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Volume 65

COPPER(I) HALIDES AND PSEUDOHALIDES

SOLUBILITY DATA SERIES

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COPPER(I) HALIDES AND PSEUDOHALIDES

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CONTENTS

Introduction to the Solubility of Solids in Liquids	ix
Preface	xvi
Copper(I) Chloride	1
Critical Evaluation of aqueous systems	1
The binary system	1
Data at or near 298 K	2
Solubility at other temperatures	3
Ternary systems involving monovalent cations	3
CuCl-HCl-H ₂ O	3
CuCl-NaCl-H ₂ O	6
CuCl-KCl-H ₂ O	8
CuCl-NH ₄ Cl-H ₂ O	9
CuCl-LiCl-H ₂ O	10
Ternary systems involving divalent or trivalent cations	10
CuCl-CaCl ₂ -H ₂ O	10
CuCl-FeCl ₂ -H ₂ O	11
CuCl-CuCl ₂ -H ₂ O	11
Other systems	11
Systems involving a soluble chloride with an indifferent salt	11
Systems involving two or more soluble chlorides	13
Systems with HCl and NaCl	13
Systems with HCl and NH ₄ Cl	16
Systems with CuCl ₂ and HCl	16
Systems with CuCl ₂ and NaCl or KCl	18
Other systems	18
Systems involving organic complexing agents	20
Unsaturated alcohols	20
Unsaturated organic acids	21
Other organic ligands	23
Double and complex salts of CuCl	24
Double salts with monovalent chlorides	24
Double salts with magnesium chloride and sodium thiosulfate	25
Salts with neutral molecules coordinated to copper	25
Phase diagrams of systems involving CuCl	27
CuCl-HCl-H ₂ O	27
CuCl-NaCl-H ₂ O	28
CuCl-KCl-H ₂ O	28
CuCl-NH ₄ Cl-H ₂ O	29
Systems with CuCl ₂	30
Other systems	31
Thermodynamic properties of aqueous systems	32
Introduction	32
Properties at zero ionic strength	33
Literature data on enthalpy changes	35
Literature data on equilibrium constants	36
Calculation of unknown solubilities	37
Virial parameters for aqueous HCl solutions	38
Virial parameters for aqueous NaCl solutions	38
Virial parameters for aqueous KCl solutions	40
Virial parameters for aqueous NH ₄ Cl solutions	40
Virial parameters for aqueous CaCl ₂ solutions	41
Other systems	42

CONTENTS (cont'd)

Copper(I) Chloride (cont'd)

Thermodynamics of systems involving organic compounds	43
Unsaturated alcohols	43
Unsaturated organic acids	45
Recommended values for solubility of CuCl	48
In aqueous HCl	52
In aqueous NaCl	54
In aqueous KCl	56
In aqueous NH ₄ Cl	57
In aqueous CaCl ₂	59
References	61
Compilation of data on aqueous systems	65
The binary system	65
Ternary systems	67
CuCl-HCl-H ₂ O	67
CuCl-NaCl-H ₂ O	82
CuCl-KCl-H ₂ O	90
CuCl-NH ₄ Cl-H ₂ O	96
CuCl-LiCl-H ₂ O	99
CuCl-CaCl ₂ -H ₂ O	100
CuCl-FeCl ₂ -H ₂ O	104
CuCl-CuCl ₂ -H ₂ O	105
CuCl-MgCl ₂ -H ₂ O	107
Systems with a soluble chloride and an indifferent salt	108
Systems with 2 or more soluble chlorides	113
Systems with HCl and NaCl	113
Systems with HCl and NH ₄ Cl	119
Systems with CuCl ₂ and HCl	121
Systems with CuCl ₂ and NaCl or KCl	131
Other systems	141
Systems involving organic complexing agents	145
Unsaturated alcohols	145
Unsaturated organic acids	155
Other organic ligands	167
Critical Evaluations of systems with organic solvents	171
Binary systems	171
Ternary systems	171
CuCl-HCl-Ethanol	171
CuCl-Tetraethylammonium Chloride-Dimethyl Sulfone	171
CuCl-KSeCN-Acetone	172
References	172
Compilation of data for systems with organic solvents	173
Copper(I) Bromide	175
Critical Evaluation of aqueous systems	175
The binary system	175
Ternary systems	175
CuBr-KBr-H ₂ O	175
CuBr-NaBr-H ₂ O	176
CuBr-HBr-H ₂ O	176

CONTENTS (cont'd)

Copper(I) Bromide (cont'd)	
CuBr-MgBr ₂ -H ₂ O	177
Other systems	177
Double salts involving CuBr	177
Thermodynamics of aqueous solutions	177
Recommended values of solubility in aqueous KBr and NaBr	178
References	181
Compilation of data for aqueous systems	182
The binary system	182
Ternary systems	183
Systems with a soluble bromide and an indifferent salt	190
Critical Evaluation of systems with an organic solvent	194
Binary systems	194
Ternary systems	194
References	194
Copper(I) Iodide	195
Critical Evaluation of aqueous systems	195
The binary system	195
Systems involving iodides	195
CuI-NaI-H ₂ O	196
CuI-KI-H ₂ O	196
CuI-HI-H ₂ O	197
Thermodynamics of solutions involving iodides	197
Recommended values of solubility in aqueous alkali iodides	199
Double salts involving CuI	202
Systems involving other soluble halides	202
Systems involving thiosulfates	202
CuI-KNbO ₃ -H ₂ O	205
CuI-I ₂ -H ₂ O	205
References	206
Compilation of data for aqueous systems	207
The binary system	207
Systems involving soluble iodides	208
Systems involving other soluble halides	213
Systems involving thiosulfates	217
Other systems	221
Critical Evaluation of systems with organic solvent	223
Binary systems	223
Ternary systems	223
References	224
Compilations of data for systems with organic solvent	225
Copper(I) Thiocyanate	230
Critical Evaluation of aqueous systems	230
The binary system	230

CONTENTS (cont'd)

Copper(I) Thiocyanate (cont'd)	
Systems involving soluble thiocyanates	231
CuSCN-KSCN-H ₂ O	231
CuSCN-NaSCN-NaClO ₄ -H ₂ O	231
CuSCN-NH ₄ SCN-H ₂ O	232
Thermodynamics of solutions in aqueous thiocyanates	232
Recommended values for solubility in aqueous KSCN	234
Systems involving soluble halides	236
Systems involving thiosulfates	237
CuSCN in aqueous NaNO ₂	238
CuSCN in aqueous HCN	239
References	240
Compilation of data for aqueous systems	241
Systems involving soluble thiocyanates	241
Systems involving soluble halides	245
Systems involving thiosulfates	247
Other systems	254
Critical Evaluation of systems with organic solvent	257
Compilation of data for systems with organic solvent	258
Copper(I) Selenocyanate	260
Copper(I) Cyanide	261
Critical Evaluation of aqueous systems	261
The binary system	261
Systems involving soluble cyanides	261
CuCN-KCN-H ₂ O	261
CuCN-NaCN-H ₂ O	262
CuCN-HCN-H ₂ O	263
CuCN-HCN-NaCN-H ₂ O	263
Equilibrium constants for complex formation	264
Other double salts containing CuCN	264
References	265
Compilation of data for aqueous systems	266
Copper(I) Cyanamide	275
Copper(I) Azide	277
System Index	279
Registry Number Index	283
Author Index	285
Solubility Data Series	290

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 dm³ 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 than 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):

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

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 v_{-i} anions, with $v_i = v_{+i} + v_{-i}$ 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:

$$x_{+i} = \frac{v_{+i} x_{+i}}{1 + \sum_{j=1}^s (v_j - 1) x_j}, \quad x_{-i} = \frac{v_{-i} x_{+i}}{v_{+i}} \quad i = 1 \dots s \quad [2]$$

$$x_{ok} = \frac{x_j}{1 + \sum_{j=1}^s (v_j - 1) x_j}, \quad k = (s+1) \dots c \quad [3]$$

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

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

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

$$x_1 = \frac{v_{+2} x_{o1}}{v_{+2} - (v_2 - 1) x_{+2}} \quad x_2 = \frac{x_{+2}}{v_{+2} - (v_2 - 1) x_{+2}} \quad [5]$$

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 $w(1)$:

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

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, $x_{s,1}$:

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

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, $x_{v,1}$:

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

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 :

$$m_1 = n_1 / n_2 M_2 \quad [9]$$

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), $m_1^{(3)}$:

$$m_1^{(3)} = m_1 \bar{M} / M_3 \quad [10]$$

SI base units: mol kg⁻¹. Here, the average molar mass of the solvent is

$$\bar{M} = x_{v,2} M_2 + (1 - x_{v,2}) M_3 \quad [11]$$

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 :

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

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 :

$$\rho_1 = g_1 / V = c_1 M_1 / V \quad [13]$$

SI base units: kg m⁻³.

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

$$r_{n,12} = n_1 / n_2 \quad [14]$$

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

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

$$I_m = \frac{1}{2} \sum_i m_i z_i^2, \quad I_c = \frac{1}{2} \sum_i c_i z_i^2 \quad [15]$$

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_- ,

$$I_m = |z_+ z_-| \nu m_i, \quad I_c = |z_+ z_-| \nu c_i \quad [16]$$

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* :

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

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

13. *Relative density, $d = \rho/\rho^\circ$* : 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	$\frac{1}{1 + \frac{M_i}{M_c} \left\{ \frac{1}{w_i} - 1 + \sum_{j \neq i}^{c-1} \left(\frac{M_c}{M_j} - 1 \right) \frac{w_j}{w_i} \right\}}$	$\frac{1}{1 + \frac{1}{m_i M_i} \left(1 + \sum_{j \neq i}^{c-1} m_j M_j \right)}$	$\frac{1}{1 + \frac{1}{M_c} \left(\frac{\rho}{c_i} - M_i \right) + \sum_{j \neq i}^{c-1} \frac{c_j}{c_i} \left(1 - \frac{M_j}{M_c} \right)}$
$w_i =$	$\frac{1}{1 + \frac{M_c}{M_i} \left\{ \frac{1}{x_i} - 1 + \sum_{j \neq i}^{c-1} \left(\frac{M_j}{M_c} - 1 \right) \frac{x_j}{x_i} \right\}}$	w_i	$\frac{1}{1 + \frac{1}{m_i M_i} \left(1 + \sum_{j \neq i}^{c-1} m_j M_j \right)}$	$\frac{c_i M_i}{\rho}$
$m_i =$	$\frac{1}{M_c \left(\frac{1}{x_i} - 1 - \sum_{j \neq i}^{c-1} \frac{x_j}{x_i} \right)}$	$\frac{1}{M_i \left(\frac{1}{w_i} - 1 - \sum_{j \neq i}^{c-1} \frac{w_j}{w_i} \right)}$	m_i	$\frac{1}{\frac{1}{c_i} \left(\rho - \sum_{j \neq i}^{c-1} c_j M_j \right) - M_i}$
$c_i =$	$\frac{\rho}{M_i + M_c \left\{ \frac{1}{x_i} - 1 + \sum_{j \neq i}^{c-1} \left(\frac{M_j}{M_c} - 1 \right) \frac{x_j}{x_i} \right\}}$	$\frac{\rho w_i}{M_i}$	$\frac{\rho}{\frac{1}{m_i} \left(1 + \sum_{j \neq i}^{c-1} m_j M_j \right) + M_j}$	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, Cu₂CN₂ and CuN₃, 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 $\leq 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$ 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 $\text{Cu}_m\text{X}_n^{m-n}$, 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 $\text{Cu}_m\text{X}_n\text{Y}_p^{m-n-p}$. Solutions of such materials as thiosulfates, unsaturated organic alcohols and unsaturated organic acids can dissolve Cu(I) halides by producing either anionic [e.g. $\text{Cu}(\text{S}_2\text{O}_3)^-$] or cationic [e.g. $\text{Cu}(\text{ROH})^+$] 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 $\text{CuCl} > \text{CuBr} > \text{CuI} > \text{CuSCN} > \text{CuCN}$. 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-H₂O with CuBr-KBr-H₂O 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 NH₄X, aqueous KX, etc.), the solubility at given conditions follows the order $\text{NH}_4^+ > \text{K}^+ > \text{Na}^+ > \text{H}^+$. Divalent cations all give similar, fairly high, solubility at low ligand concentrations; for high ligand concentrations the order is $\text{Fe}^{2+} > \text{Cu}^{2+} > \text{Ca}^{2+}$. 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 $\text{CuCl-KCl-H}_2\text{O}$. A few measurements have also been made in complex systems such as $\text{CuCl-NaCl-CuCl}_2\text{-FeCl}_2\text{-ZnCl}_2\text{-H}_2\text{O}$; 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, $\rho_i/\text{g dm}^{-3}$; mass ratios, $100\zeta_{ij}/\text{g (100 g)}^{-1}$; 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 $2\text{Cu}^+ \rightleftharpoons \text{Cu}^{2+} + \text{Cu(s)}$. 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. $10^{-3} \text{ mol dm}^{-3}$) 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 $\text{CuX}_{(s)} + \text{X}^- \rightleftharpoons \text{CuX}_2^-$. 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. Interpretation 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.

