %.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Calcium Chloride; $CaCl_2$; [10043-52-4]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Shirokova, G. N.; Shokin, I. N.; Kuznetsova, A. G.
Tr. Mosk. Inst. Khim.-Tekh. Inst. Mendeleeva 1965, *49*, 73–77.

EXPERIMENTAL VALUES:

(continued)

T/K	$100w_2$	$100w_1$	$100w_3$	m_2/mol kg^{-1}	m_1/mol kg^{-1}
323	5.4	1.6	93.0	0.5	0.2
	8.4	3.0	88.6	0.9	0.3
	9.2	2.2	88.6	0.9	0.3
	16.6	8.6	74.8	2.0	1.2
	18.	9.2	72.0	2.4	1.3
	25.8	20.6	53.6	4.3	3.9
	26.2	20.0	53.8	4.4	3.8
	30.8	24.2	45.0	6.2	4.5
	31.6	23.8	44.6	6.4	5.4
	31.8	24.4	43.8	6.5	5.6
	45.2	18.4	36.4	11.2	5.1
	47.8[b]	17.9[b]	36.3[b]	12.6[b]	5.3[b]
	47.8[b]	16.8[b]	35.4[b]	12.2[b]	4.8[b]
343	6.4	3.3	90.3	0.6	0.4
	10.1	4.6	85.3	1.1	0.9
	18.0	11.8	70.2	2.3	1.7
	25.9	22.6	51.5	4.7	4.6
	30.9	26.4	42.7	6.5	6.2
	48.2[b]	19.0[b]	32.8[b]	13.2[b]	4.5[b]
363	6.2	3.8	90.0	0.6	0.4
	8.6	5.4	86.0	0.9	0.6
	10.4	6.0	83.6	1.1	0.7
	10.8	7.2	82.0	1.1	0.9
	16.9	12.2	70.9	2.2	1.7
	19.3	14.3	66.4	2.6	2.2
	25.4	25.5	49.1	4.7	5.2
	34.0	29.2	36.8	8.3	8.0
	47.0[b]	21.4[b]	31.6[b]	13.4[b]	6.8[b]

Notes: [a] Mass percentages were read from the authors' graph. The corresponding molalities were then calculated by the compiler.

[b] For these data the solution was at equilibrium with both $CuCl$ and hydrated $CaCl_2$ — at 303 K, $CaCl_2 \cdot 6H_2O$; at other temperatures, $CaCl_2 \cdot 2H_2O$. For all other data, the solid phase was $CuCl$ only.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Calcium Chloride; $CaCl_2$; [10043-52-4]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Wilke, K.-Th.
Krist. Tech. 1968, *3*, K53–K55.

VARIABLES:

Molality of $CaCl_2$ at 298 to 328 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous $CaCl_2$

t/°C	$CaCl_2$ in Solution[a] g/100 ml H_2O	m_2/mol kg^{-1}	Solubility of CuCl[a] g/100 ml H_2O	m_1/mol kg^{-1}
25	74.5	6.71	17.6	1.77
	37.3	3.36	15.1	1.53
	18.6	1.68	7.7	0.78
35	74.5	6.71	18.4	1.86
	37.3	3.36	15.6	1.58
	18.6	1.68	8.4	0.85
45	74.5	6.71	19.7	1.99
	37.3	3.36	16.2	1.64
	18.6	1.68	9.2	0.93
55	74.5	6.71	20.7	2.09
	37.3	3.36	17.1	1.73
	18.6	1.68	10.0	1.01

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thermostated solutions with excess CuCl and metallic Cu held under nitrogen atmosphere. After 24 hours, Cu^+ was determined iodometrically after oxidation to Cu^{2+} with H_2O_2.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Calcium Chloride; $CaCl_2$; [10043-52-4]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1970, *13*, 437–439.

VARIABLES:

Concentration of $CaCl_2$ at 298 and 368 K

PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous $CaCl_2$

$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2{}^a}{\text{mol dm}^{-3}}$	t/°C = 25		t/°C = 95	
		ρ_1/g dm^{-3}	c_1/mol dm$^{-3\,a}$	ρ_1/g dm^{-3}	c_1/mol dm$^{-3\,a}$
100	0.90	25	0.25	60	0.61
200	1.80	70	0.71	150	1.52
300	2.70	130	1.31	275	2.78
400	3.60	250	2.53	395	3.99
450	4.05	305	3.08	415	4.19
500	4.51	345	3.48	430	4.34

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not stated.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1969, *12*, 706.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Iron(II) Chloride; $FeCl_2$; [7758-94-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kremann, R.; Noss, F.
Monatsh. Chem. 1912, *33*, 1205–1215.

VARIABLES:

Composition at 294.7 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System $CuCl–FeCl_2–H_2O$ at 21.5°C

$100\zeta_{2,3}$[a]	$100\zeta_{1,3}$[a]	Solid Phase	m_2/mol kg^{-1} [b]	m_1/mol kg^{-1} [b]
0	1.54	$CuCl$	0	0.156
6.02	1.33	$CuCl$	0.475	0.134
11.62	1.81	$CuCl$	0.917	0.183
16.30	3.11	$CuCl$	1.286	0.314
26.31	7.13	$CuCl$	2.076	0.720
29.35	8.06	$CuCl$	2.316	0.814
33.13	9.57	$CuCl$	2.614	0.966
43.75	12.44	$CuCl$	3.452	1.256
54.00	17.04	$CuCl$	4.260	1.721
66.40	21.60	$CuCl$	5.239	2.181
73.20	23.20	$CuCl+FeCl_2\cdot 4H_2O$	5.775	2.343
71.90	21.66	$FeCl_2\cdot 4H_2O$	5.673	2.187
69.34	11.90	$FeCl_2\cdot 4H_2O$	5.471	1.202
65.10	0	$FeCl_2\cdot 4H_2O$	5.136	0

[a] Nearly identical duplicates averaged by compiler.

[b] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook mixtures in thermostat, analyzed solutions — methods not stated.

SOURCE AND PURITY OF MATERIALS:

$FeCl_2\cdot 4H_2O$ prepared by dissolving iron in HCl, then drying in a stream of hydrogen. $CuCl$ prepared by reducing solution of $CuSO_4$ and $NaCl$ with SO_2.

Purities not stated.

ESTIMATED ERROR:

Not stated — duplicate results agree to *app.* 1%.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fedotieff, P. P.
Z. Anorg. Allg. Chem. 1928, *173*, 81-91.

VARIABLES:

Concentration of $CuCl_2$ at 292 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous $CuCl_2$ at 22°C

ρ_2/g dm^{-3}	c_2/mol dm^{-3}	ρ_1/g dm$^{-3\,a}$	c_1/mol dm$^{-3\,a}$
134.5	1.00	15.8	0.160
260.0	1.93	40.7	0.411
435.7	3.24	63.8	0.644
536.5	3.99	78.7	0.795
661.9[b]	4.92[b]	87.4[b]	0.883[b]

[a] Calculated by compiler.

[b] This solution saturated with both CuCl and $CuCl_2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not stated.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Copper(II) Chloride; $CuCl_2$; [7447-39-4] (3) Water; H_2O; [7732-18-5]	Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1970, *13*, 437–439.
VARIABLES:	**PREPARED BY:**
Concentration of $CuCl_2$ at 298 and 368 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous $CuCl_2$

ρ_2/g dm^{-3}	c_2^{a}/mol dm^{-3}	t/°C = 25		t/°C = 95	
		ρ_1/g dm^{-3}	c_1/mol dm^{-3} ^{a}	ρ_1/g dm^{-3}	c_1/mol dm^{-3} ^{a}
200	1.49	30	0.30	50	0.50
300	2.23	50	0.50	72	0.73
400	2.97	68	0.69	90	0.91
500	3.72	80	0.81	103	1.04
600	4.46	90	0.91	115	1.16

[a] Calculated by compiler.

Also gives small scale graph of solubilities at 0, 25, 50, 75 and 95°C as a function of c_{CuCl_2}/mol dm^{-3}, covering slightly wider range of $CuCl_2$ concentrations (*app.* 0.2 to 4.7 mol dm^{-3}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Not given.	Not given.
	ESTIMATED ERROR:
	Not evident.
	REFERENCES:
	Utkina, I. N.; Kunin, T. I.; Shutov, A. A. *Isv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.* 1969, *12*, 706.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Magnesium Chloride; $CuCl_2$; [7786-30-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Karimova, N. N.; Ksandrov, N. V.; Nikandrov, I. S.
Zh. Prikl. Khim. 1988, *61*, 136–138.

VARIABLES:

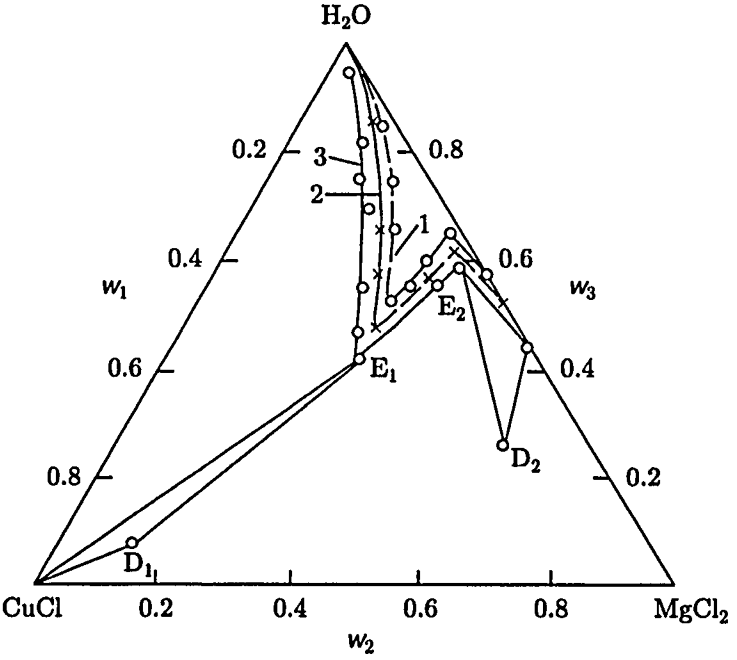
Composition at 273, 283 and 313 K

PREPARED BY:

E. Königsberger

EXPERIMENTAL VALUES:

Phase Diagram of the System $CuCl-MgCl_2-H_2O$



Temperatures: (1) 273 K, (2) 283 K, (3) 313 K. Solid phases: D_1: $12\,CuCl \cdot MgCl_2 \cdot 12\,H_2O$, D_2: $CuCl \cdot 5\,MgCl_2 \cdot 12\,H_2O$. Eutonic points: E_1: Solution at equilibrium with CuCl and D_1, E_2: Solution at equilibrium with $MgCl_2 \cdot 6\,H_2O$ and D_2.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experiments were performed by chemical analysis of solid and liquid phases and by measurement of densities of equilibrated solutions, which were correlated with values obtained from an equation for the calculation of density data of undersaturated solutions. The existence of the solid phases D_1 and D_2 was confirmed by X-ray difractometry and differential thermal analysis.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not evident.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vestin, R.; Somersalo, A.; Mueller, B.
Acta Chem. Scand. 1953, 7, 745–763.

VARIABLES:

Molality of HCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in HCl–HClO$_4$ Solutions at 25°C[a]

m_2/mol kg^{-1}	m_1/mol kg^{-1}
0.1000	0.00468
0.1500	0.00708
0.199	0.00977
0.415	0.0230
0.500	0.0293
0.600	0.0368
0.800	0.0531
1.000	0.0729
1.500	0.1318
2.00	0.210
3.00	0.427
4.00	0.735

[a] All solutions made up to constant nominal ionic strength $I_m = 4.0$ mol kg^{-1}, using $HClO_4$ as "inert" electrolyte.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Placed solid CuCl in Kjeldahl flasks, added acid mixture after purging with nitrogen. Shook flasks in thermostat at 298 K for 2.5 to 5 hours.

Analyzed for Cu^+ iodometrically after oxidation to Cu^{2+}. Found no Cu^{2+} in mixtures before analysis; no effect was produced when metallic copper was included in mixture.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Reproducible to 1%.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hikita, H.; Ishikawa, H.; Esaka, N.
Nippon Kagaku Kaiishi 1973, *(1)*, 13–18.

VARIABLES:

Concentrations of HCl and $HClO_4$ at 288, 298 and 308 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuCl in HCl–$HClO_4$ Solutions

I_c/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3} at T/K of 288	298	308
0.5	0.0499	0.451	0.00228	0.00326	0.00439
	0.0999	0.401	0.00435	0.00610	0.00846
	0.200	0.300	0.00866	0.0122	0.0169
	0.300	0.200	0.0137	0.0190	0.0255
	0.399	0.100	0.0190	0.0261	0.0348
	0.499	0.0	0.0244	0.0342	0.0446
1.0	0.100	0.900	0.00419	0.00576	0.00778
	0.201	0.795	0.00872	0.0121	0.0166
	0.402	0.597	0.0195	0.0262	0.0346
	0.603	0.398	0.0319	0.0427	0.0554
	0.804	0.199	0.0463	0.0607	0.0768
	1.01	0.0	0.0629	0.0822	0.105

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held mixture of solid and solvent in thermostat for 5 to 8 hours, then analyzed solution for copper using method of Birnbaum and Edwards (Ref. 1), *viz.*, titration with ceric sulfate using o-phenanthroline ferrous complex as indicator.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

1%. Note: Compiler was able to represent data to about this precision (Ref. 2).

REFERENCES:

1. Birnbaum, N.; Edwards, S. M. *Ind. Eng. Chem. Anal. Ed.* 1940, *12*, 155.
2. Fritz, J. J. *J. Phys. Chem.* 1980, *94*, 2241.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hikita, H.; Ishikawa, H.; Esaka, N.
Nippon Kagaku Kaiishi 1973, *(1)*, 13-18.

EXPERIMENTAL VALUES:

(continued)

I_c/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3} at T/K of		
			288	298	308
2.0	0.100	1.90	0.00396	0.00524	0.00677
	0.200	1.80	0.00842	0.0112	0.0143
	0.360	1.64	0.0166	–	–
	0.401	1.60	–	0.0249	0.0319
	0.601	1.40	0.0317	0.0414	0.0526
	0.801	1.20	0.0470	0.0608	0.0766
	1.00	1.00	0.0643	0.0824	0.105
	1.20	0.800	0.0843	0.107	0.132
	1.40	0.601	0.107	0.136	0.166
	1.60	0.400	0.131	0.165	0.202
	1.80	0.20	0.157	0.196	0.239
	2.00	0.0	0.186	0.211	0.281
3.5	0.175	3.33		0.00797	
	0.350	3.15		0.0184	
	0.526	2.98		0.0308	
	0.701	2.80		0.0457	
	0.876	2.63		0.0630	
	1.05	2.45		0.0823	
	1.23	2.28		0.105	
5.0	0.0994	4.90		0.00343	
	0.199	4.80		0.00719	
	0.398	4.60		0.0170	
	0.497	4.50		0.0230	
	0.750	4.25		0.0417	
	0.994	4.00		0.0648	
	1.24	3.75		0.0927	
	1.49	3.50		0.126	
6.5	0.130	6.38		0.00298	
	0.260	6.25		0.00657	
	0.389	6.11		0.0122	
	0.519	5.98		0.0168	
	0.649	5.85		0.0235	
	0.811	5.69		0.0332	
	0.973	5.53		0.0447	
	1.14	5.37		0.0581	
	1.30	5.20		0.0740	

continued...

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hikita, H.; Ishikawa, H.; Esaka, N.
Nippon Kagaku Kaiishi 1973, *(1)*, 13-18.

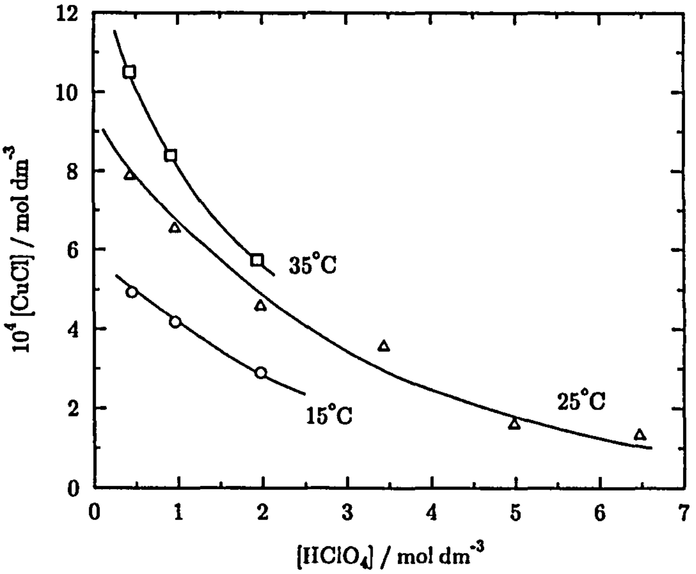
EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in HCl Solutions at 298 K

c_2/mol dm^{-3}	c_1/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.499	0.0342	3.00	0.454
0.750	0.0551	3.50	0.604
1.01	0.0822	4.00	0.774
1.50	0.146	4.50	0.959
2.00	0.231	5.00	1.16
2.50	0.333		

The authors give a graph of the solubility of CuCl in aqueous $HClO_4$ from 0.5 to 6.5 mol dm^{-3} at 298 K and from 0.5 to 2.0 mol dm^{-3} at 288 and 308 K. This graph is reproduced below. The table following the graph gives numerical values as digitized from the graph.



c_3/mol dm^{-3}	10^4 c_1/mol dm^{-3} at T/K of 288	298	308
0.43	4.92	7.95	10.51
0.95	4.10	6.63	8.40
1.97	2.90	4.52	5.72
3.42		3.67	
4.99		1.63	
6.48		1.43	

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(4) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ahrland, S.; and Rawsthorne, J.
Acta Chem. Scand. 1970, *24*(1), 157–172.

VARIABLES:

Concentration of NaCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in NaCl–$NaClO_4$–($HClO_4$) Solutions at 25°C[a]

10^3c_2 / mol dm^{-3}	10^3c_1 / mol dm^{-3}	10^3c_2 / mol dm^{-3}	10^3c_1 / mol dm^{-3}	10^3c_2 / mol dm^{-3}	10^3c_1 / mol dm^{-3}
7	0.313	500	35.8	2500	482
10	0.431	600	46.9	2800	584
30	1.27	700	56.3	3000	658
40	1.65	800	73.3	3300	776
50	2.15	900	88.2	3500	854
80	3.67	1000	102	3800	981
90	4.09	1300	154	4000	1094
100	4.68	1500	199	4300	1250
200	10.7	1800	272	4500	1344
300	18.0	2000	327	4800	1514
400	26.1	2300	418	5000	1606

[a] All measurements made at acidity of 0.1 mol dm^{-3} $HClO_4$ and at constant nominal ionic strength $I_c = 5.0$ mol dm^{-3}, using $NaClO_4$ as "indifferent" salt.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Portions of CuCl shaken under nitrogen in glass stoppered bottles with solutions given, then filtered. Solutions oxidized to Cu^{2+}, measured spectrophotometrically as complex with ammonia or cuprizone.

Authors also made extensive set of potentiometric measurements using a Cu(Hg)/Cu^+ electrode. They employed these as well as solubility measurements to calculate stability constants for complexes in the copper(I) chloride system.

SOURCE AND PURITY OF MATERIALS:

Merck *p.a.* CuCl purified and dried. Source of other materials not stated.

ESTIMATED ERROR:

±1% for c_{CuCl} greater than $5 \cdot 10^{-3}$ mol dm^{-3}, up to 4% for lower solubilities.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gokhale, S. D.
Journal of the University of Bombay 1953, *A20*, 53-60.

VARIABLES:

Concentrations of NaCl and HCl at 281 to 371 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NaCl

t/°C	c_1/mol dm^{-3} at c_2/mol dm^{-3} of 1.0	2.0	4.0
8.0 to 10	0.05	0.25	0.82
26 to 27	0.10	0.34	1.02
50 to 50.5	0.17	0.56	1.46
72 to 72.4	0.26	0.73	1.80
97 to 97.5	0.40	0.95	2.59

Effect on Solubility of Adding HCl[a] at "Room" Temperature

Amt. of HCl Added (cm^3)	c_1/mol dm^{-3}	Per Cent Increase in Solubility	c_2[b]/mol dm^{-3}	c_3[b]/mol dm^{-3}
0	1.157	-	4.0	0.0
0.1	1.135	−1.94	3.99	0.03
0.25	1.16	0.21	3.98	0.07
0.5	1.16	0.21	3.95	0.15
1.0	1.21	4.86	3.90	0.29
2.0	1.307	12.98	3.81	0.57
5.0	1.545	32.79	3.56	1.33
7.0	1.70	47.29	3.40	1.79

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added solid CuCl to solutions, along with metallic copper; solutions covered with castor oil; then held in thermostat for 18 hours before analysis. Cu^+ concentration then determined by titration with $K_2Cr_2O_7$.

Same procedure used for solutions prepared by adding concentrated HCl to aqueous NaCl and to pure water.

(Note: From data, "room" temperature would appear to be about 35°C.)

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Gokhale, S. D. *Journal of the University of Bombay* 1953, *A20*, 53-60.

EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in Aqueous HCl[c] at "Room" Temperature

Amt. of HCl Added (cm^3)	c_1/mol dm^{-3}	c_2[b]/mol dm^{-3}
0.0	–	0.0
0.5	0.008	0.15
1.0	0.0144	0.29
2.0	0.037	0.57
4.0	0.110	1.09
5.0	0.147	1.33
10.0	0.352	2.40
20.0	0.865	4.00

[a] In all cases, specified amounts of aqueous HCl (12 mol dm^{-3}) were added to 40 cm^3 of aqueous NaCl (4.0 mol dm^{-3}).

[b] Calculated by compiler.

[c] In all cases, specified amounts of aqueous HCl (12 mol dm^{-3}) were added to 40 cm^3 of water.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Peters, M. A.; Johnson, R. K;
U. S. Patent No. 4,101,315, July 18, 1978.

VARIABLES:

Concentration of NaCl at 278 to 348 K

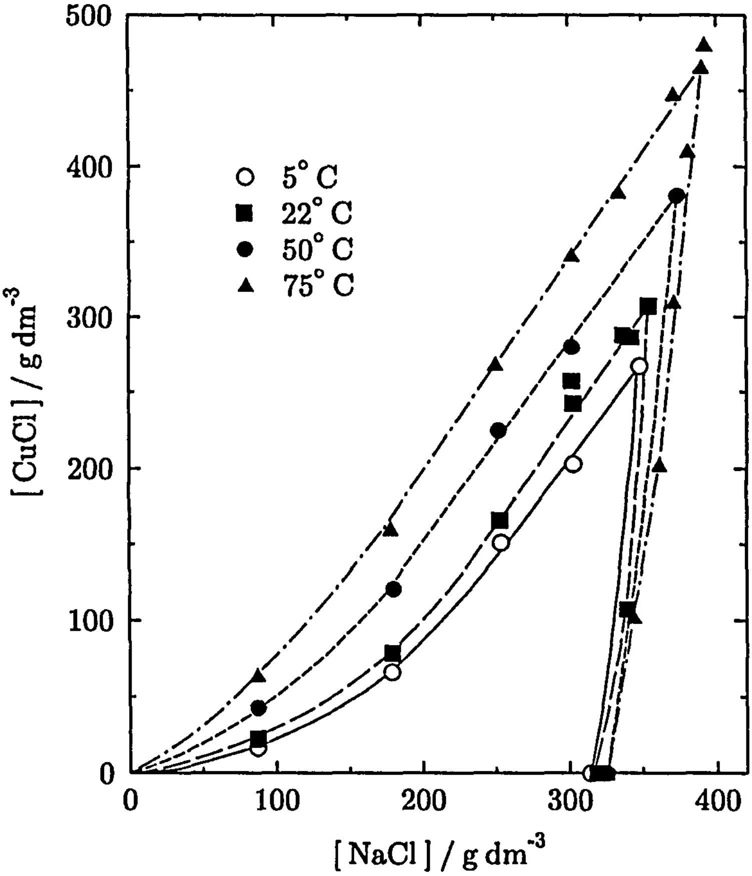
PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Phase Diagrams in the System CuCl–NaCl–(HCl)–H_2O

The authors presented their data in the form of a graph, reproduced below. Numerical results, in g dm^{-3}, were digitized from their graph and converted to mol dm^{-3}. These are listed on the following page.



continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Overall procedure not stated; the authors state that all solutions contained 8 to 11 g dm^{-3} HCl.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given; consistency about 5 per cent.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Peters, M. A.; Johnson, R. K; *U. S. Patent No. 4,101,315*, July 18, 1978.

EXPERIMENTAL VALUES:

(continued)

$t/°C$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_3{}^a}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	Solid Phase
5	1.50	0.26	0.17	CuCl
	3.06	0.26	0.67	CuCl
	4.34	0.26	1.52	CuCl
	5.18	0.26	2.05	CuCl
	5.96	0.26	2.70	CuCl + NaCl
	5.38	0.26	0.00	NaCl
22	1.50	0.26	0.22	CuCl
	3.07	0.26	0.79	CuCl
	4.33	0.26	1.67	CuCl
	5.19	0.26	2.45	CuCl
	5.17	0.26	2.60	CuCl
	5.77	0.26	2.91	CuCl
	5.86	0.26	2.90	CuCl
	6.06	0.26	3.10	CuCl + NaCl
	5.80	0.26	1.08	NaCl
	5.46	0.26	0.00	NaCl
50	1.50	0.26	0.43	CuCl
	3.08	0.26	1.22	CuCl
	4.31	0.26	2.27	CuCl
	5.17	0.26	2.83	CuCl
	6.40	0.26	3.85	CuCl + NaCl
	5.57	0.26	0.00	NaCl
75	1.50	0.26	0.65	CuCl
	3.05	0.26	1.62	CuCl
	4.29	0.26	2.72	CuCl
	5.18	0.26	3.45	CuCl
	5.73	0.26	3.87	CuCl
	6.36	0.26	4.52	CuCl
	6.68	0.26	4.71	CuCl + NaCl
	6.72	0.26	4.86	CuCl + NaCl
	6.52	0.26	4.04	NaCl
	6.35	0.26	3.04	NaCl
	6.18	0.26	2.04	NaCl
	5.88	0.26	1.04	NaCl
	5.57	0.26	0.00	NaCl

[a] This is the average of the concentration range of HCl given by the authors.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fontana, A.; van Muylder, J.; Winand, R.
Hydrometallurgy 1983, *11*, 297–314.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuCl in NaCl–HCl Solutions at 25°C[a]

$c_2 + c_3$ / mol dm^{-3}	c_2 / mol dm^{-3}	c_1 / mol dm^{-3}
0.90[b]	0.00	0.069
1.00	0.00	0.096
1.50	0.50	0.208
1.63[b]	0.63	0.233
2.00	1.00	0.351
2.50	1.50	0.490
2.62[b]	1.62	0.527
3.00	2.00	0.684
3.50	2.50	0.892
3.78[b]	2.78	1.021
4.00	3.00	1.174
4.50	3.50	1.556
4.64[b]	3.64	1.634

[a] Data read from the graph reproduced on the following page, which includes a phase diagram for the system.

[b] These data given as points on the graph; all others read from the smooth curve shown.

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The authors measured the spectra of both unsaturated and saturated solutions between 210 and 1000 nm at 298 K, for pH 0 and concentrations of (NaCl + HCl) from 0.9 to 5.0 mol dm^{-3}. These measurements were used to determine the concentrations of the complexes $CuCl_2^-$, $CuCl_3^{2-}$ and $Cu_2Cl_4^{2-}$, from which the total concentration of dissolved CuCl was obtained by summation.

SOURCE AND PURITY OF MATERIALS:

Used Riedel-de Haen "analytical quality" CuCl, NaCl and HCl — purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

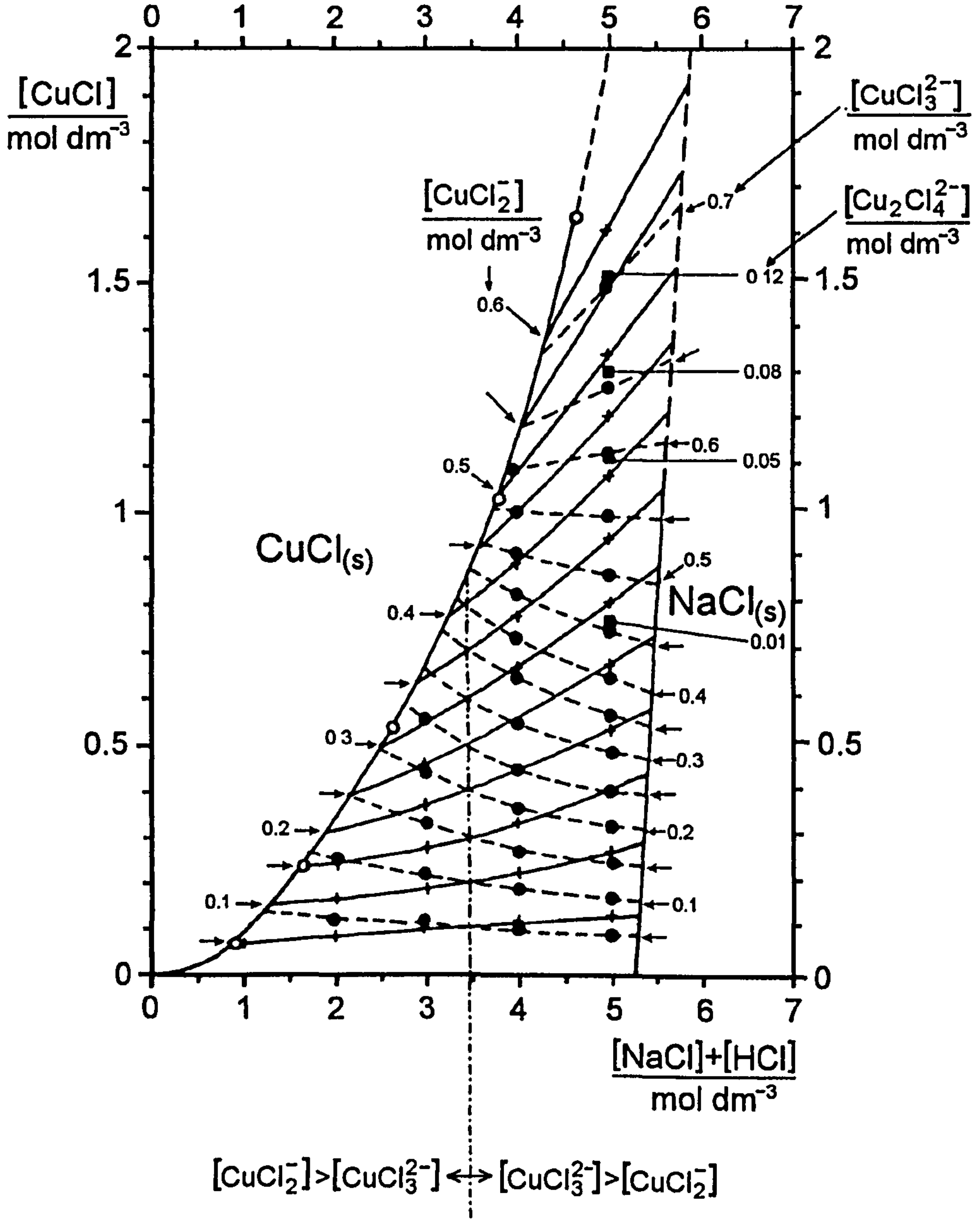
ORIGINAL MEASUREMENTS:

Fontana, A.; van Muylder, J.; Winand, R.
Hydrometallurgy 1983, *11*, 297-314.

EXPERIMENTAL VALUES:

(continued)

The graph reproduced below (Fig. 8) gives the actual results, including a phase diagram for the quaternary system.



Occurrence of complex species $CuCl_2^-$ (+), $CuCl_3^{2-}$ (•) and $Cu_2Cl_4^{2-}$ (▪) in CuCl-NaCl-HCl solutions at 25°C as a function of the copper and chloride concentrations (pH = 0).

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Ammonium Chloride; NH_4Cl;
[12125-02-9]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Iguchi, M.; Nakanishi, G.
J. Soc. Chem. Ind. Japan 1941, *44*,
S417–420.

VARIABLES:

Concentrations of NH_4Cl and HCl at 343 K

PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NH_4Cl at 70°C

$100w_2$	$100w_1$	$100w_4$	m_2/mol kg^{-1}[a]	m_1/mol kg^{-1}[a]
8.9	6.7	84.4	1.97	0.80
17.5	15.5	67.0	4.88	2.34
22.6	29.2	48.2	8.77	6.12
25.0	39.0	36.0	12.98	10.94
27.1	48.9	24.0	21.11	20.58
27.6	52.7	19.7	26.2	27.0
28.2	54.5	17.3	30.5	31.8
28.6	55.4	16.0	33.4	35.0

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Dissolved NH_4Cl in air-free water or HCl solution at 70±0.2°C, flushed apparatus with hydrogen, then nitrogen gas. Added purified CuCl and used gas stream to stir solution for two hours, then pipetted out portions of solution for analysis. Analyzed for CuCl by electrolysis, for NH_4Cl volumetrically (method not stated).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared from copper sulfate; sources and purity of materials not stated.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Ammonium Chloride; NH_4Cl; [12125-02-9]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Iguchi, M.; Nakanishi, G.
J. Soc. Chem. Ind. Japan 1941, *44*, S417–420.

EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in NH_4Cl–HCl Solutions at 70°C

$100w_3$[b]	$100w_2$	$100w_1$	$100(w_3+w_4)$	m_3/mol kg^{-1}[a]	m_2/mol kg^{-1}[a]	m_1/mol kg^{-1}[a]
0	25.0	39.0	36.0	0	12.98	10.94
1	24.6	41.7	33.7	0.28	13.78	12.63
2	23.9	40.9	35.2	0.56	12.95	11.98
3	23.4	41.6	35.0	0.85	12.89	12.38
4	23.4	42.3	34.3	1.14	13.29	12.98
7	23.0	44.4	32.6	2.06	14.18	14.79
10	21.8	44.8	33.4	3.05	13.56	15.05
0	27.6	52.7	19.7	0	26.19	27.02
1	27.9	54.9	17.2	0.28	30.63	32.57
2	27.3	54.9	17.8	0.56	29.26	31.79
3	26.4	52.9	20.7	0.85	24.58	26.61
4	26.7	54.6	18.7	1.14	27.80	30.72
7	24.6	53.2	22.2	2.06	22.27	26.03
10	22.6	51.6	25.8	3.05	18.20	22.45

[a] Calculated by compiler.

[b] Percentages of HCl were given as those of the original aqueous phase before addition of NH_4Cl (i.e., as representing the ratio of HCl to water). In calculation of molal concentrations it was assumed that the same relationship was true at the end of the experiment.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Hydrogen Chloride; HCl; [7647-01-01]
(4) Water; H_2O; [7732-18-15]

ORIGINAL MEASUREMENTS:

Poma, G.
Atti. Accad. Naz. Lincei 1909, *18-1*, 133-138.

VARIABLES:

Concentrations of $CuCl_2$ and HCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in $CuCl_2$–HCl Solutions at 25°C[a]

c_3/mol dm^{-3}	c_2/mol dm^{-3}	$[Cu^+]+[Cu^{2+}]$/mol dm^{-3}	c_1[b]/mol dm^{-3}
1	0	0.0862	0.0862
	0.1001	0.2017	0.1016
	0.2002	0.3256	0.1254
	0.3003	0.4452	0.1449
	0.4004	0.5707	0.1703
	0.5005	0.6924	0.1919
2	0	0.2365	0.2365
	0.0940	0.3528	0.2588
	0.1410	0.4160	0.2750
	0.1880	0.4766	0.2886
	0.2350	0.5385	0.3035
	0.2820	0.6038	0.3218
4	0	0.7704	0.7704
	0.0473	0.8357	0.7884
	0.0946	0.9044	0.8098
	0.1420	0.9701	0.8281
	0.1894	1.0370	0.8476
	0.2367	1.1040	0.8673
	0.3768	1.3040	0.9272
	0.4261	1.3700	0.9439
	0.4734	1.4380	0.9646

[a] The identical data are also presented in Ref. 1.

[b] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Maintained solid and solution in glass vessel in large thermostat at 25°C for several days. Determined total copper in solution electrolytically.

SOURCE AND PURITY OF MATERIALS:

CuCl from Kahlbaum, purity not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Poma, G. *Gazz. Chim. Ital.* 1910, *40I*, 193.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Edgar, G.; Cannon, L. S.
J. Am. Chem. Soc. 1922, *44*, 2842-2849.

VARIABLES:

Molalities of $CuCl_2$ and HCl at 298 and 313 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of $CuCl$ in $CuCl_2$-HCl Solutions[a]

$t/°C$	$\frac{10^3[Cu^{2+}]}{mol\ kg^{-1}}$	$\frac{10^3[H^+]}{mol\ kg^{-1}}$	$\frac{10^3[Cl^-]_{total}}{mol\ kg^{-1}}$	$\frac{10^3 m_1}{mol\ kg^{-1}}$
25	9.76	5.93	27.2	1.75
	8.13	8.67	30.4	1.85
	4.1	29.13	45.2	2.65
	1.34	70.26	95.2	5.58
	0.57	161.7	197.2	11.45
	0.48	206.3	252.4	15.03
	0.38	254.5	309.3	17.98
40	10.42	2.5	26.4	2.95
	8.14	3.88	29.5	3.14
	5.71	15.28	37.4	3.90
	3.17	30.79	52.4	4.99
	2.00	46.97	70.8	6.61
	1.24	71.22	100.4	8.90
	1.00	85.77	120.6	10.94
	0.83	182.8	201.7	17.25

[a] Nearly identical duplicate measurements averaged by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Dissolved $CuCl$ using equilibrium $CuCl_{(s)} + AgCl_{(s)} \rightleftharpoons Cu^{2+} + 2Cl^- + Ag_{(s)}$ in dilute aqueous HCl, approaching from both sides. Mixtures kept in dark amber bottles in thermostat at either 25 or 40°C (±0.02°C) to equilibrium.

Analyzed for cupric copper iodometrically; for cuprous copper by oxidation with acidic Fe(III) sulfate, followed by titration with $KMnO_4$. Analyzed for chloride by Volhard method.

SOURCE AND PURITY OF MATERIALS:

$CuCl$ — recrystallization of "imported material". $AgCl$ prepared by addition of HCl to C.P. $AgNO_3$. Silver electrolysis of $AgNO_3$.

No purities stated.

ESTIMATED ERROR:

Not stated. Duplicate results agree to 1% or less at 25°C, 4% or less at 40°C.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Copper(II) Chloride; $CuCl_2$; [7447-39-4] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. *Nauchn. Trud. Giredmeta* 1974, *62*, 52-56.
VARIABLES:	PREPARED BY:
Composition at 293 to 353 K	S. V. PETRENKO and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility Isotherm of the System $CuCl-CuCl_2-H_2O$[a]

$t/°C$	ρ_2/g dm^{-3}	ρ_1/g dm^{-3}	Solid Phase
20	593	21.6	CuCl
	621	37.3	CuCl
	652	51.0	CuCl

Solubility Isotherms of the System $CuCl-CuCl_2-HCl-H_2O$

$t/°C$	ρ_2/g dm^{-3}	ρ_3/g dm^{-3}	ρ_1/g dm^{-3}	Solid Phase
20	150	297.5	232	CuCl[b]
	170	273.0	208	CuCl[b]
	194	275.5	191	CuCl[b]
	199	258.9	206	CuCl[b]
	212	249.3	176	CuCl[b]

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility studied with saturation method. $CuCl_2$, CuCl, H_2O and HCl were loaded into the thermostated vessel and agitated for 3 hours. Amounts of salts were chosen so that both of them were in sediment.

Analyses of liquid phase were made by volume technique as described in Ref. 2.

SOURCE AND PURITY OF MATERIALS:

No information was given on the source and purity of materials.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kogan, V. B.; Ogorodnikov, S. K.; Kafarov, V. V. *Spravotchnik po Rastvorimosty Solevyh Sistem*, T. IIIL., Nauka, 1970.
2. Mel'nik, P. M.; Morgart, R. M.; Vatamanyuk, V. I.; Podlesnyak, O. Z. *Khim. Prom.* 1972, (7), 517.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Copper(II) Chloride; $CuCl_2$; [7447-39-4] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. *Nauchn. Trud. Giredmeta* 1974, *62*, 52–56.

EXPERIMENTAL VALUES:

(continued)

Solubility Isotherms of the System $CuCl–CuCl_2–HCl–H_2O$ [c]

t/°C	ρ_2/g dm^{-3}	ρ_3/g dm^{-3}	ρ_1/g dm^{-3}	Solid Phase
20	545.10	29.68	84.15	$CuCl+CuCl_2$
	480.97	65.96	97.85	$CuCl+CuCl_2$
	372.00	131.00	108.00	$CuCl+CuCl_2$
	367.05	164.10	96.00	$CuCl+CuCl_2$
	329.00	214.00	78.30	$CuCl+CuCl_2$
	310.00	307.00	144.00	$CuCl+CuCl_2$ [b]
40	571.00	51.12	88.07	$CuCl+CuCl_2$
	387.00	117.08	117.43	$CuCl+CuCl_2$
	428.00	146.76	137.00	$CuCl+CuCl_2$
	400.50	206.00	96.20	$CuCl+CuCl_2$
	525.00	214.00	178.50	$CuCl+CuCl_2$
60	548.00	41.23	187.88	$CuCl+CuCl_2$
	603.73	95.60	138.95	$CuCl+CuCl_2$
	525.69	122.90	138.95	$CuCl+CuCl_2$
	396.00	171.36	127.30	$CuCl+CuCl_2$
	505.00	189.00	109.70	$CuCl+CuCl_2$
80	672.00	42.87	129.16	$CuCl+CuCl_2$
	705.00	79.15	113.51	$CuCl+CuCl_2$
	477.00	113.00	132.00	$CuCl+CuCl_2$
	493.00	157.00	135.00	$CuCl+CuCl_2$

Notes: [a] The temperature for this set is not given in the paper; the compiler assumed 20°C.

[b] These solutions saturated with gaseous HCl.

[c] The authors also included some compositions in 'mass per cent', which are exactly 1/10th as large as the values in g dm^{-3}, indicating that they took the densities of all solutions to be 1 g cm^{-3}.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Novikov, G. I.; Voropaev, L. E.; Rud'ko, P. K.; Zharskii, I. M.
Zh. Neorg. Khim. 1979, *24*, 811–813;
Russ J. Inorg. Chem. (Engl. Transl.) 1979, *24*, 452–454.