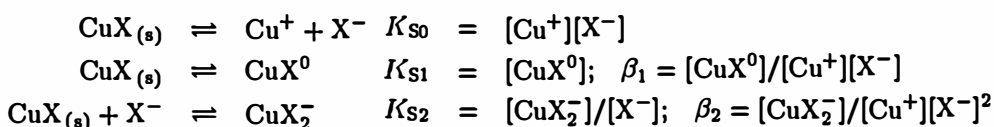
The use of the function S/C_L permits intercomparison of considerable bodies of data. Where measurements on a particular system are available from a number of sources, the function S/C_L provides a convenient way of comparing data for which the concentrations of ligand or the temperature were not the 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 serve 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 coefficients 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

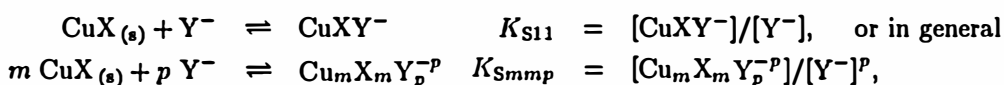


or in general



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,



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_{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_{S_2} , K_{S_3} and $K_{S_{36}}$, with K_{S_0} and K_{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 Mayorga¹ for binary systems and expanded to cover multicomponent solutions by Pitzer and Kim². 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.

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COMPONENTS:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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 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 Storbeck¹ measured the solubility (at about 293 K) under conditions where Cu²⁺ 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 Gavriš and Galinker² 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 HClO₄ 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 Fofanov⁴ (1979) deduced the solubility product of CuCl at 298.15 K, zero ionic strength, from measurement of a concentration cell. Ahrland and Rawsthorne⁵ (1970) obtained a value of the solubility product in aqueous NaClO₄-HClO₄ 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_{so} , since there is compelling evidence from Ahrland and Rawsthorne⁵ and from analysis⁶ by the compiler of the data of Hikita *et al.*³ that the neutral complex CuCl⁰ 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 CuCl₂⁻ 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 CuCl⁰ (and possibly CuCl₂⁻) 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_{so}^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 <i>et al.</i> ³	1973	298	0	-	$5.8 \cdot 10^{-4}$	See note ^c
Krestov <i>et al.</i> ¹⁶	1977	298	0	$2.1 \cdot 10^{-7}$	-	thermodynamics
Sosnitskii & Fofanov ⁴	1979	298	0	$2.5 \cdot 10^{-7}$	-	cell EMF
Kale <i>et al.</i> ¹⁷	1979	298	0*	-	$3.8 \cdot 10^{-3}$	solubility

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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- 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 CuCl⁰ formation given by the authors.
- c The solubility listed was obtained by extrapolation (by the compiler) of the data given for solubility in aqueous HClO₄ 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 Noss⁷, Kepner and Andrews⁹ and Kale *et al.*¹⁷, all of which are higher than this.

The value of K_{S0} reported by Kolthoff and Furman⁸ was given without attribution, but appears to be based on that of Bodländer and Storbeck¹. Neither Butler¹⁴ nor Chaltykyan¹⁵ gives a source for his value; the values they selected apparently represented their estimates based on other available values. Zhuk¹² 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 Storbeck¹ appears to be high, probably because they did not take in to account the increase in solubility produced by the CuCl₂ 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 · 10⁻⁷ to 3.2 · 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 Fofanov⁴, who report a value of (2.5 ± 0.8) · 10⁻⁷ from their cell measurements. The value given by Latimer¹⁰ 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 500¹¹ 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-HClO₄-H₂O and their data on solutions with low concentrations of HCl in the system CuCl-HCl-HClO₄-H₂O are best represented using a value of K_{S0} near the low end of the range given by Sosnitskii and Fofanov⁴. Overall, the other determinations confirm the result of the direct determination of K_{S0} by Sosnitskii and Fofanov⁴, 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 Rawsthorne⁵ and data of Hikita *et al.*³ on the solubility in aqueous HClO₄ (See Compilations). These are consistent with each other after allowing for the differences in the activity coefficient behaviour of the two media¹⁸. It should be noted that the solubility in aqueous NaClO₄ at ionic strength 5.0 mol dm⁻³ is distinctly higher than that in aqueous HClO₄ 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 Zhuk¹², Egorov¹³ 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. Zhuk¹² combined handbook data for K_{S0} with thermodynamic data from a variety of sources, including NBS Circular 500¹¹; his work provides no

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EVALUATOR:

J. J. FRITZ
 Department of Chemistry
 The Pennsylvania State University
 June, 1991

CRITICAL EVALUATION:

information beyond the material available in that publication. Egorov¹³ used thermodynamic information from Latimer¹⁰, Kelley¹⁹ 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 Galinker², 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 Egorov¹³ and by Krestov *et al.*¹⁶ for temperatures between 273 and 373 K are Not Recommended for use. The equations of Egorov¹³ 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 Galinker², 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, NH₄Cl 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-H₂O

Three investigations are mainly of historical interest. In the 1880's, Le Chatelier²¹ 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 Engel²² made measurements at about 293 K for four concentrations between 1.8 and 6.9 mol dm⁻³ (See Compilations). The measurements of Le Chatelier²¹ are low compared with later more extensive measurements; those of Engel²² 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, Engel²³ 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 Cha²⁴ (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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CRITICAL EVALUATION:

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

The first extensive measurements of the solubility were made by Abel²⁶ 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 Poma²⁷ measured the solubility at 298 K for 1, 2 and 4 mol dm⁻³ HCl without and with added CuCl₂. His measurements for "pure" aqueous HCl appear to be a few per cent high; measurements in solutions containing CuCl₂ will be discussed along with other quaternary systems. In 1918 Noyes and Chow²⁸ 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 CuCl₂⁻.

In 1922 Edgar and Cannon²⁹ 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 Cu²⁺ 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 Cu²⁺ was present at appreciable molalities will be discussed later. In 1928 Fedotieff³⁰ 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 Cha²⁴ 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 Ustanishkova³¹ and of Glodzińska and Zembura³², 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 Ustanishkova³¹ 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 Cha²⁴ 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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CRITICAL EVALUATION:

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 Chaltykyan³³ 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, Gokhale³⁴ 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 Ali³⁵ 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 Armington³⁶ 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, Wilke³⁷ 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 Ustanishkova³¹, 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 Gokhale³⁴ and the graphical results of O'Connor *et al.*³⁶ are given, but should not be assigned much weight.

In 1973 Hikita, Ishikawa and Esaka³ published a very extensive set of data for the solubility of CuCl in aqueous HCl and in aqueous HCl-HClO₄ 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 HClO₄ as well as HCl; these will be discussed later.

In 1974 Glodzińska and Zembura³² 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 Chaudhari¹⁷ 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 Zharskii³⁸ published data at 298 K on aqueous solutions containing HCl and CuCl₂. These included four points on aqueous HCl without added CuCl₂. Unfortunately, these points all appear high by 20 to 40 per cent. Their measurements on solutions containing CuCl₂ will be discussed later.

In 1985 Camacho Rubio, Paez Dueñas and Moreno Carretero²⁵ published an extensive set of data on the solubility of CuCl in aqueous HCl solutions, both without and with added NaCl or CuCl₂; for most sets of data, constant ionic strength was maintained by HClO₄ and/or NaClO₄. 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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CRITICAL EVALUATION:

at 298 K agree with those of Hikita *et al.*³ and Chang and Cha²⁴ 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 Cha²⁴ 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 Edgar and Cannon²⁹ 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 Ustanishkova³¹, 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 Chaltykyan³³, 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-H₂O

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 Gokhale³⁴ 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 Kuznetsova³⁹ 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 Ahrlund and Rawsthorne⁵, 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 NaClO₄; they gave only one point, at 5 mol dm⁻³, for a solution where the only anion present was Cl⁻. In 1978 Peters and Johnson⁴² 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 NaClO₄ and HClO₄ 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 Gokhale³⁴, 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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<p>CRITICAL EVALUATION:</p> <p>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.</p> <p>The earliest set of measurements reported were those published by Kremann and Noss⁷ 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 Fedotieff³⁰ 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 Chaltykyan³³ 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.</p> <p>In 1953 Gokhale³⁴ 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.</p> <p>In 1962 Kosyakina⁴⁴ reported 17 points for a phase diagram of the system CuCl-NaCl-H₂O at 298 K, of which seven points were for solutions supposedly at equilibrium 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.</p> <p>In 1964 Sin <i>et al.</i>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 Wilke³⁷ 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.</p> <p>The 1969 data of Utkina <i>et al.</i>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</p>	

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CRITICAL EVALUATION:

are generally about 10 per cent high compared with the average of all available data. Their 1970 measurements⁴¹ 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 Rawsthorne⁵ 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 than 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-H₂O

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 Chatelier²¹ 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 Storbeck¹ 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 Cu²⁺ 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 Brönsted⁴⁵ in 1912, in a study of the phase diagram of the system CuCl-KCl-H₂O at 293 K. He gave 21 measurements for which the solid phase was CuCl, many more where the solid phase was CuCl·2KCl and four points with the solid phase KCl.