VARIABLES:

Composition at 283 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubilities in the System $CuCl–CuCl_2–HCl–H_2O$ at 10°C

Composition of Solution				Composition of Solid			Solid
$100w_{3,\text{initial}}$	$100w_2$	$100w_1$	$100w_3$	$100w_2$	$100w_1$	$100w_3$	Phase
2.5	37.13	0.00	2.44	–	–	–	A
	36.95	3.54	2.42	74.38	0.87	0.59	A
	36.51	4.78	2.49	69.75	1.72	0.57	A
	36.18	5.47	2.46	43.40	37.56	0.62	A+B
	28.05	4.83	2.83	6.52	79.30	0.65	B
	16.19	3.39	3.10	4.15	81.23	0.79	B
	0.14	2.26	3.39	2.48	76.87	0.82	B
	0.00	0.66	3.62	–	–	–	B
10.0	26.29	0.00	9.18	–	–	–	A
	26.28	2.50	9.06	66.53	1.65	5.97	A
	25.46	5.91	8.52	70.13	1.28	1.79	A
	25.98	7.70	8.23	50.50	32.72	1.72	A+B
	21.21	7.37	9.23	7.05	70.58	3.06	B
	11.87	7.42	10.48	3.49	72.50	3.02	B
	0.00	7.20	11.07	–	–	–	B

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Water-salt mixtures agitated in glass ampoules sealed under nitrogen for 10–14 days at 10 ± 0.05°C.

Liquid and solid phases analyzed mercurimetrically for chloride (Ref. 1). Copper(I) and (II) determined by a "published method" (Ref. 2). Compositions of the solid phases determined by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

"Chemically pure" CuCl freed from basic salts by treatment with HCl.
"Analytical reagent" $CuCl_2$ recrystallized from weakly acidic solutions.
"Very special purity" hydrochloric acid used.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kreshkov, A. P. *Osnovy Analiticheskoi Khimii*, Izd. Khimiya, Moscow, 1970, Part II, p. 326.
2. Mel'nik, P. M.; Morgart, R. M.; Vatamanyuk, V. I. *Khim. Prom.* 1972, (7), 37.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Novikov, G. I.; Voropaev, L. E.; Rud'ko, P. K.; Zharskii, I. M.
Zh. Neorg. Khim. 1979, *24*, 811–813;
Russ J. Inorg. Chem. (Engl. Transl.) 1979, *24*, 452–454.

EXPERIMENTAL VALUES:

(continued)

Composition of Solution				Composition of Solid			Solid
$100w_{3,\text{initial}}$	$100w_2$	$100w_1$	$100w_3$	$100w_2$	$100w_1$	$100w_3$	Phase
14.5	19.64	0.00	13.57	–	–	–	A
	20.05	3.63	13.58	67.95	0.90	3.35	A
	19.62	5.98	13.14	64.62	1.55	3.32	A
	19.62	8.48	11.83	58.25	31.42	2.05	A+B
	15.24	9.22	13.27	4.95	75.00	2.35	B
	10.29	9.68	13.84	4.02	68.50	2.42	B
	6.25	10.58	14.48	1.45	88.05	2.25	B
	0.00	11.21	14.71	–	–	–	B
21.0	13.40	0.00	21.67	–	–	–	A
	13.15	3.21	21.47	70.07	0.85	5.67	A
	11.53	8.39	19.65	68.58	1.97	4.64	A
	10.49	13.81	19.96	23.60	52.25	3.75	A+B
	6.83	15.68	20.55	1.75	77.52	5.12	B
	3.74	16.55	20.42	1.07	75.07	5.83	B
	0.00	18.69	20.42	–	–	–	B

Solid phases: A: $CuCl_2{\cdot}2H_2O$; B: CuCl.

The authors also give equations for mass percentages of CuCl (1) and $CuCl_2$ (2) in saturated solutions. However, it has been found out (compiler) that the solubilities calculated from Eq. (1) are inaccurate, whereas those from Eq. (2) are completely wrong (even negative). Thus, the two equations are not reproduced here.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A.
Zh. Prikl. Khim. 1980, *53*, 2202-2206;
Russ. J. Appl. Chem. (Engl. Transl.) 1980, *53*, 1654-1658.

VARIABLES:

Composition at 293 to 353 K

PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Composition of Solutions Saturated with Both CuCl and $CuCl_2$

t/°C	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ_3/g dm^{-3}	ρ/g cm^{-3}
20	84.15	545.1	29.68	1.42
	97.85	480.97	65.96	1.41
	88.2	414.0	76.7	1.37
	108.0	372.0	131.5	1.39
	96.0	367.0	164.1	1.40
	78.28	351.9	187.7	1.40
	73.3	329.0	214.0	1.40
	97.85	332.1	277.02	1.45
	144.0	310.0	307.0	1.49
40	88.07	571.0	51.12	1.45
	137.0	428.0	146.76	1.45
	113.0	389.0	160.0	1.42
	96.2	400.5	206.0	1.45
	166.32	411.68	344.97	1.59
60	138.95	603.73	95.6	1.54
	139.05	525.69	122.9	1.51
	118.0	440.2	172.0	1.46
	205.49	438.24	303.28	1.61
80	129.16	672.0	42.87	1.54
	132.0	477.0	113.0	1.46
	146.78	378.48	216.1	1.48

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Thermostated solution in argon atmosphere with constant mixing for 3 hours.

"Analyzed solutions for Cu^{2+}, Cu^{+} and HCl by the familiar procedure" (Ref. 1).

Used chemical, X-ray and ESR methods for analysis of solids.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Pochtarev, A. N. *et al.* *Nauchn. Trud. Giredmeta* 1974, *62*, 52.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Copper(II) Chloride; $CuCl_2$; [7447-39-4] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. *Zh. Prikl. Khim.* 1980, *53*, 2202–2206; *Russ. J. Appl. Chem. (Engl. Transl.)* 1980, *53*, 1654–1658.

EXPERIMENTAL VALUES:

(continued)

Composition of Solutions Saturated with CuCl Only (t = 20°C)

ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ_3/g dm^{-3}	ρ/g cm^{-3}	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ_3/g dm^{-3}	ρ/g cm^{-3}
83.1	412.0	58.3	1.35	97.85	119.51	116.64	1.22
39.15	192.5	16.4	1.17	63.6	79.68	74.72	1.14
97.85	278.96	94.77	1.32	176.2	212.1	249.3	1.35
58.8	172.65	62.0	1.19	116.1	172.4	213.3	1.25
29.41	86.26	36.45	1.10	11.3	116.4	143.0	1.15
133.2	306.2	169.4	1.39	66.05	83.0	94.77	1.42
107.6	225.8	114.8	1.29	215.27	172.04	269.73	1.37
58.71	106.24	73.81	1.16	205.43	149.82	226.51	1.26
164.92	313.39	247.07	1.46	142.0	100.0	146.1	1.44
168.83	262.28	211.41	1.42	234.85	132.72	324.41	1.32
117.42	152.72	125.75	1.26	186.5	93.0	215.0	1.26
88.07	126.12	96.59	1.20	146.0	63.1	178.6	1.45
172.31	282.13	278.52	1.47	283.77	92.96	328.05	1.40
176.13	232.39	224.17	1.41	259.31	79.68	280.67	1.27
				171.2	46.47	196.8	1.21

Polytherm of Eutonic of Ternary System CuCl–$CuCl_2$–H_2O
(Solid Phases: CuCl and $CuCl_2$)

t/°C	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ/g cm^{-3}
19.0	87.4	661.9	1.48
40.5	97.85	796.54	1.57
68.5	58.71	810.1	1.55
80.0	83.17	813.43	1.58

Polytherm of Eutonic of Quaternary System CuCl–$CuCl_2$–HCl–H_2O
(Solid Phases: $CuCl_2$ and CuCl)

t/°C	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ_3/g dm^{-3}	ρ/g cm^{-3}
20	144.2	310.1	307.0	1.49
40	166.35	411.68	344.98	1.59
60	205.49	438.24	303.28	1.61
80	146.78	378.48	216.1	1.48

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J.
Afinidad 1987, *44 (408)*, 125–128.

VARIABLES:

Composition at 293 to 323 K

PREPARED BY:

E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCl in HCl–$HClO_4$ Solutions of I_c = 1.0, 1.5 and 2.0 mol dm^{-3} [a]

c_2 / mol dm^{-3}	c_1/mol dm^{-3} at t/°C of 20	30	40	50
2.0	0.2180	0.2540	0.3156	0.3656
1.8	0.1834	0.2160	0.2655	0.3139
1.6	0.1485	0.1800	0.2214	0.2639
1.5	0.1310	0.1652	0.1998	0.2480
1.4	0.1184	0.1464	0.1820	0.2180
1.2	0.0928	0.1179	0.1440	0.1775
1.0	0.0714	0.0912	0.1147	0.1398
0.8	0.0516	0.0666	0.0842	0.1057
0.6	0.0358	0.0458	0.0591	0.0741
0.4	0.0215	0.0276	0.0361	0.0447
0.2	0.0097	0.0122	0.0159	0.0209

[a] Ionic strength of individual experiments not specified.

Give the following equation which represents measured CuCl solubilities within 5%

$$c_{CuCl}/c_{HCl} = 331\exp(-2628\,K/T) + 1.36\exp(-1109\,K/T)c_{HCl}/\text{mol dm}^{-3} \qquad (4)$$

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All experiments were carried out in a 250 cm^3 reactor, surrounded by a glass jacket, through which water at the desired temperature was circulated from a thermostat. "High-purity" nitrogen was circulated through the solutions to prevent oxidation of Cu^+ and mechanical stirring was used to facilitate saturation of the solutions.

In the experiments, 10% HCl solutions were saturated with CuCl for 2 hours. After dilution with water and perchloric acid to achieve the desired acid concentrations, part of the dissolved CuCl precipitated out. Solutions were analyzed by the method of Hatch and Estes (Ref. 1) in which the Cu(I) was oxidized to Cu(II) using excess $FeCl_3$ solution and the Fe(II) formed titrated with standard $K_2Cr_2O_7$ solution using barium diphenylaminosulfonate as an indicator.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Hatch, L. F.; Estes, R. R.
Ind. Eng. Chem. Anal. Ed. 1946, *18*, 136.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J.
Afinidad 1987, *44 (408)*, 125-128.

EXPERIMENTAL VALUES:

(continued)

The authors also present graphs depicting CuCl solubilities in HCl–$HClO_4$–$CuCl_2$ solutions:

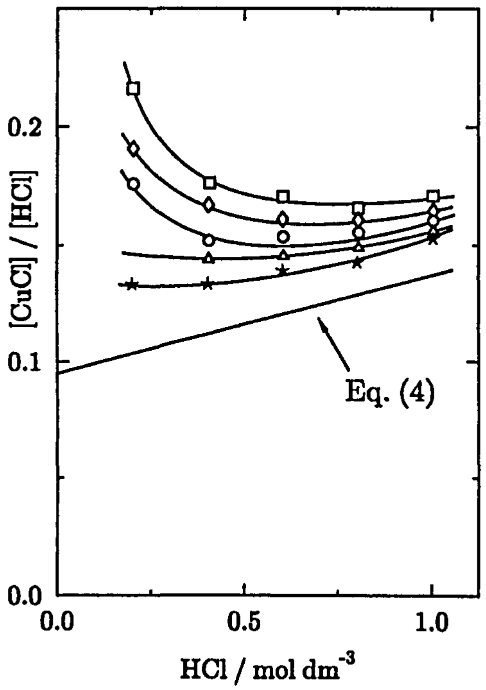


Figure 2

$[H^+]=1.0$ mol dm^{-3}

$t = 50$°C

$$\left.\begin{array}{ll}\square & 0.10\\ \diamond & 0.08\\ \circ & 0.06\\ \triangle & 0.04\\ \star & 0.02\end{array}\right\}\frac{[\mathrm{CuCl_2}]}{\mathrm{mol\,dm^{-3}}}$$

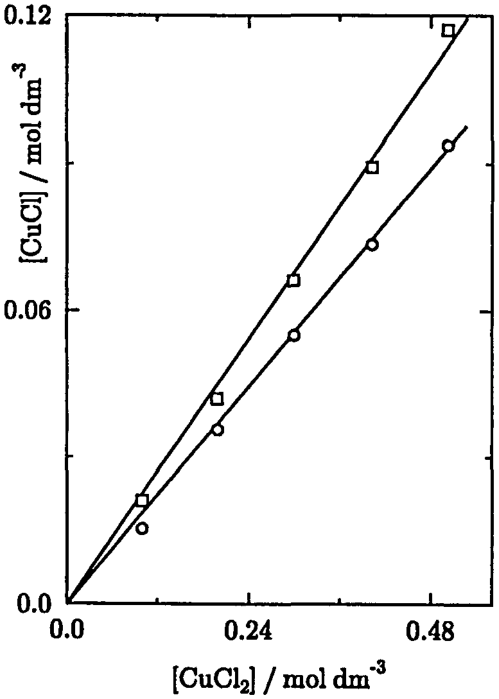


Figure 3

$2\,[\mathrm{CuCl_2}]+[\mathrm{HClO_4}] =$ 1.0 mol dm^{-3}

$$\left.\begin{array}{ll}\square & 50\\ \circ & 40\end{array}\right\} t/^\circ\mathrm{C}$$

The following equation represents CuCl solubilities in HCl–$CuCl_2$ solutions of ionic strength 1.0 to 2.0 mol dm^{-3} in the temperature range of 20 to 50°C within 10%:

$$\begin{aligned} c_{\mathrm{CuCl}}/\mathrm{mol\,dm^{-3}} &= 331\exp(-2628\,\mathrm{K}/T)c_{\mathrm{HCl}}/\mathrm{mol\,dm^{-3}}\\ &\quad +1.36\exp(-1109\,\mathrm{K}/T)(c_{\mathrm{HCl}}/\mathrm{mol\,dm^{-3}})^2\\ &\quad +119.6\exp(-2008\,\mathrm{K}/T)c_{\mathrm{CuCl_2}}/\mathrm{mol\,dm^{-3}} \end{aligned}$$

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Sulfate; Na_2SO_4; [7757-82-6]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G.
Tr. Mosk. Khim.-Tekh. Inst. 1964, *47*, 111–114.

VARIABLES:

Composition at 293 to 363 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous NaCl

$t/°C$	$100w_2$	m_2/mol kg^{-1} [a]	$100w_1$	m_1/mol kg^{-1} [a]
20	3.96	0.708	0.41	0.043
	4.04	0.724	0.45	0.048
	15.10	3.25	5.44	0.691
	15.30	3.30	5.48	0.699
30	5.35	0.977	0.95	0.102
	5.40	0.988	1.07	0.116
	10.00	1.958	2.60	0.300
	10.12	1.984	2.62	0.303
	15.80	3.47	6.24	0.808
	16.72	3.71	6.24	0.818
	22.00	5.94	14.61	2.328
	22.60	6.16	14.62	2.352
	22.60	6.16	14.66	2.360
	23.00	6.31	14.64	2.371
	23.30	6.58	16.11	2.685
	24.60	7.37	18.31	3.239
50	5.70	1.051	1.52	0.165
	5.70	1.056	1.91	0.209
	10.00	1.993	4.15	0.488
	10.20	2.029	3.78	0.444
	15.70	3.51	7.85	1.037
	15.70	3.52	7.96	1.053
	22.70	6.45	17.09	2.866
	23.00	6.54	16.80	2.818

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess solid CuCl to each solution in a glass vessel inside a water thermostat. Mechanical stirring was used and oxygen-free nitrogen was bubbled through the solution. After 2 to 3 hours samples of the liquid phase were removed for analysis (the methods used for analysis were not given).

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated. Consistency was 0.1 to 0.3 mass per cent (0.01 to 0.03 mol kg^{-1}).

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Sulfate; Na_2SO_4; [7757-82-6]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G. *Tr. Mosk. Khim.-Tekh. Inst.* 1964, *47*, 111-114.

EXPERIMENTAL VALUES:

(continued)

t/°C	$100w_2$	m_2/mol kg^{-1} [a]	$100w_1$	m_1/mol kg^{-1} [a]
70	5.64	1.050	2.45	0.269
	5.65	1.052	2.46	0.270
	10.10	2.040	5.20	0.620
	10.50	2.140	5.55	0.668
	15.30	3.51	10.10	1.367
	15.55	3.56	9.77	1.321
	15.58	3.57	9.77	1.322
	21.60	6.28	19.57	3.36
	21.72	6.33	19.59	3.37
90	5.25	0.990	3.13	0.345
	5.27	0.984	3.08	0.339
	9.58	1.979	7.61	0.928
	9.75	2.003	6.98	0.846
	14.65	3.44	12.53	1.738
	14.80	3.48	12.54	1.743
	20.70	6.19	22.10	3.90
	20.90	6.27	22.05	3.90

Solubility of CuCl in NaCl–$CuCl_2$ Solutions at 80°C

$100w_2$	m_2/mol kg^{-1} [a]	$100w_4$	m_4/mol kg^{-1} [a]	$100w_1$	m_1/mol kg^{-1} [a]
5.70	1.051	-	-	1.52	0.165
4.96	0.915	0.561	0.043	1.74	0.189
4.80	0.882	0.572	0.043	1.55	0.168
15.70	3.51	-	-	7.85	1.037
15.60	3.48	0.131	0.012	7.52	0.989
15.55	3.48	0.510	0.047	7.58	1.002
15.20	3.40	0.517	0.048	7.76	1.024
22.70	6.45	-	-	17.09	2.866
22.10	6.36	1.830	0.217	16.60	2.818
21.20	6.02	1.845	0.216	16.70	2.799

continued...

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Sulfate; Na_2SO_4; [7757-82-6]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G. *Tr. Mosk. Khim.-Tekh. Inst.* 1964, *47*, 111-114.

EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in NaCl–Na_2SO_4 Solutions at 20°C

$100w_2$	m_2/mol kg^{-1} [a]	$100w_3$	m_3/mol kg^{-1} [a]	$100w_1$	m_1/mol kg^{-1} [a]
4.04	0.723	–	–	0.45	0.048
3.96	0.708	–	–	0.41	0.043
3.84	0.694	1.03	0.077	0.47	0.050
3.85	0.696	1.03	0.077	0.47	0.050
3.85	0.703	2.01	0.151	0.44	0.047
3.85	0.704	2.18	0.164	0.44	0.048
3.73	0.687	3.00	0.228	0.44	0.048
3.78	0.697	2.95	0.224	0.45	0.049
3.65	0.685	4.71	0.364	0.44	0.049
3.76	0.706	4.67	0.361	0.42	0.047
15.10	3.25	–	–	5.44	0.691
15.30	3.30	–	–	5.28	0.671
14.80	3.27	2.72	0.248	5.16	0.674
14.60	3.22	2.72	0.247	5.15	0.671

[a] Calculated by compiler.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(3) Sodium Chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A.
Zh. Prikl. Khim. 1978, *51*, 1015–1019;
Russ. J. Appl. Chem. (Engl. Transl.) 1978, *51*, 977–980.

VARIABLES:

Composition at 299.7 K

PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Composition of Solutions Saturated with $CuCl_{(s)}$ and $CuCl_{2(s)}$ at 26.5°C

ρ_3/g dm^{-3}	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ/g cm^{-3}
60.4	88.07	609.88	1.49
110.7	127.2	556.78	1.51
158.8	146.78	531.19	1.54
190.1	132.1	557.77	1.56
177.4	146.7	537.83	1.55
169.4	152.1	497.99	1.54
190.16	149.22	514.59	1.55
201.08	149.2	554.43	1.58[a]

Composition of Solutions Saturated with $CuCl_{(s)}$ and $NaCl_{(s)}$ at 26.5°C

ρ_3/g dm^{-3}	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ/g cm^{-3}
309.5	209.52	126.15	1.42
200.0	220.17	252.32	1.43
190.6	181.03	312.08	1.43
281.5	192.31	225.6	1.45
223.45	166.34	239.04	1.41
308.3	215.27	182.6	1.45
301.0	210.38	199.2	1.45
337.0	249.1	181.2	1.5
181.55	185.9	305.44	1.43
239.9	215.27	79.67	1.34

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal saturation at constant temperature under argon. Composition of solid phase determined by ESR method and by X-ray diffraction.

Method of analysis of solutions not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Copper(II) Chloride; $CuCl_2$; [7447-39-4] (3) Sodium Chloride; NaCl; [7647-14-5] (4) Water; H_2O; [7732-18-5]	Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. *Zh. Prikl. Khim.* 1978, *51*, 1015–1019; *Russ. J. Appl. Chem. (Engl. Transl.)* 1978, *51*, 977–980.

EXPERIMENTAL VALUES:

(continued)

Composition of Solutions Saturated with $CuCl_{(s)}$ at 26.5°C

Section	app. ρ_3/ρ_2	ρ_3/g dm^{-3}	ρ_1/g dm^{-3}	ρ_2/g dm^{-3}	ρ/g cm^{-3}
1	2.	46.05	9.785	23.24	1.06
		100.06	34.25	49.80	1.13
		160.9	77.06	81.34	1.21
		200.04	124.76	99.6	1.27
		203.7	146.78	112.88	1.29
2	1.	41.55	14.68	40.7	1.07
		90.93	44.03	88.9	1.15
		144.12	90.5	148.0	1.25
		190.33	139.44	189.24	1.34
		203.95	185.92	244.03	1.41
3	0.5	39.87	14.7	76.36	1.08
		85.15	62.38	169.32	1.4
		124.0	111.31	245.68	1.3
		155.98	154.12	313.74	1.4
		190.1	156.56	418.32	1.49
4	0.33	23.93	19.57	66.40	1.07
		50.05	44.03	139.44	1.16
		91.01	92.96	272.24	1.29
		104.03	117.42	318.72	1.34
		151.02	136.99	438.24	1.46
5	0.17	14.09	10.03	126.15	1.09
		34.59	59.50	219.12	1.2
		52.35	102.74	318.72	1.3
		69.00	141.88	438.24	1.43
		83.3	117.43	498.00	1.39

[a] This solution at equilibrium with $CuCl_{(s)}$, $CuCl_{2(s)}$ and $NaCl_{(s)}$.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Potassium Chloride; KCl; [7447-40-7]
(3) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Bodländer, G.; Storbeck, O.
Z. Anorg. Chem. 1902, *31*, 1-41.

VARIABLES:

Concentration of KCl at 289 to 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous KCl

T/K	$10^3 c_2$/mol dm^{-3}	$10^3 [Cu^{2+}]$/mol dm^{-3}	$10^3 c_1$/mol dm^{-3}
293	0	2.222	0.629
292	1	1.901	0.484
292	2	1.571	0.589
292	2.5	1.421	0.534
292	3	1.523	0.460
289	5	1.008	0.514
291	10	0.475	0.761
293	15	0.322	1.022
292	20	0.324	1.122
292	30	0.1308	1.630
291	50	0.1088	2.302
289	100	0	4.702
289	200	0	9.485
292	1000	0	97.0
289	2000	0	384.0

Note: Cu^{2+} (and metallic copper) formed by disproportionation of Cu^+ at low chloride concentrations.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook air-free KCl solutions with CuCl for 6-8 hours in CO_2 atmosphere.

Analyzed for chloride gravimetrically as AgCl, for total copper present in solution electrolytically. The amount present as Cu^{2+} determined by iodometric titration using thiosulfate. The dissolved Cu^+ was then taken by difference.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(7) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J.
An. Quim. 1985, *A81*, 121–128.

VARIABLES:

Composition at 293 to 323 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Mixtures

Results are presented in the form of graphs, reproduced on the following pages, which give either the solubility, *S*, or the ratio of solubility to concentration, *S/C*, where *C* is the concentration of chloride ion supplied by the soluble chloride(s) used, with both *S* and *C* given in mol dm^{-3}. The content of each figure is given below.

Fig. 1.	Solubility in aqueous HCl at 298 K *vs.* concentration of HCl.
Fig. 4.	*S/C* *vs.* chloride concentration for equimolar NaCl–HCl mixtures of ionic strength 2 mol dm^{-3}, at 293, 303, 313 and 323 K.
Fig. 6.	*S/C* *vs.* chloride concentration for four NaCl–HCl mixtures of ionic strength 2 mol dm^{-3} at 303 K.
Fig. 7.	*S/C* *vs.* chloride concentration for equimolar NaCl–HCl mixtures of 4 different ionic strengths at 303 K.
Fig. 10.	*S/C* *vs.* total chloride concentration for four $CuCl_2$–HCl mixtures of ionic strength 2 mol dm^{-3} at 303 K.
Fig. 11.	*S/C* *vs.* HCl concentration along for the same mixtures as in Fig. 10.

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All experiments were carried out in a 250 cm^3 reactor, surrounded by a glass jacket, through which water at the desired temperature was circulated from a thermostat. "High-purity" nitrogen was circulated through the solutions to prevent oxidation of Cu^+ and mechanical stirring was used to facilitate saturation of the solutions.

For each of 13 series of measurements, 200 cm^3 portions of aqueous solution containing either chlorides or chosen mixtures of chloride and perchlorate of the same ionic strength were saturated with CuCl. Solutions were analyzed by the method of Hatch and Estes (Ref. 1) in which the Cu(I) was oxidized to Cu(II) using excess $FeCl_3$ solution and the Fe(II) formed titrated with standard $K_2Cr_2O_7$ solution using barium diphenylaminosulfonate as an indicator.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Hatch, L. F.; Estes, R. R. *Ind. Eng. Chem. Anal. Ed.* 1946, *18*, 136.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(7) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J.
An. Quim. 1985, *A81*, 121–128.

EXPERIMENTAL VALUES:

(continued)

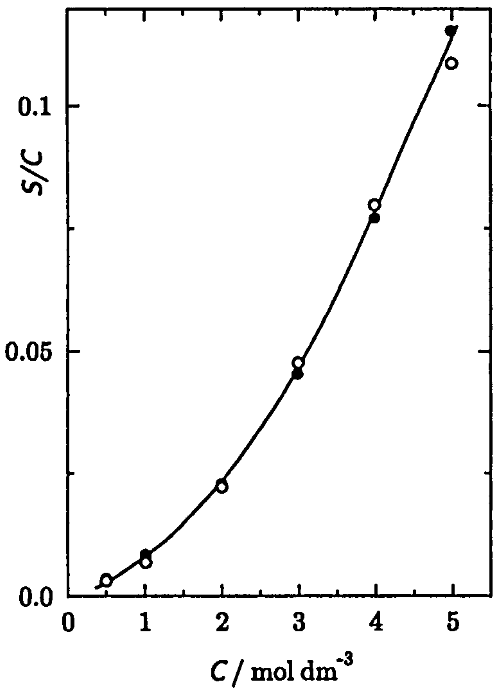


Figure 1

Solubility in HCl Solutions

$t = 25°C$

- ● Hikita *et al.*(1973)
- ○ This work

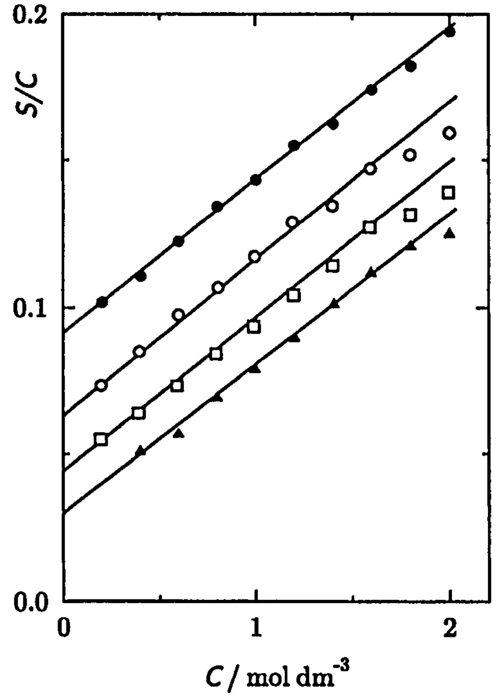


Figure 4

$I = 2$ mol dm^{-3}

$[Na^+]/[H^+]=1$

▲ 20
□ 30
○ 40
● 50
} t/°C

continued ...

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Sodium Perchlorate; $NaClO_4$; [7601-89-0] (4) Copper(II) Chloride; $CuCl_2$; [7447-39-4] (5) Hydrogen Chloride; HCl; [7647-01-0] (6) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (7) Water; H_2O; [7732-18-5]	Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J. *An. Quim.* 1985, *A81*, 121-128.

EXPERIMENTAL VALUES:

(continued)

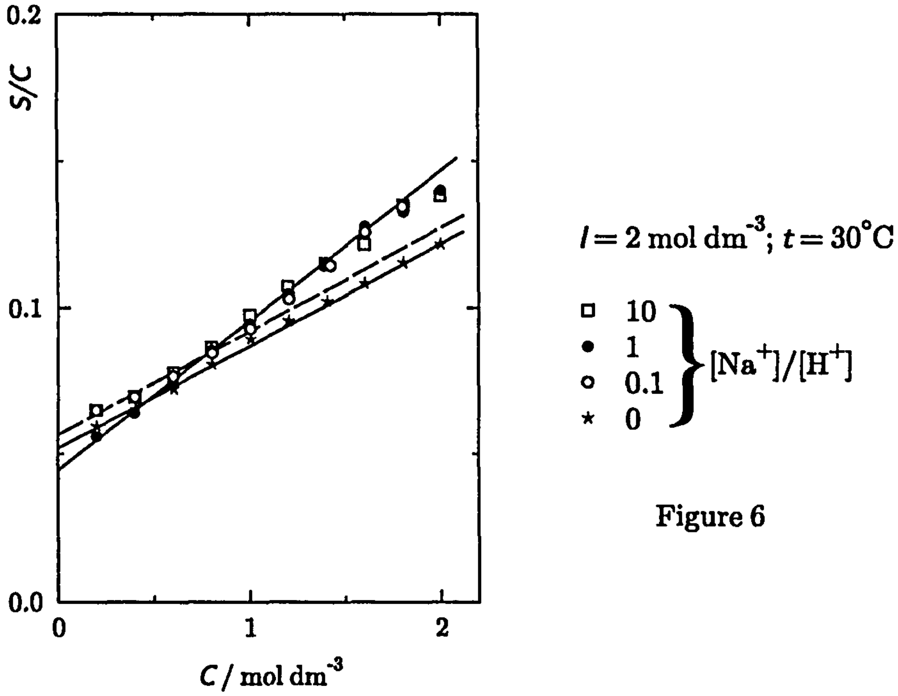


Figure 6

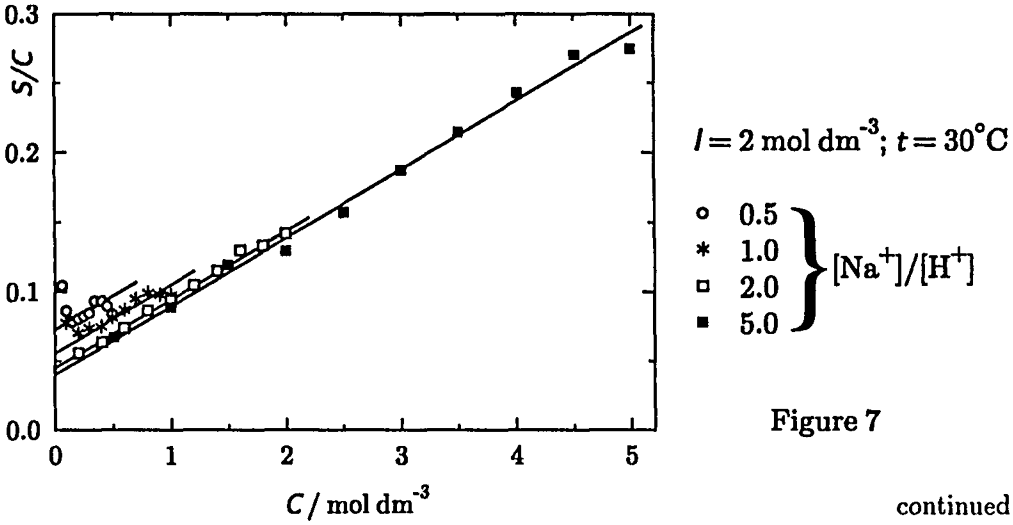


Figure 7

continued...

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(7) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J.
An. Quim. 1985, *A81*, 121–128.

EXPERIMENTAL VALUES:

(continued)

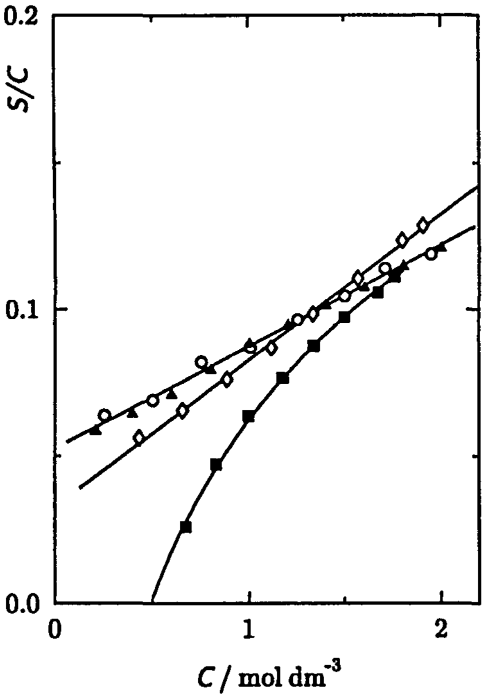


Figure 10

$I = 2$ mol dm^{-3}; $t = 30$°C

$[Na^+]/[H^+]=0$

○ 0.00
▲ 0.05
◇ 0.10
■ 0.25
} $[Cu(II)]$ / mol dm^{-3}

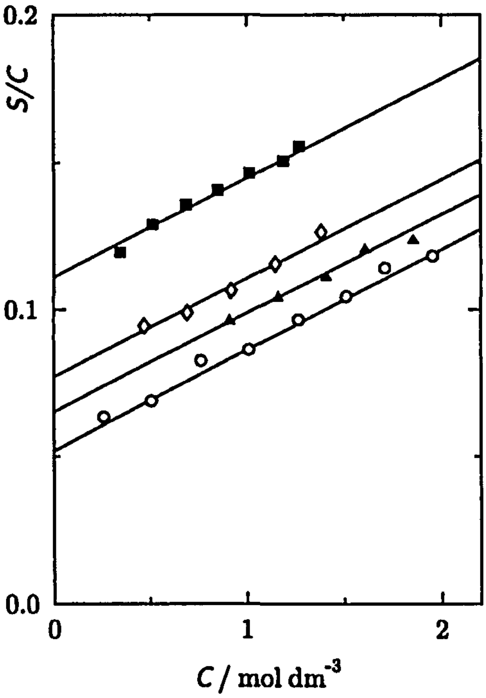


Figure 11

$I = 2$ mol dm^{-3}; $t = 30$°C

$[Na^+]/[H^+]=0$

■ 0.25
◇ 0.10
▲ 0.05
○ 0.00
} $[Cu(II)]$ / mol dm^{-3}

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-18-5]
(3) Iron(II) Chloride; $FeCl_2$; [7758-94-3]
(4) Zinc Chloride; $ZnCl_2$; [7646-85-7]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Berger, J. M.; Winand, R.
Hydrometallurgy 1984, *12 (1)*, 61-81.

VARIABLES:

Composition at 298, 303 and 363 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubilities in the System $CuCl-NaCl-FeCl_2-ZnCl_2-HCl-H_2O$

t/°C	Solid Phase	m_2 / mol kg^{-1}	m_5 / mol kg^{-1}	m_3 / mol kg^{-1}	m_4 / mol kg^{-1}	m_1 / mol kg^{-1}	ρ / kg m^{-3}
25	CuCl	0.18	0.74			0.07	1022
	CuCl	1.03	0.64			0.25	1072
	CuCl	2.57	0.21			0.57	1142
	CuCl	4.18	0.09			1.15	1214
	CuCl	5.37	0.07			1.92	1285
30	CuCl	4.76	0.11			1.46	1239
	CuCl	4.76	0.11		0.50	1.09	1253
	CuCl	4.76	0.11	0.35	0.50	1.30	1294
	CuCl	4.76	0.11	0.35		1.70	1285
	CuCl	4.76	0.11	0.50		1.78	1304
	CuCl	4.76	0.11	0.70		1.89	1322
	CuCl	4.76	0.11	1.25		2.44	1397
	CuCl	4.76	0.11	1.50		2.99	1447
	CuCl	4.76	0.11	1.75		3.27	1476
30	NaCl	4.86	0.11	1.75		3.27	1476
	NaCl	5.24	0.11	1.50		2.99	1454
	NaCl	5.76	0.72	0.85		2.49	1400
	NaCl	4.76	0.11	1.50		1.81	1380
	NaCl	4.76	0.11	0.99		0.51	1273
	NaCl	4.76	0.11	0.79		0	1225

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Brine solutions prepared by weight placed in 1 dm^3 thermostat at specified temperature 0.5°C. Weighed portion of copper salt added until small crystal (*app.* 10^{-5} kg) failed to dissolve.

SOURCE AND PURITY OF MATERIALS:

Analytical regents of Riedel-de Haen trade mark; purity not specified.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-18-5]
(3) Iron(II) Chloride; $FeCl_2$; [7758-94-3]
(4) Zinc Chloride; $ZnCl_2$; [7646-85-7]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Berger, J. M.; Winand, R.
Hydrometallurgy 1984, *12 (1)*, 61–81.

EXPERIMENTAL VALUES:

(continued)

$t/°C$	Solid Phase	$\frac{m_2}{\text{mol kg}^{-1}}$	$\frac{m_5}{\text{mol kg}^{-1}}$	$\frac{m_3}{\text{mol kg}^{-1}}$	$\frac{m_4}{\text{mol kg}^{-1}}$	$\frac{m_1}{\text{mol kg}^{-1}}$	$\frac{\rho}{\text{kg m}^{-3}}$
30	CuCl	0.58	0.15		0.64	0.16	1097
	CuCl	3.26	0.15		0.64	0.60	1196
	CuCl	5.06	0.15		0.64	1.28	1283
	CuCl	5.93	0.30		0.64	1.70	1326
	CuCl	5.88	0.45	0.48	0.63	1.98	1369
	CuCl	5.70	0.44	0.94	0.61	2.36	1424
	CuCl	5.99	0.15	1.13	0.64	2.68	1454
30	NaCl	5.99	0.15	1.13	0.64	2.60	1449
	NaCl	5.99	0.15	0.99	0.64	1.78	
	NaCl	5.99	0.15	0.49	0.64	0.61	
	NaCl	6.08	0.15		0.64	0	1236
90	CuCl	5.03	0.11		0.53	2.36	1290
	CuCl	4.76	0.11		0.50	2.13	1266
	CuCl	4.76	0.11	0.35	0.50	2.54	1310
	CuCl	4.87	0.27	0.30	0.51	2.59	1322
	CuCl	4.76	0.11	0.70	0.50	2.77	1350
	CuCl	4.73	0.29	0.68	0.49	2.98	1365
	CuCl	4.56	0.30	1.13	0.48	3.31	1395
	CuCl	4.34	0.32	1.71	0.45	3.76	1441

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Iron(II) Chloride; $FeCl_2$; [7758-94-3]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Winter, D. G.; Covington, J. W.;
Muir, D. M.
Chloride Electrometall., Proc. Symp. 1982, 167–188.

VARIABLES:

Composition at 293 to 343 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Mixtures at 50°C[a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_4/mol dm^{-3}	c_5/mol dm^{-3}	c_1/mol dm^{-3}
			4.0	1.90
1.0			4.0	1.62
1.0			4.0	1.61
1.5			4.0	1.80
2.0			3.0	1.75
2.0	1.0		1.0	1.53
2.0	1.0		2.0	1.96
2.0	1.0	1.0	1.0	1.76
2.0	1.0	1.0	2.0	1.99
3.0			2.0	1.86
3.0			2.0	1.83
3.0	1.0			1.59
3.0	1.0		1.0	2.14
3.0	1.0		2.0	2.40
3.0	1.0			1.59
3.0	2.0			2.40
4.0			0.5	1.62
4.0			1.0	1.92
4.0			1.0	1.93
4.0			2.0	1.83
4.0	1.0			2.16
4.0	2.0			2.84
5.0				2.30
5.0	1.0			3.00

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Placed 300 cm^3 of test solution in 500 cm^3 glass vessel inside waterbath controlled to 0.1°C. Bubbled oxygen-free nitrogen through solution and stirred with glass paddle. When temperature stabilized, added excess CuCl and allowed to equilibrate for 45 minutes, then withdrew samples of liquid for analysis.

Analysis performed using ferric ammonium sulfate solution to oxidize Cu(I) to Cu(II), then titrated the Fe(II) formed with standard ceric sulfate solution.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Iron(II) Chloride; $FeCl_2$; [7758-94-3]
(4) Copper(II) Chloride; $CuCl_2$; [7447-39-4]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Water; H_2O; [7732-18-5]

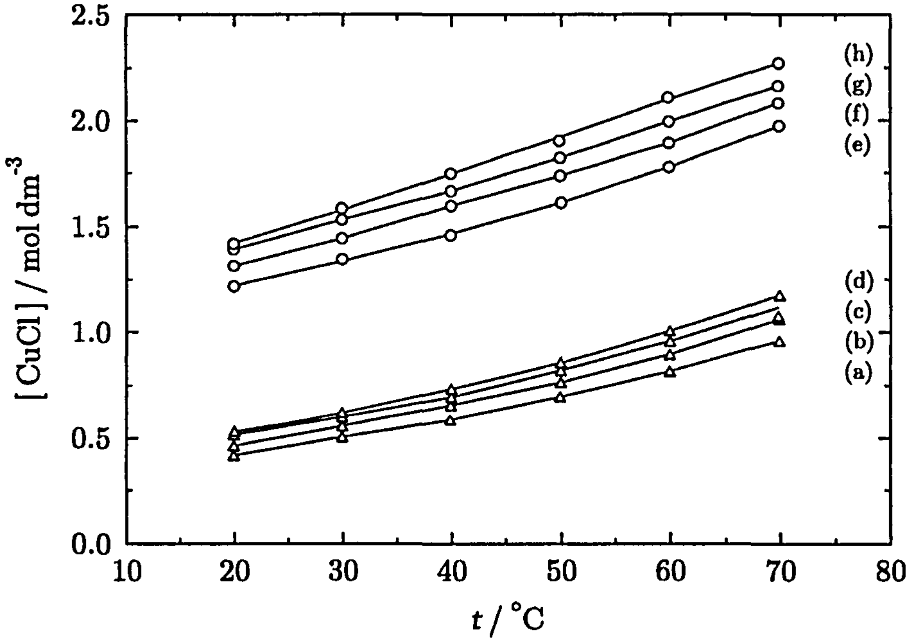
ORIGINAL MEASUREMENTS:

Winter, D. G.; Covington, J. W.;
Muir, D. M.
Chloride Electrometall., Proc. Symp. 1982,
167–188.

EXPERIMENTAL VALUES:

(continued)

The authors also give graphical presentation of the solubility of CuCl in aqueous HCl–NaCl mixtures from 293 to 363 K (their Figure 1). This figure is reproduced below.



(a) 3.0 mol dm^{-3} HCl
(b) 2.0 mol dm^{-3} HCl + 1.0 mol dm^{-3} NaCl
(c) 1.0 mol dm^{-3} HCl + 2.0 mol dm^{-3} NaCl
(d) 3.0 mol dm^{-3} NaCl
(e) 4.0 mol dm^{-3} HCl + 1.0 mol dm^{-3} NaCl
(f) 3.0 mol dm^{-3} HCl + 2.0 mol dm^{-3} NaCl
(g) 2.0 mol dm^{-3} HCl + 3.0 mol dm^{-3} NaCl
(h) 1.0 mol dm^{-3} HCl + 4.0 mol dm^{-3} NaCl

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[a] The numerical data are gathered together from Tables III and IV of the original publication.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride, HCl; [7647-01-0]
(3) Allyl Alcohol; C_3H_6O; [107-18-6]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kepner, R. E.; Andrews, L. J.
J. Org. Chem. 1948, *13*, 208–213.

VARIABLES:

Concentrations of HCl and allyl alcohol at 298 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Allyl Alcohol at 25°C[a,b]

c_3/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.0145	0.0	0.00778
0.0290	0.0	0.0137
0.0580	0.0	0.0256
0.0724	0.0	0.0300
0.1086	0.0	0.0459
0.0000	0.0	0.00238
0.0132	0.0094	0.00782
0.0264	0.0094	0.0125
0.0527	0.0094	0.0246
0.0658	0.0094	0.0298
0.0986	0.0094	0.0438
0.0000	0.0094	0.00098
0.9923	0.0094	0.406
0.5954	0.0094	0.234
0.3969	0.0094	0.153
0.0000	0.0094	0.0022

[a] The authors include an additional column labelled "Cu^+ corrected", in which the solubility recorded for zero allyl alcohol concentration is subtracted from the values listed here.

[b] The authors report evidence of hydrolysis of CuCl in the solutions which did not contain any HCl.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. After 4 hours shaking at 25°C, removed solution for volumetric analysis of cuprous content by titration against dichromate using barium diphenylaminosulfonate indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

Prepared CuCl according to method of Keller and Wycoff (Ref. 2). Commercial allyl alcohol refractionated before use. Source of HCl and purity of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Hatch, L. F.; Estes, R. R. *J. Am. Chem. Soc.* 1945, *67*, 1730.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(5) Allyl Alcohol; C_3H_6O; [107-18-6]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.
J. Am. Chem. Soc. 1949, *71*, 1723–1724.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Allyl Alcohol at 25°C

c_5/mol dm^{-3}	c_3/mol dm^{-3}	c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.0809	0	0.10	0	0.0393
0.0400	0	0.10	0	0.0226
0.0300	0	0.10	0	0.0175
0.0200	0	0.10	0	0.0128
0.0101	0	0.10	0	0.0072
0.0809	0.00938	0.0906	0	0.0378
0.0404	0.00938	0.0906	0	0.0207
0.0202	0.00938	0.0906	0	0.0117
0.0101	0.00938	0.0906	0	0.0065
0.0400	0.0938	0.0062	0	0.0196
0.0300	0.0938	0.0062	0	0.0160
0.0200	0.0938	0.0062	0	0.0125
0.0809	0	0.010	0.090	0.0394
0.0202	0	0.010	0.090	0.0131

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength using $HClO_4$ and $NaClO_4$ as needed. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator.

SOURCE AND PURITY OF MATERIALS:

Prepared CuCl according to method of Keller and Wycoff (Ref. 1). Commercial allyl alcohol refractionated before use. Source of HCl and purity of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Crotyl Alcohol; C_4H_8O; [6117-91-5]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 3906-3909.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Crotyl Alcohol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.142	0.0	0.10	0.0268
0.142	0.0102	0.0898	0.0237
0.142	0.102	0.0	0.0220
0.106	0.0102	0.0898	0.0187
0.106	0.102	0.0	0.0174
0.0708	0.102	0.0	0.0139
0.0688	0.0	0.10	0.0166
0.0342	0.0	0.10	0.0102

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Crotyl alcohol was prepared from crotonaldehyde. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) β-Methylallyl Alcohol; C_4H_8O; [513-42-8]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 3906–3909.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous β-Methylallyl Alcohol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0708	0.0	0.10	0.0178
0.0708	0.0101	0.0899	0.0150
0.0708	0.101	0.0	0.0158
0.0472	0.0	0.10	0.0132
0.0472	0.0101	0.0899	0.0108
0.0472	0.101	0.0	0.0121
0.0236	0.0	0.10	0.0081
0.0236	0.101	0.0	0.0096

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). β-Methylallyl alcohol was supplied by the Shell Chemical Corporation. It was dried and fractionated before use. Source of other and purity of materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (4) Methylvinylcarbinol; C_4H_8O; [598-32-3] (5) Water; H_2O; [7732-18-5]	Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc.* 1949, *71*, 3906-3909.
VARIABLES:	PREPARED BY:
Composition at 298 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Methylvinylcarbinol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0728	0.0	0.10	0.0306
0.0728	0.10	0.0	0.0258
0.0546	0.0	0.10	0.0246
0.0546	0.10	0.0	0.0211
0.0364	0.0	0.10	0.0180
0.0364	0.01	0.09	0.0162
0.0364	0.10	0.0	0.0160
0.0182	0.0	0.10	0.0103

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Methylvinylcarbinol prepared by hydrolysis of butenyl chloride. Source and purity of materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Ethylvinylcarbinol; $C_5H_{10}O$; [616-25-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.; Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 3906-3909.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Ethylvinylcarbinol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0929	0.0	0.10	0.0356
0.0929	0.01	0.09	0.0342
0.0929	0.10	0.0	0.0305
0.0464	0.0	0.10	0.0217
0.0464	0.01	0.09	0.0196
0.0464	0.10	0.0	0.0184
0.0232	0.0	0.10	0.0128
0.0232	0.10	0.0	0.0123
0.0116	0.0	0.10	0.0081

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Ethylvinylcarbinol prepared from ethyl magnesium bromide and acrolein. Source and purity of materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) α,α-Dimethylallyl Alcohol; $C_5H_{10}O$; [115-18-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 3906-3909.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous α,α-Dimethylallyl Alcohol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0910	0.0	0.10	0.0311
0.0910	0.10	0.0	0.0253
0.0682	0.0	0.10	0.0252
0.0682	0.01	0.09	0.0225
0.0682	0.10	0.0	0.0205
0.0455	0.0	0.10	0.0185
0.0455	0.01	0.09	0.0165
0.0455	0.10	0.0	0.0158
0.0288	0.0	0.10	0.0109

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). α,α-Dimethylallyl alcohol obtained from the University of California (Los Angeles), dried and fractionated. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J.
J. Am. Chem. Soc. 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) γ, γ-Dimethylallyl Alcohol; $C_5H_{10}O$; [556-82-1]
(5) β-Chloroallyl Alcohol; C_3H_5ClO; [5976-47-6]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 3906–3909.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous γ, γ-Dimethylallyl Alcohol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0328	0.0	0.10	0.0107
0.0328	0.01	0.09	0.0079
0.0328	0.10	0.0	0.0102
0.0164	0.01	0.09	0.0055
0.0164	0.10	0.0	0.0081

Solubility of CuCl in Aqueous β-Chloroallyl Alcohol at 25°C

c_5/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.500	0.0	0.10	0.0082
0.500	0.01	0.09	0.0058
0.500	0.10	0.0	0.0095

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). γ, γ-Dimethylallyl alcohol was supplied by the University of California (Los Angeles) and the β-chloroallyl alcohol by the Shell Chemical Corporation. Both were dried and fractionated before use. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) 3-Methyl-3-buten-2-ol; $C_5H_{10}O$; [10473-14-0]
(5) 2-Methyl-2-buten-1-ol; $C_5H_{10}O$; [479-02-9]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.; Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 3906-3909.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous 3-Methyl-3-buten-2-ol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0504	0.0	0.10	0.0091
0.0504	0.01	0.09	0.0068
0.0504	0.10	0.0	0.0100
0.0378	0.0	0.10	0.0077
0.0378	0.01	0.09	0.0055
0.0378	0.10	0.0	0.0090

Solubility of CuCl in Aqueous 2-Methyl-2-buten-1-ol at 25°C

c_5/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0189	0.0	0.10	0.0049
0.0189	0.01	0.09	0.0035
0.0189	0.10	0.0	0.0080

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). The unsaturated alcohols were supplied by the University of California (Los Angeles). They were dried and fractionated before use. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (4) 4-Methyl-4-penten-2-ol; $C_6H_{12}O$; [2004-67-3] (5) Water; H_2O; [7732-18-5]	Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc.* 1949, *71*, 3906–3909.
VARIABLES:	PREPARED BY:
Composition at 298 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous 4-Methyl-4-penten-2-ol at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0336	0.0	0.10	0.0128
0.0336	0.01	0.09	0.0103
0.0336	0.10	0.0	0.0116
0.0168	0.0	0.10	0.0076
0.0168	0.01	0.09	0.0061
0.0168	0.10	0.0	0.0090
0.0084	0.0	0.10	0.0043

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). 4-Methyl-4-penten-2-ol was supplied by the Shell Chemical Corporation, dried and fractionated before use. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (3) Maleic Acid; $C_4H_4O_4$; [110-16-7] (4) Water; H_2O; [7732-18-5]	Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* 1948, *70*, 3261-3265.
VARIABLES:	**PREPARED BY:**
Concentration of $HClO_4$ at 298 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Maleic Acid at 25°C

c_3/mol dm^{-3}	c_2/mol dm^{-3}	$c_1{}^a$/mol dm^{-3}
0.146	0.903	0.0105
0.146	0.903	0.0108
0.146	0.602	0.0115
0.146	0.421	0.0125
0.146	0.301	0.0133
0.146	0.120	0.0148
0.146	0.0602	0.0166

[a] The authors state that all solubilities were corrected for the "slight solubility of cuprous chloride in the organic acid-free medium" (amounts of correction not given).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of selected solutions in glass-stoppered nitrogen-filled Erlenmeyer flasks. Analyzed solutions for cuprous content volumetrically (Ref. 1) after two hours shaking.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Maleic acid prepared from maleic anhydride according to the directions of Robertson (Ref. 3). Source of other and purity of all materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Hatch, L. F.; Estes R. R. *J. Am. Chem. Soc.* 1945, *67*, 1730.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1
3. Robertson, G. R. *Laboratory Practice of Organic Chemistry*, MacMillan, New York, 1943, pp. 316-317.

COMPONENTS:

(1) Copper(I) Chloride; $CuCl$; [7758-89-6]
(2) Sulfuric Acid; H_2SO_4; [7664-93-9]
(3) Maleic Acid; $C_4H_4O_4$; [110-16-7]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Andrews, L. J.; Keefer, R. M.
J. Am. Chem. Soc. <u>1948</u>, *70*, 3261–3265.

VARIABLES:

Concentrations of sulfuric and maleic acids at 298 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

<u>Solubility of CuCl in Aqueous Maleic Acid at 25°C</u>

c_3/mol dm^{-3}	c_2/mol dm^{-3}	$c_1{}^a$/mol dm^{-3}
0.152	1.19	0.0105
0.150	1.19	0.0100
0.152	0.595	0.0127
0.152	0.595	0.0122
0.159	0.477	0.0132
0.0794	0.477	0.0069
0.0397	0.477	0.0034
0.150	0.298	0.0134
0.152	0.298	0.0135
0.150	0.119	0.0157
0.152	0.119	0.0146
0.150	0.0595	0.0163

[a] The authors state that all solubilites were corrected for the "slight solubility of cuprous chloride in the organic acid-free medium" (amounts of correction not given).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of selected solutions in glass-stoppered nitrogen-filled Erlenmeyer flasks. Analyzed solutions for cuprous content volumetrically (Ref. 1) after two hours shaking.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Maleic acid prepared from maleic anhydride according to the directions of Robertson (Ref. 3). Source of other and purity of all materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Hatch, L. F.; Estes R. R. *J. Am. Chem. Soc.* <u>1945</u>, *67*, 1730.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, <u>1946</u>, p. 1
3. Robertson, G. R. *Laboratory Practice of Organic Chemistry*, MacMillan, New York, <u>1943</u>, pp. 316–317.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Maleic Acid; $C_4H_4O_4$; [110-16-7]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Andrews, L. J.; Keefer, R. M.
J. Am. Chem. Soc. 1949, *71*, 2379–2380.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Maleic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.202	0.0	1.0	0.0118
0.101	0.0	1.0	0.0077
0.0504	0.0	1.0	0.0048
0.202	0.100	0.9	0.0110
0.101	0.100	0.9	0.0080
0.0503	0.100	0.9	0.0068
0.184	0.0091	0.9909	0.0092
0.101	0.0100	0.9900	0.0053
0.0503	0.0100	0.9900	0.0030
0.202	0.0	0.1	0.0192
0.152	0.0	0.1	0.0160
0.101	0.0	0.1	0.0128
0.0505	0.0	0.1	0.0083
0.202	0.100	0.0	0.0142
0.152	0.100	0.0	0.0124
0.101	0.100	0.0	0.0109
0.202	0.0100	0.09	0.0158
0.101	0.0100	0.09	0.0096

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to either 1.0 mol dm^{-3} or 0.10 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Maleic acid prepared from maleic anhydride according to the directions of Robertson (Ref. 3). Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1
3. Robertson, G. R. *Laboratory Practice of Organic Chemistry*, MacMillan, New York, 1943, pp. 316–317.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Chloride; KCl; [7447-40-7] (3) Sodium Perchlorate; $NaClO_4$; [7601-89-0] (4) Maleic Acid; $C_4H_4O_4$; [110-16-7] (5) Water; H_2O; [7732-18-5]	Andrews, L. J.; Keefer, R. M. *J. Am. Chem. Soc.* 1949, *71*, 2379–2380.
VARIABLES:	**PREPARED BY:**
Composition at 298 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Maleic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.202	0.0	0.1	0.0240
0.101	0.0	0.1	0.0170
0.0503	0.0	0.1	0.0118
0.202	0.100	0.0	0.0176
0.152	0.100	0.0	0.0154
0.101	0.100	0.0	0.0128
0.202	0.010	0.09	0.0202
0.152	0.010	0.09	0.0173
0.101	0.010	0.09	0.0141

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.100 mol dm^{-3} ionic strength with $NaClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Maleic acid prepared from maleic anhydride according to the directions of Robertson (Ref. 3). Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1
3. Robertson, G. R. *Laboratory Practice of Organic Chemistry*, MacMillan, New York, 1943, pp. 316–317.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Sulfuric Acid; H_2SO_4; [7664-93-9]
(3) Fumaric Acid; $C_4H_4O_4$; [110-17-8]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Andrews, L. J.; Keefer, R. M.
J. Am. Chem. Soc. 1948, *70*, 3261–3265.

VARIABLES:

Concentrations of sulfuric and fumaric acids at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Fumaric Acid at 25°C

c_3/mol dm^{-3}	c_2/mol dm^{-3}	$c_1{}^a$/mol dm^{-3}
0.0350	0.477	0.0093
0.0456	0.477	0.0107
0.0342	0.477	0.0091
0.0504	0.477	0.0116
0.0456	0.238	0.0100
0.0456	0.094	0.0112
0.0504	0.0496	0.0111
0.0452	0.0496	0.0115
0.0378	0.0496	0.0093
0.0339	0.0496	0.0087
0.0452	0.0	0.0103
0.0438	0.0	0.0103

[a] The authors state that all solubilities were corrected for the "slight solubility of cuprous chloride in the organic acid-free medium" (amounts of correction not given).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in glass-stoppered nitrogen-filled Erlenmeyer flask. Analyzed solutions for cuprous content volumetrically (Ref. 1) after two hours shaking.

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Fumaric acid prepared from maleic anhydride according to the directions of Robertson (Ref. 3). Source of other and purity of all materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Hatch, L. F.; Estes R. R.
   J. Am. Chem. Soc. 1945, *67*, 1730.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1
3. Robertson, G. R. *Laboratory Practice of Organic Chemistry*, MacMillan, New York, 1943, pp. 316–317.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Fumaric Acid; $C_4H_4O_4$; [110-17-8]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M. ; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 2381–2383.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Fumaric Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0465	0.0	0.10	0.0116
0.0399	0.0	0.10	0.0097
0.0232	0.0	0.10	0.0072
0.0465	0.0938	0.0062	0.0103
0.0399	0.0938	0.0062	0.0090
0.0234	0.0938	0.0062	0.0080
0.0363	0.010	0.090	0.0076
0.0272	0.010	0.090	0.0060
0.0182	0.010	0.090	0.0047

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Fumaric acid prepared from maleic anhydride according to the directions of Robertson (Ref. 3). Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1
3. Robertson, G. R. *Laboratory Practice of Organic Chemistry*, MacMillan, New York, 1943, pp. 316–317.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (4) Crotonic Acid; $C_4H_6O_2$; [107-93-7] (5) Water; H_2O; [7732-18-5]	Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc.* 1949, *71*, 2381–2383.
VARIABLES:	**PREPARED BY:**
Composition at 298 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Crotonic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.401	0.0	0.10	0.0172
0.316	0.0	0.10	0.0152
0.238	0.0	0.10	0.0131
0.158	0.0	0.10	0.0097
0.356	0.0938	0.0062	0.0130
0.267	0.0938	0.0062	0.0113
0.178	0.0938	0.0062	0.0096

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Crotonic acid was obtained from the Eastman Kodak Co. and was recrystallized from water before use. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Vinylacetic Acid; $C_4H_6O_2$; [625-38-7]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 2381–2383.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Vinylacetic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.0930	0.0	0.10	0.0350
0.0465	0.0	0.10	0.0205
0.0233	0.0	0.10	0.0123
0.0116	0.0	0.10	0.0074
0.0930	0.100	0.0	0.0288
0.0465	0.100	0.0	0.0175
0.0930	0.010	0.090	0.0321
0.0233	0.010	0.090	0.0104

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Vinylacetic acid prepared from Eastman Kodak Co. vinylacetonitrile. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Itaconic Acid; $C_5H_6O_4$; [97-65-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.; Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 2381-2383.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Itaconic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.202	0.0	0.10	0.0150
0.101	0.0	0.10	0.0099
0.0504	0.0	0.10	0.0061
0.202	0.100	0.0	0.0130
0.151	0.100	0.0	0.0115
0.101	0.100	0.0	0.0098
0.202	0.010	0.090	0.0118
0.101	0.010	0.090	0.0074

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Itaconic acid prepared from citric acid. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (4) Mesaconic Acid; $C_5H_6O_4$; [498-24-8] (5) Citraconic Acid; $C_5H_6O_4$; [498-23-7] (6) Water; H_2O; [7732-18-5]	Keefer, R. M.; Andrews, L. J.; Kepner, R. E. *J. Am. Chem. Soc.* 1949, *71*, 2381–2383.
VARIABLES:	PREPARED BY:
Composition at 298 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Mesaconic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.151	0.0	0.10	0.0045
0.113	0.0	0.10	0.0041
0.076	0.0	0.10	0.0030
0.151	0.094	0.006	0.0068
0.113	0.094	0.006	0.0066

Solubility of CuCl in Aqueous Citraconic Acid at 25°C

c_5/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.345	0.0	0.10	0.0028
0.459	0.100	0.0	0.0081

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Mesaconic and citraconic acids prepared from citric acid. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) β,β-Dimethylacrylic Acid; $C_5H_8O_2$; [541-47-9]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 2381–2383.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous β,β-Dimethylacrylic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.136	0.0	0.10	0.0029
0.136	0.100	0.0	0.0071
0.136	0.100	0.0	0.0070
0.136	0.010	0.090	0.0020

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). β,β-Dimethylacrylic acid was prepared from mesityl oxide supplied by the Shell Chemical Corporation. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Tiglic Acid; $C_5H_8O_2$; [80-59-1]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.;
Kepner, R. E.
J. Am. Chem. Soc. 1949, *71*, 2381–2383.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous Tiglic Acid at 25°C

c_4/mol dm^{-3}	c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.094	0.0	0.10	0.0031
0.082	0.0	0.10	0.0026
0.094	0.100	0.0	0.0070
0.082	0.100	0.0	0.0067
0.094	0.010	0.090	0.0022

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuCl to 50 cm^3 portions of desired solutions in nitrogen-filled glass-stoppered Erlenmeyer flask. All solutions were adjusted to 0.1 mol dm^{-3} ionic strength with $HClO_4$. After 4 hours shaking at 25°C, removed solution for analysis. Solutions were titrated for cuprous content with potassium dichromate, using barium diphenylaminosulfonate as indicator (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

CuCl prepared according to method of Keller and Wycoff (Ref. 2). Tiglic acid furnished by W. G. Young, recrystallized from water. Source of other and purity of all materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Keefer, R. M.; Andrews, L. J. *J. Am. Chem. Soc.* 1949, *71*, 1723.
2. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, vol. II, McGraw-Hill, 1946, p. 1

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Potassium Chloride; KCl; [7447-40-7]
(4) Urea; CH_4N_2O; [57-13-6]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sigal, L. N.; Kucherenko, V. I.;
Flerov, V. N.
Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 1975, *18*, 1357–1359.

VARIABLES:

Concentration of urea at 295 K

PREPARED BY:

J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl–KCl–Urea Solutions at 22°C [a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.26	1.08	0.000	0.143
0.26	1.08	0.165	0.153
0.26	1.08	0.440	0.168
0.26	1.08	0.877	0.193

[a] The numerical values in the table were digitized from the graph reproduced on the following page, containing results for the effects of three organic additives.

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess CuCl was introduced into salt solutions under argon in a thermostat at 295 K. The mixtures were stirred for three days, after which samples of solution were removed for analysis. The copper was oxidized to Cu^{2+} and then determined complexometrically.

SOURCE AND PURITY OF MATERIALS:

CuCl was prepared according to Ref. 1. All chemicals were "C.P.", no analyses given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Zvorkina, G. I. *et al.*, *Practice of Inorganic Chemistry*, Gorki, 1965.

COMPONENTS:

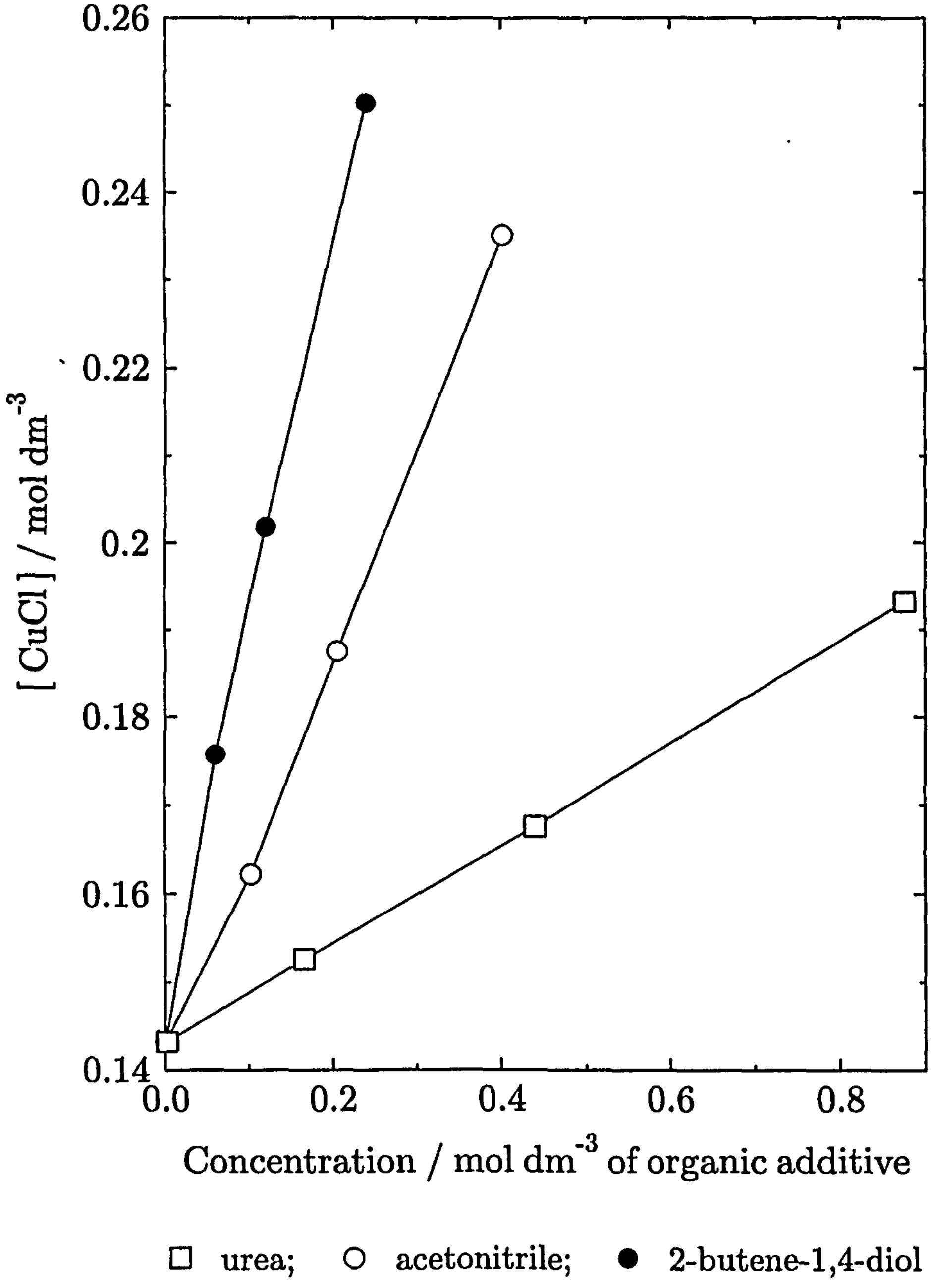
(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Potassium Chloride; KCl; [7447-40-7]
(4) Urea; CH_4N_2O; [57-13-6]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sigal, L. N.; Kucherenko, V. I.;
Flerov, V. N.
Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 1975, *18*, 1357–1359.

EXPERIMENTAL VALUES:

(continued)



COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Potassium Chloride; KCl; [7447-40-7]
(4) 2-Butene-1,4-diol; $C_4H_8O_2$; [110-64-5]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sigal, L. N.; Kucherenko, V. I.; Flerov, V. N.
Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol. 1975, *18*, 1357–1359.

VARIABLES:

Concentration of 2-butene-1,4-diol at 295 K

PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl–KCl–2-Butene-1,4-diol Solutions at 22°C[a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.26	1.08	0.000	0.143
0.26	1.08	0.061	0.176
0.26	1.08	0.121	0.202
0.26	1.08	0.240	0.250

[a] The numerical values in the table were digitized from the graph reproduced together with the data for urea, containing results for the effects of three organic additives.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess CuCl was introduced into salt solutions under argon in a thermostat at 295 K. The mixtures were stirred for three days, after which samples of solution were removed for analysis. The copper was oxidized to Cu^{2+} and then determined complexometrically.

SOURCE AND PURITY OF MATERIALS:

CuCl was prepared according to Ref. 1. All chemicals were "C.P.", no analyses given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Zvorkina, G. I. *et al.*, *Practice of Inorganic Chemistry*, Gorki, 1965.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Potassium Chloride; KCl; [7447-40-7] (4) Acetonitrile; C_2H_3N; [75-05-8] (5) Water; H_2O; [7732-18-5]	Sigal, L. N.; Kucherenko, V. I.; Flerov, V. N. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1975, *18*, 1357–1359.
VARIABLES: Concentration of acetonitrile at 295 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous HCl–KCl–Acetonitrile Solutions at 22°C[a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.26	1.08	0.000	0.143
0.26	1.08	0.103	0.162
0.26	1.08	0.206	0.188
0.26	1.08	0.402	0.235

[a] The numerical values in the table were digitized from the graph reproduced together with the data for urea, containing results for the effects of three organic additives.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Excess CuCl was introduced into salt solutions under argon in a thermostat at 295 K. The mixtures were stirred for three days, after which samples of solution were removed for analysis. The copper was oxidized for Cu^{2+} and then determined complexometrically.	CuCl was prepared according to Ref. 1. All chemicals were "C.P.", no analyses given. ESTIMATED ERROR: Not given. REFERENCES: 1. Zvorkina, G. I. *et al.*, *Practice of Inorganic Chemistry*, Gorki, 1965.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Organic Solvents	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

BINARY SYSTEMS

Only a few sets of data are available for the solubility of CuCl in organic solvents. Heines and Yntema[1] report the solubility in dioxane as 0.031 g cm^{-3} solution (0.31 mol dm^{-3}) at 300 K. Naumann and Schier[2] and Pleshkov[3] reported the solubility in acetonitrile. Naumann and Schier[2] gave 11.76 g CuCl per 100 g saturated solution (1.35 mol kg^{-1}) at 291 K. Pleshkov[3] gave 8 g CuCl per 100 g saturated solution at 298 K. While obviously in disagreement, these reports indicate the order of magnitude of the solubility of CuCl in acetonitrile.

In 1977 Machtinger *et al.*[4] gave a value of the solubility product of CuCl in molten dimethyl sulfone [$(CH_3)_2SO_2$] at 400 K as $10^{-12.7}$ ($2 \cdot 10^{-13}$) $mol^2\ kg^{-2}$ from cell measurements in which the potential of a copper electrode was measured as a function of chloride molality (provided by addition of tetraethylammonium chloride) with a molality of Cu^+ of 10^{-3} mol kg^{-1}. Their value of K_{S0} would correspond to a solubility of about $4.5 \cdot 10^{-7}$ mol kg^{-1} in the molten dimethyl sulfone.

TERNARY SYSTEMS

CuCl–HCl–Ethanol

In 1934 Chang and Liu[5] published data on the solubility of CuCl in ethanolic hydrogen chloride at 298 K, with a concentration range of 0.08 to 0.73 mol dm^{-3} HCl. They found the solubility of CuCl to be nearly proportional to the concentration of HCl used, with about 0.85 mol CuCl dissolved for every mol of HCl. With the possible exception of the lowest point, their data are smooth within 1 or 2 per cent. No other data have been found for this or any other system involving CuCl and ethanol. Their data are Accepted tentatively in view of their internal consistency and the high quality of the results obtained by Chang and Cha[6] in a similar investigation of the system CuCl–HCl–H_2O.

Their data can be fitted following the equation

$$2\,CuCl_{(s)} + HCl \rightleftharpoons HCu_2Cl_3, \qquad K_{S23} = [HCu_2Cl_3]/[HCl]$$

with both HCl and the complex essentially unionized. Their data can be fitted within 5 per cent using a value for the equilibrium constant K_{S23} of 1.47 ± 0.05. An attempt to fit the data with a reaction in which $HCuCl_2$ is formed gives a distinctly poorer fit to the data.

CuCl–Tetraethylammonium Chloride–Dimethyl Sulfone

Machtinger *et al.*[4] used titration curves to evaluate a stability constant for the ion $CuCl_2^-$ in molten dimethyl sulfone [$(CH_3)_2SO_2$] at 400 K, using chloride ion between 0.008 and 0.7 mol kg^{-1} supplied by tetraethylammonium chloride [$(C_2H_5)_4NCl$]. They give a value of $10^{16.8}$ ($6.3 \cdot 10^{16}$) $mol^{-2}\ kg^2$. Using this value with their value (above) for the solubility product of CuCl in their medium gives a value of K_{S2} for addition of Cl^- to solid cuprous chloride in molten dimethyl sulfone, *viz.*:

$$CuCl_{(s)} + Cl^- \rightleftharpoons CuCl_2^- \qquad K_{S2} = 1.2 \cdot 10^4$$

This extraordinarily large value of K_{S2} corresponds to essentially complete absorption of Cl^- by solid cuprous chloride. Machtinger *et al.*[4] do not report any actual solubilities, but indicate their expectation of a solubility of 0.008 mol kg^{-1} in the presence of only 10^{-6} mol kg^{-1} of *free* chloride ion!

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Organic Solvents	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

CuCl–KSeCN–Acetone

In 1960 Golub and Skopenko[7] published data on the solubility of CuCl in acetone solutions of potassium selenocyanate at an unspecified temperature, apparently 293 K. They found the solubility linear in (nearly proportional to) the concentration of KSeCN used, with about 0.2 mol of CuCl dissolved for every mol of KSeCN. They interpreted their measurements in terms of a reaction

$$CuCl_{(s)} + SeCN^- \rightleftharpoons Cu(SeCN)Cl^-, \qquad K = [Cu(SeCN)Cl^-]/[Cl^-]$$

and gave a value of 0.24 ± 0.01 for K. Their results are Accepted tentatively in view of the internal consistency of their data.

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4. Machtinger, M.; Vuaille, M. J.; Tremillon, B. *J. Electroanal. Chem. Interfacial Electrochem.* 1977, *83*, 273.
5. Chang, K. S.; Liu, Y.-M. *J. Chin. Chem. Soc.* 1934, *2*, 307.
6. Chang, K. S.; Cha, Y.-T. *J. Chin. Chem. Soc.* 1934, *2*, 293.
7. Golub, A. M.; Skopenko, V. V. *Zh. Neorg. Khim.* 1960, *5*, 1973; *Russ J. Inorg. Chem. (Engl. Trans.)* 1960, *5*, 961.

COMPONENTS:

(1) Copper(I) Chloride; CuCl; [7758-89-6]
(2) Hydrogen Chloride; HCl; [7647-01-0]
(3) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Chang, K. S.; Liu, Y.-M.
J. Chin. Chem. Soc. 1934, *2*, 307–310.

VARIABLES:

Concentration of HCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Ethanolic HCl Solutions at 25°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.07839	0.06078
0.1524	0.1281
0.2775	0.2336
0.3223	0.2766
0.3953	0.3338
0.4304	0.3660
0.4356	0.3660
0.4676	0.4035
0.5368	0.4663
0.6108	0.5230
0.6479	0.5538
0.7254	0.6299

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added hydrogen chloride gas to a mixture of alcohol and cuprous chloride and weighed the amount of gas added (to effect solution of the CuCl).

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Selenocyanate; KSeCN; [3425-46-5] (3) Acetone; C_2H_6O; [67-64-1]	Golub, A. M.; Skopenko, V. V. *Zh. Neorg. Khim.* 1960, *5*, 1973; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 961-963.
VARIABLES:	PREPARED BY:
Concentration of KSeCN at unspecified temperature (probably 293 K)	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCl in Acetone Solution of KSeCN

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.51	0.0980
0.55	0.1050
0.59	0.1171
0.61	0.1227
0.81	0.1520
0.86	0.1621

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook CuCl with acetone solutions of KSeCN until saturation attained. Then evaporated acetone from solution and treated residue with concentrated HNO_3 until completely dissolved. The solution was then evaporated almost to dryness, and the residue dissolved in water. The selenium in the solution was precipitated using hydrazine and weighed. The copper in the filtrate was determined iodometrically. They also describe a set of potentiometric measurements made at 293 K.

SOURCE AND PURITY OF MATERIALS:

Prepared acetone and KSeCN by method of Ref. 1 and CuCl by method of Karyakin and Angelov (Ref. 2).

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Golub, A. M. *Nauchn. Dokl. Vys. Shkoly Khim. Khim. Tekhnol.* 1958, *III (4)*, 685.
2. Karyakin, Yu. V.; Angelov, I. I. *Pure Chemical Reagents*, 1955, p. 345.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

THE BINARY SYSTEM

There are only a few data on the solubility of cuprous bromide in pure water. In 1902, Bodländer and Storbeck[1] gave a value of $4.15 \cdot 10^{-8}$ mol dm^{-3}, presumably at about 293 K. This value was quoted in 1931 by Kolthoff and Furman[2]. Four values for the solubility product at 298.15 K, zero ionic strength were found, as follows: The thermodynamic data given in U. S. National Bureau of Standards Circular 500[3] (1952) yields a value of $5.8 \cdot 10^{-9}$ mol^2 dm^{-6}. Zhuk[4] (1954) quotes a value of $5.3 \cdot 10^{-9}$ mol^2 dm^{-6}, and Chaltykyan[6] (1966) reported it without giving any source of information. Latimer[5] (1952) gives a value of $5.9 \cdot 10^{-9}$ mol^2 dm^{-6} as calculated from cell potentials. Krestov *et al.*[7] (1977) reported this same value which is somewhat uncertain because of lack of firm information about the electrode potential of the Cu/Cu^+ electrode, as in the case of CuCl. However, any of the values quoted should be within about 10 per cent of the true value. A value of $(5.5 \pm 0.5) \cdot 10^{-9}$ mol^2 dm^{-6} is Accepted tentatively. It should be noted that, as with CuCl, the solubility of CuBr in pure water will be higher than that calculated from the solubility product because of additional contributions from the formation of neutral $CuBr^0$ and the reaction $2CuBr_{(s)} \rightleftharpoons Cu^+ + CuBr_2^-$. Finally Ahrland and Tagesson[8] obtained a value of $(1.3 \pm 0.06) \cdot 10^{-9}$ mol^2 dm^{-6} at 298 K in 5.0 mol dm^{-3} $NaClO_4$.

Gavrish and Galinker[9] made measurements of the solubility of CuBr in water at 12 temperatures from 473 to 603 K. When values of the natural logarithm of solubility, $\ln(m_{CuBr}/\text{mol kg}^{-1})$, from their data are plotted against reciprocal temperature, there is some downward curvature at the higher temperatures, but there is appreciable scatter in the data. Over the entire range the data fit a straight line

$$\ln(m_{CuBr}/\text{mol kg}^{-1}) = -4457\ \text{K}/T + 7.605$$

with an average deviation of about 10 per cent (worst point 20 per cent high). Their data are Accepted tentatively with an estimated uncertainty of 10 per cent. (This sort of uncertainty is not surprising in view of the difficulty of measuring the solubility at the high temperatures.) No attempt has been made to connect their points with data at 298 K because of the large intermediate interval of temperature where no data are available.

TERNARY SYSTEMS

$CuBr-KBr-H_2O$

Five sets of measurements of the solubility of cuprous bromide in aqueous potassium bromide have been published. The earliest of these was reported in 1902 by Bodländer and Storbeck[1], who measured the solubility at a temperature of 292 ± 1 K for seven concentrations of KBr from 0.025 to 0.500 mol dm^{-3}; at concentrations below 0.1 mol dm^{-3}, their solutions contained minor amounts of Cu^{2+} due to disproportionation. In 1962 Malik *et al.*[10] reported the solubility at 323 K for 15 concentrations of KBr ranging from 0.46 to 1.56 mol dm^{-3}. In 1968 Wilke[11] reported the solubility at three KBr molalities (1.4 to 5.5 mol kg^{-1}) each at 298, 308, 318 and 328 K. In 1970 Khan and Malik[12] reported data at 293 K for ten supposedly equilibrium concentrations of Br^- from 0.10 to 0.76 mol dm^{-3}. In 1987 Fritz and Luzik[13] reported values at 298 K for 13 concentrations of KBr from 0.1 to 4.0 mol dm^{-3} and in addition 10 concentrations at nominal ionic strengths of 2.0 mol dm^{-3} (0.4 to 1.8 mol dm^{-3} KBr) and 5 concentrations at ionic strength 3.0 (0.45 to 2.4 mol dm^{-3} KBr), both of the latter sets maintained by use of KNO_3.

The data of Bodländer and Storbeck[1] and those of Fritz and Luzik[13] can be represented to a few per cent by a model using equilibrium constants for the formation of complexes and

COMPONENTS:	EVALUATOR:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

virial parameters for the ion pairs present in the solutions. The model fitted the data of Fritz and Luzik[13] to a standard deviation of 3 per cent and those of Bodländer and Storbeck[1] to 6 per cent, in each case about the consistency of the data. They are Recommended for use at or near 298 K. The data of Malik *et al.*[10] scatter badly about a smooth curve, most points by 10 per cent or more. The best fit which could be obtained with the model had an average deviation of 15 per cent (11 per cent if two inconsistent points near 0.6 mol dm^{-3} were omitted), using the parameters obtained from the data at 298 K and heats of complex formation somewhat larger than those for chlorocuprous complexes. Their data may be used to get and approximate idea of the solubility of CuBr in aqueous KBr at 323 K. The data of Khan and Malik[12] at 293 K are quite erratic, with points scattering 10 to 15 per cent from a smooth curve. In addition their reported solubilities are much larger than those reported by others for similar concentrations of KBr (as much as an order of magnitude). These data are Rejected and have not been compiled. The solubilities reported by Wilke[11] are lower by more than an order of magnitude than any other data at any temperature. They are Rejected.

Summary. The data of Fritz and Luzik[13] are recommended for use at 298 K, with an estimated uncertainty of 3 per cent, and those of Bodländer and Storbeck[1] at 292 K with an uncertainty of 6 per cent. A smooth curve through the data of Malik *et al.*[10] should give values of the solubility at 323 K within 10 per cent. The other data on this system are not satisfactory.

CuBr–NaBr–H_2O

Data on the solubility of CuBr in aqueous NaBr are much less extensive than those for its solubility in aqueous KBr. In 1967 Peters and Caldwell[14] published a set of measurements (8 points) of the solubility at 298 K for media with NaBr concentrations from 0.05 to 1.5 mol dm^{-3} at a constant nominal ionic strength of 2.0 mol dm^{-3} maintained by use of $NaNO_3$. In 1968 Wilke[11] reported solubilities at four temperatures between 298 and 328 K for three molalities (2.2, 4.4 and 8.8 mol kg^{-1}) of NaBr at each temperature. In 1977 Ahrland and Tagesson[8] reported the solubility at 298 K for five aqueous NaBr solutions with bromide concentrations from 0.11 to 0.43 mol dm^{-3}, maintained at 5 mol dm^{-3} by $NaClO_4$ with 0.1 mol dm^{-3} of $HClO_4$ present.

Of the three sets of data, those of Peters and Caldwell[14] are the smoothest and most internally consistent; they could be fitted by a model to an average of 5 per cent (r.m.s.). The data of Ahrland and Tagesson[8] at a higher ionic strength departed from smoothness by about 10 per cent. They will provide values good to about 10 per cent for the medium they employed (ionic strength 5.0 mol dm^{-3} maintained by $NaClO_4$). The solubility values given by Wilke[11] were low by at least a factor of 10 and have been Rejected.