The data of Brönsted⁴⁵ 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 Chatelier²¹ 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 Storbeck¹. The results of Le Chatelier²¹ 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 Storbeck¹ 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 Valetton and Frömel⁴⁶ studied the phase diagram of the system CuCl-KCl-H₂O at 298 K, purportedly at molalities of KCl below 1 mol kg⁻¹. They reported solutions in equilibrium with double salts CuCl·2KCl and CuCl·KCl·H₂O 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 paper³³ 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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<p>CRITICAL EVALUATION:</p> <p>quite erratic and are far lower than any other at high concentrations of KCl. Finally, in 1959 Malik <i>et al.</i>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.</p> <p>Other features of the measurements described above will be discussed in later sections, <i>viz.</i> the data of Bodländer and Storbeck¹ on the quaternary system CuCl–CuCl₂–KCl–H₂O, the phase diagram of Brönsted⁴⁵, and the double salts involving CuCl and KCl reported by Valetton and Frömel⁴⁶.</p> <p>Summary. The data of Brönsted⁴⁵ 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 Chatelier²¹ and of Bodländer and Storbeck¹. 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.</p> <p><u>CuCl–NH₄Cl–H₂O</u></p> <p>Three sets of data were found for the solubility of CuCl in aqueous NH₄Cl. In 1941 Iguchi and Nakanishi⁴⁷ published a set of data at 343 K for NH₄Cl concentrations from 9 to 29 mass per cent (2 to 33.5 mol kg⁻¹ NH₄Cl), eight points in all. At the higher concentrations the mol ratio of dissolved CuCl to NH₄Cl reached unity. In 1944 Morosov and Ustanishkova³¹ reported measurements of the solubility in solutions from 7.5 mass per cent NH₄Cl (1.6 mol kg⁻¹) to 43.5 mass per cent NH₄Cl (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 Wilke³⁷ published data for the solubility in each of three molalities of NH₄Cl (1.8 to 7) at 298, 308, 318 and 328 K.</p> <p>The results of Morosov and Ustanishkova³¹ are the most extensive. Unfortunately, their data were presented only as a set of fairly small scale graphs of mass per cent NH₄Cl 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 NH₄Cl approaches unity at high NH₄Cl concentrations. They are Accepted tentatively, within the large uncertainty reading the graphs. The data of Iguchi and Nakanishi⁴⁷ cover a larger range of NH₄Cl molalities. The two sets are in reasonable agreement at low molalities, however, the Iguchi data show much less rapid increase of solubility with NH₄Cl molalities. They should not be relied upon for intermediate NH₄Cl molalities (4 to 12 mol kg⁻¹ NH₄Cl) but can be used for the high solubility of CuCl in solutions with NH₄Cl molalities above 20. The data of Wilke³⁷ do not agree with either of the other two sets, varying from higher at low molalities of NH₄Cl to much lower at high molalities. They are Not Acceptable.</p> <p>Summary. Within the limited precision of the data available, the results of Morosov and Ustanishkova³¹ 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 Nakanishi⁴⁷ are suitable for use at 343 K for molalities from 20 to 33 mol kg⁻¹ NH₄Cl. The data of Wilke³⁷ should not be used.</p>	

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CRITICAL EVALUATION:**CuCl-LiCl-H₂O**

The only data reported for this system were those of Wilke³⁷, who gave the solubility of CuCl in aqueous 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-CaCl₂-H₂O, CuCl-FeCl₂-H₂O and CuCl-CuCl₂-H₂O; these are discussed below along with qualitative information on solutions in aqueous MgCl₂ and aqueous AlCl₃. Data available for quaternary and more complex systems containing divalent cations are discussed in a later section.

CuCl-CaCl₂-H₂O

The solubility of CuCl in aqueous solutions of CaCl₂ has been reported by Shirokova *et al.*⁴⁸, Wilke³⁷ 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). Wilke³⁷ gave data at 298, 308, 318 and 328 K for each of three CaCl₂ molalities (1.7, 3.4 and 6.7). Utkina *et al.*⁴¹ reported solubility for 298 and 368 K with six CaCl₂ 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 CaCl₂ 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 CaCl₂ concentration against the CaCl₂ 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 CaCl₂ 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 Wilke³⁷ 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.

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CRITICAL EVALUATION:
CuCl-FeCl₂-H₂O

The only data available for this system are those of Kremann and Noss⁷ for FeCl₂ 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 FeCl₂ on the solubility in more complex systems to be discussed below. Their point at zero FeCl₂ 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-CuCl₂-H₂O

Data for the solubility of CuCl in aqueous CuCl₂ have been reported by Fedotieff³⁰ and by Utkina *et al.*⁴¹. Fedotieff³⁰ measured the solubility at 292 K for five CuCl₂ 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 Fedotieff³⁰ 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 CuCl₂, 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 CuCl₂. Poma²⁷, Edgar and Cannon²⁹, 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 CuCl₂. Sin *et al.*³⁹ and Pochtarev *et al.*⁵¹ gave data for aqueous NaCl-CuCl₂ mixtures. Shirokova *et al.*⁴⁸ presented data for aqueous CaCl₂-CuCl₂. 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 coworkers⁵² reported making measurements of the solubility of CuCl in aqueous MgCl₂ at 298, 323, 348 and 368 K, but do not give numerical information on the concentrations of MgCl₂ investigated or the actual solubilities determined. They state that the solubility was greater in MgCl₂ solutions than in the corresponding concentrations of NaCl or CaCl₂. Later, members of the same group state, in another abstract⁵³, that they had measured the solubility of CuCl in aqueous AlCl₃ from 0.1 mol dm⁻³ to saturation at 273, 298, 323, 348 and 368 K, and found it greater than in aqueous MgCl₂ or NaCl. Search of the literature disclosed no detailed publication of the experiments mentioned above.

Recently, Karimova, Ksandrov and Nikandrov¹⁰⁷ presented phase diagrams of the system CuCl-MgCl₂-H₂O 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 HClO₄ or NaClO₄ 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.]

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>McConnell and Davidson⁵⁴ made five measurements in aqueous HCl–HClO₄ at 298 K, ionic strength 1.0 mol dm⁻³, with chloride concentrations from 0.2 to 0.8 mol dm⁻³. Vestin <i>et al.</i>⁵⁵ made a much more extensive set of measurements on the same system at 298 K, ionic strength 4.0 mol kg⁻¹. Hikita <i>et al.</i>³ measured the solubility in aqueous HCl–HClO₄ 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 <i>et al.</i>²⁵ measured the solubility in aqueous HCl–HClO₄ 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 <i>et al.</i>¹⁰⁸ measured the solubility in aqueous HCl–HClO₄ 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.</p> <p>Ahrland and Rawsthorne⁵ studied the solubility in aqueous NaCl–NaClO₄ 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 <i>et al.</i>³⁹ measured the solubility of CuCl in aqueous NaCl–Na₂SO₄ at 293 K for NaCl concentrations of 0.7 to 3.4 mol dm⁻³ and Na₂SO₄ concentrations from 0 to 0.36 mol dm⁻³.</p> <p>Of the four sets of measurements on aqueous HCl–HClO₄, the data of Hikita <i>et al.</i>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–H₂O, 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 <i>et al.</i>²⁵ at 303 K are uniformly about 5 per cent lower than would be expected from the data of Hikita <i>et al.</i>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 <i>et al.</i>¹⁰⁸ present a 4-parameter equation (See Compilations) which represents their data as well as those of Hikita <i>et al.</i>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 <i>et al.</i>⁵⁵ cannot be compared directly with those of Hikita <i>et al.</i>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 <i>et al.</i>³ are Recommended for the concentration and temperature ranges they cover, with estimated precision of 2 per cent. The data of Vestin <i>et al.</i>⁵⁴ are Recommended for concentration ranges not given by Hikita <i>et al.</i>³, with an estimated precision of 2 to 4 per cent. The data of Camacho Rubio <i>et al.</i>²⁵ appear to be about 5 per cent low, on the average. The data of McConnell and Davidson⁵⁴ are distinctly inferior to the previous three sets, being typically 40 to 50 per cent high; they have been Rejected and are not compiled.</p> <p>The values for the solubility of CuCl in aqueous NaCl–NaClO₄ given by Ahrland and Rawsthorne⁵ are distinctly higher than those of Hikita <i>et al.</i>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 parameters¹⁸ 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–NaClO₄</p>	

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CRITICAL EVALUATION:

solutions of CuCl.

The data of Sin *et al.*³⁹ on aqueous NaCl–Na₂SO₄ are Not Recommended for use. They cover only a small range of concentration of Na₂SO₄, 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 Rawsthorne⁵ 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 NaClO₄ by NaNO₃) 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 CuCl₂, 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–H₂O were first reported by Gokhale³⁴ 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 Johnson⁴² 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–H₂O 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,II)Cl–(Na,II)ClO₄–H₂O. 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.

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<p>CRITICAL EVALUATION:</p> <p>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 Gokhale³⁴, Winter <i>et al.</i>⁵⁶ and Camacho Rubio <i>et al.</i>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 Rawsthorne⁵, discussed earlier, were for a mol ratio Na/H of 49, and give essentially no information about the effect of mixing the two cations.)</p> <p>The data of Gokhale³⁴ 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.</p> <p>Winter <i>et al.</i>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.</p> <p>The work of Camacho Rubio <i>et al.</i>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 (<i>app.</i> 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 <i>et al.</i>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</p>	

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
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CRITICAL EVALUATION:

HCl-HClO₄ 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 Johnson⁴² 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 Rawsthorne⁵ 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 Gokhale³⁴ 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 Johnson⁴² 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

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>10 per cent. The data of Fontana <i>et al.</i>⁴³ appear uniformly high, and should not be relied upon.</p> <p><u>Systems Containing HCl and NH₄Cl</u></p> <p>Two reports have been found of the solubility of CuCl in aqueous mixtures of HCl and NH₄Cl. In 1941 Iguchi and Nakanishi⁴⁷ 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 NH₄Cl. In 1945 Morosov and Ustanishkova³¹ presented isotherms for the quaternary system CuCl–HCl–NH₄Cl–H₂O 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 NH₄Cl 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 NH₄Cl, 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 Nakanishi⁴⁷ are Accepted tentatively. Morosov and Ustanishkova³¹ discuss the presence of a double salt at 343 K but not at higher temperatures; this will be considered in a later section.</p> <p><u>Systems Involving CuCl₂ and HCl</u></p> <p>A number of investigations have been made in aqueous systems involving copper(II) chloride along with HCl. In 1909 Poma²⁷ 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 CuCl₂ added (6 to 8 points for each HCl concentration, 30 in all). In 1922 Edgar and Cannon²⁹ 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 Cu²⁺ 0.01 to 0.0004 mol kg⁻¹, 15 points in all (see Compilations). In 1974 Pochtarev <i>et al.</i>⁴⁹ published isotherms at 293, 313, 333 and 353 for solutions in equilibrium with both solid CuCl and solid CuCl₂ (19 points in all). In 1979 Novikov <i>et al.</i>³⁸ published a set of measurements at 283 K for HCl from 0 to 9.2 mol kg⁻¹ and CuCl₂ 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 CuCl₂·2H₂O as the solid phase, and four had a mixture of the two salts; their solutions had mol ratios of Cu²⁺/H⁺ from 0 to 4.0 at low H⁺ molalities and from 0 to 0.14 at high H⁺ molalities. In 1980 Pochtarev <i>et al.</i>⁵⁰ published many data for the system CuCl–HCl–CuCl₂–H₂O, including the data reported by Pochtarev <i>et al.</i>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 CuCl₂ (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 CuCl₂. 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 CuCl₂; it contained 9 points at 293 K, with 5, 4 and 3 points at the other temperatures, respectively. Finally, Camacho Rubio <i>et al.</i>²⁵ made measurements on the system CuCl–HCl–CuCl₂–HClO₄–H₂O 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, Cu²⁺ 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 HClO₄ used to maintain the desired ionic strength. In a second paper, Camacho Rubio <i>et al.</i>¹⁰⁸ presented measurements at 40 and 50°C in graphical form.</p> <p>The solubility behaviour of CuCl in aqueous HCl is very well known and that in aqueous CuCl₂ 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–CuCl₂ 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 CuCl₂. This criterion can be used to estimate the reliability of data where direct comparison with other data is not possible.</p>	