CuBr–HBr–H_2O

The only data reported for the solubility of CuBr in aqueous HBr are those of Wilke[11] (1968) and those of Khan and Malik[12] (1970). Wilke[11] gave the solubility for one concentration of HBr at four temperatures (298, 308, 318 and 328 K). Khan and Malik[12] gave twenty values of solubility at 323 K for supposedly equilibrium concentrations of Br^- from 0.06 to 1.00 mol dm^{-3}. Their procedure was to dilute a concentrated solution of CuBr in aqueous KBr so as to precipitate out much of the CuBr, after which the Cu^+ concentration was determined analytically and the bromide concentration was derived from a mass balance. Their results scatter badly about a smooth curve (as much as 30 per cent); the results at their highest concentrations are comparable with those obtained by Malik *et al.*[10] for aqueous KBr at 323 K, but all others are distinctly higher. These data are Rejected and have not been compiled. The results reported by Wilke[12] are exceedingly low and have also been Rejected.

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]

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

EVALUATOR:

J. J. Fritz
Department of Chemistry
The Pennsylvania State University
June, 1991

CRITICAL EVALUATION:

$CuBr–MgBr_2–H_2O$

The only data reported for the solubility of CuBr in aqueous $MgBr_2$ are those of Khan and Malik[12] (1970) who gave ten values of solubility at 293 K for supposedly equilibrium concentrations of Br^- from 0.10 to 1.02 mol dm^{-3}. Their procedure was the same as with aqueous HBr, described above. Again, their results scatter badly about a smooth curve and in addition are very high compared with other solubilities in aqueous solutions of soluble bromides. Their data are Rejected and have not been compiled.

Other Systems

Wilke[11] reported values for the solubility of CuBr in aqueous LiBr and aqueous NH_4Br for three concentrations each at four temperatures (298, 308, 318 and 328 K). His results appear quite low and are not recommended for use.

DOUBLE SALTS INVOLVING CuBr

Numerous double salts have been reported for CuBr. Malik *et al.*[10] claimed that $CuBr{\cdot}2KBr$, $CuBr{\cdot}3KBr$ and $CuBr{\cdot}4KBr$ were formed at 323 K in their solubility study of the system $CuBr–KBr–H_2O$, but they neither isolated the solid phases nor indicated clearly which double salt was present at any given solution composition. The other double salts have not been observed in solubility measurements, but it is always possible that one will appear when CuBr is dissolved under conditions other than those for which measurements are available. Wells and Hurlburt[15] prepared the double salts $CuBr{\cdot}2NH_4Br$ and $CuBr{\cdot}NH_4Br{\cdot}H_2O$. The crystal structure of the first of these was determined by Brink and van Arkel[16]. Mellor[17] discusses a variety of early work on compounds containing CuBr combined with ammonia. In a series of papers, Harris[18–20] reported a number of compounds involving CuBr with ammoniacal ligands, as follows: (a) 3 mixed compounds containing both CuBr and $CuBr_2$, *viz.* $Cu(NH_3)_4Br_2{\cdot}CuBr$, $Cu(en)_2Br_2 \cdot CuBr$ and $Cu(en)_2Br_2 \cdot CuBr \cdot 2.5H_2O$ (en = ethylene diamine); (b) 3 compounds containing CuBr and CuI, *viz.* $[Cu^{II}(NH_3)_4][Cu^{I}IBr]_2$, $[Cu^{II}(en)_2][Cu^{I}IBr]_2$, and pyridinium bromoiodocuprate $[C_5H_5NH][CuIBr]$. In all cases the compounds were verified by chemical analysis. Rosenheim and Steinhauser[21] prepared the salt $CuBr \cdot NH_4Br \cdot (NH_4)_2S_2O_3$. They verified its composition by chemical analysis and described its crystal structure. Canneri and Luchini[22] prepared $CuBr \cdot Cu_2S_2O_3 \cdot 9Na_2S_2O_3$, verifying the composition by chemical analysis.

Gilliland *et al.*[23] prepared the compound $CuBr{\cdot}C_2H_4$ and measured its (large) vapor pressure between 273 and 290 K. Somewhat later Gilliland and coworkers[24] prepared $CuBr \cdot C_4H_6$ and $CuBr \cdot C_2H_2$ and measured their vapor pressures, in the range 273 to 320 K for the first and 203 to 255 K for the second compound.

The double salts observed suggest that CuBr probably has appreciable solubility in aqueous solutions of a variety of materials where measurements have not been made, such as thiosulfates, ammonia, ethylene diamine, pyridine and unsaturated organic acids and alcohols.

THERMODYNAMICS OF AQUEOUS SOLUTIONS OF CuBr

The data for aqueous KBr and NaBr were used to obtain a set of equilibrium constants for bromocuprous complexes and a set of virial parameters for ion pairs between Na^+ and K^+ and the complexes $CuBr^0$, $CuBr_2^-$, $CuBr_3^{2-}$ and $Cu_3Br_6^{3-}$. Virial parameters for the ion pairs Na^+-Br^-, K^+-Br^- and K^+-NO_3^- were taken from Pitzer and Mayorga[25], those for ion pairs involving the complexes derived from the data. All of the parameters were chosen to optimize fit to the various data. The data at 298 K were used to establish the values of equilibrium constants and virial parameters at that temperature. The data of Malik *et al.*[10] were used to get approximate values for the enthalpy changes associated with formation

COMPONENTS:	EVALUATOR:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

of complexes from CuBr and bromide ion. There were sufficient data available to evaluate temperature dependence of the virial parameters. The equilibrium constants are given in Table 23 and the virial parameters for KBr and NaBr solutions in Table 24.

In the case of aqueous KBr the parameters of Tables 23 and 24 represent the data of Fritz and Luzik[13] to 3 per cent (r.m.s.) and those of Bodländer and Storbeck[1] to about 6 per cent. They represent the data of Malik *et al.*[10] at 323 K to about 10 per cent, the consistency of the data. For NaBr, the parameters fit the data of Peters and Caldwell[14] to 5 per cent, about the consistency of these data.

Table 23. Equilibrium Constants and Enthalpies of Reaction for Formation of Complexes from $CuBr_{(s)}$ and Bromide Ion at 298 K, Zero Ionic Strength[a]

Species	K_{Smn} / $(\text{mol dm}^{-3})^{(1-m-n)}$	$\Delta_r H^\ominus$ / kJ mol^{-1}
$CuBr^0$	$1.8 \cdot 10^{-5}$	-
$CuBr_2^-$	0.00389	32.1
$CuBr_3^{2-}$	0.01429	22.0
$Cu_3Br_6^{3-}$	$3.21 \cdot 10^{-4}$	43.9

[a] The equilibrium constants, K_{Smn}, and enthalpies of reaction, $\Delta_r H^\ominus$, are for the reactions $m\ CuBr_{(s)} + (n-m)Br^- \rightleftharpoons Cu_mBr_n^{m-n}$ with standard state in mol dm^{-3}.

Table 24. Virial Parameters for Ion Pairs of Bromide Species with K^+ and Na^+ a 298 K (for Concentrations in mol dm^{-3})

Species	Pairs with K^+			Pairs with Na^+		
	$\beta^{(0)}$	$\beta^{(1)}$	C	$\beta^{(0)}$	$\beta^{(1)}$	C
Br^-	0.0569	0.2212	−0.0009	0.0973	0.2791	0.00058
$CuBr^0$	0.235	0.322	−0.031	0.235	0.322	−0.031
$CuBr_2^-$	0.200	0.117	0.0881	0.115	−0.833	0.05414
$CuBr_3^{2-}$	0.137	1.216	−0.0261	0.1358	1.441	0.00678
$Cu_3Br_6^{3-}$	0.132	3.13	0.00972	0.1466	4.035	−0.00616

The only values for the equilibrium constants found in the literature were a value of $4.6 \cdot 10^{-3}$ given by Latimer[5] for $CuBr_2^-$ at 298.15 K, zero ionic strength (obviously based on K_{S0} and β_2 of Bodländer and Storbeck[1]), and a set of values given for $CuBr^0$, $CuBr_2^-$ and $CuBr_3^{2-}$ given by Peters and Caldwell[14] for solutions in aqueous NaBr at 298.15 K, 2.0 mol dm^{-3} ionic strength; these values represent their data within about 5 per cent, but are suitable only for their experimental conditions. Ahrland and Tagesson[8] give values of stability constants for the complexes they considered, and these can be used along with their value for the solubility product to reproduce or interpolate within their data.

RECOMMENDED VALUES FOR SOLUBILITY OF CuBr

Table 25 gives smoothed values of the solubility of CuBr and the ratio of solubility to concentration of KBr from 0.1 to 4.0 mol dm^{-3} at 298.15 K, calculated using the constants of Tables 23 and 24. Values at other temperatures, which could be calculated from the same parameters, are not given because of the uncertainty of the only experimental data above 298 K. The values in Table 25 should be accurate to about 3 per cent, and the values of the solubility are given to about this precision. The ratio c_{CuBr}/c_{KBr} is given to facilitate

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]

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

EVALUATOR:

J. J. Fritz

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

interpolation; it varies only 60-fold over the entire range, while the solubility varies by a factor of nearly 3000. It is given to considerably higher precision as an aid to interpolation. It is by no means linear in concentration, but can be interpolated quadratically over much of the concentration range.

Table 25. Solubility and Ratio of Solubility to KBr Concentration for CuBr in Aqueous KBr at 298.15 K

$\frac{c_{\mathrm{KBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{c_{\mathrm{KBr}}}$	$\frac{c_{\mathrm{KBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{c_{\mathrm{KBr}}}$
0.100	$0.63 \cdot 10^{-3}$	0.00633	1.600	0.187	0.11703
0.200	$1.84 \cdot 10^{-3}$	0.00918	1.700	0.223	0.13118
0.300	$3.76 \cdot 10^{-3}$	0.01255	1.800	0.263	0.14622
0.400	$6.57 \cdot 10^{-3}$	0.01643	1.900	0.308	0.16209
0.500	0.0104	0.02081	2.000	0.357	0.17867
0.600	0.0154	0.02573	2.200	0.470	0.21347
0.700	0.0219	0.03132	2.400	0.599	0.24921
0.800	0.0286	0.03758	2.600	0.741	0.28517
0.900	0.0401	0.04450	2.800	0.895	0.31961
1.000	0.0522	0.05217	3.000	1.056	0.35188
1.100	0.0668	0.06068	3.200	1.221	0.38145
1.200	0.0841	0.07006	3.400	1.39	0.40806
1.300	0.1045	0.08036	3.600	1.55	0.43163
1.400	0.128	0.09162	3.800	1.72	0.45223
1.500	0.156	0.10384	4.000	1.87	0.46995

Table 26 gives a set of recommended values for the solubility of CuBr in aqueous NaBr from 0.1 to 2.0 mol dm^{-3} at 298.15 K. Since there were no reliable data on the solubility in aqueous NaBr without the presence of an "indifferent" electrolyte, the constants of Tables 23 and 24 were used to calculate a set of values for the solubility in "neat" aqueous NaBr. These parameters fitted the data of Peters and Caldwell[14] within 5 per cent and should give about this order of precision to the values in Table 26. The entries in Table 26 are terminated at 2.0 mol dm^{-3} NaBr because there were no reliable experimental data above this concentration. It is of interest to note that the solubility is nearly the same at low concentrations of both KBr and NaBr; however, the solubility increases more rapidly with increase in concentration of KBr, and by 2.0 mol dm^{-3} the solubility in aqueous KBr is nearly 50 per cent larger.

Table 26. Solubility and Ratio of Solubility to NaBr Concentration for CuBr in Aqueous NaBr at 298.15 K

$\frac{c_{\mathrm{NaBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{c_{\mathrm{NaBr}}}$	$\frac{c_{\mathrm{NaBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{\mathrm{mol\ dm^{-3}}}$	$\frac{c_{\mathrm{CuBr}}}{c_{\mathrm{NaBr}}}$
0.100	$0.68 \cdot 10^{-3}$	0.00683	1.100	0.0535	0.04866
0.200	$1.98 \cdot 10^{-3}$	0.00991	1.200	0.0655	0.05455
0.300	$3.98 \cdot 10^{-3}$	0.01327	1.300	0.0792	0.06093
0.400	$6.72 \cdot 10^{-3}$	0.01684	1.400	0.0950	0.06782
0.500	0.01029	0.02057	1.500	0.1130	0.07532
0.600	0.01474	0.02456	1.600	0.1335	0.08346
0.700	0.0201	0.02878	1.700	0.157	0.09233
0.800	0.0267	0.03324	1.800	0.184	0.1020
0.900	0.0342	0.03803	1.900	0.214	0.1125
1.000	0.0431	0.04317	2.000	0.248	0.1240

COMPONENTS:	EVALUATOR:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

The values of c_{CuBr}/c_{MBr} of Tables 25 and 26 are shown graphically in Fig. 4. Note that the solubility in the two media are essentially identical at low bromide concentrations, but that the solubility in KBr rapidly becomes larger than that in NaBr as the bromide concentration is increased.

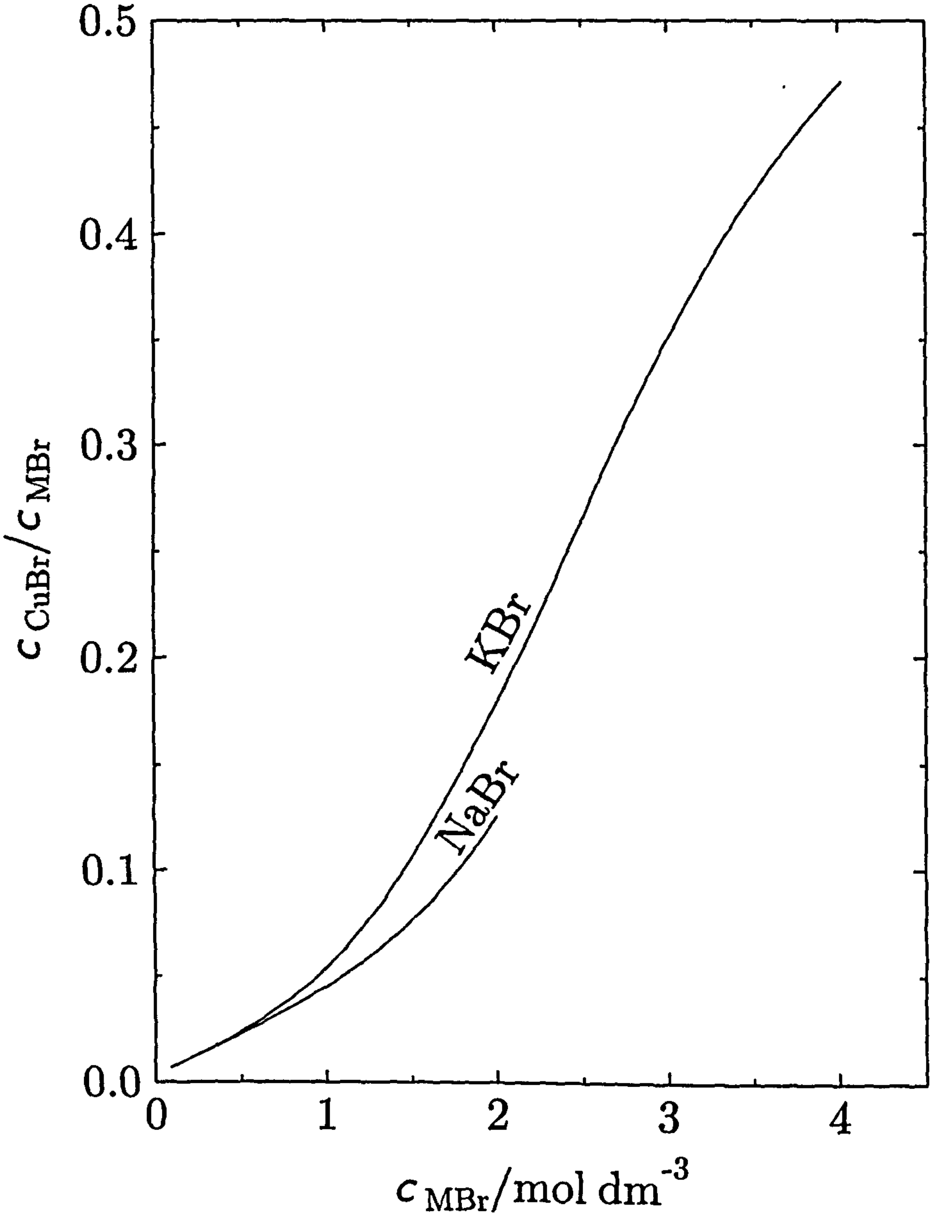

Fig. 4. Ratio of CuBr Solubility to Initial Concentration of Aqueous Bromide Plotted Against Concentration for KBr and NaBr at 298 K

COMPONENTS:	EVALUATOR:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H_2O; [7732-18-5]	Gavrish, M. L.; Galinker, I. S. *Dokl. Akad. Nauk SSSR* 1955, *102*, 89-91.
VARIABLES:	PREPARED BY:
$T/K = 473$ to 603	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in Water

$t/°C$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/°C$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/°C$	$\frac{m_1}{\text{mol kg}^{-1}}$
200	0.149	260	0.49	300	0.820
220	0.217	270	0.66	310	0.930
230	0.286	280	0.716	320	1.01
240	0.369	290	0.790	330	1.07
250	0.411				

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions prepared in 140 cm^3 quartz bomb inside autoclave maintained at desired temperatures. Samples of salt pressed into pellets under 2000 atm, then weighed carefully. Samples put into equilibrium with known mass of water over 2-hour period at selected temperature. Solubility determined by loss of mass of pellet.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Potassium Bromide; KBr; [7758-02-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Bodländer, G.; Storbeck, O.
Z. Anorg. Chem. 1902, *31*, 458–476.

VARIABLES:

Composition at 291 to 293 K[a]

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous KBr

$10^3 c_2$/mol dm^{-3}	$10^3 [Cu^{2+}]$/mol dm^{-3} [b]	$10^3 c_1$/mol dm^{-3}
25	0.012	0.107
40	0.013	0.187
60	0.025	0.285
80	0.012	0.411
100	–	0.5836
120	–	0.6934
500	–	8.719

Notes: [a] The exact temperature of each measurement was not given.

[b] The concentrations of Cu^{2+} given arose through disproportionation of dissolved Cu^+ to produce metallic Cu and Cu^{2+}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Air-free KBr solutions kept with excess solid CuBr for 15–20 hours, with shaking. Determined the total copper present in solution by electrolysis, the amount present as Cu^{2+} by iodometric titration using thiosulfate. The dissolved Cu^+ was then taken by difference.

SOURCE AND PURITY OF MATERIALS:

Prepared CuBr by reduction of an aqueous mixture of $CuSO_4$ and KBr with SO_2. Source and purity of materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Potassium Bromide; KBr; [7758-02-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Malik, W. U.; Rahman, S. M. F.; Malik, A.
Z. Anorg. Allg. Chem. 1962, *314*, 276-280.

VARIABLES:

Concentration of KBr at 323 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous KBr at 50°C

ρ_2/g dm^{-3}	c_2/mol dm^{-3} [a]	ρ_1/g dm^{-3}	c_1/mol dm^{-3} [a]
185.39	1.558	65.4	0.524
170.31	1.431	58.2	0.406
164.3	1.381	41.5	0.289
152.6	1.282	33.3	0.232
140.9	1.184	31.6	0.220
134.6	1.131	26.4	0.184
128.9	1.083	20.3	0.142
120.3	1.011	15.87	0.111
73.03	0.614	8.71	0.061
70.98	0.596	6.88	0.048
69.1	0.581	4.9	0.034
63.4	0.533	3.9	0.027
62.6	0.526	3.6	0.025
61.2	0.514	3.2	0.023
54.8	0.461	2.8	0.020

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Diluted portions of an unsaturated solution, held them in sealed tubes at 323 K (time not specified), then analyzed both solution and wet residue. Cuprous ion determined by titration with NH_4SCN using feric alum indicator. Potassium determined by precipitation with sodium cobaltinitrite. From analysis of wet residues, they concluded that the solid phase contained double salts of KBr and CuBr, but they don't indicate clearly which double salt was present at any given solution composition. (See Critical Evaluation.)

SOURCE AND PURITY OF MATERIALS:

CuBr prepared from an aqueous mixture of $CuSO_4$ and NaBr by reduction with SO_2. Source of materials not given. No purities stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Potassium Bromide; KBr; [7758-02-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Wilke, K.-Th.
Krist. Tech. 1968, *3*, K53–K55.

VARIABLES:

Molality of KBr at 298 to 328 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous KBr

t/°C	KBr in Solution[a]		Solubility of CuBr[a]	
	g/100 ml H_2O	m_2/mol kg^{-1}	g/100 ml H_2O	m_1/mol kg^{-1}
25	65.6	5.51	2.3	0.16
	32.8	2.76	0.5	0.03
	16.4	1.38	0.07	0.005
35	65.6	5.51	2.3	0.16
	32.8	2.76	0.5	0.03
	16.4	1.38	0.08	0.006
45	65.6	5.51	2.4	0.17
	32.8	2.76	0.6	0.04
	16.4	1.38	0.08	0.006
55	65.6	5.51	2.4	0.17
	32.8	2.76	0.6	0.04
	16.4	1.38	0.1	0.007

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Sodium Bromide; NaBr; [7647-15-6]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Wilke, K.-Th.
Krist. Tech. 1968, *3*, K53–K55.

VARIABLES:

Molality of NaBr at 298 to 328 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous NaBr

t/°C	NaBr in Solution[a]		Solubility of CuBr[a]	
	g/100 ml H_2O	m_2/mol kg^{-1}	g/100 ml H_2O	m_1/mol kg^{-1}
25	90.5	8.79	2.5	0.17
	45.3	4.40	0.6	0.04
	22.6	2.20	0.1	0.007
35	90.5	8.79	2.6	0.18
	45.3	4.40	0.7	0.05
	22.6	2.20	0.1	0.007
45	90.5	8.79	2.8	0.20
	45.3	4.40	0.7	0.05
	22.6	2.20	0.1	0.007
55	90.5	8.79	2.8	0.20
	45.3	4.40	0.8	0.06
	22.6	2.20	0.2	0.014

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Hydrogen Bromide; HBr; [10035-10-6]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Wilke, K.-Th.
Krist. Tech. 1968, *3*, K53–K55.

VARIABLES:

$T/K = 298$ to 328

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous HBr

$t/°C$	HBr in Solution[a]		Solubility of CuBr[a]	
	g/100 ml H_2O	m_2/mol kg^{-1}	g/100 ml H_2O	m_1/mol kg^{-1}
25	40	4.9	2.9	0.20
35	40	4.9	3.0	0.21
45	40	4.9	3.1	0.22
55	40	4.9	3.1	0.22

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Lithium Bromide; LiBr; [7550-35-8] (3) Water; H_2O; [7732-18-5]	Wilke, K.-Th. *Krist. Tech.* 1968, *3*, K53–K55.
VARIABLES:	**PREPARED BY:**
Molality of LiBr at 298 to 328 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous LiBr

t/°C	LiBr in Solution[a]		Solubility of CuBr[a]	
	g/100 ml H_2O	m_2/mol kg^{-1}	g/100 ml H_2O	m_1/mol kg^{-1}
25	177.	20.4	3.9	0.27
	88.5	10.2	2.1	0.15
	44.3	5.1	0.4	0.03
35	177.	20.4	4.1	0.29
	88.5	10.2	2.2	0.15
	44.3	5.1	0.5	0.04
45	177.	20.4	4.4	0.31
	88.5	10.2	2.3	0.16
	44.3	5.1	0.5	0.04
55	177.	20.4	4.6	0.32
	88.5	10.2	2.4	0.17
	44.3	5.1	0.5	0.04

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Not given.	Not given.
	ESTIMATED ERROR:
	Not given.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Ammonium Bromide; NH_4Br; [12124-97-9] (3) Water; H_2O; [7732-18-5]	Wilke, K.-Th. *Krist. Tech.* 1968, *3*, K53-K55.
VARIABLES:	**PREPARED BY:**
Molality of NH_4Br at 298 to 328 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous NH_4Br

t/°C	NH_4Br in Solution[a]		Solubility of CuBr[a]	
	g/100 ml H_2O	m_2/mol kg^{-1}	g/100 ml H_2O	m_1/mol kg^{-1}
25	73.9	7.54	3.3	0.23
	36.9	3.77	0.5	0.03
	18.5	1.89	0.07	0.005
35	73.9	7.54	3.4	0.24
	36.9	3.77	0.6	0.04
	18.5	1.89	0.07	0.005
45	73.9	7.54	3.4	0.24
	36.9	3.77	0.6	0.04
	18.5	1.89	0.08	0.006
55	73.9	7.54	3.4	0.24
	36.9	3.77	0.6	0.04
	18.5	1.89	0.08	0.006

[a] Molalities were calculated by the compiler, taking the author's "g/100 ml H_2O" to mean g/100 g H_2O within the precision of the data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Potassium Bromide; KBr; [7758-02-3]
(3) Potassium Nitrate; KNO_3; [7757-79-1]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fritz, J. J.; Luzik, E.
J. Solution Chem. 1987, *16*, 79-85.

VARIABLES:

Concentrations of KBr and KNO_3 at 298.0 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous KBr at 24.8°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.0989	0.00064
0.1978	0.00185
0.3955	0.00633
0.4738	0.00959
0.5933	0.01539
0.7910	0.0289
0.9888	0.0496
1.483	0.1511
1.978	0.334
2.472	0.647
2.966	1.005
3.461	1.418
3.955	1.860

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added excess CuBr to KBr solutions, held mixture in a sealed flask under nitrogen for at least 8 hours at 298.0 ± 0.1 K with intermittent shaking, then analysed solutions for copper iodometrically after oxidation to Cu^{2+} with HNO_3. The KBr solutions used were standardized using the Volhard method. Traces of Cu^{2+} in saturated solutions were determined colorimetrically as $Cu(NH_3)_4^{2+}$. All solutions were prepared at least in duplicate and each was analyzed at least in triplicate.

SOURCE AND PURITY OF MATERIALS:

Used reagent grade KBr and KNO_3. Prepared CuBr following the method described by Keller and Wycoff for CuCl (Ref. 1). The CuBr was washed with dilute H_2SO_3 and with glacial acetic acid, then dried with absolute ethanol and anhydrous diethyl ether, after which it was stored in a dark air-tight bottle until used. All distilled water used to prepare solutions was boiled in a stream of pure nitrogen to remove oxygen.

ESTIMATED ERROR:

2% for all but lowest concentrations (4%).

REFERENCES:

1. Keller, R. N.; Wycoff, H. O. *Inorganic Syntheses*, 1942, 2, 1.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Potassium Bromide; KBr; [7758-02-3] (3) Potassium Nitrate; KNO_3; [7757-79-1] (4) Water; H_2O; [7732-18-5]	Fritz, J. J.; Luzik, E. *J. Solution Chem.* 1987, *16*, 79-85.

EXPERIMENTAL VALUES:

(continued)

Solubility of CuBr in KBr–KNO_3 Solutions at 24.8°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.3955	1.605	0.0101
0.5159	1.483	0.0171
0.5933	1.404	0.0226
0.7910	1.204	0.0415
0.9888	1.003	0.0683
1.384	0.602	0.1483
1.582	0.401	0.197
1.780	0.201	0.266
0.450	2.553	0.0157
0.901	2.102	0.0691
1.501	1.502	0.224
1.801	1.201	0.335
2.402	0.601	0.643

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Sodium Bromide; NaBr; [7647-15-6]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Peters, D. G.; Caldwell, R. L.
Inorg. Chem. 1967, *6*, 1478–1483.

VARIABLES:

Bromide ion concentration at 298 K, ionic strength[a] of 2.0 mol dm^{-3}

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuBr in NaBr–$NaNO_3$ Solutions at 25°C

$[Br^-]$/mol dm^{-3}	c_1/mol dm^{-3}
0.051	0.00035 ± 0.00002
0.102	0.00079 ± 0.00001
0.206	0.00223 ± 0.00001
0.495	0.0104 ± 0.0001
0.595	0.0151 ± 0.0001
0.798	0.0282 ± 0.0002
1.01	0.0456 ± 0.0018
1.52	0.118 ± 0.008

[a] Ionic strength maintained using $NaNO_3$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stock solutions were prepared with specified amounts of $CuBr_2$, NaBr and $NaNO_3$. The Cu^{2+} was then reduced electrochemically to produce solid CuBr in equilibrium with solution. Dissolved CuBr was determined electrolytically and bromide by titration with $AgNO_3$.

SOURCE AND PURITY OF MATERIALS:

Reagent grade chemicals used; purities not given.

ESTIMATED ERROR:

Estimated errors given in table above.

REFERENCES:

COMPONENTS:

(1) Copper(I) Bromide; CuBr; [7787-70-4]
(2) Sodium Bromide; NaBr; [7647-15-6]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ahrland, S.; Tagesson, B.
Acta Chem. Scand. 1977, *A31*, 615-624.

VARIABLES:

Concentration of NaBr at 298 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuBr in $NaBr-NaClO_4-(HClO_4)$ Solutions at 25°C

$[Br^-]_{free}$ / mol dm^{-3}	c_3 / mol dm^{-3}	c_4 / mol dm^{-3}	$[Br^-]_{total}$[a] / mol dm^{-3}	c_1 / mol dm^{-3}
0.113	0.10	4.887	0.113	0.00039
0.201	0.10	4.698	0.202	0.00156
0.226	0.10	4.673	0.227	0.00218
0.283	0.10	4.616	0.284	0.00367
0.429	0.10	4.469	0.431	0.00743

[a] The total bromide concentrations were calculated by the compiler using the free bromide concentrations given and the equilibrium constants for complex formation given by the authors. Observe that very little of the bromide was involved in the complexes.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The main work of the investigation was a potentiometric study of the stability constants of the cupro-bromide complexes, using mainly unsaturated CuBr solutions at an ionic strength of 5.0 mol dm^{-3}. When the potential measurements showed that the solution had become saturated, that solution was treated with concentrated $HClO_4$ to oxidize the copper to Cu^{2+}, which was then determined spectrometrically as the cuprizone complex.

SOURCE AND PURITY OF MATERIALS:

Used BDH copper(I) bromide; $NaClO_4$ (Fluka) purified by recristallization; NaBr (*Mallinckrodt* p. a.) used without further purification.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Organic Solvents	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

BINARY SYSTEMS

There have been two reports of the solubility of CuBr in an organic solvent without any added salt. In 1914 Naumann and Schier[1] reported that the solubility of CuBr in acetonitrile at 291 K was approximately 0.0386 g CuBr per g acetonitrile.

In 1977 Machtinger *et al.*[2] gave a value of the solubility product of CuBr in molten dimethyl sulfone $[(CH_3)_2SO_2]$ at 400 K as $10^{-12.4}$ $(4 \cdot 10^{-13})$ $mol^2\ kg^{-2}$ from cell measurements in which the potential of a copper elecrode was measured as a function of bromide molality (provided by addition of tetraethylammonium bromide) with a Cu^+ molality of 10^{-3} $mol\ kg^{-1}$. Their value of K_{S0} would correspond to a solubility of about $6.3 \cdot 10^{-7}$ $mol\ kg^{-1}$ in the molten dimethyl sulfone.

TERNARY SYSTEMS

Machtinger *et al.*[2] also used titration curves to evaluate a stability constant for the ion $CuBr_2^-$ in molten dimethyl sulfone $[(CH_3)_2SO_2]$ at 400 K, with bromide ion between 0.008 and 0.2 $mol\ kg^{-1}$. They gave the stability constant as $10^{15.1}$ $(1.3 \cdot 10^{15})$ $mol^{-2}\ kg^2$. Using this value with their value for the solubility product of CuBr in their medium gives a value of K_{S2} for addition of Br^- to $CuBr_{(s)}$, *viz.*:

$$CuBr_{(s)} + Br^- \rightleftharpoons CuBr_2^- \qquad K_{S2} = 520$$

This value of K_{S2} would correspond to essentially complete absorption of Br^- by solid cuprous bromide. Machtinger *et al.*[2] do not report any actual solubilities, but indicate their expectation of a solubility of 0.008 $mol\ kg^{-1}$ in the presence of only about 10^{-5} $mol\ kg^{-1}$ of free Br^-!

REFERENCES

1. Naumann, A.; Schier, A. *Ber. Dtsch. Chem. Ges.* 1914, *47*, 247.
2. Machtinger, M.; Vuaille, M. J.; Tremillon, B. *J. Electroanal. Chem. Interfacial Electrochem.* 1977, *83*, 273.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

THE BINARY SYSTEM

There are very few data on the solubility of cuprous iodide in pure water. In 1902 Bodländer and Storbeck[1] reported a value of $5.06 \cdot 10^{-12}$ mol^2 dm^{-6} for the solubility product at a temperature of about 293 K, based on cell measurements and their value for the solubility product of CuBr. This value was quoted in 1931 by Kolthoff and Furman[2]. At 298.15 K five values for the solubility product (K_{S0}) at zero ionic strength were found, as follows: The thermodynamic data given in U. S. National Bureau of Standards Circular 500[3] (1952) yields a value of $1.2 \cdot 10^{-12}$ mol^2 dm^{-6}; Zhuk[4] (1954) quotes a value of $1.1 \cdot 10^{-12}$ mol^2 dm^{-6}, as do Latimer[5] (1952) and Chaltykyan[6] (1966); Krestov *et al.*[7] (1977) quote a value of $1.3 \cdot 10^{-12}$ mol^2 dm^{-6}. A value of $(1.2 \pm 0.1) \cdot 10^{-12}$ mol^2 dm^{-6} is Accepted tentatively. (Note that the solubility of CuI in pure water will be higher than that calculated from the solubility product because of additional unknown contributions from the formation of neutral CuI^0 and the reaction $2CuI_{(s)} \rightleftharpoons Cu^+ + CuI_2^-$.) Ahrland and Tagesson[8] reported a value of $(1.92 \pm 0.06) \cdot 10^{-13}$ mol^2 dm^{-6} at 298.16 K, 5.0 mol dm^{-3} ionic strength maintained by acidified $NaClO_4$. This value is surprisingly low, but could be valid for the high ionic strength they used. Golub, Sazhienko and Romanenko[9] (1962) reported a value of $9.4 \cdot 10^{-13}$ mol^2 dm^{-6} at 20°C (293 K); this is not unreasonable for that temperature.

Gavrish and Galinker[10] made measurements of the solubility (mol kg^{-1}) of CuI in water at 9 temperatures from 453 to 613 K. When values of the natural logarithm of solubility (S) from their data are plotted against reciprocal temperature (K), there is some downward curvature at the higher temperatures, but there is appreciable scatter in the data. Over the entire range the data fit a straight line

$$\ln(m_{\mathrm{CuI}}/\mathrm{mol\ kg^{-1}}) = -5692\ \mathrm{K}/T + 6.920$$

with an average deviation of about 12 per cent (worst point 20 per cent high). Their data are Accepted tentatively with an estimated uncertainty of 12 per cent. (This sort of uncertainty is not surprising in view of the difficulty of measuring the solubility at the high temperatures.) No attempt has been made to connect their points with data at 298 K because of the large intermediate interval of temperature where no data are available.

SYSTEMS INVOLVING IODIDES

Two sets of measurements of the solubility of cuprous iodide in aqueous sodium iodide have been reported. In 1968, Gyunner and Yakhkind[11] made 13 measurements at 293 K in a nominal ionic strength of 3.9 mol dm^{-3}, using $NaNO_3$ to maintain ionic strength as the concentration of NaI was varied from 0.400 to 3.900 mol dm^{-3}. In connection with an extensive potentiometric study of complex formation between CuI and I^-, Ahrland and Tagesson[8] (1977) measured the solubility at 298.16 K, 5.0 mol dm^{-3} ionic strength maintained by $NaClO_4$ with 0.1 mol dm^{-3} $HClO_4$ added. Their graph covers the range 0.2 to 1.0 mol dm^{-3} concentration of NaI, but shows only four measured points, with the remainder of the graph calculated from values they give for the stability constants of the complexes and their solubility product, given above.

Three sets of measurements were found for the solubility of CuI in aqueous potassium iodide. In 1959, Fridman and Sarbaev[12] reported two sets of five measurements each at 298 K, one in which the medium contained only KI at concentrations from 1.0 to 5.9 mol dm^{-3}, and another in which the concentration of KI was varied from 1.0 to 4.9 mol dm^{-3}, with a constant nominal ionic strength of 5.0 mol dm^{-3} maintained by use of $NaNO_3$. In 1962, Golub *et al.*[9] reported two series of measurements at 293 K, one (8 points) at ionic strength of 0.6 mol dm^{-3} (KI from 0.1 to 0.6 mol dm^{-3}) and the other (13 points) at ionic strength

COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

of 4.0 mol dm^{-3}, with KI from 0.5 to 3.3 mol dm^{-3}. In 1964 Gavrish and Galinker[13] reported a limited set of measurements at four temperatures between 473 and 593 K. They present their results at 573 K in the form of a graph of log[I$^-$] plotted against log[CuI_2^-], where [I$^-$] is the equilibrium concentration of iodide ion in mol dm^{-3} and [CuI_2^-] is the corresponding concentration of the only complex believed formed (thus the solubility). Their results at the other three temperatures are given only as the value of K_{S2}, the equilibrium constant for the formation of CuI_2^- from $CuI_{(s)}$ and I$^-$.

Because of the differences in conditions employed, it was not possible to compare the measurements in the aqueous alkali iodides directly. Instead, a model including equilibrium constants (for complex formation) and virial parameters was constructed to fit all of the data at 298 K simultaneously. The model is described in a section on Thermodynamics, later. With the exception of a few points, it fitted the data set (52 points) to about 6 per cent. The results of the comparison of data are given below for the CuI–NaI and CuI–KI systems separately.

Only one set of measurements has been reported for the solubility of CuI in aqueous hydrogen iodide. These were made by Popolitov *et al.*[14] at temperatures of 200, 250 and 300°C, with four points at each temperature, for HI concentrations of 0.33 to 3.4 mol dm^{-3}. These will be considered separately below.

No solubility data were found for the system $CuI–NH_4I–H_2O$, but Wells and Hurlburt[15] were able to prepare a double salt $CuI{\cdot}NH_4I$ from a solution of the two salts in aqueous HI. The solubility of CuI in aqueous NH_4I should be at least as large as in corresponding concentrations of aqueous KI.

$CuI–NaI–H_2O$

The results of Gyunner and Yakhkind[11] at 293 K are smooth and consistent to a few per cent for NaI concentrations of 2.0 mol dm^{-3} and above. Points at lower NaI concentrations are consistently high compared with the other data available (a factor of 3 at the lowest concentration). The data at 2.0 mol dm^{-3} and above are Accepted tentatively as appropriate for the measurement conditions they used. Their data below this concentration are apparently too high. Values resulting from the constants given by Ahrland and Tagesson[8] are consistent with data for other conditions to about 6 per cent, and should be suitable for their conditions within this uncertainty.

$CuI–KI–H_2O$

The data of Fridman and Sarbaev[12] for systems containing only KI agreed with other data to about 6 per cent. The data they obtained using $NaNO_3$ to maintain a nominal ionic strength of 5.0 mol dm^{-3} agreed to about 8 per cent except for their lowest point (1.002 mol dm^{-3} KI), which was distinctly high. Except for this point, their data are Accepted, with the uncertainties given above. Those of Golub *et al.*[9] were somewhat less consistent. Their point for KI concentration of 0.521 mol dm^{-3}, ionic strength 4.0, appears to be almost 50 per cent low; their remaining points agree with other data to about 10 per cent. Except for the point cited, their data are Accepted tentatively with precision of 10 per cent.

The data given by Gavrish and Galinker[13] can be used to estimate the solubility of cuprous iodide at high temperatures. Their equilibrium constants are discussed in the section on Thermodynamics, below. They imply solubility proportional to the original concentration of KI. For KI concentration of 1 mol dm^{-3}, their constants predict solubilities at the various temperatures of 0.063 (473 K), 0.174 (533 K), 0.324 (573 K) and 0.426 (593 K) mol dm^{-3}. There is no way of evaluating the reliability of these estimates, but they should give at least the proper order of magnitude of the high temperature solubility.

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]

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

EVALUATOR:

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Department of Chemistry
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June, 1991

CRITICAL EVALUATION:

CuI–HI–H_2O

It is not possible to make an unambiguous interpretation of the data of Popolitov *et al.*[14]. They give their data in two graphical forms. Their Fig. 1 shows the solubility of CuI in mass per cent plotted against concentration of HI in mol dm^{-3}; their Fig. 2 gives log S (units unspecified) plotted against mass per cent HI. It would appear that concentrations of HI in Fig. 2 correspond (at least approximately) to those used in Fig. 1. However, the values of log S shown are several-fold smaller than correspond to the values shown in Fig. 1. The best interpretation that can be made is that the values of solubility given in Fig. 1 do indeed correspond to concentrations of HI of 5, 15, 25 and 35 mass per cent. As such, the values given for 473 K are 3 to 5 times as large as the corresponding values for aqueous KI at 298 K, with those at 573 K six to ten times larger than those for KI at 298 K. In the region 473 to 573 K they give an average enthalpy of solution of 20 ± 2 kJ. Their results cannot be considered definitive, but can be taken to give an approximate idea of the solubility of CuI in aqueous HI in the temperature range they investigated.

THERMODYNAMICS OF SOLUTIONS INVOLVING IODIDES

The model mentioned above used virial parameters for ion pairs involving I^-, NO_3^- and ClO_4^- from Pitzer and Mayorga[16]; all other parameters were optimized so as to minimize the sum of squares of the per cent deviation of calculated from observed solubilities. The complexes considered were CuI^0, CuI_2^-, CuI_3^{2-} and $Cu_3I_6^{3-}$. Table 27 gives the equilibrium constants and enthalpies of reactions for formation of the various complexes from $CuI_{(s)}$ and I^-. Table 28 gives virial parameters for solutions in aqueous NaI and KI. There were not adequate data for obtaining parameters for aqueous HI.

Table 27. Equilibrium Constants[a,b] and Enthalpies of Reaction[c] at 298 K for Formation of Complexes from $CuI_{(s)}$ and I^-

Species	$\frac{K_{Smn}}{(\text{mol dm}^{-3})^{(1+m-n)}}$	$\frac{\Delta_r H^\ominus}{\text{kJ mol}^{-1}}$
CuI^0	$1.5 \cdot 10^{-5}$	—
CuI_2^-	$7.9 \cdot 10^{-5}$	33.9
CuI_3^{2-}	$7.8 \cdot 10^{-4}$	58.6
$Cu_3I_6^{3-}$	$4.4 \cdot 10^{-6}$	32.2

[a] The neutral complex CuI^0 did not contribute significantly to the solubilities and a value near that for $CuBr^0$ improved the fit for the few points where it contributed noticeably. No attempt was made to obtain an enthalpy change for this reaction.

[b] The equilibrium constants are the K_{Smn} for reactions $m\,CuI_{(s)} + (n-m)I^- \rightleftharpoons Cu_mI_n^{m-n}$, with standard state in mol dm^{-3}.

[c] The enthalpy changes are those for the reactions of Note b. Because of the small temperature range covered and the lack of precision of the data, they are approximate only.

Values previously reported for formation constants of iodocuprous complexes are: In 1902 Bodländer and Storbeck[1] gave a value of $1.55 \cdot 10^8$ for the stability constant of CuI_2^- at about 293 K, corresponding to a value of $7.8 \cdot 10^{-4}$ for the formation constant K_{S2}. In 1952 Latimer[5] gave a value of $6.3 \cdot 10^{-4}$ for K_{S2} at 298 K; he did not specify his source, but quoted Bodländer and Storbeck[1], apparently modifying their result somewhat. In 1964 Gavrish and Galinker[13] gave a set of values for K_{S2} at temperatures from 473 to 593 K with values of 0.067 (473 K), 0.211 (533 K), 0.479 (573 K) and 0.741 (593 K). The variation

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

of these constants with temperature corresponds to a heat of reaction of 46 kJ, somewhat higher than that given in Table 25. In 1977 Ahrland and Tagesson[8] gave a set of stability constants at 298.15 K for a medium maintained at ionic strength 5.0 mol dm^{-3}. They considered CuI_2^- and CuI_3^{2-}, but used a different set of complexes of higher charge. Values corresponding to the constants of Table 25 calculated from their results are of the same magnitude as those given above; they would not be expected to be the same, considering the large effect their medium could have on the constants.

Table 28. Virial Parameters[a] at 298 K for Ion Pairs Formed by Iodide Species with Na$^+$ and K$^+$ (for Concentrations in mol dm^{-3})

Species	Pairs with Na$^+$			Pairs with K$^+$		
	$\beta^{(0)}$	$\beta^{(1)}$	C	$\beta^{(0)}$	$\beta^{(1)}$	C
I^-	0.1195	0.3439	0.0009	0.0746	0.2517	−0.00207
CuI^0	0.235	0.322	−0.031	0.235	0.322	−0.031
CuI_2^-	−0.1171	−2.821	−0.0029	−0.082	−3.673	0.11234
CuI_3^{2-}	0.3438	−1.289	0.03312	0.122	−1.124	0.01198
$Cu_3I_6^{3-}$	0.2467	3.547	−0.003098	0.123	3.37	−0.00732

[a] The parameters for the 'salting out' effect for CuI^0 were put in the same form as for the charged complexes for convenience in calculation and assigned the same values as for CuBr; in any case this species did not contribute significantly to the solubility.

RECOMMENDED VALUES FOR SOLUBILITY IN AQUEOUS ALKALI IODIDES

Since virtually none of the data available are for an alkali iodide without another added salt, the parameters of Tables 27 and 28 were used to get reasonable estimates of these solubilities. Tables 29 and 30 give a set of smoothed values for the solubility of CuI in aqueous NaI and aqueous KI at 293 and 298 K, calculated in this manner. The values given should be valid within about 10 per cent and perhaps somewhat better than this. As an aid in interpolation, values of c_{CuI}/c_{MI}, the ratio of solubility to iodide concentration, is given for each concentration, to somewhat greater precision than the solubility itself. c_{CuI}/c_{MI} is plotted against iodide concentration for both iodide solutions in Fig. 5. It will be noted that at low iodide concentrations the difference between the solubility in the two media is almost negligible. For iodide concentrations above 0.5 mol dm^{-3} the solubility in aqueous KI increases more rapidly than that in aqueous NaI, and becomes over 50 per cent larger for an iodide concentration of 5 mol dm^{-3}. No recommended values are given for the solubility of CuI in aqueous HI because of the scarcity of the data and the difficulty in interpreting that which is available.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Table 29. Solubility and Ratio of Solubility to Initial Iodide Concentration for CuI in Aqueous NaI

c_{NaI} / mol dm^{-3}	$T = 293$ K		$T = 298$ K	
	c_{CuI}/mol dm^{-3}	c_{CuI}/c_{NaI}	c_{CuI}/mol dm^{-3}	c_{CuI}/c_{NaI}
0.100	$3.60 \cdot 10^{-5}$	$3.60 \cdot 10^{-4}$	$4.47 \cdot 10^{-5}$	$4.47 \cdot 10^{-4}$
0.200	$1.106 \cdot 10^{-4}$	$5.53 \cdot 10^{-4}$	$1.530 \cdot 10^{-4}$	$7.65 \cdot 10^{-4}$
0.300	$2.715 \cdot 10^{-4}$	$9.05 \cdot 10^{-4}$	$3.89 \cdot 10^{-4}$	$1.298 \cdot 10^{-3}$
0.400	$5.52 \cdot 10^{-4}$	$1.380 \cdot 10^{-3}$	$8.03 \cdot 10^{-4}$	$2.008 \cdot 10^{-3}$
0.500	$9.84 \cdot 10^{-4}$	$1.967 \cdot 10^{-3}$	$1.440 \cdot 10^{-3}$	$2.879 \cdot 10^{-3}$
0.600	$1.595 \cdot 10^{-3}$	$2.658 \cdot 10^{-3}$	$2.338 \cdot 10^{-3}$	$3.897 \cdot 10^{-3}$
0.700	$2.412 \cdot 10^{-3}$	$3.446 \cdot 10^{-3}$	$3.533 \cdot 10^{-3}$	$5.047 \cdot 10^{-3}$
0.800	$3.45 \cdot 10^{-3}$	$4.316 \cdot 10^{-3}$	$5.06 \cdot 10^{-3}$	$6.322 \cdot 10^{-3}$
0.900	$4.74 \cdot 10^{-3}$	$5.262 \cdot 10^{-3}$	$6.93 \cdot 10^{-3}$	$7.703 \cdot 10^{-3}$
1.000	$6.27 \cdot 10^{-3}$	$6.271 \cdot 10^{-3}$	$9.17 \cdot 10^{-3}$	$9.165 \cdot 10^{-3}$
1.100	$8.06 \cdot 10^{-3}$	$7.236 \cdot 10^{-3}$	$1.175 \cdot 10^{-2}$	$1.086 \cdot 10^{-2}$
1.200	$1.011 \cdot 10^{-2}$	$8.428 \cdot 10^{-3}$	$1.469 \cdot 10^{-2}$	$1.224 \cdot 10^{-2}$
1.300	$1.244 \cdot 10^{-2}$	$9.573 \cdot 10^{-3}$	$1.799 \cdot 10^{-2}$	$1.384 \cdot 10^{-2}$
1.400	$1.490 \cdot 10^{-2}$	$1.064 \cdot 10^{-2}$	$2.166 \cdot 10^{-2}$	$1.547 \cdot 10^{-2}$
1.500	$1.770 \cdot 10^{-2}$	$1.180 \cdot 10^{-2}$	$2.567 \cdot 10^{-2}$	$1.711 \cdot 10^{-2}$
1.600	$2.069 \cdot 10^{-2}$	$1.293 \cdot 10^{-2}$	$2.997 \cdot 10^{-2}$	$1.873 \cdot 10^{-2}$
1.700	$2.393 \cdot 10^{-2}$	$1.408 \cdot 10^{-2}$	$3.455 \cdot 10^{-2}$	$2.032 \cdot 10^{-2}$
1.800	$2.737 \cdot 10^{-2}$	$1.521 \cdot 10^{-2}$	$3.94 \cdot 10^{-2}$	$2.188 \cdot 10^{-2}$
1.900	$3.102 \cdot 10^{-2}$	$1.633 \cdot 10^{-2}$	$4.44 \cdot 10^{-2}$	$2.339 \cdot 10^{-2}$
2.000	$3.49 \cdot 10^{-2}$	$1.744 \cdot 10^{-2}$	$4.97 \cdot 10^{-2}$	$2.485 \cdot 10^{-2}$
2.200	0.0431	0.01958	0.0608	0.02763
2.400	0.0520	0.02164	0.0726	0.03024
2.600	0.0614	0.02363	0.0852	0.03276
2.800	0.0716	0.02558	0.0986	0.03520
3.000	0.0827	0.02756	0.1128	0.03762
3.200	0.0948	0.02962	0.1283	0.04010
3.400	0.1082	0.03181	0.1453	0.04273
3.600	0.1231	0.03420	0.1653	0.04564
3.800	0.1398	0.03687	0.1859	0.04893
4.000	0.1597	0.03993	0.2108	0.05270
4.200	0.1825	0.04345	0.2396	0.05705
4.400	0.2090	0.04751	0.2732	0.06210
4.600	0.2400	0.05217	0.3126	0.06795
4.800	0.2758	0.05747	0.3588	0.07475
5.000	0.3122	0.06343	0.4131	0.08262

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]

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

EVALUATOR:

J. J. Fritz

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

Table 30. Solubility and Ratio of Solubility to Initial Iodide Concentration for CuI in Aqueous KI

c_{KI}	$T = 293$ K		$T = 298$ K	
mol dm^{-3}	c_{CuI}/mol dm^{-3}	c_{CuI}/c_{KI}	c_{CuI}/mol dm^{-3}	c_{CuI}/c_{KI}
0.100	$3.66 \cdot 10^{-5}$	$3.66 \cdot 10^{-4}$	$4.53 \cdot 10^{-5}$	$4.53 \cdot 10^{-4}$
0.200	$1.132 \cdot 10^{-4}$	$5.66 \cdot 10^{-4}$	$1.560 \cdot 10^{-4}$	$7.80 \cdot 10^{-4}$
0.300	$2.739 \cdot 10^{-4}$	$9.13 \cdot 10^{-4}$	$3.93 \cdot 10^{-4}$	$1.309 \cdot 10^{-3}$
0.400	$5.58 \cdot 10^{-4}$	$1.396 \cdot 10^{-3}$	$8.10 \cdot 10^{-4}$	$2.024 \cdot 10^{-3}$
0.500	$1.002 \cdot 10^{-3}$	$2.004 \cdot 10^{-3}$	$1.450 \cdot 10^{-3}$	$2.908 \cdot 10^{-3}$
0.600	$1.634 \cdot 10^{-3}$	$2.724 \cdot 10^{-3}$	$2.377 \cdot 10^{-3}$	$3.962 \cdot 10^{-3}$
0.700	$2.490 \cdot 10^{-3}$	$3.557 \cdot 10^{-3}$	$3.663 \cdot 10^{-3}$	$5.188 \cdot 10^{-3}$
0.800	$3.50 \cdot 10^{-3}$	$4.500 \cdot 10^{-3}$	$5.26 \cdot 10^{-3}$	$6.577 \cdot 10^{-3}$
0.900	$5.00 \cdot 10^{-3}$	$5.556 \cdot 10^{-3}$	$7.31 \cdot 10^{-3}$	$8.117 \cdot 10^{-3}$
1.000	$6.71 \cdot 10^{-3}$	$6.710 \cdot 10^{-3}$	$9.79 \cdot 10^{-3}$	$9.793 \cdot 10^{-3}$
1.100	$8.76 \cdot 10^{-3}$	$7.961 \cdot 10^{-3}$	$1.275 \cdot 10^{-2}$	$1.159 \cdot 10^{-2}$
1.200	$1.165 \cdot 10^{-2}$	$9.304 \cdot 10^{-3}$	$1.622 \cdot 10^{-2}$	$1.352 \cdot 10^{-2}$
1.300	$1.396 \cdot 10^{-2}$	$1.074 \cdot 10^{-2}$	$2.024 \cdot 10^{-2}$	$1.557 \cdot 10^{-2}$
1.400	$1.715 \cdot 10^{-2}$	$1.225 \cdot 10^{-2}$	$2.483 \cdot 10^{-2}$	$1.774 \cdot 10^{-2}$
1.500	$2.073 \cdot 10^{-2}$	$1.382 \cdot 10^{-2}$	$2.994 \cdot 10^{-2}$	$1.996 \cdot 10^{-2}$
1.600	$2.470 \cdot 10^{-2}$	$1.544 \cdot 10^{-2}$	$3.56 \cdot 10^{-2}$	$2.223 \cdot 10^{-2}$
1.700	$2.908 \cdot 10^{-2}$	$1.711 \cdot 10^{-2}$	$4.18 \cdot 10^{-2}$	$2.456 \cdot 10^{-2}$
1.800	$3.389 \cdot 10^{-2}$	$1.883 \cdot 10^{-2}$	$4.85 \cdot 10^{-2}$	$2.694 \cdot 10^{-2}$
1.900	$3.91 \cdot 10^{-2}$	$2.060 \cdot 10^{-2}$	$5.58 \cdot 10^{-2}$	$2.936 \cdot 10^{-2}$
2.00	$4.48 \cdot 10^{-2}$	$2.242 \cdot 10^{-2}$	$6.37 \cdot 10^{-2}$	$3.183 \cdot 10^{-2}$
2.200	0.0578	0.02628	0.0811	0.03685
2.400	0.0724	0.03016	0.1007	0.04196
2.600	0.0888	0.03416	0.1225	0.04711
2.800	0.1077	0.03826	0.1465	0.05231
3.000	0.1274	0.04247	0.1727	0.05758
3.200	0.1498	0.04682	0.2014	0.06295
3.400	0.1746	0.05136	0.2327	0.06845
3.600	0.2022	0.05616	0.2671	0.07419
3.800	0.2329	0.06130	0.3049	0.08023
4.000	0.2675	0.06687	0.3464	0.08661
4.200	0.3192	0.07301	0.394	0.09372
4.400	0.3514	0.07987	0.447	0.1016
4.600	0.403	0.08767	0.509	0.1106
4.800	0.464	0.09666	0.582	0.1209
5.000	0.536	0.10719	0.665	0.1331

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-18-5] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

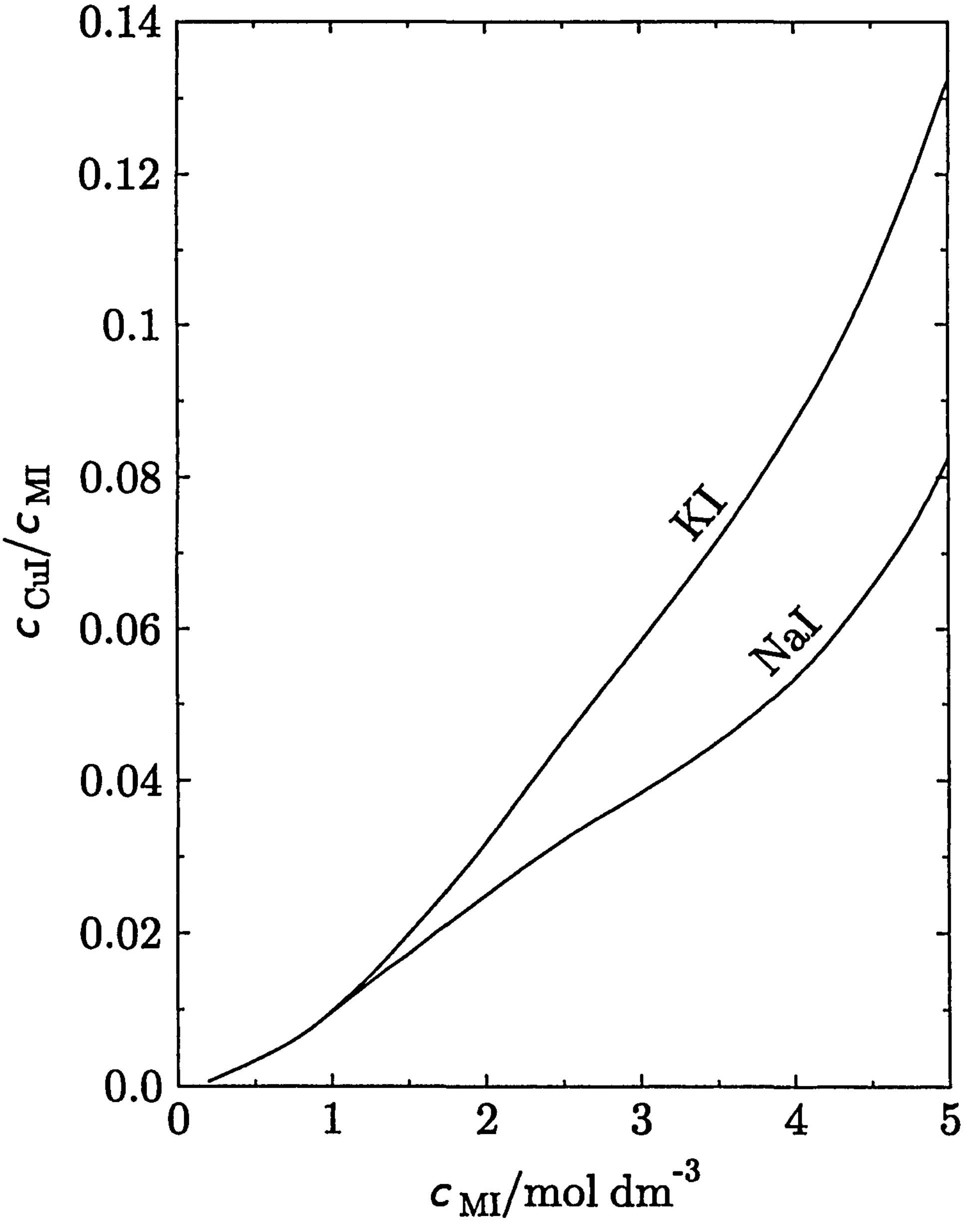

Fig. 5. Ratio of CuI Solubility to Initial Concentration of Aqueous Iodide Plotted Against Concentration for NaI and KI at 298.15 K

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

DOUBLE SALTS INVOLVING CuI

Mellor[17] describes early studies of compounds containing ammonia and/or NH_4I along with CuI. In a series of papers, Harris[18–21] reported a number of complex compounds involving CuI. These include 2CuI·NaI, compounds between CuI and ammonia or ethylene diamine, compounds between CuI and pyridinium or methylpyridinium iodide, compounds between CuI and CuI_2 complexed with ammonia or ethylene diamine and a variety of compounds of Cu(I) containing both iodine and bromine. These results suggest that cuprous iodide should be soluble in aqueous solutions of ammonia and amines, although no solubility measurements have been found for such systems.

SYSTEMS INVOLVING OTHER SOLUBLE HALIDES

There are four reports of the solubility of cuprous iodide in aqueous solutions of salts other than iodides. In 1909 Kohn[22] published results on the solubility of CuI in aqueous solutions of KBr from 2 to 4 mol dm^{-3} at temperatures from 291 to 297 K. In 1912, Kohn and Klein[23] gave results for the solubility in 2 to 4 mol dm^{-3} NH_4Br at 294 K. Finally, in 1959 Fridman and Sarbaev[12] gave values for the solubility at 298 K in aqueous KBr, 0.5 to 5 mol dm^{-3}, and in aqueous KCl, 2 to 4 mol dm^{-3}; in both cases the ionic strength was maintained at 5.0 mol dm^{-3} by use of $NaNO_3$. The data given by Fridman and Sarbaev[12] are the most extensive (10 points).

Of the two sets of data for aqueous KBr, the solubilities given by Fridman and Sarbaev[12] are larger than those of Kohn[22] for a given concentration of KBr (See Compilations). The solubilities are about the same as the authors gave for aqueous KI at the lower Br^- concentrations, but increase much less rapidly with increasing halide concentration. The solubilities given by Kohn and Klein[23] for aqueous NH_4Br are roughly the same as those of Kohn[21] for aqueous KBr. The solubilities given by Fridman and Sarbaev[12] for aqueous KCl are nearly 10-fold smaller than those they give for aqueous KBr. In view of differences in conditions and results for the various investigations, it is not possible to state what values should be accepted. It is clear from the results that the solubility of CuI in aqueous KBr or NH_4Br is equal to or less than in aqueous KI, and its solubility in aqueous KCl is much smaller than in aqueous KI.

For all of the data, the ratio of solubility to halide concentration (c_{CuI}/c_{L^-}) increases with increasing concentration of the soluble halide. Fridman and Sarbaev[12] attribute the solubility to the formation of mixed complexes $CuIL^-$ and $CuIL_2^{2-}$, where L is either Br or Cl, with the increase in c_{CuI}/c_{L^-} due to formation of the second complex with increasing ligand concentration. They give stability constants for these complexes based on their measurements.

SYSTEMS INVOLVING THIOSULFATES

Three sets of measurements have been reported for the solubility of cuprous iodide in aqueous $Na_2S_2O_3$ and one for the solubility of CuI in aqueous $K_2S_2O_3$. In 1952, Yatsimirskii and Panova[24] gave values for the solubility at 298 K in aqueous solutions of $Na_2S_2O_3$ from 0.02 to 0.54 mol kg^{-1} (10 points). In 1968 Gyunner and Yakhkind[11] published 8 values of solubility for CuI in aqueous $Na_2S_2O_3$ from 0.2 to 1.0 mol dm^{-3} at 20°C. In 1975 Golub, Butsko and Dobryanskaya[25] published results for aqueous $Na_2S_2O_3$ from 0.09 to 1.25 mol dm^{-3} (15 points) at an unspecified temperature (probably 25°C). Of these three sets of measurements, the first and last involved determination of the solubility by ordinary analytical techniques; Gyunner and Yakhkind[11] measured solubility by changes in the refractive index of the

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

solution. Finally, in 1976 a second paper by Golub and coworkers[26] gave values for the solubility in aqueous $K_2S_2O_3$ for concentrations from 0.01 to 0.40 mol dm^{-3}, again at an unspecified temperature.

In all of the investigations listed above, the solubilities observed were 2 to 3 orders of magnitude larger than would be found for solution of CuI in aqueous iodides under similar conditions. The various investigators all interpreted their data in terms of formation of a mixed complex by a reaction:

$$CuI_{(s)} + S_2O_3^{2-} \rightleftharpoons CuIS_2O_3^{2-} \qquad K_1 = [CuIS_2O_3^{2-}]/[S_2O_3^{2-}]$$

Independent least-squares analysis of the data confirmed that such a treatment worked, and also that the formation of a complex $Cu(S_2O_3)^-$ by the reaction $CuI_{(s)} + S_2O_3^{2-} \rightleftharpoons Cu(S_2O_3)^- + I^-$ could not be made to represent the data. All sets of data are internally consistent and appear to agree with each other to the extent they can be compared. The various pieces of research are discussed below.

Yatsimirskii and Panova[24] give a value of 3.5 ± 0.5 for the constant K_1 at 298 K, but do not state the precision to which this represented their data. A least-squares fit to the values of the solubility gives $K_1 = 3.51$, with a standard deviation of 0.004 mol kg^{-1} (for solubilities from 0.016 to 0.43 mol kg^{-1}); a least-squares fit based on percentage deviation between observed and calculated solubility give $K_1 = 3.45$, with average deviation of 2.7%. Yatsimirskii and Panova[24] also used a literature values of the solubility product of CuI to get a value for the reciprocal of the stability constant β for formation of their complex

$$Cu^+ + I^- + S_2O_3^{2-} \rightleftharpoons CuIS_2O_3^{2-} \qquad \beta = [CuIS_2O_3^{2-}]/[Cu^+][I^-][S_2O_3^{2-}]$$

Their value corresponds to $\beta = 3.2 \cdot 10^{12}$ mol^{-2} kg^2.

Gyunner and Yakhkind[11] give a value for K_1 of 2.66 ± 0.16 at 293 K; it fitted their data to an average of ±0.004 mol dm^{-3} for solubilities from 0.15 to 0.72 mol dm^{-3}. A least-squares fit on the values of solubility gave $K_1 = 2.61$, with a standard deviation of 0.005 mol dm^{-3}; that on percentage deviations gave $K_1 = 2.66$, with fit to 1.4 per cent. They calculated the reciprocal of β, corresponding to $\beta = 2.4 \cdot 10^{12}$ mol^{-2} dm^6 at 293 K. They also made four solubility measurements on systems in which the concentration of $Na_2S_2O_3$ was between 0.56 and 0.67 mol dm^{-3}, with NaI concentrations from 0.15 (highest $[S_2O_3^{2-}]$) to 0.6 mol dm^{-3} (lowest $[S_2O_3^{2-}]$). The solubilities observed in these cases were not significantly different from those observed for the same concentration of $S_2O_3^{2-}$ alone, as might have been expected in view of the much greater affinity for CuI of the thiosulfate.

The paper of Golub *et al.*[25] for the solubility of CuI in aqueous $Na_2S_2O_3$ gives a value of 3.3 for K_1 without stating the precision to which this fits their data. A least-squares treatment of the actual values of solubility gives a value of 3.29, with standard deviaton of 0.009 mol dm^{-3}; one based on percentage deviations gives a value of 3.22, with standard deviation of 1.8 per cent. Their value of $1/\beta$ corresponds to β of $3.48 \cdot 10^{12}$ mol^{-2} dm^6. Their failure to report a temperature makes it difficult to compare their results with those of the other investigators. On the one hand, they use a value for K_{S0} which had been determined by Golub, Sazhienko and Romaneko[9] at 293 K. On the other hand, they also present a series of potentiometric measurements made on unsaturated solutions at 298 K, and their value of K_1 agrees better with the one given above for 298 K than that for 293 K. It seems best to interpret their solubility measurements as applying to 298 K, with the effect of temperature on K_{S0} neglected in their calculation of $1/\beta$.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

In connection with their solubility measurements Golub *et al.*[25] isolated two salts, whose chemical composition corresponded to $Na_2[CuIS_2O_3] \cdot 2H_2O$ and $Na_4[CuI(S_2O_3)_2] \cdot 2H_2O$, and described their solubility properties. Their potentiometric measurements were made with Cu(I) concentrations of 0.005 mol dm^{-3} and $Na_2S_2O_3$ concentrations of 0.2 to 1.44 mol dm^{-3}, with Na_2SO_4 added to maintain constant nominal ionic strength (value not specified).

These measurements indicated formation under these conditions of a series of complexes of Cu^+ with $S_2O_3^{2-}$ but without iodide. They gave values for stability constants of four such; these were, with $S_2O_3^{2-}$ represented as L^{-2}, CuL^-, CuL_2^{3-}, CuL_3^{5-} and CuL_4^{7-}, the last of these predominant. They also isolated a series of salts whose chemical compositions corresponded to $Na_3CuL_2 \cdot 2H_2O$, $Na_5CuL_3 \cdot 6H_2O$ and $Na_7CuL_4 \cdot 7H_2O$ and described their solubility properties.

The measurements of Golub *et al.*[26] on the solubility of CuI in aqueous $K_2S_2O_3$ (temperature unspecified) were interpreted to give a K_1 of 10.7 ± 0.2; they did not state the precision to which this fitted their data. However, an independent least-squares fit gave a value of 10.85 which fitted the data with a standard deviation of 0.0001 mol dm^{-3} for solubilities from 0.01 to 0.36 mol dm^{-3}; a treatment based on the percentage deviations gave K_1 of 10.72, with standard deviation of 0.2 per cent. The authors give a value of $1.1 \cdot 10^{13}$ for the stability constant of $CuIS_2O_3^{2-}$. As with their previous paper, it seems most reasonable to take their results as applying to 298 K. A set of potentiometric measurements on unsaturated solutions at 298 K (temperature specified), with Cu(I) concentration of 0.005 mol dm^{-3}, was interpreted to give a set of complexes CuL^-, CuL_2^{3-}, CuL_3^{5-} and CuL_4^{7-}, where L represents the ion $S_2O_3^{2-}$. The authors give a set of stability constants for these complexes, derived from their measurements. They also reported isolation of salts whose chemical compositions corresponded to K_2CuIL, K_4CuIL_2, K_6CuIL_3, K_3CuL_2, $K_4Cu_2L_3$, K_5CuL_3 and K_7CuL_4. Rosenheim and Steinhauser[27] prepared the double salt $CuI \cdot NH_4I \cdot 4(NH_4)_2S_2O_3$ and verified its composition by chemical analysis.

Summary. All of the measurements reported for the solubility of CuI in aqueous $Na_2S_2O_3$ or $K_2S_2O_3$ can be interpreted in terms of the formation of a mixed complex $CuIS_2O_3^{2-}$ by the reaction:

$$CuI_{(s)} + S_2O_3^{2-} \rightleftharpoons CuIS_2O_3^{2-} \qquad K_1 = [CuIS_2O_3^{2-}]/[S_2O_3^{2-}]$$

All of the results are internally consistent and smooth within 2 to 3 per cent. Except for the uncertainty in the temperature for the data of Golub *et al.*[25,26], they can all be taken to agree with each other to the extent that they can be compared. The results of Yatsimirskii and Panova[24] and those of Gyunner and Yakhkind[11] are Accepted for their respective conditions. The results of Golub *et al.*[25,26] for solubility of CuI in aqueous $Na_2S_2O_3$ and in aqueous $K_2S_2O_3$ are Accepted tentatively as applying to measurements at 298 K. It is of interest to note that solubility in the latter medium is about three times as large as in the former, similar to the difference between solubilities observed in aqueous NaI and aqueous KI.

The isolation of a variety of salts, both with and without iodide content, by Golub *et al.*[25,26] indicates that many complexes of both sorts can be present in solution. The fact that only one suffices to interpret the solubility data indicates that this is probably the main species present in solution at equilibrium with solid CuI. The values of the stability constant β for this complex can be order of magnitude only, in view of uncertainty as to the value of the solubility product of CuI which should be used to obtain β from the experimentally determined K_1.

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]

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

EVALUATOR:

J. J. FRITZ

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

$CuI–KNbO_3–H_2O$

Tanirbergenov[28] measured the solubility of CuI in aqueous potassium metaniobate ($KNbO_3$) at 293 K, using concentrations of $KNbO_3$ from 0.05 to 0.33 mol dm^{-3} (10 points), with ionic strength held constant at 0.33 mol dm^{-3} by use of KNO_3. He also made a series of potentiometric measurements with a Cu(I) concentration of 0.0027 mol dm^{-3} amd $KNbO_3$ concentrations from 0.04 to 0.213 mol dm^{-3}. In the solubility measurements, the concentration of dissolved CuI was in all cases about 12 per cent as large as the concentration of NbO_3^-.

Tanirbergenov[28] attributed the solubility of CuI to formation of the mixed complex $CuINbO_3^-$ by the reaction $CuI_{(s)} + NbO_3^- \rightleftharpoons CuINbO_3^-$, with an equilibrium constant equal to 0.14 ± 0.02. This interpretation fitted both the solubility and the potentiometric data. His results are Accepted tentatively, in the absence of other data for comparison.

$CuI–I_2–H_2O$

In 1910 Fedotieff[29] made an interesting series of measurements on the solubility of CuI in unsaturated solutions of iodine in water. He measured ten points at 293 K in which the amount of CuI dissolved varied from 4.5 to $19.4 \cdot 10^{-3}$ mol dm^{-3}, with iodine concentrations in solution varying from 4.6 to $59.9 \cdot 10^{-3}$ mol dm^{-3} (note that these concentrations are all greater than the solubility of iodine in pure water). He also gives 8 points for solutions saturated with iodine and unsaturated with CuI, and presents a phase diagram for the entire system at 293 K. He also measured the compositions of solutions with both CuI and I_2 present as solids at 273, 293 and 313 K. All of the measurements of Fedotieff are internally consistent and are Accepted tentatively.

Fedotieff attributed solution of CuI to the reaction

$$2\,CuI_{(s)} + I_2 \rightleftharpoons 2\,Cu^{2+} + 4I^-, \qquad K = [Cu^{2+}]^2[I^-]^4/[I_2]$$

with the subsequent reaction

$$I_{2(s)} + I^- \rightleftharpoons I_3^- \qquad K' = [I_3^-]/[I^-]$$

increasing the total iodine present in solution and driving the first reaction to the right. After taking into account the partition of the dissolved iodine between the simple and complex ion, Fedotieff gives the constant K as $10.7 \cdot 10^{-9}$ mol^5 dm^{-15}. The value of this constant, along with his value for the solubility of iodine and for K', represent his observations within about 2 per cent.

In 1990 Kapler[30] made a series of measurements on the solubility of CuI in solutions of iodine in 7 polar solvents at 20°C. Kapler[30] found that his results can be correlated by the equation

$$\log c_{CuI}/\text{mol dm}^{-3} = a \log c_{I_2}/\text{mol dm}^{-3} + \log b.$$

He did not report actual solubility data for water as solvent, however, the constants $a = 0.56$ and $b = 0.14$ provided represent Fedotieff's[29] data within a few per cent. Kapler[30] confirmed the existence of Cu^{2+} by ESR spectroscopy and also detected higher polyiodide anions I_{2n+1}^- $(n = 1 - 4)$ by UV-VIS spectroscopy.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H_2O; [7732-18-5]	Gavrish, M. L.; Galinker, I. S. *Dokl. Akad. Nauk SSSR* 1955, *102*, 89–91.
VARIABLES:	PREPARED BY:
$T/K = 453$ to 613	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuI in Water

$t/°C$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/°C$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/°C$	$\frac{m_1}{\text{mol kg}^{-1}}$
180	0.003621	240	0.01323	300	0.04945
200	0.0065	260	0.029	320	0.06239
220	0.008299	280	0.040	340	0.08993

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions prepared in 140 cm^3 quartz bomb inside autoclave maintained at desired temperatures. Samples of salt pressed into pellets under 2000 atm, then weighed carefully. Samples put into equilibrium with known mass of water over 2-hour period at selected temperature. Solubility determined by loss of mass of pellet.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Sodium Iodide; NaI; [7681-82-5]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gyunner, E. A.; Yakhkind, N. D.
Russ. J. Inorg. Chem. (Engl. Transl.) 1968, *13*, 1420–1422.
Zh. Neorg. Khim. 1968, *13*, 2758.

VARIABLES:

Concentrations of NaI and $NaNO_3$ at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous NaI–$NaNO_3$ at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.400	3.5	0.003
0.800	3.1	0.006
1.100	2.8	0.010
1.400	2.5	0.016
1.700	2.2	0.023
2.000	1.9	0.029
2.300	1.6	0.039
2.600	1.3	0.055
2.900	1.0	0.068
3.200	0.7	0.090
3.500	0.4	0.113
3.900	–	0.158

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method described in Ref. 1

SOURCE AND PURITY OF MATERIALS:

Prepared CuI by method of Ref. 2. Used "C. P." salts in solutions.

ESTIMATED ERROR:

Not stated.

REFERENCES:

1. Gyunner, E. A.; Yakhkind, N. D. *Russ. J. Inorg. Chem.* 1968, *13*, 128.
2. Karyakin, Yu. V.; Angelov, I. I. *Pure Chemical Reagents*, 1955, p. 348.

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Sodium Iodide; NaI; [7681-82-5]
(3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3]
(4) Sodium Perchlorate; $NaClO_4$; [7601-89-0]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ahrland, S.; Tagesson, B.
Acta Chem. Scand. 1977, *A31*, 615-624.

VARIABLES:

Concentration of NaI at 298 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuI in NaI–$NaClO_4$–($HClO_4$) Solutions at 25°C

$[I^-]_{free}$ / mol dm^{-3}	c_3 / mol dm^{-3}	c_4 / mol dm^{-3}	$[I^-]_{total}$[a] / mol dm^{-3}	c_1 / mol dm^{-3}
0.201	0.10	4.699	0.201	0.00019
0.343	0.10	4.556	0.344	0.00062
0.490	0.10	4.409	0.491	0.00136
0.733	0.10	4.167	0.736	0.00316

[a] The total iodide concentrations were calculated by the compiler using the free iodide concentrations given and the equilibrium constants for complex formation given by the authors. Observe that very little of the iodide was involved in the complexes.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The main work of the investigation was a potentiometric study of the stability constants of the cupro-iodide complexes, using mainly unsaturated solutions at an ionic strength of 5.0 mol dm^{-3}. When the potential measurements showed that the solution had become saturated, that solution was treated with concentrated $HClO_4$ to oxidize the copper to Cu^{2+}, which was then determined spectrophotometrically as the cuprizone complex.

SOURCE AND PURITY OF MATERIALS:

Used BDH copper(I) iodide; $NaClO_4$ (Fluka) purified by recrystallization; NaI (*Merck p. a.*) used without further purification.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Potassium Iodide; KI; [7681-11-0]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fridman, Ya. D.; Sarbaev, Dzh. S.
Zh. Neorg. Khim. 1959, *4*, 1849–1859;
Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 835–841.

VARIABLES:

Concentrations of KI and $NaNO_3$ at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous KI at 25°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
1.014	0.0104
2.00	0.061
3.050	0.167
3.959	0.366
5.878	1.218

Solubility of CuI in KI–$NaNO_3$ Solutions at 25°C[a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
1.002	4.0	0.0103
2.012	3.0	0.050
3.002	2.0	0.153
3.980	1.0	0.373
4.949	–	0.716

[a] Constant ionic strength of 5 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stirred mixtures of solid and solution for 8–10 hours. Evaporated a measured volume of solution to dryness with concentrated HNO_3, dissolved residue in water. CuO was precipitated with KOH, dried and weighed. Concentration of iodide was determined argentimetrically. Solid phases were analyzed periodically.

SOURCE AND PURITY OF MATERIALS:

CuI was prepared either by reducing an aqueous mixture of $CuSO_4$ and KI with SO_2 or by hydrolysis of a solution of CuO in concentrated NH_4I. Sources and purities of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Potassium Iodide; KI; [7681-11-0]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Golub, A. M.; Sazhienko, S. M.; Romanenko, L. I.
Ukr. Khim. Zh. 1962, *28*, 561-565.

VARIABLES:

Concentrations of KI and $NaNO_3$ at 293 K, ionic strength 0.6 or 4.0 mol dm^{-3}

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in KI–$NaNO_3$ Solutions of $I_C = 0.6$ mol dm^{-3} at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.104	0.496	$9.44 \cdot 10^{-5}$
0.150	0.450	$1.37 \cdot 10^{-4}$
0.199	0.401	$2.25 \cdot 10^{-4}$
0.250	0.350	$3.38 \cdot 10^{-4}$
0.300	0.300	$4.83 \cdot 10^{-4}$
0.349	0.251	$5.25 \cdot 10^{-4}$
0.499	0.151	$9.23 \cdot 10^{-4}$
0.626	–	$2.28 \cdot 10^{-3}$

Solubility of CuI in KI–$NaNO_3$ Solutions of $I_C = 4.0$ mol dm^{-3} at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.521	3.479	0.0009
0.728	3.272	0.0031
0.834	3.166	0.0032
1.034	2.966	0.0075
1.252	2.748	0.0102
1.293	2.707	0.0124
1.758	2.242	0.0269
2.177	1.823	0.0492
2.585	1.415	0.0804
2.608	1.392	0.0766
2.895	1.105	0.1103
2.921	1.079	0.1092
3.309	0.691	0.1718

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held mixtures of solid and solution for 7 days in the dark, with frequent shaking, then kept in thermostat at 293 K for 5 hours before withdrawing solutions for analysis. Oxidized copper to Cu^{2+}, then analyzed iodometrically.

SOURCE AND PURITY OF MATERIALS:

Prepared CuI the "usual way", confirmed by analysis. KI recrystallized from aqueous solution. Used "C.P." $NaNO_3$. Purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-43]
(2) Hydrogen Iodide; HI; [10034-85-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Popolitov, V. I.; Mininzon, Yu. M.; Nikitenko, V. A.; Stoyukhin, S. G.
Kristallografiya 1984, *29*, 779–784;
Sov. Phys. Crystallogr. (Engl. Transl.) 1984, *29*, 460–463.

VARIABLES:

Concentration of HI at T/K of 473 to 573

PREPARED BY:

J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous HI

Solubility is presented in the form of two figures reproduced below. Numerical values digitized from their Fig. 1 are in the following table.

c_2/mol dm^{-3}	$100w_1$ at t/°C of		
	200	250	300
0.31	0.38	0.77	1.06
1.27	1.83	2.45	3.68
2.31	3.84	5.45	8.44
3.49	8.46	10.36	14.73

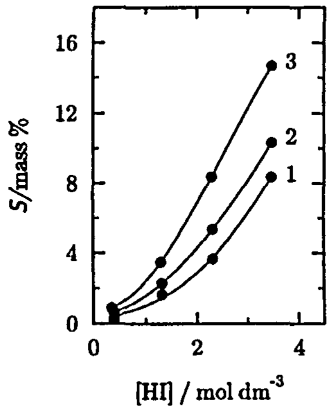

FIG. 1. Solubility of CuI *vs.* HI concentration. t / °C = (1) 200; (2) 250; (3) 300.

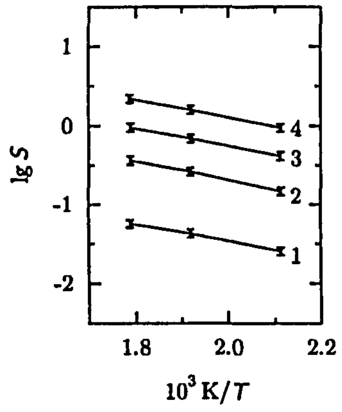

FIG. 2. Graphs of log S *vs.* reciprocal of temperature[a]. Mass percentage of HI: (1) 5; (2) 15; (3) 25; (4) 35.

[a] Units of S not specified. Note that the first point of each graph corresponds to $T \approx 285$ K.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Placed weighed amount of CuI crystals with HI solution in an ampoule, which was then sealed under a pressure of 500 atmospheres and placed in an autoclave at the desired temperature. After allowing 4 days for equilibration, the ampoule was quenched, opened and the undissolved crystals weighed after drying. The amount of CuI dissolved was then taken from the observed loss in weight.

SOURCE AND PURITY OF MATERIALS:

Used CuI crystals obtained by crystallization. HI solutions were prepared from C. P. hydriodic acid and distilled water.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Potassium Chloride; KCl; [7447-40-7] (3) Sodium Nitrate; $NaNO_3$; [7631-99-4] (4) Water; H_2O; [7732-18-5]	Fridman, Ya. D.; Sarbaev, Dzh. S. *Zh. Neorg. Khim.* 1959, *4*, 1849–1859; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, *4*, 835–841.
VARIABLES:	**PREPARED BY:**
Concentrations of KCl and $NaNO_3$ at 298 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuI in KCl–$NaNO_3$ Solutions at 25°C[a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
2.028	3.0	0.0065
2.505	2.5	0.0088
3.030	2.0	0.0106
3.535	1.5	0.0128
4.00	1.0	0.0143

[a] Constant ionic strength of 5 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stirred mixtures of solid and solution for 8–10 hours. Evaporated a measured volume of solution to dryness with concentrated HNO_3, dissolved residue in water. CuO was precipitated with KOH, dried and weighed. Concentration of halogenide was determined argentimetrically. Solid phases were analyzed periodically.