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<p>CRITICAL EVALUATION:</p> <p>The data of Poma²⁷ 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 Cannon²⁹ 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 CuCl₂ 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.</p> <p>The data of Novikov <i>et al.</i>³⁸, those of Pochtarev <i>et al.</i>⁴⁹ and those of Pochtarev <i>et al.</i>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 concentration was below 7 mol dm⁻³ can be compared directly with the solubilities which would be found if either HCl or CuCl₂ 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 CuCl₂ present; one gave a solubility far lower than that in either aqueous HCl or aqueous CuCl₂ 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-CuCl₂. The data of Novikov <i>et al.</i>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.</p> <p>The data of Camacho Rubio <i>et al.</i>²⁵ appear generally satisfactory. Their results for the system CuCl-HCl-HClO₄-H₂O 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-CuCl₂-H₂O with no HClO₄ 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-CuCl₂-HClO₄-H₂O. Most of these data are in satisfactory agreement with predictions of a model using parameters based on the behaviour of the systems CuCl-HCl-H₂O and CuCl-CuCl₂-H₂O, however, their data for low chloride concentrations in solutions containing 0.1 and 0.25 mol dm⁻³ of CuCl₂ are surprisingly low. In their second paper, Camacho Rubio <i>et al.</i>¹⁰⁸ present a 6-parameter equation (See Compilations) which represents their results as well as literature data within 10% and can be used for CuCl₂-HCl-HClO₄ 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.</p> <p><i>Summary.</i> The data of Poma²⁷ are Recommended for the temperature and concentration range they cover, as are the limited data of Edgar and Cannon²⁹. The data of Camacho Rubio <i>et al.</i>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 <i>et al.</i>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 <i>et al.</i>³⁸, those of Pochtarev <i>et al.</i>⁴⁹ and those of Pochtarev <i>et al.</i>⁵⁰ should be taken only to give an approximate idea of the solubility of CuCl at high concentrations of aqueous HCl-CuCl₂ mixtures.</p>	

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p><u>Systems Involving CuCl₂ and NaCl or KCl</u></p> <p>Two sets of measurements were found for the system CuCl–NaCl–CuCl₂–H₂O. In 1964 Sin <i>et al.</i>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 CuCl₂ at 323 K. In 1978 Pochtarev <i>et al.</i>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 CuCl₂ from 4.5 to 0.2 mol dm⁻³. As in their 1980 measurements on CuCl–HCl–CuCl₂–H₂O 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 CuCl₂ were at equilibrium with the solution. In 1902 Bodländer and Storbeck¹ 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 Cu²⁺ produced by disproportionation during the course of the experiment. These are the only measurements reported for the system CuCl–KCl–CuCl₂–H₂O.</p> <p>The data of Sin <i>et al.</i>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 CuCl₂ as well as 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 <i>et al.</i>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 CuCl₂, 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 CuCl₂ 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 CuCl₂, 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.</p> <p>The results of Bodländer and Storbeck¹ are of little utility. They reported the presence of Cu²⁺ 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.</p> <p>Summary. Of the two sets of data available for the solubility of CuCl in aqueous NaCl–CuCl₂ mixtures, the results of Sin <i>et al.</i>³⁹ at 323 K cover only a very limited range of concentration of CuCl₂ and are of doubtful validity. The much more extensive results of Pochtarev <i>et al.</i>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 Storbeck¹ 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.</p> <p><u>Other Systems</u></p> <p>The only measurements found for the system CuCl–CaCl₂–CuCl₂–H₂O are those of Shirokova <i>et al.</i>⁴⁸, who found no significant change in solubility produced by addition of 1 or 2 per cent of CuCl₂ to aqueous solutions of CaCl₂. Two sets of measurements are available of systems involving up to four soluble chlorides. In 1982 Winter <i>et al.</i>⁵⁶ published data on the solubility of CuCl at 323 K for systems in which various amounts of FeCl₂ were added to aqueous HCl–NaCl (12 points in all, of which two contained CuCl₂ as well). In 1984 Berger and Winand⁵⁷ studied the effect on the solubility of adding FeCl₂ and/or ZnCl₂ 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</p>	

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<p>CRITICAL EVALUATION:</p> <p>as the solid phase and were presumably not saturated with CuCl.</p> <p>Winter <i>et al.</i>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 FeCl₂ 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 > FeCl₂ > CuCl₂. 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 CuCl₂ was used for that purpose; similarly replacement of Na⁺ by H⁺ or Fe²⁺ at constant total chloride reduces the solubility, quite substantially in the case of Fe²⁺. Where duplicate measurements were available, they agreed within about 5 per cent. The results of Winter <i>et al.</i>⁵⁶ on the complex system are Accepted to this precision.</p> <p>Berger and Winand⁵⁷ 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, FeCl₂ and ZnCl₂) studied. (Note that theirs are the only results available for the effect of dissolved ZnCl₂ 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 FeCl₂ was increased (this series also contained two measurements in which ZnCl₂ was added, one with and one without FeCl₂ present). In another series at this temperature, the concentration of ZnCl₂ was held constant, while those of the other salts were varied. At 363 K the concentrations of NaCl, HCl and ZnCl₂ were held constant while that of FeCl₂ 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 FeCl₂ increased the solubility (as would be expected), but addition in the form of ZnCl₂ actually <u>decreased</u> the solubility. Unfortunately, the increases they report are not a smooth function of the amount of chloride added; in their first series (FeCl₂ 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 ZnCl₂ 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.</p> <p><i>Summary.</i> The measurements of Shirokova <i>et al.</i>⁴⁸ on the effect on CuCl solubility of adding CuCl₂ to aqueous CaCl₂ are too limited in scope to be useful. The results of Winter <i>et al.</i>⁵⁶ on the system CuCl–NaCl–HCl–FeCl₂–H₂O appear to be valid to about 5 per cent. These data describe mainly the effect of FeCl₂ and contain only a small indication of the effect of CuCl₂ in the mixed system. The data of Berger and Winand⁵⁷ for the system CuCl–NaCl–HCl–FeCl₂–ZnCl₂–H₂O appear to be valid within about 10 per cent. Within this limit, they describe the effects of both FeCl₂ and CuCl₂ in their complex system and give an indication of the effect of ZnCl₂ on the solubility.</p>	

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<p>CRITICAL EVALUATION:</p> <p style="text-align: center;">SYSTEMS CONTAINING ORGANIC COMPLEXING AGENTS</p> <p>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.</p> <p><u>Systems Involving Unsaturated Alcohols</u></p> <p>In 1948 Kepner and Andrews⁹ published a set of data on the solubility of CuCl at 298 K in aqueous allyl alcohol [2-propenol, CH₂=CH-CH₂OH] 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 Andrews⁶⁰ 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 HClO₄ 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 HClO₄, and NaClO₄ 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 Kepner⁶¹ 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 HClO₄; 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.</p> <p>The original results of Kepner and Andrews⁹ 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 Andrews⁶⁰ 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 Andrews⁶⁰ 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 CuCl₂⁻ and two complexes involving the alcohol; this matter will be discussed in a later section on Thermodynamics.</p>	

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

The series of alcohols studied by Keefer, Andrews and Kepner⁶¹ 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, CH₂=CH-CH(OH)-CH₃] and in aqueous ethylvinylcarbinol [1-penten-3-ol, CH₂=CH-CH(OH)-CH₂-CH₃]. Solubilities were about 25 per cent less for α , α -dimethylallyl alcohol [2-methyl-3-buten-2-ol, CH₂=CH-C(CH₃)₂OH], with two methyl groups substituted on the carbinol carbon, and about 1/3 less for 4-methyl-4-penten-2-ol [CH₂=C(CH₃)-CH₂-CH(OH)-CH₃], 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, CH₂=CCl-CH₂OH] 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 · 10⁻⁴ mol dm⁻³ for HCl concentration of zero or 0.01 mol dm⁻³ and about 6 · 10⁻³ mol dm⁻³ for HCl concentration 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, CH₃-C(CH₃)=CH-CH₂OH], β -methylallyl alcohol [2-methyl-2-propenol, CH₂=C(CH₃)-CH₂OH], crotyl alcohol (2-buten-1-ol, CH₃-CH=CH-CH₂OH), 2-methyl-2-buten-1-ol [CH₃-CH=C(CH₃)-CH₂OH] and 3-methyl-3-buten-2-ol [CH₂=C(CH₃)-CH(OH)-CH₃].

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 authors 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 Andrews⁶⁰ on aqueous allyl alcohol and those of Keefer, Andrews and Kepner⁶¹ on more complex alcohols are Accepted tentatively in view of their internal consistency and smoothness of data. The early results of Kepner and Andrews⁹ for low concentrations of allyl alcohol 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 Keefer⁶² 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.

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>In this same paper they reported the solubility (12 points) in aqueous fumaric acid [(<i>E</i>)-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 Keefer⁶³ 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 HClO₄. 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 (HClO₄), 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 NaClO₄, 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 Kepner⁶⁴ 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 (HClO₄) 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.</p> <p>The largest number of measurements were made on media containing maleic acid. In the 1948 set⁶² 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 1949⁶³ 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.</p> <p>Measurements of the solubility of CuCl in media containing fumaric acid are given in the 1948 paper⁶² and by Keefer, Andrews and Kepner⁶⁴ 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 work⁶², 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 work⁶⁴, at acidity and ionic strength of 0.1 mol dm⁻³, solubility was reduced by addition of chloride</p>	

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<p>CRITICAL EVALUATION:</p> <p>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.</p> <p>The other seven acids investigated by Keefer, Andrews and Kepner⁶⁴ 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-butenic acid, CH₂=CH-CH₂-COOH) dissolved even more CuCl than aqueous 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(CH₃)=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(=CH₂)-COOH] and crotonic acid [(E)-2-butenic acid, CH₃-CH=CH-COOH] giving somewhat less solubility than maleic acid. Mesaconic acid [(E)-2-methyl-2-butenedioic acid, HOOC-C(CH₃)=CH-COOH], tiglic acid [(E)-2-methyl-2-butenic acid, CH₃-CH=C(CH₃)-COOH] and β,β-dimethyl acrylic acid [3-methyl-2-butenic acid, (CH₃)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.</p> <p><i>Summary.</i> 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.</p> <p><u>Systems Involving Other Organic Ligands</u></p> <p>In 1975 Sigal <i>et al.</i>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 [C₄H₈O₂, H₂C(OH)-CH=CH-CH₂OH], acetonitrile (CH₃CN) and urea (CH₄N₂O, H₂NCONH₂). 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.</p>	

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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 NH₄Cl, 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 Mellor⁶⁶, 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 Neumann⁶⁷ claimed to have produced a 1 : 1 salt, CuCl·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 H₂CuCl₃ (CuCl·2HCl) was formed at the lower ranges of HCl concentration and H₃CuCl₄ (CuCl·3HCl) at the higher ranges, but they did not isolate these salts. No other investigators of the system CuCl-HCl-H₂O have found any double salts, so that the existence of any of the three salts described above is doubtful.

Chassevant⁶⁸ 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 Mitscherlich⁶⁹, who was the first to describe the preparation and properties of CuCl itself. He prepared what he believed to be CuCl·2NaCl. In 1893 Chassevant⁶⁸ 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 Mitscherlich⁶⁹, who isolated a salt believed to be CuCl·2KCl as colorless octahedra. The same salt was reported by Deherain⁷⁰ in 1862, Chassevant⁶⁸ in 1893, Brönsted⁴⁵ in 1912, Korreng⁷¹ in 1914, Valetton and Frömel⁴⁶ in 1924, Brink and MacGillavry⁷² in 1949 and Malik *et al.*³⁵ in 1959. Of all of these the most definitive work was that of Valetton and Frömel⁴⁶, who gave a chemical analysis corresponding to this composition, and that of Brink and MacGillavry⁷², who determined the structure of the compound by X-ray analysis. The existence of this salt is beyond question. Brönsted⁴⁵ found a region of the system CuCl-KCl-H₂O in which the solid phase was a double salt

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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 $\text{CuCl}_{(s)} + 2\text{KCl} \rightleftharpoons \text{CuCl} \cdot 2\text{KCl}$. Korreng⁷¹ 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. Valetton and Frömel⁴⁶ prepared a second double salt whose analysis corresponded to CuCl·KCl·H₂O. This salt had been obtained by Schiff⁷³ in 1858 and by Le Chatelier²¹ in 1884, but neither had identified it positively. Malik *et al.*³⁵ also claimed such a salt from their Method of Wet Residues. However, Brönsted⁴⁵ found indications of only one double salt in his solubility measurements.