SOURCE AND PURITY OF MATERIALS:

CuI was prepared either by reducing an aqueous mixture of $CuSO_4$ and KI with SO_2 or by hydrolysis of a solution of CuO in concentrated NH_4I. Sources and purities of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Potassium Bromide; KBr; [7758-02-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kohn, M.
Z. Anorg. Chem. 1909, *63*, 337–339.

VARIABLES:

Concentration of KBr at 291 to 297 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous KBr

$t/°C$	c_2/mol dm^{-3}	ρ_1/g dm^{-3}	c_1/mol dm^{-3} [a]
18	2.0	1.4653	0.0077
19.5	2.0	1.4666	0.0077
24	2.0	1.5576	0.0082
19.5	3.0	3.4094	0.0179
20	3.0	3.4656	0.0182
23	3.0	3.5949	0.0189
22	4.0	7.1263	0.0374
22	4.0	6.9768	0.0366
23	4.0	7.0581	0.0371

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook CuI with KBr solutions at room temperature for several days. Precipitated copper from solution with KOH, washed till free of halogenide, then converted to CuO by heating in air. The copper content was then calculated from the mass of CuO.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated; consistency about 2%.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Potassium Bromide; KBr; [7758-02-3]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fridman, Ya. D.; Sarbaev, Dzh. S.
Zh. Neorg. Khim. 1959, *4*, 1849–1859;
Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 835–841.

VARIABLES:

Concentrations of KBr and $NaNO_3$ at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in KBr–$NaNO_3$ Solutions at 25°C[a]

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.505	4.5	0.0098
1.010	4.0	0.0118
1.535	3.5	0.0141
2.02	3.0	0.0211
2.545	2.5	0.0276
3.05	2.0	0.0317
3.575	1.4	0.0392
4.121	0.9	0.0523
4.767	0.2	0.0666
5.050	–	0.0771

[a] Constant ionic strength of 5 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stirred mixtures of solid and solution for 8–10 hours. Evaporated a measured volume of solution to dryness with concentrated HNO_3, dissolved residue in water. CuO was precipitated with KOH, dried and weighed. Concentration of halogenide was determined argentimetrically. Solid phases were analyzed periodically.

SOURCE AND PURITY OF MATERIALS:

CuI was prepared either by reducing an aqueous mixture of $CuSO_4$ and KI with SO_2 or by hydrolysis of a solution of CuO in concentrated NH_4I. Sources and purities of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Ammonium Bromide; NH_4Br; [12124-97-9]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kohn, M.; Klein, A.
Z. Anorg. Chem. 1912, *77*, 252–254.

VARIABLES:

Concentration of NH_4Br at 291 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous NH_4Br at 18°C

c_2/mol dm^{-3}	ρ_1/g dm^{-3}	c_1/mol dm^{-3} [a]
2.0	1.9068	0.0100
3.0	3.6540	0.0192
4.0	6.0588	0.0318

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook CuI with NH_4Br solutions at 293 K. Heated with HNO_3 to drive out bromine and iodine while oxidizing copper to Cu^{2+}. Precipitated copper as Cu_2S which was dried and weighed.

SOURCE AND PURITY OF MATERIALS:

Confirmed purity of CuI by determination of copper and iodine content. Purity of other materials not given.

ESTIMATED ERROR:

Not stated; consistency about 1%

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Sodium Thiosulfate; $Na_2S_2O_3$; [7772-98-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Yatsimirskii, K. B.; Panova, V. E.
Zh. Obshch. Khim. 1952, *22*, 1284–1289.

VARIABLES:

Molality of $Na_2S_2O_3$ at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous $Na_2S_2O_3$ at 25°C

$10^2 m_2$/mol kg^{-1}	$10^2 m_1$/mol kg^{-1}
1.927	1.555
3.624	2.780
4.210	3.446
7.029	5.270
7.940	6.084
8.708	6.654
18.05	13.85
32.54	25.03
44.20	33.55
53.76	42.82

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuI in contact with $Na_2S_2O_3$ solution in thermostat at 25 ± 0.1°C for several days, with continuous shaking. Analyzed for total $S_2O_3^{2-}$ and Cu^+ iodometrically, for copper separately after oxidation to Cu^{2+} with HNO_3.

SOURCE AND PURITY OF MATERIALS:

Prepared CuI from chemically pure KI and $CuSO_4 \cdot 5H_2O$. Source of materials not given.

ESTIMATED ERROR:

Not given; internal consistency *app.* 3%.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Sodium Thiosulfate; $Na_2S_2O_3$; [7772-98-7] (3) Water; H_2O; [7732-18-5]	Golub, A. M.; Butsko, S. S.; Dobryanskaya, L. P. *Zh. Neorg. Khim.* 1975, *20*, 2728-2732; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1975, *20*, 1510-1512.
VARIABLES:	PREPARED BY:
Concentration of $Na_2S_2O_3$ at unspecified temperature (probably about 298 K)	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous $Na_2S_2O_3$

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.090	0.068
0.131	0.098
0.199	0.152
0.270	0.208
0.352	0.270
0.456	0.351
0.590	0.427
0.651	0.497
0.713	0.550
0.811	0.633
0.854	0.649
0.952	0.736
1.061	0.829
1.110	0.850
1.180	0.902
1.250	0.951

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Added dry CuI to solutions of $Na_2S_2O_3$, shook mixture in the dark until equilibrium was attained. Analyzed solutions for copper iodometrically.	Prepared CuI by treating aqueous $CuSO_4$ with KI, washed and dried it before use. Used "C.P." $Na_2S_2O_3$.
	ESTIMATED ERROR: Not given.
	REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Sodium Thiosulfate; $Na_2S_2O_3$; [7772-98-7]
(3) Sodium Iodide; NaI; [7681-82-5]
(4) Sodium Sulfate; Na_2SO_4; [7757-82-6]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gyunner, E. A.; Yakhkind, N. D.
Zh. Neorg. Khim. 1968, *13*, 2758–2761;
Russ. J. Inorg. Chem. (Engl. Transl.) 1968, *13*, 1420–1422.

VARIABLES:

Composition at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in $Na_2S_2O_3$–Na_2SO_4 Solutions at 20°C

c_2/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.200	0.8	0.148
0.400	0.6	0.288
0.500	0.5	0.374
0.600	0.4	0.431
0.700	0.3	0.506
0.800	0.2	0.580
0.900	0.1	0.645
1.000	–	0.723

Solubility of CuI in NaI–$Na_2S_2O_3$–Na_2SO_4 Solutions at 20°C

c_3/mol dm^{-3}	c_2/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.150	0.665	0.285	0.483
0.300	0.630	0.270	0.456
0.450	0.595	0.255	0.427
0.600	0.560	0.240	0.403

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method described in Ref. 1

SOURCE AND PURITY OF MATERIALS:

Prepared CuI by method of Ref. 2. Used "C. P." salts in solutions.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Yakhkind, N. D.; Gyunner, E. A. *Russ. J. Inorg. Chem.* 1968, *13*, 1005.
2. Karyakin, Yu. V.; Angelov, I. I. *Pure Chemical Reagents*, 1955, p. 348.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Potassium thiosulfate; $K_2S_2O_3$; [10294-66-3] (3) Water; H_2O; [7732-18-5]	Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. *Ukr. Khim. Zh.* 1976, *42 (4)*, 343-347.
VARIABLES:	**PREPARED BY:**
Concentration of $K_2S_2O_3$ at unspecified temperature (probably 298 K)	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous $K_2S_2O_3$

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.0124	0.0113
0.0485	0.0442
0.0997	0.0913
0.1454	0.1332
0.1952	0.1788
0.2408	0.2204
0.2969	0.2720
0.3421	0.3133
0.3983	0.3645

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Maintained solid CuI in contact with $K_2S_2O_3$ solution in the dark, with vigorous stirring until equilibrium attained. Then analyzed solutions for copper content (method not stated).

SOURCE AND PURITY OF MATERIALS:

Prepared copper iodide according to method of Ref. 1. Used C. P. $K_2S_2O_3$. No other information given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Karyakin, Yu. V.; Angelov, I. I. *Pure Chemical Reagents*, 1955, p. 348.

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Potassium Metaniobate; $KNbO_3$; [12030-85-2]
(3) Potassium Nitrate; KNO_3; [7757-79-1]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Tanirbergenov, B.
Ukr. Khim. Zh. 1980, *46 (3)*, 262–264;
Sov. Prog. Chem. (Engl. Transl.) 1980, *46 (3)*, 39–41.

VARIABLES:

Concentrations of $KNbO_3$ and KNO_3 at 293 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuI in $KNbO_3$–KNO_3 Solutions at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.05	0.28	0.006
0.08	0.25	0.009
0.11	0.22	0.013
0.14	0.19	0.017
0.17	0.16	0.020
0.21	0.12	0.025
0.24	0.09	0.029
0.27	0.06	0.033
0.30	0.03	0.036
0.33	0.00	0.039

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Added dry CuI to solutions with desired $KNbO_3$ concentration held at constant ionic strength of 0.33 with KNO_3. Mixtures were shaken for a week at 293 K, then analyzed for copper according to Ref. 1.

SOURCE AND PURITY OF MATERIALS:

CuI and $KNbO_3$ synthesized by "known methods". Sources and purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kolthoff, I. M. *et. al.*, *Volumetric Analysis (Russ. Transl.)* 1961, *3*, 430.

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Iodine; I_2; [7553-56-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fedotieff, P. P.
Z. Anorg. Chem. 1910-11, *69*, 22-37.

VARIABLES:

Concentration of iodine at 273 to 313 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Aqueous Iodine at 20°C

I_2 Supplied		Solubility of CuI[a]		Total I_2[b]
ρ_2/g dm^{-3}	10^3c_2/mol dm^{-3}	ρ_1/g dm^{-3}	10^3c_1/mol dm^{-3}	10^3c_2/mol dm^{-3}
0.5848	2.30	0.285	4.48	4.54
1.3053	5.14	0.482	7.58	8.93
1.9218	7.57	0.583	9.17	12.16
2.5573	10.08	0.678	10.66	15.41
3.2042	12.62	0.756	11.89	18.57
3.9539	15.58	0.844	13.27	22.22
4.4359	17.48	0.898	14.12	24.54
5.0854	20.04	0.964	15.15	27.62
5.6854	22.40	1.032	16.23	30.52
6.2816	24.75	1.090	17.13	33.32
6.5301	25.73	1.112	17.50	34.48
7.6529	30.15	1.232	19.37[c]	39.84

Solubility of CuI in Aqueous Iodine Saturated also with I_2

t/°C	I_2 Supplied		Solubility of CuI[a]		Total I_2[b]
	ρ_2/g dm^{-3}	10^3c_2/mol dm^{-3}	ρ_1/g dm^{-3}	10^3c_1/mol dm^{-3}	10^3c_2/mol dm^{-3}
0	5.4609	21.52	0.925	14.54	28.79
20	7.6529	30.15	1.232	19.37	39.84
40	11.3658	44.78	1.658	26.07	57.82

Notes: [a] CuI goes into solution by oxidation to Cu^{2+}.
[b] Total includes iodine derived from dissolved CuI.
[c] This solution is in equilibrium with both CuI and I_2.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solutions in contact with solid CuI inside 200 cm^3 glass-stoppered flasks for 15 or 30 hours at a temperature slightly above 293 K, with continuous shaking. Removed one specimen for analysis at 15 hours, another at 30 hours. The specimens were then put in a thermostat at 293 K, shaken occasionally over 30 minutes, then allowed to settle. Analysis of liquid phase for iodine was made by titration with $K_2S_2O_3$. Copper was determined electrolytically after oxidation to Cu^{2+} with HNO_3.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	EVALUATORS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Organic Solvents	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

BINARY SYSTEMS

In 1914 Naumann and Schier[1] reported the solubility of CuI in acetonitrile at 293 K as 0.0352 g CuI/g acetonitrile. In 1977 Machtinger *et al.*[2] gave a value of the solubility product of CuI in molten dimethyl sulfone [$(CH_3)_2SO_2$] at 400 K as $10^{-13.3}$ $(5 \cdot 10^{-14})$ mol^2 kg^{-2} from cell measurements in which the potential of a copper electrode was measured as a function of iodide molality (provided by addition of tetraethylammonium iodide) with a molality of Cu^+ of 10^{-3} mol kg^{-1}. Their value of K_{S0} would correspond to a solubility of about $2.3 \cdot 10^{-7}$ mol kg^{-1} in the molten dimethyl sulfone.

TERNARY SYSTEMS

Machtinger *et al.*[2] used titration curves to evaluate a stability constant for the ion CuI_2^- in molten dimethyl sulfone at 400 K, with iodide ion molalities between 0.008 and 0.2 . They gave the stability constant as $10^{14.1}$ $(1.2 \cdot 10^{14})$ mol^{-2} kg^{-2}. Using this value with their value for the solubility product of CuI in their medium gives a value of K_{S2} for addition of I^- to $CuI_{(s)}$, *viz.*:

$$CuI_{(s)} + I^- \rightleftharpoons CuI_2^- \qquad K_{S2} = 6$$

This value of K_{S2} corresponds to substantial absorption of I^- by solid cuprous iodide. Machtinger *et al.*[2] do not report any actual solubilities, but indicate their expectation of a solubility of 0.008 mol kg^{-1} in the presence of 10^{-3} mol kg^{-1} of free I^-.

There have been three reports of the solubility of CuI in non-aqueous solutions of alkali halides. In 1962, Golub, Sazhienko and Romanenko[3] reported measurements of the solubility in both acetone and ethanol solutions of NaI at 293 K, using concentrations of NaI from 0.4 to 1.5 mol dm^{-3} (8 points for acetone and 7 for ethanol). In 1970 Khan, Zaidi and Malik[4] gave five points for the solubility of CuI in acetone solutions of KI, with KI concentrations from 0.03 to 0.09 mol dm^{-3}. All three investigations found substantial solubility of CuI in the non-aqueous medium. All of them indicate a much higher solubility of CuI in non-aqueous solutions of alkali iodides than in the corresponding aqueous solutions.

All three of the sets of measurements are consistent within 1 to 2 per cent, with the relative solubility highest for the system KI–acetone, where the ratio S/C_L of solubility to iodide concentration was approximately unity. For the system NaI–acetone, this ratio varied from about 0.9 at the lowest concentrations to about 0.7 at the highest. The solubility was lowest in NaI–ethanol, where the ratio was nearly constant at about 0.64. All of these measurements are Recommended provisionally, subject to further results becoming available.

The values of the solubility suggest the formation of the simple complex CuI_2^- in solution. Khan *et al.*[4] believed that this species was present in their solutions, and Golub *et al.*[3] believe it to be the major component of solution in the system NaI–ethanol. However, the latter authors obtained a considerably better fit to their data for NaI–acetone by attributing the solubility to formation of the dinuclear complex $Cu_2I_3^-$. For NaI–ethanol, they give the reaction

$$CuI_{(s)} + I^- \rightleftharpoons CuI_2^- \qquad K_{S2} = 1.7;$$

for NaI–acetone, they find a better fit for the reaction

$$2CuI_{(s)} + I^- \rightleftharpoons Cu_2I_3^- \qquad K_{S23} = 0.6.$$

It is of course possible that all of the solutions contained a variety of complexes, and the measurements do not rule out the possibility that some CuI dissolves as a neutral salt.

COMPONENTS:	EVALUATORS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Organic Solvents	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

In 1990 Kapler[5] made an interesting series of measurements on the solubility of CuI in solutions of iodine in 7 polar solvents at 20°C. Kapler[5] found that his results can be correlated by the equation

$$\log c_{\mathrm{CuI}}/\mathrm{mol\ dm^{-3}} = a \log c_{\mathrm{I_2}}/\mathrm{mol\ dm^{-3}} + \log b.$$

He reported actual solubility data in graphical form only for two systems (See Compilations) but provided the following set of a and b values:

Solvent	*a*	*b*
Methanol	1.03	0.26
Ethanol	1.02	0.16
Acetonitrile	0.65	0.86
Water	0.56	0.14
Methanol:Water = 1:1	0.83	0.21
Ethanol:Water = 1:1	0.83	0.14
Dioxane:Water = 1:1	0.82	0.25

Kapler[5] attributed solution of CuI to the reaction

$$2\,\mathrm{CuI}_{(s)} + \mathrm{I_2} \rightleftharpoons 2\,\mathrm{Cu^{2+}} + 4\,\mathrm{I^-}$$

with the subsequent reaction

$$n\,\mathrm{I}_{2\,(s)} + \mathrm{I^-} \rightleftharpoons \mathrm{I}^-_{2n+1}$$

increasing the total iodine present in solution and driving the first reaction to the right.

Kapler[5] confirmed the existence of $\mathrm{Cu^{2+}}$ by ESR spectroscopy and also detected higher polyiodide anions I^-_{2n+1} ($n = 1 - 4$) by UV-VIS spectroscopy.

Kapler's[5] values of the constants a and b for the correlation of CuI solubilities in solutions of iodine in organic solvents are Accepted tentatively, in view of good agreement of his correlation for the system $\mathrm{CuI{-}I_2{-}H_2O}$ with the data of Fedotieff[6].

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5. Kapler, R. *Z. Chem. (Leipzig)* 1990, *30*, 226.
6. Fedotieff, P. P. *Z. Anorg. Chem.* 1910-11, *69*, 22.

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Sodium Iodide; NaI; [7681-82-5]
(3) Acetone; C_2H_6O; [67-64-1]

ORIGINAL MEASUREMENTS:

Golub, A. M.; Sazhienko, S. M.; Romanenko, L. I.
Ukr. Khim. Zh. 1962, *28*, 561–565.

VARIABLES:

Concentration of NaI at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Acetone Solutions of NaI at 20°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.4585	0.4015
0.5923	0.4977
0.7031	0.5769
0.8176	0.6324
0.8875	0.7125
1.0368	0.8032
1.2438	0.9162
1.4680	1.0520

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held mixtures of solid and solution for 7 days in the dark, with frequent shaking, then kept in thermostat at 293 K for 5 hours before withdrawing solutions for analysis. Oxidized copper to Cu^{2+}, then analyzed iodometrically.

SOURCE AND PURITY OF MATERIALS:

Prepared CuI the "usual way", confirmed by analysis. Used "pure" NaI, recrystallized from water solution and dried at 180–200°C. Acetone distilled over $KMnO_4$. Purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Sodium Iodide; NaI; [7681-82-5] (3) Ethanol; C_2H_6O; [64-17-5]	Golub, A. M.; Sazhienko, S. M.; Romanenko, L. I. *Ukr. Khim. Zh.* 1962, *28*, 561-565.
VARIABLES:	**PREPARED BY:**
Concentration of NaI at 293 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Ethanolic NaI Solutions at 20°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.3798	0.2262
0.7163	0.4637
0.9766	0.6334
1.0526	0.6674
1.3044	0.8256
1.4352	0.9048
1.5299	0.9501

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held mixtures of solid and solution for 7 days in the dark with frequent shaking, then kept in thermostat at 293 K for 5 hours before withdrawing solutions for analysis. Oxidized copper to Cu^{2+}, then analyzed iodometrically.

SOURCE AND PURITY OF MATERIALS:

Prepared CuI the "usual way", confirmed by analysis. Used "pure" NaI, recrystallized from water solution and dried at 180–200°C. Absolute ethanol distilled with benzol. Purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Potassium Iodide; KI; [7681-11-0]
(3) Acetone; C_2H_6O; [67-64-1]

ORIGINAL MEASUREMENTS:

Khan, M. M.; Zaidi, S. A. A.; Malik, A. U.
Z. Anorg. Allg. Chem. 1970, *375*, 291–296.

VARIABLES:

Concentration of KI at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuI in Acetone Solutions of KI at 20°C

ρ_2/g (20 cm^3)$^{-1}$	c_2/mol dm^{-3} [a]	ρ_1/g (20 cm^3)$^{-1}$	c_1/mol dm^{-3} [a]
0.104	0.0313	0.113	0.0297
0.130	0.0392	0.146	0.0383
0.229	0.0690	0.257	0.0675
0.272	0.0819	0.316	0.0830
0.295	0.0889	0.349	0.0889

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Prepared saturated solutions of CuI in acetone containing KI. After filtering these, the CuI was precipitated by adding water, dried and weighed. The iodide content of the solution was determined as AgI.

SOURCE AND PURITY OF MATERIALS:

Prepared CuI by reducing an aqueous mixture of $CuSO_4$ and KI. A. R. grades of acetone and KI were used.

ESTIMATED ERROR:

Not stated.

REFERENCES:

COMPONENTS:

(1) Copper(I) Iodide; CuI; [7681-65-4]
(2) Iodine; I_2; [7553-56-2]
(3) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Kapler, R.
Z. Chem. (Leipzig) 1990, *30*, 226–227.

VARIABLES:

Concentration of I_2 at 293 K

PREPARED BY:

E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuI in Ethanolic I_2 Solutions at 20°C[a]

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.131	0.020
0.219	0.033
0.230	0.037
0.292	0.045
0.347	0.052
0.448	0.076
0.548	0.093
0.666	0.115
0.730	0.115
0.756	0.133
0.925	0.153
0.969	0.164
1.125	0.188
1.291	0.204
1.352	0.219
1.544	0.238
1.654	0.258

[a] The values given in the table were digitized from the graph presented by the author.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method for solubility measurements not given. Oxidized copper to Cu^{2+}, then analyzed photometrically as Cu^{2+} tetrammin complex. Iodine determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

Not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Iodide; CuI; [7681-65-4] (2) Iodine; I_2; [7553-56-2] (3) Methanol; CH_4O; [67-56-1] (4) Water; H_2O; [7732-18-5]	Kapler, R. *Z. Chem. (Leipzig)* 1990, *30*, 226-227.
VARIABLES:	**PREPARED BY:**
Concentration of I_2 at 293 K	E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuI in Solutions of I_2 in Methanol–Water (1:1) at 20°C[a]

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.110	0.033
0.140	0.046
0.170	0.047
0.220	0.061
0.251	0.069
0.290	0.077
0.327	0.091
0.389	0.098
0.424	0.109
0.470	0.121
0.527	0.127
0.595	0.140
0.648	0.149

[a] The values given in the table were digitized from the graph presented by the author.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Method for solubility measurements not given. Oxidized copper to Cu^{2+}, then analyzed photometrically as Cu^{2+} tetrammin complex. Iodine determined iodometrically.	Not given.
	ESTIMATED ERROR:
	Not given.
	REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

THE BINARY SYSTEM

No reliable data are available on the solubility of cuprous thiocyanate in pure water, although numerous reports have been made of its solubility product. In 1893, Kohlrausch and Rose[1] gave the solubility as $4 \cdot 10^{-6}$ mol dm^{-3} at 291 K, based on measurements of electrical conductivity of a supposedly saturated solution. In 1950 Ragg[2] gave a value of $4.4 \cdot 10^{-3}$ g dm^{-3} ($3.6 \cdot 10^{-5}$ mol dm^{-3}) at 293 K. In 1931 Kolthoff and Furman[3] gave a value for the solubility product at 298 K of $1.6 \cdot 10^{-11}$ mol^2 dm^{-6} without stating its source, though it would appear to have been derived from the result of Kohlrausch and Rose[1] cited above. In 1950 Vladimirova and Kakovsky[4] reported a value of $4.8 \cdot 10^{-15}$ mol^2 dm^{-6} at the same temperature, based on some potentiometric measurements and a study of equilibria involving CuSCN and CN^-. In 1952 Latimer[5] gave value of $4 \cdot 10^{-14}$ mol^2 dm^{-6} at 298.15 K, zero ionic strength, based on admittedly approximate values of cell potentials involving Cu^+ and SCN^-. In 1956 Golub[6] gave a value of $1.85 \cdot 10^{-13}$ mol^2 dm^{-6} at 293 K for aqueous solutions in which SCN^- was supplied by KSCN, with a constant ionic strength of 4.5 mol dm^{-3} maintained by $NaNO_3$; his value was calculated by combination of solubility measurements and a set of potentiometric measurements on unsaturated solutions. In 1966 Swinarski *et al.*[7] gave values at 293 K of $4.82 \cdot 10^{-12}$ mol^2 dm^{-6} in 2 mol dm^{-3} $NaNO_3$ and $7.08 \cdot 10^{-12}$ mol^2 dm^{-6} in 4 mol dm^{-3} $NaNO_3$. Also in 1966, Chaltykyan[8] gave a value of $4.0 \cdot 10^{-14}$ mol^2 dm^{-6} without stating its source (probably Latimer[5]). In 1977, Ahrland and Tagesson[9] give a value (based on solubility and potentiometric measurements of solutions of CuSCN in aqueous NaSCN) of $(1.71 \pm 0.16) \cdot 10^{-15}$ mol^2 dm^{-6} at 298.16 K and a constant ionic strength of 5.0 mol dm^{-3} maintained by $NaClO_4$ with 0.1 mol dm^{-3} of $HClO_4$ added. Finally, in 1982 Mazo *et al.*[10] published a value of $(5 \pm 1) \cdot 10^{-15}$ mol^2 dm^{-6} for the solubility product at 298 K in a solution of ionic strength 4 mol dm^{-3} maintained by use of $NaClO_4$.

Of the values given for the solubility product, the value given by Kolthoff and Furman[3] is almost certainly too high. The values given by Golub[6], Ahrland and Tagesson[9] and Mazo *et al.*[10] all apply to special media at high ionic strength, and there are no data available to convert them to values at zero or any other ionic strength. The values given by Swinarski *et al.*[7] were based on solubility measurements alone and are almost certainly high because of contributions to the solubility by a neutral complex $CuSCN^0$; the contribution of this species is not known, but data on other cuprous salts indicate that its contribution could be as large as that from the ion pairs. The only values designed to apply to zero ionic strength are those of Latimer[5] and of Vladimirova and Kakovsky[4], both subject to some uncertainty. Latimer[5] considered the cell potentials used in his calculation as approximate only, without indicating the degree of uncertainty. The approach used by Vladimirova and Kakovsky[4] was very indirect, involving the reaction of $CuSCN_{(s)}$ with HCN to produce $Cu(CN)_2^-$, and required knowledge of the properties of $Cu(CN)_2^-$ and of HCN, as well as the activity coefficients in various solutions. Thus, their result has an unknown uncertainty which could be substantial. Most likely the true value for the solubility product at 298 K, zero ionic strength, lies between the values of the latter two authors, *i. e.* between $5 \cdot 10^{-15}$ and $4 \cdot 10^{-14}$ mol^2 dm^{-6} (order of magnitude 10^{-15} mol^2 dm^{-6}).

The value given for 298.16 K by Ahrland and Tagesson[9] was determined from a combination of solubility and potentiometric methods in solutions of 5 mol dm^{-3} ionic strength maintained by acidified $NaClO_4$, and is probably reliable to their quoted uncertainty for such a medium. That given by Golub[6] at 293 K was obtained by similar procedures in a medium of ionic strength 4.5 mol dm^{-3} maintained by use of $NaNO_3$; they give no estimate of the uncertainty of their result. It is only suitable for the medium and temperature they employed. The value given by Mazo *et al.*[10] was obtained for a medium of ionic strength 4 mol dm^{-3} maintained by use of $NaClO_4$. It lies between the values given by the other two sets of investigators, much closer to that of Ahrland and Tagesson[9]. It would appear that

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

the values given by Ahrland and Tagesson[9] and by Mazo *et al.*[10] are the more appropriate for media of high ionic strength.

CuSCN IN AQUEOUS SOLUTIONS OF SOLUBLE THIOCYANATES

Five sets of measurements have been reported for the solubility of CuSCN in aqueous solutions of soluble thiocyanates. In 1956 Golub[6] made a series of measurements at 293 K in aqueous $KSCN-NaNO_3$ solutions, with SCN^- concentrations from 0.75 to 4.5 mol dm^{-3} (13 points) at a constant nominal ionic strength of 4.5 maintained by use of $NaNO_3$. In 1958 Fridman and Sarbaev[11] made two sets of measurements in aqueous KSCN solutions at 298 K. In one of these KSCN concentrations were varied from 0.73 to 6.8 mol dm^{-3} (6 points), with no indifferent electrolyte present. In the other the concentration of KSCN was varied from 0.97 to 4.93 mol dm^{-3} (5 points) with a constant ionic strength of 5 mol dm^{-3} maintained using $NaNO_3$. In 1968 Gyunner and Yakhkind[12] made observations of the solubility at 293 K in aqueous $NH_4SCN-NH_4NO_3$ solutions, with SCN^- concentrations from 2.4 to 4.4 mol dm^{-3} (10 points) with a constant ionic strength of 4.4 mol dm^{-3} maintained by NH_4NO_3. In 1977 Ahrland and Tagesson[9] made measurements of the solubility of CuSCN in aqueous NaSCN at 298.16 K with a constant ionic strength of 5.0 mol dm^{-3} maintained by $NaClO_4$ with 0.1 mol dm^{-3} of $HClO_4$ present. Finally, in 1982 Mazo *et al.*[10] published a set of solubilities at 298.16 K in aqueous NaSCN maintained at an ionic strength of 4 mol dm^{-3} by use of $NaClO_4$ (no acid added).

Certain features are common to all of the measurements. In the first place, for similar conditions the solubilities are all smaller than for any of the cuprous halides (for solutions in the potassium salt, half or somewhat less). Second, the solubilities generally increase more rapidly than the square of the SCN^- concentration. Third, at a given temperature the solubilities at large ionic strengths depend only slightly on the cation used to suppply SCN^-. Finally, the solubilities at 293 K are smaller than those at 298 K, as would be expected. Since the various measurements were made under conditions too different to compare results directly, a set of equilibrium constants for complex formation and virial parameters for activity coefficients was developed to fit all of the data except those of Mazo *et al.*[10]; this data set consisted of 49 points. With the exception of 6 inconsistent points, this set of parameters fitted the data set used to about 6 per cent. The results of the representation were used to assess the consistency and reliability of the various sets of data, considered individually below.

Solubility in Aqueous KSCN

The data of Golub[6] are rather erratic. Two points, at SCN^- concentrations of 0.75 and 3.07 mol dm^{-3}, are quite inconsistent with the rest. At other concentrations, adjacent points can vary by 5 per cent (in some cases more) from a smooth curve, although the overall fit to the model (except for the two points cited) is about 7 per cent. The results are probably reliable to about this extent for the conditions used [293 K, 4.5 mol dm^{-3} ionic strength ($NaNO_3$)]. The data of Fridman and Sarbaev[11] for "pure" KSCN solutions are consistent to about 3 per cent except for the lowest point (0.73 mol dm^{-3} KSCN), which is much too high; adjacent points vary about this much from smoothness. Their data can probably be relied on to about this extent for KSCN without indifferent electrolyte at 298 K. For solutions maintained at constant ionic strength, their results are generally high and erratic compared to other measurements and should not be relied on.

Solubility in Aqueous $NaSCN-NaClO_4$.

Ahrland and Tagesson[9] give their results for the solubility in the form of a graph on which only four points are shown, along with a curve calculated from the stability constants they

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]

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

EVALUATOR:

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Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

give for a series of complexes. Over the range for which they show actual points, solubilities calculated from their stability constants are consistent within a few per cent and are probably reliable to that extent for the medium they used. The data of Mazo *et al.*[10] were erratic compared to the others. They were generally higher than those of Ahrland and Tagesson[9] and could be fitted only to an average of about 20 per cent by parameters which fitted all of the other data to 6 per cent.

Solubility in Aqueous NH_4SCN

The data of Gyunner and Yakhkind[12] are consistent overall to about 6 per cent (somewhat better except for a rather low point at 2.4 mol dm^{-3}). However, adjacent points depart from smoothness by 2 to 6 per cent. Their data are probably reliable to this precision.

THERMODYNAMICS OF SOLUTIONS IN AQUEOUS THIOCYANATES

The model used to represent the solubilities considered the complexes $CuSCN^0$, $Cu(SCN)_2^-$, $Cu(SCN)_3^{2-}$ and $Cu_3(SCN)_6^{3-}$. Representation of the entire body of data gave at least tentative values for the equilibrium constants and enthalpy changes associated with the formation from $CuSCN_{(s)}$ of this set of complexes, along with virial parameters for ion pairs formed between the complexes and the cation(s) present in solution. Table 31 gives these quantities along with virial parameters for ion pairs formed with K^+. The parameters obtained for the other cations are not presented, since they apply only to a limited (high) range of ionic strength and are should not be used under other conditions.

Table 31. Equilibrium Constants and Virial Parameters[a] at 298 K for Complexes Formed from $CuSCN_{(s)}$ in Aqueous KSCN

Species	K_{Smn} [b] / $(mol\ dm^{-3})^{(1-m-n)}$	$\Delta_r H^\ominus$ [b] / $kJ\ mol^{-1}$	$\beta^{(0)}$	$\beta^{(1)}$	C
$CuSCN^0$	$2 \cdot 10^{-6}$	–	0.235	0.322	−0.031[c]
$Cu(SCN)_2^-$	$6.8 \cdot 10^{-6}$	23	0.003	−1.373	0.0182
$Cu(SCN)_3^{2-}$	$1.02 \cdot 10^{-3}$	19	0.263	−0.404	0.0027
$Cu_3(SCN)_6^{3-}$	$4.0 \cdot 10^{-6}$	5	0.0939	2.86	0.00766

[a] The virial parameters given apply only to solutions where SCN^- is supplied by KSCN; they can be used in conjuction with the parameters given for this and other soluble salts by Pitzer and Mayorga[13].

[b] The equilibrium constants and enthalpy changes are for the reaction $m\ CuSCN_{(s)} + (n-m)SCN^- \rightleftharpoons Cu_m(SCN)_n^{m-n}$.

[c] There was not sufficient data to evaluate parameters for $CuSCN^0$. Because of this, the data were fitted using a set of parameters which had proved suitable for cuprous halides.

Although it was not possible to obtain a firm estimate of the uncertainty of the equilibrium constants of Table 31, a fit to the data could not be obtained for values of the constants more than 10 per cent different from those in the Table (except for the formation constants of $CuSCN^0$ and $Cu(CN)_2^-$, to which the data were relatively insensitive).

Stability and/or formation constants have been given for a considerable number of possible complexes by a variety of investigators, including Mazo *et al.*[10], Ahrland and Tagesson[9], Fridman and Sarbaev[11], Golub[6], Gyunner and Yakhkind[12] and Korshunov and Malyugina[14]. With the exception of the last authors, those who gave stability constants also gave values for a solubility product, so that their results could be converted to formation constants such

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

as those in Table 31. Table 32 gives the values of these constants for each complex considered by each set of investigators. In the table K_{Smn} represents the equilibrium constant for the formation of $Cu_m(SCN)_n^{m-n}$ from $CuSCN_{(s)}$ and SCN^-, for the experimental conditions used in each case (note that the subscript m is omitted when its value is 1). [Note: Korshunov and Malyugina[14] give a value for the dissociation constant of $Cu(SCN)_4^{3-}$ of $7 \cdot 10^{-10}$ mol^4 dm^{-12}, but this is at least an order of magnitude low.]

Table 32. **Solubility Product and Formation Constants for Complexes of CuSCN**

	Reference No.[a]				
Constant[b]	6	9	10	11	12
K_{S0}	$1.85 \cdot 10^{-13}$	$1.71 \cdot 10^{-15}$	$5 \cdot 10^{-15}$	$4 \cdot 10^{-14}$	$4.8 \cdot 10^{-15}$
K_{S1}	–	–	$6.5 \cdot 10^{-7}$	–	–
K_{S2}	–	$< 4 \cdot 10^{-5}$	$6.0 \cdot 10^{-5}$	$4 \cdot 10^{-3}$	–
K_{S3}	$1.5 \cdot 10^{-3}$	$6.9 \cdot 10^{-4}$	$1.8 \cdot 10^{-3}$	$3.2 \cdot 10^{-3}$	–
K_{S4}	$2.3 \cdot 10^{-3}$	$1.8 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$1.2 \cdot 10^{-3}$	$1.95 \cdot 10^{-3}$
K_{S5}	$7.1 \cdot 10^{-4}$	–	$6.0 \cdot 10^{-4}$	–	–
K_{S6}	$1.1 \cdot 10^{-3}$	–	–	–	–
K_{S26}	–	$6.4 \cdot 10^{-6}$	–	–	–

[a] Experimental conditions were:

Ref. 6: $T = 293$ K, KSCN, $I_c = 4.5$ mol dm^{-3} ($NaNO_3$); values are also given for K_{14} at 313 and 333 K
Ref. 9: $T = 298$ K, NaSCN, $I_c = 5.0$ mol dm^{-3} ($NaClO_4$–$HClO_4$)
Ref. 10: $T = 298$ K, NaSCN, $I_c = 4.0$ mol dm^{-3} ($NaClO_4$)
Ref. 11: $T = 298$ K, KSCN, $I_c = 1$ to 4 mol dm^{-3}
Ref. 12: $T = 293$ K, NH_4SCN, $I_c = 4.4$ mol dm^{-3} (NH_4NO_3)

[b] Units of K_{Smn} are (mol dm^{-3})$^{(1-m-n)}$.

The differences between the values given in Table 32 and the zero ionic strength values of Table 31 are due partly to the fact that all the values in Table 32 are for media at substantial ionic strength and partly to the set of complexes selected to represent the solubility. Comparison of the two tables demonstrates the large effect of ionic strength on the ability of various complexes to form. For References 6 and 9, correction of the constants of Table 32 to zero ionic strength using suitable virial parameters gives results in substantial agreement with Table 31 for the species considered there (note that K_{S36} is equivalent to $3 \cdot K_{S4}$). The constants given in these two references adequately represent the solubility under their experimental conditions and could be used to estimate unknown solubilities under these conditions. The constants given in references 10, 11 and 12 do not represent the solubilities adequately and should not be used to estimate unknown solubilities. The values given by Fridman and Sarbaev[11] are certainly much too large. The values for K_{S5} given by Golub[6] and by Mazo *et al.*[10], and the value for K_{S6} given by Golub[6] from potentiometric measurements may be artifacts of their experiments, since inclusion of these species is not needed to fit their solubility data.

The values given in Table 31 for the enthalpy changes associated with the formation of complexes from $CuSCN_{(s)}$ are only approximate, due to the small temperature range of the available data. They are required in order to represent data at both 298 and 293 K.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

RECOMMEDED VALUES FOR SOLUBILITY OF CuSCN IN AQUEOUS KSCN

The parameters of Table 31 were used to prepare smoothed tables of solubility for CuSCN in aqueous KSCN of concentration 1.0 to 5.0 mol dm^{-3} at 298 K. These are given in Table 33, along with the corresponding values of c_{CuSCN}/c_{KSCN}. The values of c_{CuSCN}/c_{KSCN} are plotted against KSCN concentration in Fig. 6. The values in the table agree with the results of Fridman and Sarbaev[11] within the internal consistency of the experimental data (about 6 per cent). Values are not given for solutions in the other soluble thiocyanates because lack of experimental data at other than high ionic strengths prevented evaluating parameters which would be valid over a range of ionic strength. The values in Table 33 are presented only at and above 1.0 mol dm^{-3} because of uncertainty as to the proper values below this range. Values of the ratio of solubility to the concentration of the soluble thiocyanate are given to facilitate interpolation. Although the values of Table 33 cannot be used for solubility in solutions of other soluble thiocyanates, they at least give an approximation to the values which might be expected.

Table 33. **Solubility and Ratio of Solubility to Initial Thiocyanate Concentration for CuSCN in Aqueous KSCN at 298 K**

c_{KSCN}/mol dm^{-3}	c_{CuSCN}/mol dm^{-3}	c_{CuSCN}/c_{KSCN}
1.00	$5.23 \cdot 10^{-3}$	$5.233 \cdot 10^{-3}$
1.10	$6.57 \cdot 10^{-3}$	$5.976 \cdot 10^{-3}$
1.20	$8.08 \cdot 10^{-3}$	$6.736 \cdot 10^{-3}$
1.30	$9.76 \cdot 10^{-3}$	$7.506 \cdot 10^{-3}$
1.40	$1.160 \cdot 10^{-2}$	$8.286 \cdot 10^{-3}$
1.50	$1.361 \cdot 10^{-2}$	$9.072 \cdot 10^{-3}$
1.60	$1.578 \cdot 10^{-2}$	$9.861 \cdot 10^{-3}$
1.70	$1.812 \cdot 10^{-2}$	$1.066 \cdot 10^{-2}$
1.80	$2.063 \cdot 10^{-2}$	$1.146 \cdot 10^{-2}$
1.90	$2.331 \cdot 10^{-2}$	$1.227 \cdot 10^{-2}$
2.00	0.0262	0.01309
2.20	0.0325	0.01475
2.40	0.0395	0.01645
2.60	0.0473	0.01818
2.80	0.0559	0.01997
3.00	0.0655	0.02182
3.20	0.0761	0.02377
3.40	0.0879	0.02584
3.60	0.1010	0.02807
3.80	0.1157	0.03046
4.00	0.1321	0.03303
4.20	0.1502	0.03577
4.40	0.1699	0.03869
4.60	0.1922	0.04179
4.80	0.2160	0.04508
5.00	0.2428	0.04855

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

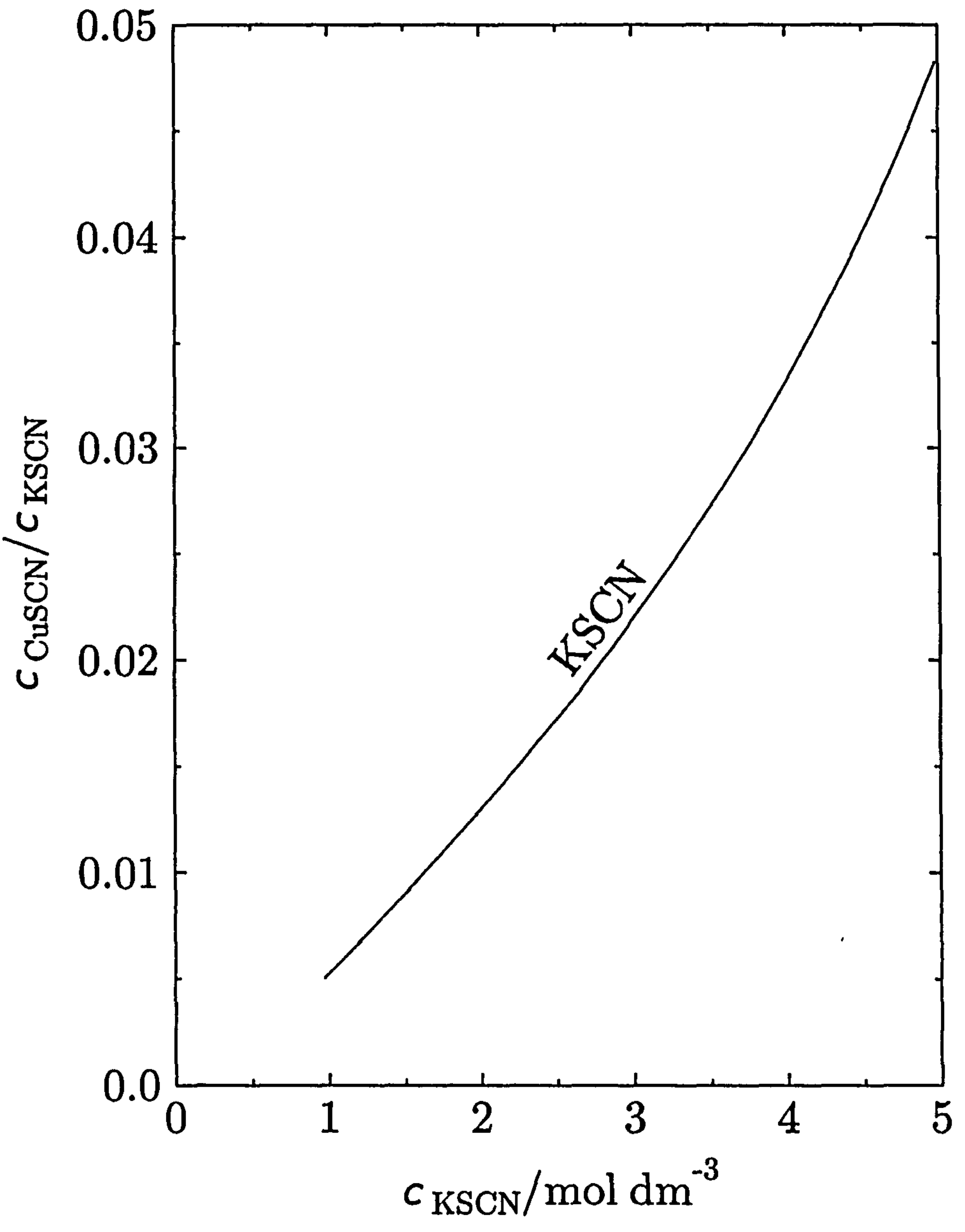

Fig. 6. Ratio of CuSCN Solubility to KSCN Concentration Plotted Against Concentration of KSCN at 298.15 K

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

SOLUBILITY IN AQUEOUS SOLUTIONS OF SOLUBLE HALIDES

Fridman and Sarbaev[11] investigated the solubility of CuSCN at 298 K in aqueous KI and in aqueous mixtures of KI and KSCN. In the former case they made measurements for KI concentrations of 1 to 6 mol dm^{-3} (8 points) without any indifferent electrolyte added and at concentrations from 1 to 5 mol dm^{-3} (7 points) with ionic strength maintained at 5 mol dm^{-3} by use of $NaNO_3$. They found that for concentrations of KI up to 2 mol dm^{-3} the solubility of CuSCN was higher than in the corresponding concentrations of KSCN for both types of experiment. However, at concentrations of 3 mol dm^{-3} and above, the solubility was greater in aqueous KSCN.

Fridman and Sarbaev[11] made 28 measurements of solubility in aqueous mixtures of KI and KSCN, with KI concentrations ranging from 1 mol dm^{-3} to 3.6 mol dm^{-3} and total concentrations of soluble salts from 2.5 to 7.9 mol dm^{-3}. In all cases the solubility was less than would be found for the same total anion concentration in either aqueous KI or aqueous KSCN, but in most cases greater than obtained by adding the solubilities expected for I^- and SCN^- at their separate concentrations, acting independently. (Note that the significance of this observation is diminished by the fact that a mixture is at a distinctly higher ionic strength than would be present for either salt solution separately.) Fridman and Sarbaev[11] attribute the solubility in aqueous KI to the formation of addition products $Cu(SCN)I^-$, $Cu(SCN)I_2^{2-}$ and $Cu(SCN)I_3^{3-}$. For the mixed solutions they postulate complexes of the form $Cu(SCN)_nI_m^{1-n-m}$. They give values for stability constants for 7 complexes containing SCN^- and I^-, ranging from $Cu(SCN)I^-$ to $Cu(SCN)_3I_2^{4-}$.

The measurements they presented on these systems appear internally consistent to about the same amount as those cited previously (about 6 per cent), and are Accepted tentatively to this precision, in the absence of other evidence on these systems. The authors' contention that the solubility in solutions containing KI is due to the formation of mixed complexes is a reasonable one, and they are able to use it to give a satisfactory representation of their data. They observed that no $CuI_{(s)}$ was formed in their experiments and that CuSCN, but not CuI, was precipitated on hydrolysis of the solutions, indicating reactions such as $CuSCN + 2I^- \rightleftharpoons CuI_2^- + SCN^-$ or $2CuSCN + 2I^- \rightleftharpoons CuI_2^- + Cu(SCN)_2^-$ did not play a significant part in the solution process. In view of complexities produced by varying ionic strength and composition of their solutions (not taken into account by the authors), the nature of the complexes formed and their stability constants remain subject to question pending further investigation of the systems.

Fridman and Sarbaev[11] stated that the solubility of CuSCN in aqueous KBr and KCl was negligible, and made no measurements on these systems. Swinarski *et al.*[7] made measurements at 293 K of the solubility of CuSCN in aqueous solutions of NaBr and NaCl. For NaBr they made measurements between 0.4 and 2.0 mol dm^{-3} bromide (9 points) in solutions maintained at 2.0 mol dm^{-3} ionic strength by use of $NaNO_3$; for NaCl they made measurements between 2.0 and 4.0 mol dm^{-3} chloride (9 points) at constant ionic strength of 4.0 mol dm^{-3} ($NaNO_3$). The solubilities they report are indeed smaller than those given by Fridman and Sarbaev[11] for KI solutions by nearly two orders of magnitude (See Compilations). In both cases, the solubility is linear in the concentration of the soluble halide; at 2.0 mol dm^{-3}, the solubility in NaBr is almost twice as high as in NaCl.

Swinarski *et al.*[7] interpret their solubilities in terms of formation of a single mixed complex $Cu(SCN)X^-$ (X = Cl or Br) and give stability constants for the two complexes, corrected to zero ionic strength, using the results of their measurement of the solubility product of CuSCN. These constants are almost 4 orders of magnitude lower than that reported by Fridman and Sarbaev[11] for the complex $Cu(SCN)I^-$ at 298 K. The measurements are internally consistent to 1 or 2 per cent in the case of NaCl, but only to 5 per cent in the

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

case of NaBr solutions. Their measurements should be of the correct order of magnitude, but there is strong suspicion that they are too high.

For aqueous NaCl the ratio S/C_L of solubility to chloride concentration decreases linearly with chloride concentration, and the solubilities themselves extrapolate linearly to a value at zero chloride concentration much higher than the value they report for 4 mol dm^{-3} $NaNO_3$ without chloride present. Similar behaviour, though not so pronounced, is seen for the measurements in NaBr solutions. In both cases it would appear that there is a (possibly constant) experimental error or unaccounted source of solubility present in the measurements. Swinarski *et al.*[7] considered these anomalies to be within their experimental error. With this interpretation, their results for NaCl are Accepted tentatively with uncertainties of 5 to 10 per cent in each case.

SOLUBILITY IN AQUEOUS $Na_2S_2O_3$ AND $K_2S_2O_3$

Three sets of measurements have been reported on the solubility of CuSCN in aqueous solutions of $Na_2S_2O_3$ and one set in aqueous $K_2S_2O_3$. In 1952, Yatsimirski and Panova[15] reported a set of solubility measurements at 298 K for $Na_2S_2O_3$ solutions from 0.017 to 0.83 mol kg^{-1} (13 points). In 1968 Gyunner and Yakhkind[12] reported solubility measurements at 293 K for $Na_2S_2O_3$ concentrations from 0.2 to 1.0 mol dm^{-3} (8 points) with ionic strength maintained at 3.0 mol dm^{-3} by use of Na_2SO_4; they also reported four measurements with $Na_2S_2O_3$ concentrations from 0.45 to 0.81 mol dm^{-3}, with NaSCN added as well. In 1976 Golub *et al.*[16] reported both solubility and potentiometric measurements on CuSCN in both aqueous $Na_2S_2O_3$ and aqueous $K_2S_2O_3$ at 298 K with ionic strength maintained at 2.4 mol dm^{-3} by use of the corresponding alkali sulfate. For $Na_2S_2O_3$ they reported solubilities for 16 concentrations of thiosulfate from 0.22 to 1.4 mol dm^{-3}; for $K_2S_2O_3$ they gave 10 solubilities for thiosulfate concentrations from 0.1 to 0.75 mol dm^{-3}. For potentiometric measurements on unsaturated solutions in both systems they used thiosulfate concentrations from 0.10 to 0.86 mol dm^{-3} with a small (unspecified) concentration of Cu^+. The measurements of Gyunner and Yakhkind[12] were made by observation of the refractive index of the solutions; all others were made using chemical analysis. All of the solubilities were much higher than those observed for CuSCN in aqueous solutions of soluble thiocyanates.

The solubilities determined by Gyunner and Yakhkind[12] and by Golub *et al.*[16] on aqueous $Na_2S_2O_3$ at fixed ionic strength were nearly proportional to the concentration of thiosulfate used; both sets are internally consistent to 1 per cent or less. For a given thiosulfate concentration, Gyunner and Yakhkind's results were about 2 per cent higher than those of Golub *et al.*, despite being carried out at a lower temperature. This may be due to the fact that they were made at a higher ionic strength. Both sets are Accepted tentatively.

The measurements of Yatsimirski and Panova[15] were apparently made at whatever ionic strength was provided by the concentration of $Na_2S_2O_3$ used. The solubilities they report increase more rapidly than the concentration of thiosulfate, with the ratio S/C_L of solubility to thiosulfate concentration increasing about 40 per cent over the range of their measurements. For thiosulfate concentrations between 0.3 and 0.8 mol kg^{-1}, S/C_L lies between the values for the other measurements. Their data are not as consistent, with individual points scattering 5 per cent or more from a smooth curve. Yatsimirski and Panova[15] considered the deviation of solubility from proportionality to thiosulfate concentration to be due to experimental error. It might also be due to variations in ionic strength, although this would be expected to affect the results in the opposite direction (solubility less than proportional). Their results can be taken to confirm the general correctness of the other results, but should not be relied upon by themselves.

The results of Golub *et al.*[16] on aqueous $K_2S_2O_3$ are consistent to a per cent or less, but are nearly three times as large as for $Na_2S_2O_3$ solutions; this is in line with the generally

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

greater ability of potassium salts to dissolve cuprous salts. Their results are Accepted tentatively because of their quality and that of the authors' results on $Na_2S_2O_3$ solutions.

All of the investigators agreed that the observed solubilities were produced by the formation of an addition complex by a reaction such as $CuSCN_{(s)} + S_2O_3^{2-} \rightleftharpoons CuSCN \cdot S_2O_3^{2-}$ rather than a replacement reaction such as $CuSCN_{(s)} + S_2O_3^{2-} \rightleftharpoons Cu(S_2O_3)^- + SCN^-$. This conclusion is borne out by two lines of evidence. First, the replacement reaction would require the solubility to be approximately proportional to the square root of the thiosulfate concentration, rather than to the first power, as observed. Second, Gyunner and Yakhkind[12] observed that the solubility was virtually unaffected by addition of NaSCN to the solution, whereas it should be decreased if a replacement reaction was occurring. All of the investigators calculated equilibrium constants for the reaction

$$CuSCN_{(s)} + S_2O_3^{2-} \rightleftharpoons CuSCN \cdot S_2O_3^{2-} \qquad K_{s11} = [CuSCN \cdot S_2O_3^{2-}]/[S_2O_3^{2-}]$$

and stability constants for formation of the complex from the three ions. In $Na_2S_2O_3$ solutions the results for K_{s11} vary from 0.3 to 0.4, with uncertainties of 2 (Golub) to 13 per cent (Yatsimirskii); the differences are most likely due to differences in temperature and in ionic strength. The values of stability constants vary from $1.6 \cdot 10^{12}$ (Golub) to $8 \cdot 10^{13}$ mol^{-2} dm^6 (Gyunner); these differences come mainly from the choice for the (uncertain) value of the solubility product of CuSCN. For solutions in aqueous $K_2S_2O_3$ Golub *et al.*[16] obtained a K_{s11} of 1.95 ± 0.13 and a stability constant of $1.05 \cdot 10^{13}$ mol^{-2} dm^6. (Note: It is possible that other addition complexes may also be formed, but the experimental results provide no basis for identifying any.)

Golub *et al.*[16] used their potentiometric measurements on unsaturated solutions to evaluate stability constants for complexes formed between Cu^+ and $S_2O_3^{2-}$; they considered complexes CuL^-, CuL_2^{3-}, CuL_3^{5-} and CuL_4^{7-}, where L represents S_2O_3. For $Na_2S_2O_3$ solutions they gave values ranging from $8 \cdot 10^8$ mol^{-1} dm^3 for the first complex to $3.2 \cdot 10^{11}$ mol^{-4} dm^{12} for the last, and values about 10 times higher for $K_2S_2O_3$ solutions. The values for the higher complexes may be artifacts of the experiment, but the results do reinforce the belief that these complexes are distinctly less stable than the addition complex.

SOLUBILITY IN AQUEOUS $NaNO_2$

Swinarski *et al.*[7] reported the solubility of CuSCN in aqueous $NaNO_2$ at 293 K, in solutions maintained at a constant ionic strength of 2.0 mol dm^{-3} by use of $NaNO_3$. They give 9 measurements at $NaNO_2$ concentrations ranging from 0.4 to 2.02 mol dm^{-3}, with solubility nearly proportional to the concentration of NO_2^-. Above 0.6 mol dm^{-3} the ratio S/C_L of solubility to NO_2^- concentration is constant within 2 per cent. At 0.6 and 0.4 mol dm^{-3}, the ratio is higher by an amount much larger than would be due to their measured solubility of CuSCN in aqueous $NaNO_3$ without added $NaNO_2$. This suggests a positive experimental error corresponding to 10 per cent or more of the solubility at 0.4 mol dm^{-3} and possibly 5 per cent at 2.0 mol dm^{-3}. They do not comment on this feature of the results, and average the low concentration data with the rest to get equilibrium data. Overall their measurements appear reliable within 5 to 10 per cent.

Swinarski *et al.*[7] interpreted their solubility in terms of the formation of a mixed complex $CuSCN \cdot NO_2^-$, and this is consistent with their observations. They give a value of $2.37 \cdot 10^8$ mol^{-2} dm^6 for the stability constant of this ion, based on their value of $4.8 \cdot 10^{-12}$ mol^2 dm^{-6} for the solubility product at 293 K, $I = 2.0$ mol dm^{-3}. This corresponds to an equilibrium constant of $1.14 \cdot 10^{-3}$ for the equilibrium

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

$$CuSCN_{(s)} + NO_2^- \rightleftharpoons CuSCN \cdot NO_2^-.$$

Their stability constant is almost certainly too low, since their value for the solubility product is unreasonably high. The equilibrium constant for formation of the complex from solid CuSCN is probably valid within about 5 per cent.

SOLUBILITY IN AQUEOUS HCN

The only measurements of solubility of CuSCN in aqueous HCN are those of Vladimirova and Kakovsky[4] (1950), who carried out experiments at 298 K in HCN concentrations from 0.06 to 1.15 mol dm^{-3} (10 points) and in addition made a number of measurements in which CuSCN was dissolved in HCN from 0.5 to 1.1 mol dm^{-3} with an unspecified amount of HCl added to the reaction medium. They report equilibrium concentrations of HCN, $Cu(CN)_2^-$ and H^+, which they considered came from the reaction

$$CuSCN_{(s)} + 2HCN \rightleftharpoons Cu(CN)_2^- + SCN^- + 2H^+ \qquad (5)$$

with an equilibrium constant $K = [Cu(CN)_2^-][SCN^-][H^+]^2/[HCN]^2$. They report a value for this equilibrium constant of $1.31 \cdot 10^{-9}$ mol^2 dm^{-6}, corrected to zero ionic strength.

There are serious difficulties with their measurements. The worst of these is that it not possible to say which of their reported concentrations represents the solubility of CuSCN in the aqueous acid. According to Equation (5), the concentrations of $Cu(CN)_2^-$ and SCN^- should be equal, each representing the solubility of CuSCN, whereas in fact the concentrations they give for SCN^- are about 3 times as large as those reported for $Cu(CN)_2^-$ (See Compilations). Either could be taken to represent the actual solubility, but in either case one is left with some component of the solution unaccounted for. Less serious, although both concentrations vary approximately with $[HCN]^{1/2}$, as would be expected from Equation (5), they vary erratically from smoothness by 5 to 15 per cent, leading to uncertainties of at least this magnitude in their equilibrium constant. The authors observed these deviations and attributed them to experimental uncertainties. The measurements they made with HCl present did show that the reaction was inhibited somewhat by small additions of strong acid, but the results were considerably more erratic than those without it.

The experimental results of Vladimirova and Kakovsky[4] cannot be considered reliable measurements of the solubility of CuSCN in aqueous HCN, but only to give an estimate of the small solubility of CuSCN in this medium.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

REFERENCES

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16. Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. *Zh. Neorg. Khim.* 1976, *21*, 2733; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1976, *21*, 1504.

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Potassium Thiocyanate; KSCN; [333-20-0]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Golub, A. M.
Zh. Neorg. Khim. 1956, *1*, 2517–2531;
J. Inorg. Chem. USSR (Engl. Transl.) 1956, *1*, 87–100.

VARIABLES:

Concentrations of KSCN and $NaNO_3$ at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in KSCN–$NaNO_3$ Solutions at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
0.7508	3.75	0.006150
0.7674	3.73	0.00122
1.2788	3.22	0.004516
1.3642	3.14	0.00569
1.5017	3.00	0.005936
2.0463	2.45	0.01626
2.2525	2.25	0.02046
2.7284	1.78	0.03780
2.8156	1.68	0.04096
3.0695	1.53	0.07259
3.3788	1.12	0.07373
3.9429	0.56	0.1082
4.505	–	0.1775

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solutions of nominal ionic strength 4.5 mol dm^{-3} in contact with solid CuSCN at 293 K for 6 days, with occasional stirring. Analyzed solutions for copper iodometrically after precipitating it as sulfide and oxidizing to Cu^{2+} with nitric acid. KSCN concentrations of starting solutions was determined by mercurometry.

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by dissolving Cu_2O in concentrated NH_4SCN solution. It was then washed, recrystallized and dried. Used recrystallized C. P. KSCN. No other information about materials given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Ammonium Thiocyanate; NH_4SCN; [1762-95-4]
(3) Ammonium Nitrate; NH_4NO_3; [6484-52-2]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gyunner, E. A.; Yakhkind, N. D.
Zh. Neorg. Khim. 1968, *13*, 2758–2763;
Russ. J. Inorg. Chem. (Engl. Transl.) 1968, *13*, 1420–1422.

VARIABLES:

Concentrations of NH_4SCN and NH_4NO_3 at 293 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in NH_4SCN–NH_4NO_3 Solutions at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	c_1/mol dm^{-3}
2.400	2.0	0.019
2.600	1.8	0.030
2.800	1.6	0.037
3.000	1.4	0.045
3.200	1.2	0.052
3.400	1.0	0.067
3.600	0.8	0.078
3.800	0.6	0.090
4.000	0.4	0.104
4.400	–	0.142

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method described in Ref. 1

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by dissolving Cu_2O in concentrated NH_4SCN solution; Washed, recrystallized and dried the product. Used "C.P." NH_4SCN and NH_4NO_3.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Gyunner, E. A.; Yakhkind, N. D. *Russ. J. Inorg. Chem* 1968, *13*, 128.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I)thiocyanate; CuSCN; [1111-67-7] (2) Sodium thiocyanate; NaSCN; [540-72-7] (3) Sodium perchlorate; $NaClO_4$; [7601-90-0] (4) Water; H_2O; [7732-18-5]	Mazo, L. H.; Neves, E. de A.; De Azevedo, L. A. *An. Simp. Bras. Eletroquim. Eletroanal. 3rd*, 1982, *1*, 333-338.
VARIABLES:	**PREPARED BY:**
Concentration of NaSCN at 298 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in NaSCN-$NaClO_4$ Solutions at 25°C [a]

c_2/mol dm^{-3}	10^3c_1/mol dm^{-3}
0.238	0.125
0.358	0.463
0.528	1.06
0.763	2.55
1.000	4.94
1.250	6.66
1.53	10.10

[a] The table gives the data read from the graph of Mazo *et al.* by the compiler. Nominal ionic strength of 4.0 mol dm^{-3} maintained by addition of $NaClO_4$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Analyzed solutions for Cu^+ after allowing 48 hours for equilibration at 25.0 ± 0.1°C.

SOURCE AND PURITY OF MATERIALS:

CuSCN prepared and purified in accord with Reference 1.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Vogel, A. I. *Quantitative Inorganic Analysis*, Longman, London, 1955, p. 431.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Sodium Thiocyanate; NaSCN; [540-72-7] (3) Hydrogen Perchlorate; $HClO_4$; [7601-90-3] (4) Sodium Perchlorate; $NaClO_4$; [7601-89-0] (5) Water; H_2O; [7732-18-5]	Ahrland, S.; Tagesson, B. *Acta Chem. Scand.* 1977, *A31*, 615-624.
VARIABLES:	**PREPARED BY:**
Concentration of Thiocyanate at 298 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in $NaSCN-NaClO_4-(HClO_4)$ Solutions at 25°C

$[SCN^-]_{free}$ / mol dm^{-3}	c_3 / mol dm^{-3}	c_4 / mol dm^{-3}	$[SCN^-]_{total}$[a] / mol dm^{-3}	c_1 / mol dm^{-3}
0.449	0.10	4.551	0.449	0.00033
0.640	0.10	4.259	0.641	0.00068
1.000	0.10	3.897	1.003	0.00235
1.230	0.10	3.666	1.234	0.00439
1.683	0.10	3.206	1.694	0.01030
1.811	0.10	3.076	1.824	0.01127

[a] The total thiocyanate concentrations were calculated by the compiler using the free thiocyanate concentrations given and the equilibrium constants for complex formation given by the authors. Observe that very little of the thiocyanate was involved in the complexes.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The main work of the investigation was a potentiometric study of the stability constants of the cuprothiocyanate complexes, using mainly unsaturated solutions at an ionic strength of 5.0 mol dm^{-3}. When the potential measurements showed that the solution had become saturated, that solution was treated with concentrated $HClO_4$ to oxidize the copper to Cu^{2+}, which was then determined spectrophotometrically as the cuprizone complex.

SOURCE AND PURITY OF MATERIALS:

Used BDH copper(I) thiocyanate; $NaClO_4$ (Fluka) purified by recrystallization; NaSCN (*Mallinckrodt* p. a.) used without further purification.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Sodium Chloride; NaCl; [7647-14-5]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Swinarski, A.; Danilczuk, E.; Gogolin, R.
Roczniki Chem. 1966, *40*, 737–741.

VARIABLES:

Concentrations of NaCl and $NaNO_3$ at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in NaCl–$NaNO_3$ Solutions at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	10^4c_1/mol dm^{-3}
4.0	-	5.36
3.8	0.2	5.12
3.4	0.6	4.80
3.0	1.0	4.26
2.8	1.2	4.16
2.6	1.4	3.84
2.4	1.6	3.65
2.2	1.8	3.39
2.0	2.0	3.21

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuSCN in contact with NaCl–$NaNO_3$ solutions of ionic strength 4.0 mol dm^{-3} to equilibrium at 293 ± 1 K. Analyzed solution for copper colorimetrically as pyridine-thiocyanate complex after oxidation of the copper to Cu^{2+}.

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by reduction of aqueous mixtures of $CuSO_4$ and KSCN. Used "C. P." salts throughout. Purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Sodium Bromide; NaBr; [7647-15-6] (3) Sodium Nitrate; $NaNO_3$; [7631-99-4] (4) Water; H_2O; [7732-18-5]	Swinarski, A.; Danilczuk, E.; Gogolin, R. *Roczniki Chem.* 1966, *40*, 737-741.
VARIABLES:	**PREPARED BY:**
Concentrations of NaBr and $NaNO_3$ at 293 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in NaBr–$NaNO_3$ Solutions at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	10^4c_1/mol dm^{-3}
2.0	–	5.47
1.8	0.2	4.98
1.6	0.4	4.27
1.4	0.6	3.79
1.2	0.8	3.21
1.0	1.0	2.65
0.8	1.2	2.26
0.6	1.4	1.82
0.4	1.6	1.15

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuSCN in contact with NaBr–$NaNO_3$ solutions of ionic strength 2.0 mol dm^{-3} to equilibrium at 293 ± 1 K. Analyzed solution for copper colorimetrically as pyridine-thiocyanate complex after oxidation of the copper to Cu^{2+}.

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by reduction of aqueous mixtures of $CuSO_4$ and KSCN. Used "C. P." salts throughout. Purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Sodium Thiosulfate; $Na_2S_2O_3$; [7772-98-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Yatsimirskii, K. B.; Panova, V. E.
Zh. Obshch. Khim. 1952, *22*, 1284–1289.

VARIABLES:

Molality of $Na_2S_2O_3$ at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in Aqueous $Na_2S_2O_3$ at 25°C

$10^2 m_2$/mol kg^{-1}	$10^2 m_1$/mol kg^{-1}
1.720	0.3368
2.109	0.4194
3.542	0.7705
4.900	0.9652
6.370	1.305
7.750	1.748
11.94	2.822
18.41	4.304
24.32	6.127
33.72	8.645
42.46	11.01
52.16	13.54
83.23	23.98

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuSCN in contact with $Na_2S_2O_3$ solution in thermostat at 25 ± 0.1°C for several days, with continuous shaking. Analyzed for total $S_2O_3^{2-}$ and Cu^+ iodometrically, for copper separately after oxidation to Cu^{2+} with HNO_3.

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN from chemically pure $CuSO_4 \cdot 5H_2O$ and KSCN. Source of materials not given.

ESTIMATED ERROR:

Not given; internal consistency *app.* 2%.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Sodium Thiosulfate; $Na_2S_2O_3$; [7772-98-7] (3) Sodium Sulfate; Na_2SO_4; [7757-82-6] (4) Water; H_2O; [7732-18-5]	Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. *Zh. Neorg. Khim.* 1976, *21*, 2733–2737; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1976, *21*, 1504–1506.
VARIABLES:	**PREPARED BY:**
Concentration of $Na_2S_2O_3$ at 298 K	J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuSCN in $Na_2S_2O_3$–Na_2SO_4 Solutions at 25°C [a]

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.219	0.0524
0.257	0.0602
0.299	0.0704
0.333	0.0794
0.445	0.1050
0.500	0.1170
0.527	0.1280
0.555	0.1340
0.667	0.1580
0.713	0.1680
0.833	0.1990
0.984	0.2260
1.020	0.2320
1.140	0.2620
1.250	0.2850
1.428	0.3230

[a] Nominal ionic strength of 2.4 mol dm^{-3} maintained by addition of Na_2SO_4.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Shook solid CuSCN with $Na_2S_2O_3$ solutions at 298.1 ± 0.2 K until equilibrium reached, then analyzed solutions for copper content (method not given).

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by reaction of $CuSO_4$ solutions with KSCN, then washed and dried precipitated CuSCN. Source and purity of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Potassium Thiosulfate; $K_2S_2O_3$; [10294-66-3] (3) Potassium Sulfate; K_2SO_4; [7778-80-5] (4) Water; H_2O; [7732-18-5]	Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. *Zh. Neorg. Khim.* 1976, *21*, 2733–2737; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1976, *21*, 1504–1506.
VARIABLES:	PREPARED BY:
Concentration of $K_2S_2O_3$ at 298 K	J. J. Fritz and E. Königsberger

EXPERIMENTAL VALUES:

Solubility of CuSCN in $K_2S_2O_3$–K_2SO_4 Solutions at 25°C [a]

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.098	0.065
0.158	0.104
0.207	0.137
0.261	0.172
0.342	0.227
0.404	0.269
0.508	0.333
0.553	0.364
0.612	0.403
0.715	0.498

[a] Nominal ionic strength of 2.4 mol dm^{-3} maintained by addition of K_2SO_4.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Shook solid CuSCN with $K_2S_2O_3$ solutions at 298.1 ± 0.2 K until equilibrium reached, then analyzed solutions for copper content (method not given).	Prepared CuSCN by reaction of $CuSO_4$ solutions with KSCN, then washed and dried precipitated CuSCN. Source and purity of materials not given.
	ESTIMATED ERROR:
	Not given.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Sodium Thiosulfate; $Na_2S_2O_3$; [7772-98-7] (3) Sodium Thiocyanate; NaSCN; [540-72-7] (4) Sodium Sulfate; Na_2SO_4; [7757-82-6] (5) Water; H_2O; [7732-18-5]	Gyunner, E. A.; Yakhkind, N. D. *Zh. Neorg. Khim.* 1968, *13*, 2758-2763; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 1420-1422.
VARIABLES:	**PREPARED BY:**
Concentrations of $Na_2S_2O_3$, NaSCN and Na_2SO_4 at 293 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in $Na_2S_2O_3$–Na_2SO_4 Solutions at 20°C

c_2/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.200	0.8	0.050
0.400	0.6	0.105
0.500	0.5	0.139
0.600	0.4	0.169
0.700	0.3	0.199
0.800	0.2	0.224
0.900	0.1	0.254
1.000	–	0.289

Solubility of CuSCN in NaSCN–$Na_2S_2O_3$–Na_2SO_4 Solutions at 20°C

c_3/mol dm^{-3}	c_2/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.500	0.450	0.282	0.125
0.300	0.630	0.270	0.175
0.200	0.720	0.213	0.199
0.100	0.810	0.157	0.224

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method described in Ref. 1

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by dissolving Cu_2O in concentrated NH_4SCN solution; Washed, recrystallized and dried the product. Used "C. P." salts in solution.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Gyunner, E. A.; Yakhkind, N. D. *Russ. J. Inorg. Chem.* 1968, *13*, 128.

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Potassium Thiocyanate; KSCN; [333-20-0]
(3) Potassium Iodide; KI; [7681-11-0]
(4) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fridman, Ya D.; Sarbaev, Dzh. S.
Zh. Neorg. Khim. 1959, *4*, 1849–1859;
Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 835–841.

VARIABLES:

Concentrations of KSCN, KI and $NaNO_3$ at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in KSCN–NaNO$_3$ Solutions at 25°C

c_2/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
0.730	0.0	0.0054
1.481	0.0	0.0139
2.080	0.0	0.0292
3.928	0.0	0.1472
5.60	0.0	0.4484
6.8	0.0	0.8339
0.97	4.0	0.0095
1.237	3.8	0.0188
1.980	3.0	0.0262
2.97	2.0	0.0591
4.93	–	0.2710

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Stirred mixtures of solid and solution for 8–10 hours. Evaporated a measured volume of solution to dryness with concentrated HNO_3, dissolving residue in water. CuO was precipitated with KOH, dried and weighed. Concentration of thiocyanate and iodide were determined argentimetrically. Solid phases were analyzed periodically.

SOURCE AND PURITY OF MATERIALS:

CuSCN was prepared either by reducing an aqueous mixture of $CuSO_4$ and KSCN with SO_2 or by hydrolysis of a solution of CuO in concentrated NH_4SCN. Sources and purities of materials not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Potassium Thiocyanate; KSCN; [333-20-0]
(3) Potassium Iodide; KI; [7681-11-0]
(4) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fridman, Ya D.; Sarbaev, Dzh. S.
Zh. Neorg. Khim. 1959, *4*, 1849–1859;
Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 835–841.

EXPERIMENTAL VALUES:

(continued)

Solubility of CuSCN in KI–$NaNO_3$ Solutions at 25°C

c_3/mol dm^{-3}	c_4/mol dm^{-3}	c_1/mol dm^{-3}
1.020	0.0	0.0094
1.065	0.0	0.0090
2.036	0.0	0.0359
3.060	0.0	0.0661
4.044	0.0	0.140
5.00	0.0	0.2110
5.10	0.0	0.218
6.042	0.0	0.399
0.994	4.0	0.0133
1.487	3.5	0.0221
2.008	3.0	0.0342
2.505	2.5	0.0465
3.022	2.0	0.0661
3.976	1.0	0.1307
5.10	–	0.2183

continued...

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Potassium Thiocyanate; KSCN; [333-20-0]
(3) Potassium Iodide; KI; [7681-11-0]
(4) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fridman, Ya D.; Sarbaev, Dzh. S.
Zh. Neorg. Khim. 1959, *4*, 1849-1859;
Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 835-841.

EXPERIMENTAL VALUES:

(continued)

Solubility of CuSCN in KI-KSCN Solutions at 25°C

c_3/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}
1.5	1.025	0.0209
1.5	1.473	0.0460
2.0	1.00	0.0252
1.5	1.995	0.0638
2.0	1.50	(0.05)
2.5	1.075	0.0346
1.5	2.52	0.0994
2.0	2.0	(0.0955)
2.5	1.514	0.0668
1.5	3.045	0.1071
2.5	2.0	0.09316
3.6	1.10	0.0965
0.978	3.912	0.218
1.235	3.705	0.205
1.50	3.477	0.210
1.98	3.16	0.177
2.5	2.53	0.166
2.93	2.0	0.139
3.57	1.54	0.128
1.5	4.035	0.2715
2.50	3.03	0.2039
3.60	1.80	0.1910
2.50	3.364	0.289
1.50	5.109	0.571
2.50	4.04	0.4873
3.6	3.0	0.3735
2.5	4.809	0.762
1.5	6.377	0.991

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Sodium Nitrite; $NaNO_2$; [7632-00-0]
(3) Sodium Nitrate; $NaNO_3$; [7631-99-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Swinarski, A.; Danilczuk, E.; Gogolin, R.
Roczniki Chem. 1966, *40*, 737–741.

VARIABLES:

Concentrations of $NaNO_2$ and $NaNO_3$ at 293 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in $NaNO_2$–$NaNO_3$ Solutions at 20°C

c_2/mol dm^{-3}	c_3/mol dm^{-3}	pH	10^4c_1/mol dm^{-3}
2.020	–	6.79	22.12
1.818	0.2	6.88	19.89
1.616	0.4	6.96	18.02
1.414	0.6	6.86	15.85
1.212	0.8	6.82	13.295
1.010	1.0	6.70	11.05
0.808	1.2	6.64	9.11
0.606	1.4	6.51	7.19
0.404	1.6	6.40	5.48

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuSCN in contact with $NaNO_2$–$NaNO_3$ solutions of ionic strength 2.0 mol dm^{-3} to equilibrium at 293 ± 1 K. Analyzed solution for copper colorimetrically as pryidine-thiocyanate complex after oxidation of the copper to Cu^{2+}.

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by reduction of aqueous mixtures of $CuSO_4$ and KSCN. Used "C. P." salts throughout. Purities not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Hydrogen Cyanide; HCN; [420-05-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vladimirova, M. G.; Kakovsky, I. A.
Zh. Prikl. Khim. 1950, *23*, 580-598;
J. Appl. Chem. (USSR) (Engl. Transl.) 1950, *23*, 615-632.

VARIABLES:

Concentration of HCN at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in Aqueous HCN at 25°C

[HCN]/mol dm^{-3}	[SCN^-]/mol dm^{-3}	[H^+]/mol dm^{-3}	[$Cu(CN)_2^-$]/mol dm^{-3}
1.152	0.00692	0.0124	0.00196
0.860	0.00643	0.0110	0.00190
0.739	0.00580	0.0100	0.00184
0.604	0.00565	0.0089	0.00155
0.478	0.00565	0.0073	0.00136
0.364	0.00326	0.0064	0.00130
0.307	0.00288	0.0059	0.00130
0.207	0.00215	0.0048	0.00100
0.143	0.00195	0.0038	0.00090
0.059	0.00174	0.0024	0.00060

Note: The concentration given for $Cu(CN)_2^-$ should represent the solubility of CuSCN, according to the method of analysis described by the authors. However, it should be equal to the concentration of SCN^- produced. The authors give no explanation for the fact that the SCN^- concentration is always much higher.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuSCN and HCN solution at 298 K until equilibrium reached. Determined HCN concentration by titration with $AgNO_3$, copper by method of Kolthoff (Ref. 1) and thiocyanate from mass of sulfur produced when solution was oxidzed by H_2O_2.

SOURCE AND PURITY OF MATERIALS:

Prepared HCN by method of Karyakin (Ref. 2), CuSCN by reducing $CuSO_4$ solution (with thiocyanate added?). No purities given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kolthoff, I. M. *Volumetric Analysis (Russ. Ed.)* 1950.
2. Karyakin, Yu. V. *Pure Chemical Reagents* 1936.

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]
(2) Hydrogen Cyanide; HCN; [420-05-3]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vladimirova, M. G.; Kakovsky, I. A.
Zh. Prikl. Khim. 1950, *23*, 580-598;
J. Appl. Chem. (USSR) (Engl. Transl.) 1950, *23*, 615-632.

VARIABLES:

Concentrations of HCN and HCl at 298 K

PREPARED BY:

J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in HCN-HCl Solutions at 25°C

[HCN]/mol dm^{-3}	[SCN^-]/mol dm^{-3}	[H^+]/mol dm^{-3}	[$Cu(CN)_2^-$]/mol dm^{-3}
0.519	0.00289	0.00698	0.00103
0.739	0.00524	0.00962	0.00152
0.800	0.00528	0.01074	0.00138
1.038	0.0060	0.012288	0.001798
0.978	0.00588	0.012425	0.001645
0.876	0.0047	0.01251	0.00169
0.876	0.00468	0.01270	0.00169
1.119	0.00782	0.01949	0.00177

Note: The concentration given for $Cu(CN)_2^-$ should represent the solubility of CuSCN, according to the method of analysis described by the authors. However, it should be equal to the concentration of SCN^- produced. The authors give no explanation for the fact that the SCN^- concentration is always much higher.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuSCN and HCN solution at 298 K until equilibrium reached. Determined HCN concentration by titration with $AgNO_3$, copper by method of Kolthoff (Ref. 1) and thiocyanate from mass of sulfur produced when solution was oxidzed by H_2O_2.

SOURCE AND PURITY OF MATERIALS:

Prepared HCN by method of Karyakin (Ref. 2), CuSCN by reducing $CuSO_4$ solution (with thiocyanate added?). Source of HCl not given. No purities given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kolthoff, I. M. *Volumetric Analysis (Russ. Ed.)*, 1950.
2. Karyakin, Yu. V. *Pure Chemical Reagents* 1936.

COMPONENTS:	EVALUATOR:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Organic Solvents	J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

No measurements were found on any binary systems involving CuSCN and an organic solvent. The results on ternary systems are given below.

Golub[1] made measurements of the solubility of CuSCN in KSCN–ethanol and KSCN–acetone solutions at 293 K. For the ethanol system he gave five points for KSCN concentrations from 0.07 to 0.41 mol dm^{-3}. For KSCN–acetone he reported 10 measurements at KSCN concentrations from 0.24 to 1.17 mol dm^{-3}.

The solubility in KSCN–ethanol was relatively modest, the maximum value being 0.0116 mol dm^{-3} in 0.406 mol dm^{-3} KSCN (See Compilations). The data follow a smooth curve within about 1 per cent. They are Accepted tentatively subject to possible further study of the system. Golub attributed the solubility to formation of two complexes, $Cu(SCN)_2^-$ and $Cu(SCN)_3^{2-}$, but did not attempt to evaluate equilibrium constants for formation of either of them, merely showing that neither would represent the data individually. The data can in fact be represented to 1 or 2 per cent by this assumption, with equilibrium constants of about 0.015 and 0.035 mol^{-1} dm^3, respectively, for formation of the singly and doubly charged complexes from solid CuSCN.

Golub[1] found the solubility of CuSCN in KSCN–acetone to be quite substantial, typically 60 to 80 per cent of the KSCN concentration employed. The measurements for this system are less consistent than for the ethanolic system. The ratio S/C_L of solubility to initial KSCN concentration varies about linearly with KSCN concentration, but with individual points varying 2 to 3 per cent from linearity. In addition, the ratio increases with decreasing KSCN concentration, and a direct plot of solubility versus KSCN concentration extrapolates to a value of 0.04 mol dm^{-3} at zero KSCN concentration. This behaviour could be due to formation of neutral $CuSCN^0$ or to a constant positive experimental error. Golub does not comment on this tendency or present any data on the solubility of CuSCN in acetone in the absence of another salt. The data do not permit choosing between these alternatives. Consequently, the data can only be Accepted tentatively, with possible errors up to 5 per cent.

Golub[1] interpreted his data on the solubility in acetone in terms of formation of a single complex $Cu(SCN)_2^-$ and evaluated an average equilibrium constant for formation of this complex from solid CuSCN of 2.84, treating this complex as the only source of solubility. However, individual values for the constant vary over a range of about 0.9. The data are represented much better by including a constant contribution (of unknown source) to the results and an slightly smaller equilibrium constant (2.78).

In 1956 Golub and Kilimnik[2] succeeded in preparing a compound $K_2Cu(SCN)_3$ from an acetone solution of CuSCN and KSCN. They also found crystals believed to be $KCu(SCN)_2$ but were unable to identify them unambiguously. Harris[3] succeeded in preparing the pyridinium compounds $(C_5H_5NH)Cu^I(SCN)_2$ and $(C_5H_5NH)Cu^IISCN$, also from acetone solution. Rosenheim and Steinhauser[4] prepared the salt $CuSCN \cdot NH_4SCN \cdot 4(NH_4)_2S_2O_3$ and verified its composition by chemical analysis. Canneri and Luchini[5] prepared the salt $2CuSCN \cdot 5Na_2S_2O_3$ and verified its composition by chemical analysis.