In 1895 Wells⁷⁴ prepared three double salts containing cesium chloride, viz. 2CuCl·CsCl, 2CuCl·3CsCl and a hydrated salt 2CuCl·3CsCl·H₂O. 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-H₂O, in which it might be found. There have been no further reports of the other two salts reported by Wells⁷⁴.

There have been numerous reports of double salts formed between CuCl and ammonium chloride, beginning with the work of Mitscherlich⁶⁹, who prepared what he believed to be CuCl·2NH₄Cl. Deherain⁷⁰ prepared a salt which he believed to be a hemi-hydrate of the 1 : 2 salt [his formula 4NH₄Cl·Cu₂Cl₂·H₂O] but Wells and Hurlburt⁷⁶ were able to prepare it only in anhydrous form. They gave a chemical analysis verifying the composition they claimed. In 1952 Brink and van Arkel⁷⁷ 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 Hurlburt⁷⁶ prepared a salt whose chemical analysis corresponded to 3CuCl·2NH₄Cl (their 4NH₄Cl·3Cu₂Cl₂), and assigned this formula to a salt prepared earlier by Ritthausen⁷⁸, who gave a slightly different composition. A 1 : 1 salt, CuCl·NH₄Cl, was claimed by Deherain⁶⁸ and by Morosov and Ustanishkova³¹, but neither gave definitive evidence of the composition of their materials. Both of these also claimed to have produced material of the composition 2CuCl·NH₄Cl. In the Morosov work, the 2 : 1 salt was believed to be in equilibrium with some solutions of CuCl in aqueous NH₄Cl at 298 K and the 1 : 1 salt at 323 K. Finally, Rosenheim and Steinhauser⁷⁹ prepared a salt of the formula CuCl·NH₄Cl·4(NH₄)₂S₂O₃ and verified its composition by chemical analysis. All of the double salts with cesium chloride described by Wells⁷⁴ produced this material when treated with aqueous ammonium thiosulfate.

Remy and Laves⁸⁰ 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·CH₃NH₃Cl and CuCl·2CH₃NH₃Cl). With dimethyl ammonium chloride, (CH₃)₂NH₂Cl, they obtained a 1 : 1 salt for large ratios of the ammonium chloride to CuCl and a 2 : 1 salt for equimolar ratios. Trimethylammonium chloride produced a 2 : 1 salt and an 1 : 2 salt. Tetramethyl ammonium chloride (CH₃)₄NCl gave only a 1 : 1 salt.

Double Salts with Magnesium Chloride and Sodium Thiosulfate

Karimova, Ksandrov and Nikandrov¹⁰⁷ prepared double salts 12CuCl·MgCl₂·12H₂O and CuCl·5MgCl₂·12H₂O. Their existence was confirmed by chemical analysis, X-ray diffractometry and differential thermal analysis. Canneri and Luchini⁸¹ prepared a double salt CuCl·Na₂S₂O₃ 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. Mellor⁶⁶ discusses compounds between CuCl and NH₃. Marykyan⁸² prepared a compound between CuCl and pyridine

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<p>CRITICAL EVALUATION:</p> <p>to which he assigned the formula Cu₂(C₅H₅N)₄Cl₂ - more simply CuCl · 2C₅H₅N. He measured its limited solubility in water from 298 to 343 K. Chaltykyan¹⁵ reported preparing CuCl · PH₃. Harris⁸³ produced a double salt in which CuCl was combined with cupric tetrammine chloride to form CuCl · Cu(NH₃)₄Cl₂ and another with cupric ethylenedi-amine chloride of the formula 3CuCl · Cu(en)₂Cl₂. In later work⁸⁴ he and a coworker were able to prepare and identify the hydrated salt CuCl · Cu(en)₂Cl₂ · 1.5H₂O. Ritthausen⁷⁸ claimed to have produced a monohydrate CuCl · Cu(NH₃)₄Cl₂ · H₂O.</p> <p>Compounds have also been prepared in which CuCl is coordinated to mono- or di-olefins. In 1939 Gilliland, Seabold, Fitzhugh and Morgan⁸⁵ reported preparation of 1 : 1 compounds between CuCl and ethene (C₂H₄), propene (C₃H₆) and isobutene (C₄H₈) and measured their (fairly large) vapor pressures as a function of temperature. In 1935 Koblyanskii <i>et al.</i>⁸⁶ reported production of two compounds with butadiene, 2CuCl · C₄H₆ and its monohydrate 2CuCl · C₄H₆ · H₂O. In 1941 Gilliland, Bliss and Kip⁵⁸ reported preparation of the anhydrous compound with butadiene, along with similar compounds with isoprene (2-methyl-1,3-butadiene), of formula 2CuCl · C₅H₈, and with ethine, of formula 2CuCl · C₂H₂; they gave the vapor pressures of these compounds as a function of temperature. Ward and Makin⁵⁹ also prepared the compound with isoprene and in addition a similar compound with piperylene (1,3-pentadiene) of formula 2CuCl · C₅H₈; they measured the vapor pressures for each of these compounds.</p> <p>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 Mellor⁶⁶ for details and references on these compounds.</p> <p>Summary. The double salts reported to have been formed between CuCl and other chlorides can be grouped as follows:</p> <ol style="list-style-type: none"> 1. Existence and identity have been firmly established for CuCl · 2KCl, CuCl · KCl, CuCl · 2NH₄Cl and 2CuCl · 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 · 2NaCl, CuCl · NH₄Cl, 2CuCl · NH₄Cl, CuCl · 2NH₄Cl, 3CuCl · 2NH₄Cl, CuCl · NH₄Cl · 4(NH₄)₂S₂O₃, 12 CuCl · MgCl₂ · 12 H₂O and CuCl · 5 MgCl₂ · 12 H₂O. 3. Salts reported by one or two observers, but with weak or conflicting evidence, so that their existence is doubtful, include CuCl · HCl, CuCl · 2HCl, CuCl · 3HCl, CuCl · xLiCl, and 2CuCl · 4NH₄Cl · H₂O. 4. The series of salts of CuCl with the various methylammonium chlorides reported by Remy and Laves⁸⁰ almost certainly exist, but there is no confirmatory evidence that the formulas they assigned are correct in all cases. <p>Of the salts listed above, only six have been observed in the course of solubility measurements of CuCl. These are CuCl · 2KCl, CuCl · KCl, CuCl · NH₄Cl, 2CuCl · NH₄Cl, 12 CuCl · MgCl₂ · 12 H₂O and CuCl · 5 MgCl₂ · 12 H₂O. 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.</p> <p>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</p>	

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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-H₂O

The only phase diagram data for this system reported in the literature are those of Morosov and Ustanishkova³¹, 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 Chaltykyan¹⁵.) 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

<i>T</i> /K	100 <i>w</i> _{CuCl}	100 <i>w</i> _{HCl}	$\frac{m_{\text{CuCl}}}{\text{mol kg}^{-1}}$	$\frac{m_{\text{HCl}}}{\text{mol kg}^{-1}}$
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

<i>T</i> /K	100 <i>w</i> _{HCl}	$\frac{m_{\text{HCl}}}{\text{mol kg}^{-1}}$
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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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-H₂O

Phase diagram data for this system have been reported in mass units by Kremann and Noss⁷ and Kosyakina⁴⁴ and in volume units by Fedotieff³⁰, Utkina *et al.*⁴⁰, Peters and Johnson⁴² 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 Johnson⁴², 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.

Fedotieff³⁰ 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 Johnson⁴² 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 Johnson⁴² or Fedotieff³⁰. 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 Johnson⁴² and of Fedotieff³⁰ 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 Noss⁷ 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 Kosyakina⁴⁴ 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 Fedotieff³⁰ at 292 K and those of Peters and Johnson⁴² 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-H₂O

Three sets of phase diagrams have been reported for solutions of CuCl in aqueous KCl. In 1912 Brönsted⁴⁵ gave 44 points for a phase diagram at 295 K (see Compilations). In 1924 Valetton and Frömel⁴⁶ gave a phase diagram for 298 K, and in 1966 Chaltykyan¹⁵ gave phase diagrams for 298 and 323 K.

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

Brönsted⁴⁵ 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·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 Valetton and Frömel⁴⁶ investigated the system at 298 K, they found a region where a hydrated salt CuCl·KCl·H₂O was the solid phase, along with a large region where the solid phase was CuCl·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 Chaltykyan¹⁵ 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 Brönsted⁴⁵ and that of Valetton and Frömel⁴⁶ and the ambiguity in the work of Chaltykyan¹⁵, none of the published phase diagrams for CuCl–KCl–H₂O can be recommended for use.

CuCl–NH₄Cl–H₂O

Morosov and Ustanishkova³¹ studied the systems CuCl–NH₄Cl–H₂O and CuCl–NH₄Cl–HCl–H₂O 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 Chaltykyan¹⁵.) For the ternary system they reported finding CuCl·NH₄Cl as the solid phase over a range of CuCl concentrations at 323 K, 2CuCl·NH₄Cl as the solid phase at 298 and an unspecified double salt (presumably also 2CuCl·NH₄Cl) 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 NH₄Cl was the only solid phase present are listed in the Compilations.

Table 4. Composition of Solutions in Equilibrium with Double Salts for CuCl–NH₄Cl–H₂O

T/K	100w _{NH₄Cl}	100w _{CuCl}	$\frac{m_{\text{NH}_4\text{Cl}}}{\text{mol kg}^{-1}}$	$\frac{m_{\text{CuCl}}}{\text{mol kg}^{-1}}$	Solid Phases
273	17.5	13	4.7	1.9	CuCl, 2CuCl·NH ₄ Cl
	22.	13	6.3	2.0	2CuCl·NH ₄ Cl
	26	14	8.1	2.4	2CuCl·NH ₄ Cl, NH ₄ Cl
298	20	26.5	7.0	5.1	CuCl, 2CuCl·NH ₄ Cl
	23.5	28.5	9.2	6.0	2CuCl·NH ₄ Cl
	31	34.5	17.	10.1	2CuCl·NH ₄ Cl, NH ₄ Cl
323	26.7	47.3	19.2	18.4	CuCl, CuCl·NH ₄ Cl
	29.	48.	24.	21.	CuCl·NH ₄ Cl
	31.95	48.88	31.2	25.7	CuCl·NH ₄ Cl, NH ₄ Cl

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>Morosov and Ustanishkova³¹ also gave phase diagrams for the quaternary system CuCl-NH₄Cl-HCl-H₂O 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:</p> <ol style="list-style-type: none"> 1. CuCl and CuCl·NH₄Cl were present as solids in a solution at equilibrium with one atmosphere of gaseous HCl, containing 5.25 mass per cent NH₄Cl, 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·NH₄Cl and NH₄Cl were present as solids in a solution at equilibrium with one atmosphere of gaseous HCl, containing 8.9 mass per cent NH₄Cl, 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 NH₄Cl 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 NH₄Cl, 16.44 mass per cent HCl and 25.33 mass per cent CuCl (5.14, 9.87 and 5.60 mol kg⁻¹, respectively). <p><i>Summary.</i> The data of Morosov and Ustanishkova³¹ are Accepted tentatively for systems involving NH₄Cl. 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 NH₄Cl in the presence of dissolved CuCl is distinctly higher than in pure water and that the solubilities of NH₄Cl and CuCl both reach very high values, especially at higher temperatures.</p> <p><u>Systems Involving CuCl₂</u></p> <p>A number of publications give phase diagram data for CuCl in aqueous CuCl₂, most with another soluble chloride also present. In 1928 Fedotieff³⁰ presented data for the solubility of CuCl in aqueous CuCl₂ at 292 K up to the point where the solution was saturated with both salts; this solution contained 661.9 g dm⁻³ of CuCl₂ and 97.4 g dm⁻³ of CuCl (4.92 and 0.88 mol dm⁻³, respectively). In 1979 Novikov <i>et al.</i>³⁸ published data at 283 K for the system CuCl-CuCl₂-HCl-H₂O, 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 <i>et al.</i>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 CuCl₂. They had previously published⁵¹ a similar set of data for the system CuCl-CuCl₂-NaCl-H₂O at 299.5 K.</p> <p>Both the data of Novikov <i>et al.</i>³⁸ and those of Pochtarev <i>et al.</i>⁵⁰ on the system CuCl-CuCl₂-HCl-H₂O show that increase in mass percentage of HCl <u>decreases</u> that of CuCl₂ and <u>increases</u> 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 CuCl₂ 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 <i>et al.</i>³⁸ are smooth within a few per cent, while those of Pochtarev <i>et al.</i>⁵⁰ scatter over 10 per cent or more when the concentrations of the copper salts are plotted against the HCl concentration. The Novikov <i>et al.</i>³⁸ data are also in better agreement with what would be expected from the ternary systems CuCl-HCl-H₂O and CuCl-CuCl₂-H₂O; 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 CuCl₂ appears as a solid phase. Novikov <i>et al.</i>³⁸ identify it as CuCl₂·2H₂O, while Pochtarev <i>et al.</i>⁵⁰ describe it simply as CuCl₂.</p> <p>The earlier results of Pochtarev <i>et al.</i>⁵¹ contain data for solutions with both CuCl and solid NaCl present as well as solutions where CuCl and CuCl₂ were present as solids together. These data are somewhat smoother than those for CuCl-CuCl₂-HCl-H₂O but are still</p>	