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3. Harris, C. M. *J. Proc. Roy. Soc. New South Wales* 1951, *84*, 111.
4. Rosenheim, A.; Steinhauser, S. *Z. Anorg. Chem.* 1900, *25*, 103.
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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Thiocyanate; CuSCN; [1111-67-3] (2) Potassium Thiocyanate; KSCN; [333-20-0] (3) Ethanol; C_2H_6O; [64-17-5]	Golub, A. M. *Zh. Neorg. Khim.* 1956, *1*, 2517-2531; *J. Inorg. Chem. USSR* 1956, *1*, 87-100.
VARIABLES:	PREPARED BY:
Concentration of KSCN at 293 K	J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in Ethanolic KSCN at 20°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.06768	0.9678
0.1160	2.2258
0.2031	4.516
0.2901	7.42
0.4061	11.61

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions kept at 20°C for a week, then analyzed for copper by precipitation as sulfide, followed by iodometric determination of copper after solution in sulfuric acid.

SOURCE AND PURITY OF MATERIALS:

CuSCN prepared by dissolving Cu_2O in concentrated, purified NH_4SCN. Thereafter the precipitate was reprecipitated, washed and dried. Recrystallized KSCN and redistilled absolute ethanol were used.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Thiocyanate; CuSCN; [1111-67-3]
(2) Potassium Thiocyanate; KSCN; [333-20-0]
(3) Acetone; C_2H_6O; [67-64-1]

ORIGINAL MEASUREMENTS:

Golub, A. M.
Zh. Neorg. Khim. 1956, *1*, 2517–2531;
J. Inorg. Chem. USSR 1956, *1*, 87–100.

VARIABLES:

Concentration of KSCN at 293 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuSCN in Acetone Solutions of KSCN at 20°C

c_2/mol dm^{-3}	c_1/mol dm^{-3}
1.1660	0.7884
0.9388	0.6502
0.7058	0.5017
0.4659	0.3430
0.5956	0.4300
0.5933	0.4249
0.2375	0.1843
0.2708	0.2048
0.6267	0.4693
0.5044	0.3799

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions kept at 20°C for a week, then analyzed for copper by precipitation as sulfide, followed by iodometric determination of copper after solution in sulfuric acid.

SOURCE AND PURITY OF MATERIALS:

CuSCN prepared by dissolving Cu_2O in concentrated, purified NH_4SCN. Thereafter the precipitate was reprecipitated, washed and dried. Recrystallized KSCN and redistilled dehydrated acetone were used.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Selenocyanate; CuSeCN; [no registry number known]

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

EVALUATOR:

J. J. Fritz

Department of Chemistry
The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

THE BINARY SYSTEM

The only data available on the solubility of copper(I) selenocyanate comes from potentiometric measurements on a saturated aqueous solution of this salt at 293 K reported by Golub and Skopenko[1] in 1960. They utilized their results to obtain a value for the solubility product at 293 K of (*app.*) $1.8 \cdot 10^{-10}$ (distinctly higher than values given for CuSCN but comparable to values for CuI; the authors observe that this is in accord with the relationship between the solubility products for the two silver salts.)

REFERENCE

1. Golub, A. M.; Skopenko, V. V. *Zh. Neorg. Khim.* 1960, *5*, 1973; *Russ J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 961.

COMPONENTS:	EVALUATORS:
(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

THE BINARY SYSTEM

The only measurement of the solubility of cuprous cyanide in pure water found in the literature was that of Ragg[1] (1950), who gave a value of $2.6 \cdot 10^{-3}$ g dm^{-3} at 288 K; he also gave a value of $6.0 \cdot 10^{-3}$ g dm^{-3} in sea water. Vladimirova and Kakovsky[2] (1950) give a value for the solubility product at 298 K of $3.2 \cdot 10^{-20}$ mol^2 dm^{-6}. Their value was obtained indirectly by measurement of the equilibrium constants of the reactions $CuCN_{(s)} + HCN \rightleftharpoons Cu(CN)_2^- + H^+$ and $CuSCN_{(s)} + 2\,HCN \rightleftharpoons Cu(CN)_2^- + SCN^- + 2\,H^+$. Butler[3] reported the same value for the solubility product in 1964, without attribution.

The value given by Ragg[1] for the solubility of CuCN in pure water corresponds to a concentration of $2.9 \cdot 10^{-5}$ mol dm^{-3}, much higher than would result from dissociative solution of CuCN. Another possibility is the reaction $2\,CuCN_{(s)} \rightleftharpoons Cu^+ + Cu(CN)_2^-$, for which the results of Vladimirova and Kakovsky[2] give an equilibrium constant of $5.1 \cdot 10^{-16}$ mol^2 dm^{-6}. However, this would yield a solubility of only about $2 \cdot 10^{-8}$ mol dm^{-3}. The additional solubility observed by Ragg[1] could have been due to the production of neutral $CuCN^0$ (properties unknown) or possibly to acidity in the water used.

The value of $3.2 \cdot 10^{-20}$ mol^2 dm^{-6} given by Vladimirova and Kakovsky[2] for the solubility product appears to be correct, at least to order of magnitude. The actual solubility of CuCN in pure water could be no higher than the value given by Ragg[1] and could be as low as the value $2 \cdot 10^{-8}$ mol dm^{-3} derived from the measurements of Vladimirova and Kakovsky[2].

SOLUBILITY IN AQUEOUS SOLUTIONS OF ALKALI CYANIDES AND HCN

There have been three investigations of the solubility of CuCN in aqueous solutions of alkali cyanides. In 1924 Bassett and Corbet[4] published a complete phase diagram for the system $CuCN\text{-}KCN\text{-}H_2O$ at 298 K. In 1938 Plaksin and Fishkova[5] made similar measurements on this system and the system $CuCN\text{-}NaCN\text{-}H_2O$ at 288, 298 and 308 K. In 1950 Vladimirova and Kakovsky[2] measured the solubility of CuCN in 7 concentrations of aqueous HCN at 298 K.

A common feature of the measurements involving alkali cyanides is the fact that as CuCN is dissolved, it is transformed to one of a number of double salts so that the saturated solutions produced are in equilibrium with a double salt rather than with CuCN itself. No solid double salt was observed with aqueous HCN, the solid phase in equilibrium with solution being always CuCN.

Results with Aqueous KCN

The only medium for which more than one set of results is available is aqueous KCN at 298 K, which was studied by both Bassett and Corbet[4] and Plaksin and Fishkova[5]. The first of these reported results for 20 molalities of KCN ranging from 0.21 to 12.8 mol kg^{-1}, with dissolved CuCN from zero to 6.0 mol kg^{-1}. They found no solutions in equilibrium with solid CuCN, but reported finding four different complex salts in equilibrium with their solutions, *viz.* $KCu_2(CN)_3 \cdot H_2O$, $KCu(CN)_2$, $K_3Cu(CN)_4 \cdot H_2O$ and $K_3Cu(CN)_4$, with KCN the solid phase for the highest molalities of KCN. The first of these salts appeared at KCN molalities from 0.21 to 1.86, with the molality of dissolved cuprous salt 0.07 to 1.02. $KCu(CN)_2$ was at equilibrium with solution in a range 2.35 to 12.52 mol kg^{-1} and cuprous molalities from 1.25 to 5.91. $K_3Cu(CN)_4$ and its hydrate were found at KCN molalitiess between 10.2 and 12.8 and cuprous molalities from 1.23 to 6.0. [Note that they report the equilibrium molalities of KCN and CuCN; with double salts present, the molalities of KCN would be less than the (unspecified) molalities of KCN supplied at the start of the experiments.]

COMPONENTS:	EVALUATORS:
(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

Plaksin and Fishkova[5] measured the solubility of CuCN in aqueous KCN at 288, 298 and 308 K, with KCN concentrations from 10 to 600 g dm^{-3} (0.15 to 9.2 mol dm^{-3}), 13 concentrations at each temperature. They report solubility of CuCN as a function of KCN concentration (apparently the KCN concentration originally supplied, since they state only that they analyzed their solutions for copper content.) They found that solutions in the lower range of KCN concentration had CuCN as the solid phase, those in the intermediate range $KCu(CN)_2$, at higher ranges $K_2Cu(CN)_3$, then finally mixtures of KCN and the second complex salt. For some ranges of concentration they reported mixtures of solid CuCN and $KCu(CN)_2$ and mixtures of the two complexes. They did not report finding the other complex salts reported by Bassett and Corbet[3] and there is no indication that they were aware of this research. They also report mixtures of solid phases over a range of concentration, which could happen only if equilibrium was not fully reached in conversion of CuCN to a double salt (Bassett and Corbet[3] observed that conversion of CuCN to double salt was incomplete, even after 2 days equilibration.)

The two sets of solubilities at 298 K can be compared after conversion of the data of Plaksin and Fishkova[5] to mol kg^{-1} using the densities they report for their solutions. In the range where both groups reported values, those of Plaksin and Fishkova[5] are 5 to 10 per cent higher than those of Bassett and Corbet[4]. The latter would appear to be the more reliable and are Recommended for use. The data of Plaksin and Fishkova[5] at 288 and 308 K are Accepted tentatively, subject to an uncertainty of 10 per cent on the high side.

The question of the double salts produced between KCN and CuCN has been the subject of many past investigations. For example, in 1902 Itzig[6] reported salts corresponding to $KCu_2(CN)_3 \cdot H_2O$, $KCu(CN)_2$, $K_2Cu_3(CN)_5$ and $K_3Cu(CN)_4$ at room temperature. In 1904 Kunschert[7] reported observation of three of these (excepting $K_2Cu_3(CN)_5$). In 1912 Truthe[8] identified $KCu_2(CN)_3$, $KCu(CN)_2$ and $K_3Cu(CN)_4$ in his study of the phase diagram of the system CuCN–KCN in the temperature range 500 to 900 K. Bassett and Corbet[4] (1924) confirmed the presence of $KCu_2(CN)_3 \cdot H_2O$, $KCu(CN)_2$ and $K_3Cu(CN)_4 \cdot H_2O$ by chemical analysis. Finally, Staritsky and coworkers described the preparation and crystal structure of $KCu(CN)_2$9, $KCu_2(CN)_3 \cdot H_2O$[10] and $K_3Cu(CN)_4$[11]. Thus the three compounds $KCu_2(CN)_3$, $KCu(CN)_2$ and $K_3Cu(CN)_4$ all appear to be stable at ordinary temperatures, with the first and third of these probably hydrated in the presence of aqueous KCN.

Results with Aqueous NaCN

Plaksin and Fishkova[5] reported the solubility in aqueous NaCN at 288, 298 and 308 K, with 13 points at each temperature, again reporting double salts present as solid phases. Their results have about the same consistency as those in aqueous KCN, but cannot be compared with any other investigations. Based on these facts, they are Accepted tentatively, with a possible error of as much as 10 per cent.

There is some information in the literature about double salt formation between CuCN and NaCN. Truthe[8] identified compounds corresponding to $NaCu(CN)_2$, $Na_2Cu(CN)_3$ and $Na_3Cu(CN)_4$ in his study of the phase behaviour of the system CuCN–NaCN between 550 and 820 K. Plaksin and Fishkova[5] claimed to find the first two of these in equilibrium with NaCN solutions, along with two pentacyano salts, $Na_3Cu_2(CN)_5$ and (at their lowest temperature) $Na_4Cu(CN)_5$. The three salts found by Truthe[8] appear well established, with the other two questionable. It is also possible that one or more of the salts may exist as a hydrate at ordinary temperature.

COMPONENTS:	EVALUATORS:
(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

Results with Aqueous HCN

The only results reported for the solubility of CuCN in aqueous HCN are those of Vladimirova and Kakovsky[2]. They measured the solubility at 298 K in 6 concentrations of HCN, ranging from 0.14 to 1.44 mol dm^{-3}. They also reported solubilities for media in which a small amount of either HCl or H_2SO_4 was added to the HCN solution. They found that in "pure" aqueous HCN the solubility varied with the square root of the HCN concentration. The ratio $(S/C_L)^{1/2}$, where S is the solubility and C_L the concentration of HCN, increases by only 7 per cent over the entire range of concentrations, and individual points all lie within 2 per cent of a straight line. Addition of either HCl or H_2SO_4 to the medium reduces the solubility for a given HCN concentration.

Vladimirova and Kakovsky[2] interpreted their solubility data in terms of the reaction

$$\mathrm{CuCN_{(s)} + HCN \rightleftharpoons Cu(CN)_2^- + H^+}, \qquad K = [\mathrm{Cu(CN)_2^-}][\mathrm{H^+}]/[\mathrm{HCN}].$$

They derived a value of $1.22 \cdot 10^{-5}$ mol dm^{-3} for this equilibrium constant. With estimated corrections for ionic strength effects, this fitted their data for "pure" aqueous HCN within a few per cent and the data for solutions containing strong acid to a poorer precision of 10 to 20 per cent, apparently because of difficulty in determination of the final concentration of H^+.

Vladimirova and Kakovsky[2] found no evidence for double salt formation, with the solid phase being only CuCN in all cases. Their results are Accepted tentatively in view of their excellent consistency.

Results with Aqueous HCN–NaCN

In 1994 Königsberger *et al.*[15] presented a solubility study of CuCN in HCN–NaCN solutions at 25°C and 4 nominal ionic strengths (0.15, 0.25, 0.50 and 1.0 mol dm^{-3} NaCl), the concentrations of HCN and NaCN ranging from 0.0025 to 0.05 mol dm^{-3}. Solutions were prepared by adding appropriate amounts of HCl to NaCN–NaCl solutions of desired ionic strength so that part of the NaCN was converted to HCN. Königsberger *et al.*[15] used a thermostated, percolation-type solubility apparatus where the solution was recirculated by a nitrogen gas stream which was presaturated with H_2O and HCN so that their partial pressures in the incoming and leaving gas streams were essentially equal. The H^+ concentration was measured as $p[H] = \log[H^+]/\mathrm{mol\ dm^{-3}}$ using a galvanic cell with glass electrode and Ag/AgCl reference electrode. The p[H] was also recorded before adding the solid phase in order to calculate the dissociation constants of HCN in NaCl media (which were found to be in very good agreement with literature values). The p[H] was then monitored during the dissolution of CuCN; constant p[H] values indicated that solubility equilibrium was attained (typically after 5 to 10 hours).

Königsberger *et al.*[15] used the stability constants of Cu(I)–CN^- complexes given by Hefter *et al.*[16] (see below) to simulate solubility equilibria of CuCN under the conditions of their work. It turned out that CN^- dissolves $CuCN_{(s)}$ by forming $Cu(CN)_2^-$ [*app.* 75 to 85 per cent of total Cu(I)] and $Cu(CN)_3^{2-}$ as predominant species while the initial concentration of HCN remains virtually unchanged. Thus the results were interpreted in terms of the equilibria

$$\begin{array}{lcll} \mathrm{CuCN_{(s)} + HCN} & \rightleftharpoons & \mathrm{H^+ + Cu(CN)_2^-} & {}^*K_{S2} = [\mathrm{Cu(CN)_2^-}][\mathrm{H^+}]/[\mathrm{HCN}], \\ \mathrm{CuCN_{(s)} + 2\,HCN} & \rightleftharpoons & \mathrm{2\,H^+ + Cu(CN)_3^{2-}} & {}^*K_{S3} = [\mathrm{Cu(CN)_3^{2-}}][\mathrm{H^+}]^2/[\mathrm{HCN}]^2. \end{array}$$

COMPONENTS:	EVALUATORS:
(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

The neutral complex $CuCN^0$ became important only at the lowest CN^- concentrations used.

By taking the Cu(I) speciation into account, Königsberger *et al.*[15] derived log $^*K_{S2}$ values for the 4 ionic strengths investigated and obtained $\log {}^*K_{S2}/\text{mol dm}^{-3} = -4.9 \pm 0.1$ by extrapolation to zero ionic strength. It should be noted that the estimated error is due to uncertainties in speciation and extrapolation; it is much larger than suggested by the excellent consistency of the experiments. The value of log $^*K_{S2}$ given by Königsberger *et al.*[15] agrees perfectly with that of Vladimirova and Kakovsky[2], however, Königsberger *et al.*[15] investigated a well-buffered system and were able to measure p[H] values very precisely.

Equilibrium Constants for Complex Formation

In the course of their measurements Vladimirova and Kakovsky[2] obtained a value of $5 \cdot 10^{-5}$ for the equilibrium constant of the reaction $CuCN_{(s)} + CN^- \rightleftharpoons Cu(CN)_2^-$. This can be compared with a value of $3.2 \cdot 10^{-4}$ derived from their solubility product and a value of $1 \cdot 10^{-16}$ mol^2 dm^{-6} for the dissociation constant of $Cu(CN)_2^-$ given by Latimer[12]. They also give values for the Gibbs energy changes involved in formation of $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ from the singly charged complex ion, but the meaning of their numbers is unclear. [In 1931 Kolthoff and Furman[13] had given a value of $5 \cdot 10^{-28}$ mol^4 dm^{-12} for the dissociation constant of $Cu(CN)_4^{3-}$ (source not given).] In 1964 Butler[3] gave values for the equilibrium constants for formation of $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$ from $CuCN_{(s)}$ and CN^-, supposedly corrected to zero ionic strength; he did not give the source of his information.

In 1993 Hefter *et al.*[16] used a new method for studying Cu(I)–CN^- stability constants by potentiometric titration. Cu(I) solutions were produced by reduction of Cu(II) with an excess of copper and stabilized by chloride. Their values for $\log\beta_1/\text{mol}^{-1}\,\text{dm}^3 = 16.33$, $\log\beta_2/\text{mol}^{-2}\,\text{dm}^6 = 23.97$, $\log\beta_3/\text{mol}^{-3}\,\text{dm}^9 = 29.40$ and $\log\beta_4/\text{mol}^{-4}\,\text{dm}^{12} = 31.87$, are valid for $I_c = 1$ mol dm^{-3} NaCl and 25°C. Hefter *et al.*[16] present a table where their results are compared with data given in a comprehensive review[17]. It should be noted that $CuCN^0$ is not normally detected in this type of measurement; the value given by Hefter *et al.*[16] was estimated. In fact, the results of the CuCN solubility study of Königsberger *et al.*[15] suggest that $\log\beta_1$ may actually be lower by about half an order of magnitude.

Other Double Salts Containing CuCN

In 1891 Fleurent[14] reported a compound $NH_4Cu_2(CN)_3\cdot 3NH_3$ with its composition verified by chemical analysis. Itzig[6] isolated a mixed compound $K_3Cu(CN)_3SCN\cdot H_2O$ when CuCN was dissolved in an aqueous mixture of KCN and KSCN.

Other Information

No table of recommended values of solubility is given, for lack of sufficient data. No information was found on the solubility of CuCN in any organic solvent.

COMPONENTS:	EVALUATORS:
(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H_2O; [7732-18-5]	J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996

CRITICAL EVALUATION:

REFERENCES

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17. Beck, M. T. *Pure Appl. Chem.* 1987, *59*, 1703.

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(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*, 1660-1675.

VARIABLES:

Composition at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCN in Aqueous KCN at 25°C

$100w_2$	m_2/mol kg^{-1} [a]	$100w_1$	m_1/mol kg^{-1} [a]	Solid Phase [b]
1.34	0.210	0.60	0.068	A
3.27	0.528	1.68	0.197	A
4.21	0.688	1.87	0.222	A
6.03	1.028	3.88	0.481	A
6.05	1.032	3.93	0.487	A
9.97	1.856	7.52	1.017	A
12.10	2.35	8.84	1.248	B
19.95	4.62	13.78	2.321	B
22.32	5.44	14.71	2.607	B
34.77	12.52	22.59	5.913	B
35.28	12.84	22.52	5.957	C
34.82	11.45	18.47	4.414	C
36.24	10.95	12.92	2.837	C
41.94	12.40	6.13	1.318	C
33.86	10.23	15.30	3.359	D
35.96	10.39	10.86	2.279	D
41.70	12.10	5.84	1.243	D
40.31	11.16	4.20	0.845	E
40.53	10.86	2.16	0.421	E
41.7	10.99	-	-	E

Notes: [a] Calculated by compiler.

[b] Solid phases were: A: $KCu_2(CN)_3 \cdot H_2O$; B: $KCu(CN)_2$; C: $K_3Cu(CN)_4 \cdot H_2O$; D: $K_3Cu(CN)_4$; E: KCN.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of CuCN, KCN and water were sealed in wax bottles, which were then rotated in a thermostat at 298 K for several days. After 4 or 5 days, both liquid phase and moist solid were analyzed. CuCN was precipitated from the liquid phase with H_2SO_4; dried at 293-393 K and weighed. To determine KCN content, the liquid was distilled with H_2SO_4, the HCN produced collected in an alkaline solution and titrated against $AgNO_3$. The double salts inferred to be present were isolated in separate experiments and analyzed.

SOURCE AND PURITY OF MATERIALS:

CuCN prepared by adding hot aqueous KCN solution to a hot solution of $CuSO_4$, after which CuCN was precipitated by addition of dilute H_2SO_4. Used "best commercial" KCN, which contained as much as 3% KOH.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Potassium Cyanide; KCN; [151-50-8]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Plaksin, I. N.; Fishkova, Ts. E.
Isv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim., Akad. Nauk SSSR 1938, *10*, 229–244.

VARIABLES:

Composition at 288 to 308 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCN in Aqueous KCN

$t/°C$	ρ_2 / g dm^{-3}	c_2[a] / mol dm^{-3}	ρ_1 / g dm^{-3}	c_1[a] / mol dm^{-3}	ρ / g cm^{-3}	Solid Phase[b]
15	10	0.154	11.938	0.133	-	A
	60	0.922	54.94	0.613	-	A
	100	1.536	75.03	0.837	-	A
	160	2.457	102.15	1.140	-	-
	180	2.764	109.88	1.226	-	-
	200	3.072	138.67	1.548	-	A+B
	220	3.379	159.72	1.783	-	A+B
	240	3.686	165.91	1.852	-	B
	260	3.993	179.29	2.001	-	B
	300	4.608	189.93	2.120	-	B
	400	6.143	190.35	2.125	-	B
	500	7.679	197.27	2.203	-	B+C
	600	9.215	196.37	2.192	-	B+C

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Carried out experiments in thermostat at temperatures specified ±0.2 K. After equilibrium was attained (*app.* 3 hours), analyzed solutions for copper content (method not given). Measured density of solutions at 298 and 308 K.

SOURCE AND PURITY OF MATERIALS:

To obtain CuCN, produced cyano-complexes by adding KCN to $CuSO_4$ solutions, then precipitated CuCN by adding H_2SO_4. Used Kahlbaum KCN of 99 to 99.8% purity; other chemicals "C. P.", purity not given.

ESTIMATED ERROR:

Not given.

REFERENCES:

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Potassium Cyanide; KCN; [151-50-8]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Plaksin, I. N.; Fishkova, Ts. E.
Isv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim., Akad. Nauk SSSR 1938, *10*, 229-244.

EXPERIMENTAL VALUES:

(continued)

t/°C	ρ_2 / g dm^{-3}	c_2[a] / mol dm^{-3}	ρ_1 / g dm^{-3}	c_1[a] / mol dm^{-3}	ρ / g cm^{-3}	Solid Phase[b]
25	10	0.154	11.25	0.127	1.010	A
	60	0.922	55.85	0.623	1.058	A
	100	1.536	88.46	0.987	1.088	A
	160	2.457	126.44	1.411	1.152	A
	180	2.764	144.76	1.616	1.170	A
	200	3.072	159.06	1.775	1.185	A
	220	3.379	164.87	1.840	1.205	A
	240	3.686	180.5	2.015	1.219	B
	260	3.993	195.25	2.179	1.237	B
	300	4.608	221.16	2.469	1.254	B
	400	6.143	255.12	2.848	1.308	B
	500	7.679	266.47	2.974	1.355	B+C
	600	9.215	262.87	2.934	1.348	B+C
35	10	0.154	12.95	0.144	1.009	A
	60	0.922	59.04	0.659	1.059	A
	100	1.536	89.28	0.996	1.085	A
	160	2.457	132.69	1.481	1.143	A
	180	2.764	153.59	1.714	1.165	A
	200	3.072	162.63	1.815	1.176	A
	220	3.379	195.25	2.179	1.195	A
	240	3.686	197.93	2.209	1.212	A
	260	3.993	205.53	2.294	1.229	A+B
	300	4.608	226.077	2.527	1.245	A+B
	400	6.143	257.35	2.872	1.287	B
	500	7.679	277.91	3.102	1.345	B+C
	600	9.215	273.88	3.057	1.331	B+C

Notes: [a] Molar concentrations calculated by compiler.

[b] Solid phases were: A: CuCN; B: "Complex" [probably $KCu(CN)_2$ at low concentrations and $K_2Cu(CN)_3$ at higher concentrations (not precisely identified)]; C: KCN.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Sodium Cyanide; NaCN; [143-33-9] (3) Water; H_2O; [7732-18-5]	Plaksin, I. N.; Fishkova, Ts. E. *Isv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim., Akad. Nauk SSSR* 1938, *10*, 229-244.

VARIABLES:	PREPARED BY:
Concentration of NaCN at 288 to 308 K	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuCN in Aqueous NaCN

$t/°C$	ρ_2 / g dm^{-3}	c_2^{a} / mol dm^{-3}	ρ_1 / g dm^{-3}	c_1^{a} / mol dm^{-3}	ρ / g cm^{-3}	Solid Phase^b
15	10	0.204	25.23	0.282	1.050	A
	60	1.224	78.25	0.873	1.085	A
	100	2.040	121.59	1.357	1.138	A
	160	3.264	168.295	1.879	1.194	A+B
	180	3.672	178.295	1.990	1.217	A+B
	200	4.080	185.20	2.067	1.228	A+B
	220	4.488	149.30	1.666	1.149	A+B
	240	4.896	155.16	1.732	1.181	A+B
	260	5.304	154.64	1.726	1.193	A+B
	300	6.120	149.50	1.669	1.177	A+B
	400	8.160	181.60	2.027	1.222	B+C
	500	10.200	201.38	2.253	1.237	B+C
	600	12.240	198.11	2.155	1.347	B+C

continued...

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Carried out experiments in thermostat at temperatures specified ±0.2 K. After equilibrium was attained (*app.* 3 hours), analyzed solutions for copper content (method not given.) Measured density of solutions.	To obtain CuCN, produced cyano-complexes by adding NaCN to $CuSO_4$ solutions, then precipitated CuCN by adding H_2SO_4. Used Kahlbaum NaCN of 99 to 99.8% purity; other chemicals "C. P.", purity not given.
	ESTIMATED ERROR: Not given.
	REFERENCES:

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Sodium Cyanide; NaCN; [143-33-9]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Plaksin, I. N.; Fishkova, Ts. E.
Isv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim., Akad. Nauk SSSR 1938, *10*, 229–244.

EXPERIMENTAL VALUES:

(continued)

$t/°C$	ρ_2 / g dm^{-3}	c_2[a] / mol dm^{-3}	ρ_1 / g dm^{-3}	c_1[a] / mol dm^{-3}	ρ / g cm^{-3}	Solid Phase[b]
25	10	0.204	25.29	0.282	1.063	A
	60	1.224	81.94	0.915	1.085	A
	100	2.040	129.51	1.447	1.092	A
	160	3.264	196.14	2.178	1.189	A
	180	3.672	191.23	2.134	1.193	A
	200	4.080	188.55	2.105	1.201	A+B
	220	4.488	177.83	1.985	1.215	A+B
	240	4.896	238.76	2.553	1.224	A+B
	260	5.304	239.48	2.670	1.238	B
	300	6.120	253.33	2.828	1.263	B
	400	8.160	268.08	2.992	1.292	B
	500	10.200	265.40	2.962	1.291	B+C
	600	12.240	260.93	2.912	1.292	B+C
35	10	0.204	28.77	0.321	1.062	A
	60	1.224	84.44	0.943	1.086	A
	100	2.040	130.30	1.426	1.125	A
	160	3.264	201.50	2.249	1.187	A
	180	3.672	215.35	2.404	1.197	A
	200	4.080	245.29	2.737	1.203	A
	220	4.488	252.88	2.823	1.212	A+B
	240	4.896	258.25	2.883	1.223	A+B
	260	5.304	262.23	2.927	1.251	A+B
	300	6.120	270.02	3.014	1.291	B
	400	8.160	274.33	3.062	1.315	B
	500	10.200	273.71	3.055	1.313	B+C
	600	12.240	272.07	3.037	1.315	B+C

Notes: [a] Calculated by compiler.

[b] Solid phases were: A: CuCN; B: "Complex" [probably $NaCu(CN)_2$ at low concentrations and $Na_2Cu(CN)_3$ at higher concentrations (not precisely identified)]; C: NaCN.

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Hydrogen Cyanide; HCN; [420-05-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vladimirova, M. G.; Kakovsky, I. A.
Zh. Prikl. Khim. 1950, *23*, 580;
J. Appl. Chem. USSR (Engl. Transl.) 1950, *23*, 615–632.

VARIABLES:

Concentration of HCN at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCN in Aqueous HCN at 25°C

c_2/mol dm^{-3}	c_2^{initial}/mol dm^{-3} [a]	c_1/mol dm^{-3}
0.138	0.1394	0.00136
0.200	0.2017	0.00166
0.374	0.3763	0.00228
0.381	0.3834	0.00235
0.726	0.7293	0.00326
1.086	1.090	0.00400
1.444	1.449	0.00468

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuCN and HCN solution at 298 K until equilibrium reached. Determined HCN concentration by titration with $AgNO_3$, copper by method of Kolthoff (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

Prepared HCN by method of Karyakin (Ref. 2), CuCN by reducing $CuSO_4$ solution (with cyanide added?).

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kolthoff, I. M. *Volumetric Analysis (Russ. Ed.)* 1950.
2. Karyakin, Yu. V. *Pure Chemical Reagents* 1936.

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Hydrogen Cyanide; HCN; [420-05-3]
(3) Hydrogen Chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vladimirova, M. G.; Kakovsky, I. A.
Zh. Prikl. Khim. 1950, *23*, 580;
J. Appl. Chem. USSR (Engl. Transl.) 1950, *23*, 615-632.

VARIABLES:

Concentrations of HCN and HCl at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCN in HCN–HCl Solutions at 25°C

c_2/mol dm^{-3}	c_2^{initial}/mol dm$^{-3\,\text{a}}$	c_3/mol dm$^{-3\,\text{a}}$	c_1/mol dm^{-3}	I_c/mol dm^{-3}
1.160	1.164	0.00022	0.00362	0.00384
1.180	1.184	0.00077	0.00353	0.00430
1.080	1.084	0.00157	0.00304	0.00461
1.020	1.023	0.00207	0.00272	0.00479
1.060	1.063	0.00287	0.00253	0.00540
1.020	1.023	0.00333	0.00250	0.00583
1.060	1.062	0.00448	0.00227	0.00675
1.040	1.042	0.00528	0.00205	0.00733
1.118	1.120	0.00578	0.00219	0.00797
1.078	1.080	0.00619	0.00205	0.00824
1.088	1.090	0.00659	0.00199	0.00858
0.996	0.998	0.00682	0.00177	0.00859
1.018	1.020	0.00865	0.00162	0.01028
1.058	1.060	0.00925	0.00163	0.01088
1.096	1.098	0.00987	0.00162	0.01149
1.058	1.060	0.01067	0.00152	0.01219
1.058	1.060	0.01107	0.00150	0.01257
1.038	1.039	0.01147	0.00146	0.01293
1.058	1.059	0.01189	0.00139	0.01328
1.038	1.039	0.01273	0.00136	0.01409

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuCN and HCN–HCl solution at 298 K until equilibrium reached. Determined HCN concentration by titration with $AgNO_3$, copper by method of Kolthoff (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

Prepared HCN by method of Karyakin (Ref. 2), CuCN by reducing $CuSO_4$ solution (with cyanide added?). Source of HCl not given; no purites given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kolthoff, I. M. *Volumetric Analysis (Russ. Ed.)* 1950.
2. Karyakin, Yu. V. *Pure Chemical Reagents* 1936.

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Hydrogen Cyanide; HCN; [420-05-3]
(3) Sulfuric Acid; H_2SO_4; [7664-93-9]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Vladimirova, M. G.; Kakovsky, I. A.
Zh. Prikl. Khim. 1950, *23*, 580;
J. Appl. Chem. USSR (Engl. Transl.) 1950, *23*, 615-632.

VARIABLES:

Concentrations of HCN and H_2SO_4 at 298 K

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of CuCN in HCN–H_2SO_4 Solutions at 25°C

c_2/mol dm^{-3}	c_2^{initial}/mol dm$^{-3\,a}$	c_3/mol dm$^{-3\,a}$	c_1/mol dm^{-3}	I_c/mol dm^{-3}
0.050	0.051	0.00031	0.00059	0.001540
0.500	0.502	0.00048	0.00209	0.003545
0.520	0.522	0.00124	0.00166	0.005395
0.520	0.521	0.00185	0.00123	0.00678
0.500	0.501	0.00206	0.00132	0.00749
0.700	0.702	0.00249	0.00150	0.00896
1.400	1.403	0.00356	0.00252	0.01308
1.200	1.201	0.00815	0.00128	0.02572
1.060	1.061	0.01458	0.00079	0.04455

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Held solid CuCN and HCN–H_2SO_4 solution at 298 K until equilibrium reached. Determined HCN concentration by titration with $AgNO_3$, copper by method of Kolthoff (Ref. 1).

SOURCE AND PURITY OF MATERIALS:

Prepared HCN by method of Karyakin (Ref. 2), CuCN by reducing $CuSO_4$ solution (with cyanide added?). Source of H_2SO_4 not given; no purites given.

ESTIMATED ERROR:

Not given.

REFERENCES:

1. Kolthoff, I. M. *Volumetric Analysis (Russ. Ed.)* 1950.
2. Karyakin, Yu. V. *Pure Chemical Reagents* 1936.

COMPONENTS:

(1) Copper(I) Cyanide; CuCN; [544-92-3]
(2) Sodium Cyanide; NaCN; [143-33-9]
(3) Hydrogen Cyanide; HCN; [420-05-3]
(4) Sodium Chloride; NaCl; [7647-14-5]
(5) Hydrogen Chloride; HCl; [7647-01-0]
(6) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Königsberger, E.; Solis, J. S.; May, P. M.; Hefter, G. T.
6th International Symposium on Solubility Phenomena 1994, Buenos Aires, Argentina.

VARIABLES:

Concentrations of NaCN and HCN at 298 K

PREPARED BY:

E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuCN in NaCN–HCN–NaCl Solutions at 25°C

I_c[a] / mol dm^{-3}	$c_{2,\text{initial}}$ / mol dm^{-3}	c_3 / mol dm^{-3}	p[H]$_{\text{initial}}$	p[H]$_{\text{eq}}$	10^3 [Cu$^+$] / mol dm^{-3}
0.15	0.010	0.010	9.003	4.585	9.29
	0.010	0.020	8.698	4.270	9.09
	0.010	0.005	9.298	4.879	9.03
0.25	0.010	0.010	8.976	4.539	9.28
	0.010	0.020	8.668	4.226	9.12
	0.010	0.005	9.270	4.833	9.20
0.50	0.010	0.010	8.959	4.508	9.38
	0.010	0.040	8.342	3.877	9.29
	0.010	0.0025	9.516	5.064	9.30
1.00	0.010	0.010	8.985	4.450	(9.15)
	0.010	0.020	8.690	4.144	9.67
	0.010	0.005	9.281	4.748	9.69
	0.050	0.050	9.000	4.250	41.18
	0.040	0.040	9.005	4.294	34.38
	0.030	0.030	8.996	4.332	26.24
	0.015	0.015	8.991	4.418	13.37
	0.005	0.005	8.990	4.502	5.04

[a] Ionic strength maintained by addition of NaCl.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Prepared HCN–NaCN–NaCl solutions by adding appropriate amounts of HCl to NaCN–NaCl solutions of desired ionic strength. Used percolation-type solubility apparatus and galvanic cell with glass electrode and Ag/AgCl reference electrode for continuous potentiometric measurement of p[H] = –log [H$^+$]/mol dm^{-3}. Solution was saturated with CuCN under nitrogen until p[H] remained constant, then oxidized to Cu^{2+} which was determined electrolytically.

SOURCE AND PURITY OF MATERIALS:

Janssen CuCN recrystallized from NaCN solution. Reagent grade chemicals used. Purity of NaCN determined to be 99%.

ESTIMATED ERROR:

± 0.01 for p[H], ± 2% for [Cu$^+$], ± 0.05 K for T.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Copper(I) Cyanamide; Cu_2CN_2; [35380-03-1] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

The only data found on the solubility of cuprous cyanamide were those of Kitaev *et al.*[1]. They made five measurements of its solubility at 298 K in nitric acid from $2.6 \cdot 10^{-4}$ to 0.1 mol dm^{-3}, with ionic strength maintained at 1.0 mol dm^{-3} by use of KNO_3. They presented their results as a graph of log(solubility) *vs.* pH. Then using the dissociation constant of cyanamide as an acid, they calculated the solubility product of the cuprous salt. The value obtained for the solubility product of Cu_2CN_2 was $1.6 \cdot 10^{-24}$ mol^3 dm^{-9}.

The values obtained for the solubility of copper(I) cyanamide in nitric acid vary as $[H^+]^{0.64}$ (see Compilations). This is consistent with the interpretation that most of the solubility occurs mainly as a result of the reaction $Cu_2CN_2 + H^+ \rightleftharpoons HCN_2^- + 2\,Cu^+$ (which would give solubility varying approximately as the square root of hydrogen ion concentration), with part of it occurring due to the reaction $Cu_2CN_2 + 2\,H^+ \rightleftharpoons H_2CN_2 + 2\,Cu^+$, which would give solubility varying with the first power of $[H^+]$. The results over the wide range of $[H^+]$ follow the exponential law to about 5 per cent, within the precision of reading their graph. They are Accepted tentatively in view of their excellent consistency.

REFERENCE

1. Kitaev, G. A.; Bol'shchikova, T. P.; Yatlova, L. E. *Zh. Neorg. Khim.* 1971, *16*, 3173; *Russ J. Inorg. Chem. (Engl. Transl.)* 1971, *16*, 1683.

COMPONENTS:

(1) Copper(I) Cyanamide; Cu_2CN_2; [35380-03-1]
(2) Potassium Nitrate; KNO_3; [7757-79-1]
(3) Nitric Acid; HNO_3; [7697-37-2]
(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;
Russ. J. Inorg. Chem. (Engl. Transl.) 1971, *16*, 1683-1684.

VARIABLES:

Concentration of HNO_3 at 298 K, ionic strength 1 mol dm^{-3}

PREPARED BY:

J. J. Fritz

EXPERIMENTAL VALUES:

Solubility of Cu_2CN_2 in HNO_3–$NaNO_3$ Solutions at 25°C[a]

c_3/mol dm^{-3}	c_2/mol dm^{-3}	c_1/mol dm^{-3}
0.100	0.9	0.0537
0.0107	0.99	0.0166
0.0055	0.99	0.0100
0.00112	1.0	0.00355
0.00026	1.0	0.00135

[a] The concentrations of HNO_3 and Cu_2CN_2 were read from a logarithmic graph given by the authors, which contains data on solubility of several cyanamides as a function of pH.

The authors calculated the solubility product of Cu_2CN_2 as $10^{-23\ 8}$ ($1.6 \cdot 10^{-24}$) mol^2 dm^{-6}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid Cu_2CN_2 was placed in 1 mol dm^{-3} aqueous KNO_3, and the pH adjusted by addition of dilute HNO_3. The concentration of copper in the resulting solution was determined trilonometrically using Murexide as an indicator.

SOURCE AND PURITY OF MATERIALS:

To obtain Cu_2CN_2, ammoniacal $CuSO_4$ was reduced with 2 mol dm^{-3} hydroxylammonium chloride, after which the desired material was precipitated by addition of cyanamide. The solid Cu_2CN_2 was then washed with water containing a small amount of hydroxylammonium chloride before use.

ESTIMATED ERROR:

Not given. The graph of the data could be read to about 1%.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Copper(I) Azide; CuN_3; [14215-30-6] (2) Water; H_2O; [7732-18-5]	J. J. Fritz Department of Chemistry The Pennsylvania State University June, 1991

CRITICAL EVALUATION:

Two rather fragmentary investigations of the solubility properties of copper(I) azide have been reported. In 1943 Straumanis and Círulis[1] reported the solubility at "room temperature" (probably about 293 K) in pure water and in 2 mass per cent (*app.* 0.5 mol dm^{-3}) aqueous hydrazoic acid (See Compilation). In 1953 Suzuki[2] carried out a potentiometric investigation of of the system CuN_3–NaN_3–H_2O at five temperatures between 288 and 308 K, from which he derived a value of the solubility product of CuN_3 at 298 K.

The value obtained for the solubility product by Straumanis and Círulis[1] was $5 \cdot 10^{-9}$ mol^2 dm^{-6} and that obtained by Suzuki[2] was $4.9 \cdot 10^{-9}$ mol^2 dm^{-6}. The latter value is accepted in view of the close agreement between the two results. The value for the solubility in aqueous hydrazoic acid given by Straumanis and Círulis[1] is presented in the Compilations without recommendation as an indication of the approximate solubility of CuN_3 in the aqueous acid.

REFERENCES

1. Straumanis, M.; Círulis, A. *Z. Anorg. Allg. Chem.* 1943, *251*, 315.
2. Suzuki, K. *J. Chem. Soc. Japan, Pure Chem. Sect.* 1953, *74*, 269.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) Azide; CuN_3; [14215-30-6] (2) Hydrogen Azide; HN_3; [7782-79-8] (3) Water; H_2O; [7732-18-5]	Straumanis, M.; Církulis, A. *Z. Anorg. Allg. Chem.* 1943, *251*, 315-331.
VARIABLES:	**PREPARED BY:**
Concentration of HN_3 at room temperature (probably about 293 K)	J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuN_3 in Aqueous HN_3

ρ_2/g dm^{-3}	c_2/mol dm^{-3} [a]	ρ_1/g dm^{-3}	c_1/mol dm^{-3} [a]
0.0	0.0	0.0075	$7.1 \cdot 10^{-5}$
20.	0.47	0.2897	$2.73 \cdot 10^{-3}$

[a] Calculated by compiler.

The authors give the solubility product of CuN_3 as $5 \cdot 10^{-9}$ mol^2 dm^{-6}, which is the square of $7.1 \cdot 10^{-5}$ mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Not given.

SOURCE AND PURITY OF MATERIALS:

Prepared CuN_3 from powdered copper and 2% hydrazoic acid. Source and purity of materials not stated.

ESTIMATED ERROR:

Not given.

REFERENCES:

SYSTEM INDEX

Page numbers preceded by E refer to evaluation text whereas those not preceded by E refer to compiled tables.

REGISTRY NUMBER INDEX

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