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

somewhat erratic. They indicate a decrease in saturation mass percentage of CuCl₂ 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 Fedotieff³⁰ at 292 K for a solution saturated with both CuCl and CuCl₂ agrees with what would be expected from extrapolation of the data on the two ternary systems and is considered Satisfactory. For the system CuCl-CuCl₂-HCl-H₂O, 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.*⁶¹ on the system CuCl-CuCl₂-NaCl-H₂O 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 CuCl₂ should be considered fully reliable without independent verification.

Other Systems

In 1912 Kremann and Noss⁷ published data on the system CuCl-FeCl₂-H₂O 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 FeCl₂·4H₂O and one point where the solution was saturated with both salts. They indicate a modest increase in the solubility of FeCl₂ 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 Chaltykian¹⁵ published phase diagrams for this system at 298 and 323 K, apparently derived from the results of Kremann and Noss⁷; his results are questionable.

In 1965 Shirokova *et al.*⁴⁸ measured the solubility of CuCl in aqueous CaCl₂ at four temperatures (303, 323, 343 and 363 K) up to molalities where hydrated CaCl₂ 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 CaCl₂

<i>T</i> /K	100 <i>w</i> _{CaCl₂}	100 <i>w</i> _{CuCl}	$\frac{m_{\text{CaCl}_2}}{\text{mol kg}^{-1}}$	$\frac{m_{\text{CuCl}}}{\text{mol kg}^{-1}}$	Solid Phases
303	46.8	16.8	11.6	4.7	CuCl, CaCl ₂ ·6H ₂ O
323	47.8	17.9	12.6	5.3	CuCl, CaCl ₂ ·2H ₂ O
	47.8	16.8	12.2	4.8	CuCl, CaCl ₂ ·2H ₂ O
343	48.2	19.0	13.2	4.5	CuCl, CaCl ₂ ·2H ₂ O
363	47.0	21.4	13.4	6.8	CuCl, CaCl ₂ ·2H ₂ O

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 CaCl₂ 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.

Chaltykian¹⁵ gives graphical phase diagrams for CuCl in aqueous CaCl₂ 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.

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Berger and Winand⁵⁷ observed the phase behaviour in the complex system CuCl–NaCl–HCl–FeCl₂–ZnCl₂–H₂O 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 ZnCl₂ 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 ZnCl₂, the curves show breaks at intermediate concentrations of CuCl suggestive of possible double salt formation, but Berger and Winand⁵⁷ 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

$c_{\text{NaCl}}/\text{mol dm}^{-3}$	$c_{\text{HCl}}/\text{mol dm}^{-3}$	$c_{\text{FeCl}_2}/\text{mol dm}^{-3}$	$c_{\text{ZnCl}_2}/\text{mol dm}^{-3}$	$c_{\text{CuCl}}/\text{mol dm}^{-3}$
4.80±0.04	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.

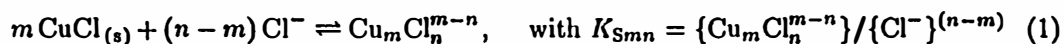
Their results cannot be compared directly with any other. They are in general smooth to about 10 per cent and are Accepted tentatively as good to at least this precision.

Summary. All of the results cited above are Accepted tentatively. The data of Kremann and Noss⁷ appear to have a precision of 5 per cent or better. Those of Shirokova *et al.*⁴⁸ and those of Berger and Winand⁵⁷ 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):



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:



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

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CRITICAL EVALUATION:

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:

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

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-HClO₄; it has been reported in the literature⁶. 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 Kunin⁸⁷. They measured heats of solution of CuCl in aqueous HCl-HClO₄ 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 CuCl⁸⁸. 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 Kunin⁸⁹ (this agreed with the early value given in NBS Circular 500¹¹ within the precision of the latter), the standard

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CRITICAL EVALUATION:

enthalpy of formation of Cl⁻ given in NBS Circular 500¹¹ and that for Cu⁺ given by Wagman⁹⁰.

- The solubility product at 298.15 K determined by Sosnitskii and Fofanov⁴ 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 HClO₄ and in aqueous HCl-HClO₄ 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 Fofanov⁴.
- 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 CuCl₃²⁻ and Cu₂Cl₄²⁻, but not adequate to distinguish between the possible triply charged species. The latter were represented in terms of a single complex Cu₃Cl₆³⁻, 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	$\frac{K_{Smn}}{(\text{mol dm}^{-3})^{(1+m-n)}}$	$\frac{\Delta_r H^\ominus}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r C_p^\ominus}{\text{J K}^{-1} \text{ mol}^{-1}}$	$\frac{\Delta_r G^\ominus}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r S^\ominus}{\text{J K}^{-1} \text{ mol}^{-1}}$
Cu ⁺ + Cl ⁻	1.83 · 10 ⁻⁷	40.33	-	38.46	6.29
CuCl ⁰	3.74 · 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 ₂ Cl ₄ ²⁻	8.16 · 10 ⁻⁴	28.03	-	17.6	34.9
Cu ₃ Cl ₆ ³⁻	3.34 · 10 ⁻⁵	5.94	-	25.56	-65.8

^a The dashed entries under $\Delta_r C_p^\ominus$ 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	$\frac{\beta_{mn}}{(\text{mol dm}^{-3})^{(1-m-n)}}$	$\frac{\Delta_r H^\ominus}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r G^\ominus}{\text{kJ mol}^{-1}}$	$\frac{\Delta_r S^\ominus}{\text{J K}^{-1} \text{ mol}^{-1}}$
CuCl ⁰	2043	-17.32	-18.90	5.3
CuCl ₂ ⁻	3.38 · 10 ⁵	-13.01	-31.56	62.2
CuCl ₃ ²⁻	6.88 · 10 ⁴	-25.98	-27.62	5.48
Cu ₂ Cl ₄ ²⁻	2.43 · 10 ¹⁰	-52.63	-59.28	22.3
Cu ₃ Cl ₆ ³⁻	5.43 · 10 ¹⁵	-115.	-89.8	-84.7

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:
Literature Data on Enthalpy Changes

Outside of the data of Vasil'ev and Kunin⁸⁷ 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 Chow²⁸ 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 Chow²⁸ is an average over the temperature range 273 to 348 K.

The values given by Vasil'ev and Kunin⁸⁷ were obtained by them from a large set of measured heats of solution of CuCl in aqueous HCl-HClO₄, using what they described as 'most probable stability constants' for CuCl₂⁻ and CuCl₃²⁻ obtained from previous publications; they did not consider the uncharged complex CuCl⁰ 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 CuCl₂⁻ and 0.1 to 0.15 kcal mol⁻¹ (0.4 to 0.6 kJ mol⁻¹) to those for CuCl₃²⁻. 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 CuCl₂⁻ and lower in the case of CuCl₃²⁻. 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-HClO₄ 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 Chow²⁸ 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 Tuhtar⁹¹ used titration calorimetry to obtain the enthalpy change for the reaction CuCl₂⁻ + Cl⁻ ⇌ CuCl₃²⁻ at ionic strength 5.0 mol dm⁻³ (4.9 mol dm⁻³ NaClO₄, 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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CRITICAL EVALUATION:

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 Cu⁺ and Cl⁻ of 12(!) complexes, mostly polynuclear, which they believed were present in solutions of CuCl in aqueous NH₄Cl at 10 mol dm⁻³ ionic strength maintained by use of NH₄NO₃. 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 Kunin⁸⁷ 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 Chow²⁸ 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 Martell⁹³, of Smith and Martell⁹⁴ and most recently by Fontana *et al.*⁴³. Of the many values in the literature, the majority refer to formation of the complexes from Cu⁺ and Cl⁻ (stability constants, as in Table 8), some to the $K_{S_{mn}}$ 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 $K_{S_{mn}}$ 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 Chaltykyan⁹⁵ (CuCl₂⁻, KCl), Carlson and Wettermark⁹⁶ (CuCl₂⁻, CuCl₃²⁻, 1.0 mol dm⁻³ HCl-HClO₄), Braun and Nobe⁹⁷ (CuCl₂⁻, CuCl₃²⁻, HCl-KCl), Hikita *et al.*³ (CuCl₂⁻, CuCl₃²⁻, CuCl₄³⁻, HCl-HClO₄), Noyes and Chow²⁸ (CuCl₂⁻, dilute HCl), Chang and Cha²⁴ (CuCl₂⁻, CuCl₃²⁻, HCl), Bodländer and Storbeck⁹⁸ (CuCl₂⁻, dilute KCl), Ahrland and Rawsthorne⁵ (CuCl₂⁻, CuCl₃²⁻, Cu₂Cl₄²⁻, CuCl₄³⁻, 5.0 mol dm⁻³ NaCl-NaClO₄), McConnell and Davidson⁵⁴ (CuCl₂⁻, CuCl₃²⁻, 1.0 mol dm⁻³ HCl-HClO₄), Latimer¹⁰ (CuCl₂⁻, zero ionic strength) and Butler¹⁴ (CuCl₂⁻, 1.0 mol dm⁻³ ionic strength). Sugasaka and Fujii⁹⁹ give a value of $K_{S_{13}}/K_{S_{12}}$ at 298 K (5.0 mol dm⁻³ NaCl-NaClO₄-HClO₄) obtained in the course of a spectroscopic study. (Note that Noyes and Chow²⁸ 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 Cha²⁴ and Ahrland and Rawsthorne⁵ 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 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.

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
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CRITICAL EVALUATION:

Sugasaka and Fujii⁹⁹ 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⁻, CuCl₂OH²⁻, CuCl(OH)₂²⁻, and give values (all greater than 10^3) for equilibrium constants for formation of these species from CuCl₂⁻. 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 Storbeck⁹⁸ (CuCl₂⁻, dilute KCl), Chang and Cha²⁴ (CuCl₂⁻, HCl), Náráy-Szabó and Szabó¹⁰⁰ (CuCl₂⁻, CuCl₃²⁻, CuCl₄³⁻, concentrated KCl), Chaltykyan⁹⁵ (CuCl₂⁻, CuCl₃²⁻, KCl), Sukhova *et al.*^{92,101} (13 complexes, concentrated NH₄Cl-NH₄NO₃), Ahrland and Rawsthorne⁵ (CuCl₂⁻, CuCl₃²⁻, Cu₂Cl₄²⁻, CuCl₄³⁻, 5.0 mol dm^{-3} NaCl-NaClO₄), Pestrikov and Kranilov¹⁰² (CuCl₂⁻, 4.0 mol dm^{-3} NaClO₄), Braun and Nobe⁹⁷ (CuCl₂⁻, CuCl₃²⁻, HCl-KCl). Vasil'ev and Kunin⁸⁷ give a set of values for the stability constants of CuCl₂⁻ and CuCl₃²⁻ 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 Rawsthorne⁵. 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 Mayorga¹⁸, as applied to mixtures of electrolytes by Pitzer and Kim¹⁰³, 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 pair¹⁰⁴.

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 literature¹⁸ and in many cases their temperature derivatives¹⁰⁵. 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

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

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

$$\ln \gamma_N = z_N^2 f^\gamma + 2 \sum_c M_a [B_{Na} + (\sum_c M_c z_c) C_{Na}] + \sum_c \sum_a M_c M_a [z_N^2 B'_{ca} + z_N C_{ca}]$$

$$\ln \gamma_X = z_X^2 f^\gamma + 2 \sum_c M_c [B_{cX} + (\sum_a M_a |z_a|) C_{cX}] + \sum_c \sum_a M_c M_a [z_X^2 B'_{ca} + |z_X| C_{ca}]$$

with

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

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

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

$$C_{NX} = C_{NX}^\phi / (2|z_N z_X|^{1/2}).$$

^a Note that for 2-2 and higher valence type electrolytes an additional parameter $\beta^{(2)}$ must be added; see Pitzer and Kim¹⁰³.

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 function¹⁸.

Virial Parameters for Aqueous HCl Solutions

Virial parameters for use with solutions of CuCl in aqueous HCl, with or without HClO₄ 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 Cha²⁴ 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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

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	$d\beta^{(0)}/dT$ ·10 ⁴	$d\beta^{(1)}/dT$ ·10 ⁴	dC/dT ·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 ₂ Cl ₄ ²⁻	0.3686	1.794	0.0064	-	-	-
H ⁺ -Cu ₃ Cl 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⁺-ClO₄⁻ are from Pitzer and Mayorga¹⁸ and their temperature derivatives from Silvester and Pitzer¹⁰⁵. 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 CuCl⁰ 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	$d\beta^{(0)}/dT$ ·10 ⁴	$d\beta^{(1)}/dT$ ·10 ⁴	dC/dT ·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 ₂ Cl ₄ ²⁻	-0.0159	0.6372	0.01188	24.7	135.0	-12.
Na ⁺ -Cu ₃ Cl 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⁺-ClO₄⁻ are from Pitzer and Mayorga¹⁸ and their temperature derivatives from Silvester and Pitzer¹⁰⁵. 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 Ahrlund and Rawsthorne⁵, 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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Brönsted⁴⁵ 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 ₂ Cl ₄ ²⁻	0.0161	0.500	0.00964
K ⁺ -Cu ₃ Cl 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 Mayorga¹⁸. Those for pairs involving complexes were obtained by fitting the solubility data.

The parameters of Table 13 represent the data of Brönsted⁴⁵ 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 Chatelier²¹ 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 NH₄Cl Solutions

A set of parameters for use in calculating the solubility of CuCl in aqueous NH₄Cl solutions (molalities) are given in Table 14. They were derived from the graphical data of Morosov and Ustanishkova³¹. No parameters are given for CuCl⁰, 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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

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	$d\beta^{(0)}/dT$ ·10 ⁴	$d\beta^{(1)}/dT$ ·10 ⁴	dC/dT ·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 ₂ Cl ₄ ²⁻	-0.0277	0.891	0.0004	-0.4	41.4	-12.9
NH ₄ ⁺ -Cu ₃ Cl ₆ ³⁻	-0.0825	2.133	0.012	1.4	67.1	-15.2

^a The values given for the parameters for NH₄⁺-Cl⁻ are from Pitzer and Mayorga¹⁸. 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 Ustanishkova³¹ with an estimated standard deviation of 5 per cent for NH₄Cl 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 CaCl₂ Solutions.

A set of parameters suitable for calculating the solubility of CuCl in aqueous solutions of CaCl₂ 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 CaCl₂ molalities from 0.5 mol kg⁻¹ to saturation with CaCl₂ (about 7.5 mol kg⁻¹ CaCl₂). 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 CaCl₂, 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 ₂ Cl ₄ ²⁻	0.520	4.30	-5.6	0.0174
Ca ²⁺ -Cu ₃ Cl ₆ ³⁻	0.973	9.208	-1.2	0.01755

^a The values given for the parameters for Ca²⁺-Cl⁻ are from Pitzer and Mayorga¹⁸. Those for pairs involving complexes were obtained by fitting the solubility data. No parameters are given for the neutral complex CuCl⁰, since the measurements did not extend into CaCl₂ 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 Kim¹⁰³.

Table 15B. Temperature Coefficients at 298 K for CaCl₂ Parameters^{a,b} (for Molalities)

Ion Pair	$d\beta^{(0)}/dT$ ·10 ⁴	$d\beta^{(1)}/dT$ ·10 ⁴	dC/dT ·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 ₂ Cl ₄ ²⁻	-1.4	59.	3.
Ca ²⁺ -Cu ₃ Cl ₆ ³⁻	-5.1	110.	2.

^a The coefficients for Ca²⁺-Cl⁻ were taken from Silvester and Pitzer¹⁰⁵. 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 (Cu²⁺, Fe²⁺, Zn²⁺) 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 Cu²⁺ or Fe²⁺ 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 CuCl₂ and FeCl₂ solutions is available in the literature¹⁰⁴.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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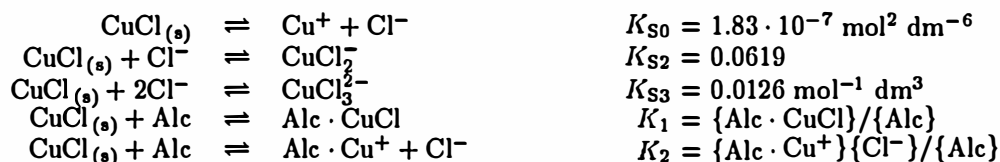
**THERMODYNAMICS OF SYSTEMS INVOLVING
ORGANIC COMPOUNDS**

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 CuCl₂⁻, 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 CuCl₃²⁻ was included in the calculation along with the CuCl₂⁻ 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:



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 squares program was then used to obtain the unknown 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	$\frac{K_2}{\text{mol dm}^{-3}}$	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

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>^a The alcohols have been given the names as reported by Andrews and coworkers^{60,61}. For formulas and registry numbers, see Compilations.</p> <p>^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.</p> <p>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.</p> <p>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 CuCl₃²⁻ 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.</p> <p>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.</p>	

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>														
<p>CRITICAL EVALUATION:</p> <p><u>Systems Involving Unsaturated Organic Acids</u></p> <p>Andrews and coworkers⁶²⁻⁶⁴ 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 [(<i>Z</i>)-2-butenedioic acid]^{62,63} with fewer observations on other acids, including fumaric acid [(<i>E</i>)-2-butenedioic acid] and the remaining seven. The other acids for which measurements were made were vinylacetic (3-butenic acid, CH₂=CH-CH₂-COOH), itaconic [methylenebutanedioic acid, HOOC-C(=CH₂)-CH₂-COOH], crotonic [(<i>E</i>)-2-butenic acid, CH₃-CH=CH-COOH], tiglic [(<i>E</i>)-2-methyl-2-butenic acid, CH₃-CH=C(CH₃)-COOH], β, β-dimethylacrylic acid [3-methyl-2-butenic acid, (CH₃)₂C=CH-COOH], mesaconic [(<i>E</i>)-2-methyl-2-butenedioic acid, HOOC-C(CH₃)=CH-COOH] and citraconic [(<i>Z</i>)-2-methyl-2-butenedioic acid, HOOC-C(CH₃)=CH-COOH].</p> <p>A considerable variety of measurements were made in the case of maleic acid. In preliminary work, Andrews and Keefer⁶² 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 paper⁶² 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 HClO₄; 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 NaClO₄. In all cases the maleic acid concentration was varied from 0.05 to 0.2 mol dm⁻³.</p> <p>In the case of fumaric acid, their first paper⁶² 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 Kepner⁶⁴ measured the solubility at constant ionic strength of 0.1 mol dm⁻³ maintained by HClO₄, 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 acids⁶⁴.</p> <p>In the process of dissolution, complexes analogous to those for unsaturated alcohols can be formed, viz. H₂A·CuCl and H₂A·Cu⁺, where H₂A represents the organic acid. Complexes HA·CuCl⁻ and HA·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 CuCl₂. 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.</p> <p>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 H₂A 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.</p> <table style="width: 100%; border: none;"> <tr> <td style="padding: 5px;">CuCl_(s) ⇌ Cu⁺ + Cl⁻</td> <td style="padding: 5px;">$K_{S0} = 1.83 \cdot 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$</td> </tr> <tr> <td style="padding: 5px;">CuCl_(s) + Cl⁻ ⇌ CuCl₂⁻</td> <td style="padding: 5px;">$K_{S2} = 0.0619$</td> </tr> <tr> <td style="padding: 5px;">H₂A ⇌ H⁺ + H₂A⁻</td> <td style="padding: 5px;">$K_A = \{H^+\}\{H_2A^-\}/\{H_2A\}$</td> </tr> <tr> <td style="padding: 5px;">H₂A + CuCl_(s) ⇌ H₂A·CuCl</td> <td style="padding: 5px;">$K_4 = \{H_2A \cdot CuCl\}/\{H_2A\}$</td> </tr> <tr> <td style="padding: 5px;">H₂A + CuCl_(s) ⇌ H₂A·Cu⁺ + Cl⁻</td> <td style="padding: 5px;">$K_5 = \{H_2A \cdot Cu^+\}\{Cl^-\}/\{H_2A\}$</td> </tr> <tr> <td style="padding: 5px;">H₂A⁻ + CuCl_(s) ⇌ HA·CuCl⁻</td> <td style="padding: 5px;">$K_6 = \{HA \cdot CuCl^-\}/\{HA^-\}$</td> </tr> <tr> <td style="padding: 5px;">HA⁻ + CuCl_(s) ⇌ HA·Cu + Cl⁻</td> <td style="padding: 5px;">$K_7 = \{HA \cdot Cu\}\{Cl^-\}/\{HA^-\}$</td> </tr> </table>		CuCl _(s) ⇌ Cu ⁺ + Cl ⁻	$K_{S0} = 1.83 \cdot 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$	CuCl _(s) + Cl ⁻ ⇌ CuCl ₂ ⁻	$K_{S2} = 0.0619$	H ₂ A ⇌ H ⁺ + H ₂ A ⁻	$K_A = \{H^+\}\{H_2A^-\}/\{H_2A\}$	H ₂ A + CuCl _(s) ⇌ H ₂ A·CuCl	$K_4 = \{H_2A \cdot CuCl\}/\{H_2A\}$	H ₂ A + CuCl _(s) ⇌ H ₂ A·Cu ⁺ + Cl ⁻	$K_5 = \{H_2A \cdot Cu^+\}\{Cl^-\}/\{H_2A\}$	H ₂ A ⁻ + CuCl _(s) ⇌ HA·CuCl ⁻	$K_6 = \{HA \cdot CuCl^-\}/\{HA^-\}$	HA ⁻ + CuCl _(s) ⇌ HA·Cu + Cl ⁻	$K_7 = \{HA \cdot Cu\}\{Cl^-\}/\{HA^-\}$
CuCl _(s) ⇌ Cu ⁺ + Cl ⁻	$K_{S0} = 1.83 \cdot 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$														
CuCl _(s) + Cl ⁻ ⇌ CuCl ₂ ⁻	$K_{S2} = 0.0619$														
H ₂ A ⇌ H ⁺ + H ₂ A ⁻	$K_A = \{H^+\}\{H_2A^-\}/\{H_2A\}$														
H ₂ A + CuCl _(s) ⇌ H ₂ A·CuCl	$K_4 = \{H_2A \cdot CuCl\}/\{H_2A\}$														
H ₂ A + CuCl _(s) ⇌ H ₂ A·Cu ⁺ + Cl ⁻	$K_5 = \{H_2A \cdot Cu^+\}\{Cl^-\}/\{H_2A\}$														
H ₂ A ⁻ + CuCl _(s) ⇌ HA·CuCl ⁻	$K_6 = \{HA \cdot CuCl^-\}/\{HA^-\}$														
HA ⁻ + CuCl _(s) ⇌ HA·Cu + Cl ⁻	$K_7 = \{HA \cdot Cu\}\{Cl^-\}/\{HA^-\}$														

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

For evaluation of the best set of complexation constants for each acid, the dissociation constants for the acids, K_A , were taken from the compilation of Kortum, Vogel and Andrussov¹⁰⁶. 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 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 $K_7/\text{mol dm}^{-3}$ 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 respect 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 $\text{H}_2\text{A} \cdot \text{CuCl}$ (or $\text{HA} \cdot \text{CuCl}$), but are about half as large as the Andrews values for the charged species $\text{H}_2\text{A} \cdot \text{Cu}^+$, 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:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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 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 H₂A·Cu⁺ (*K*₄) (in the case of maleic acid, HA·Cu (*K*₇) also), which is the major contributor to the solubility in the absence of chloride. At the same time the concentration of CuCl₂⁻ 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·CuCl⁻ (*K*₆) and HA·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 H₂A·Cu⁺, with a smaller contribution from H₂A·CuCl and very little from CuCl₂⁻. When the principal anion present is Cl⁻, the main contributors are H₂A·CuCl (little affected by the addition of chloride) and CuCl₂⁻. Maleic acid, being much stronger than the others, has major contributions from HA·CuCl⁻ and HA·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·Cu dominant and a minor contribution from H₂A·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·Cu and H₂A·Cu⁺ while increasing that of CuCl₂⁻, 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 CH₃ 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.

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p style="text-align: center;">RECOMMENDED VALUES FOR SOLUBILITY OF CuCl</p> <p>General</p> <p>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, NH₄Cl and CaCl₂. 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.</p> <p>The values of the solubility can be represented compactly by giving the ratio $c_{\text{CuCl}}/c_{\text{MCl}}$ of CuCl solubility to the initial concentration of the aqueous chloride used or, equivalently, the ratio $c_{\text{CuCl}}/c_{\text{Cl}^-}$ 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 $c_{\text{CuCl}}/c_{\text{MCl}}$ at given concentration, then obtaining the desired value of $c_{\text{CuCl}}/c_{\text{MCl}}$ by exponentiation.</p> <p>The general behaviour of $c_{\text{CuCl}}/c_{\text{MCl}}$ 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 $c_{\text{CuCl}}/c_{\text{MCl}}$ 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 CaCl₂, the ratio plotted is $m_{\text{CuCl}}/m_{\text{Cl}^-}$, where m_{Cl^-} is the molality of chloride ion provided by the media (twice the molality of the salt in the case of CaCl₂). The effects of NH₄Cl and KCl in dissolving CuCl are quite similar, and are much greater than those of HCl and NaCl at high concentrations. CaCl₂, 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 $c_{\text{CuCl}}/c_{\text{MCl}}$ 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.</p> <p>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 $c_{\text{CuCl}}/c_{\text{MCl}}$ 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.</p>	

COMPONENTS:

- (1) Copper(I) Chloride; CuCl [7758-89-6]
- (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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June, 1991

CRITICAL EVALUATION:

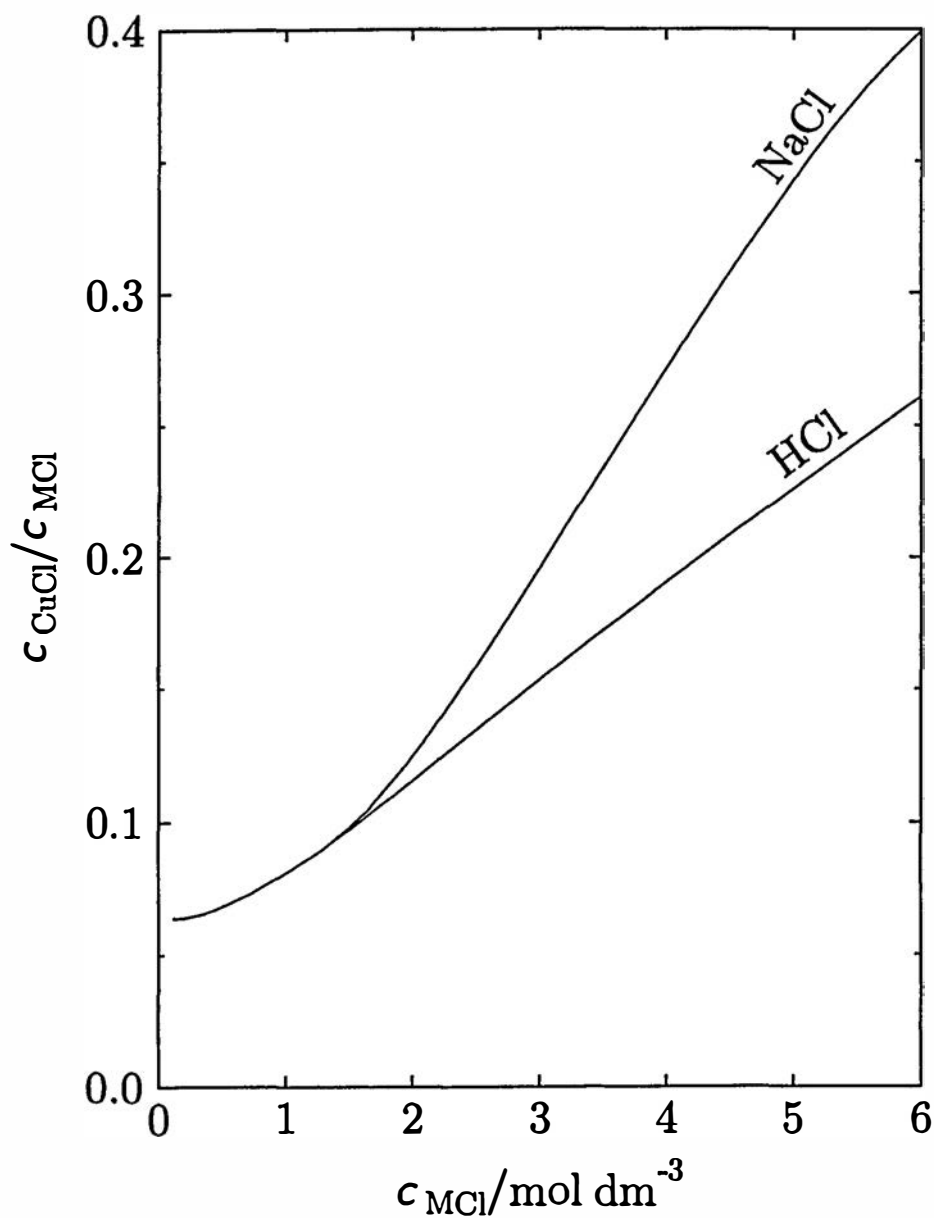


Fig. 1. Ratio of CuCl Solubility to Initial Concentration of Aqueous Chloride Plotted Against Concentration for NaCl and HCl at 298.15 K

COMPONENTS:

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

(2) Water; H₂O; [7732-18-5]

EVALUATOR:

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The Pennsylvania State University

June, 1991

CRITICAL EVALUATION:

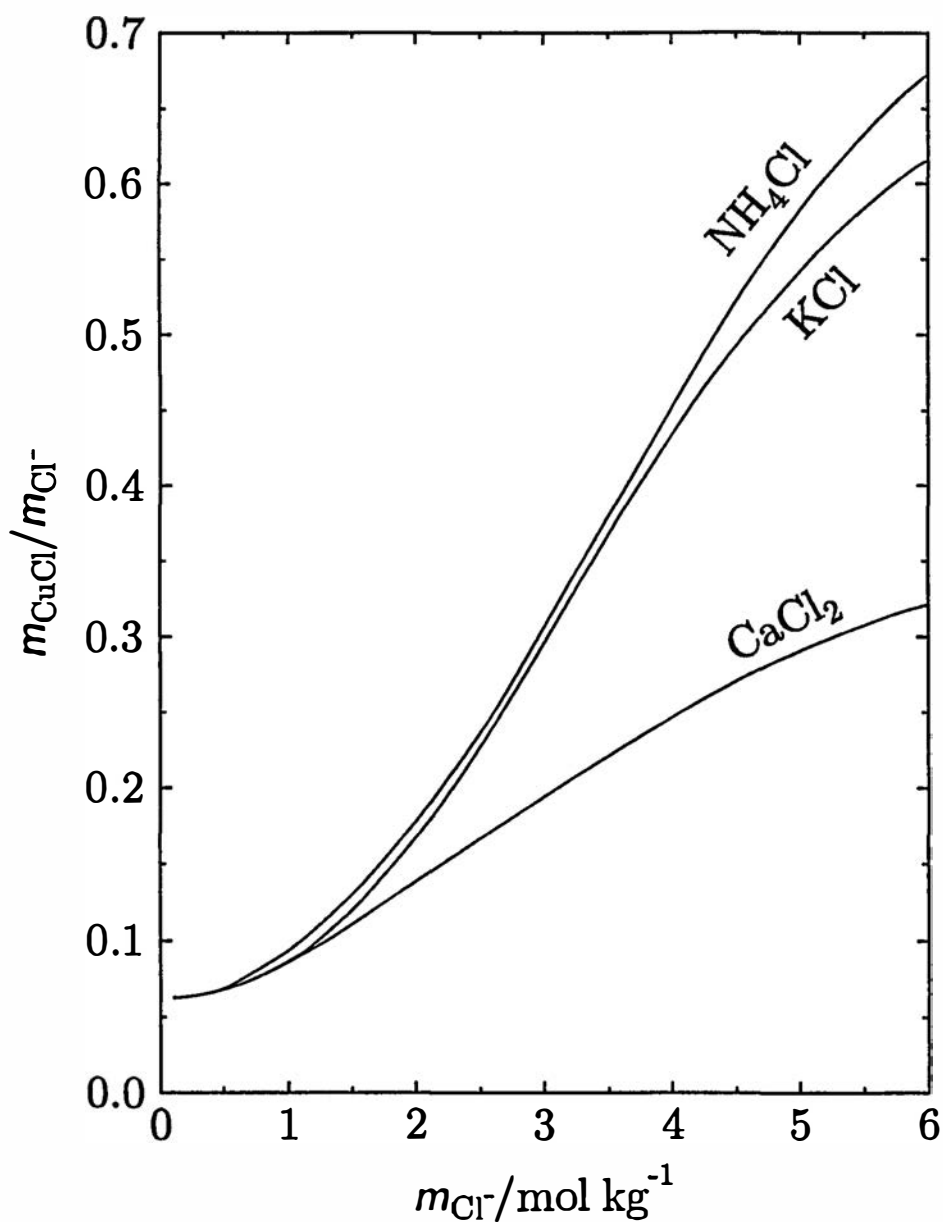


Fig. 2. Ratio of CuCl Solubility to Molality of Chloride Ion Supplied by the Aqueous Chloride, Plotted Against the Chloride Ion Molality for NH_4Cl , KCl and CaCl_2 at 298 K

COMPONENTS:

- (1) Copper(I) Chloride; CuCl [7758-89-6]
- (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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CRITICAL EVALUATION:

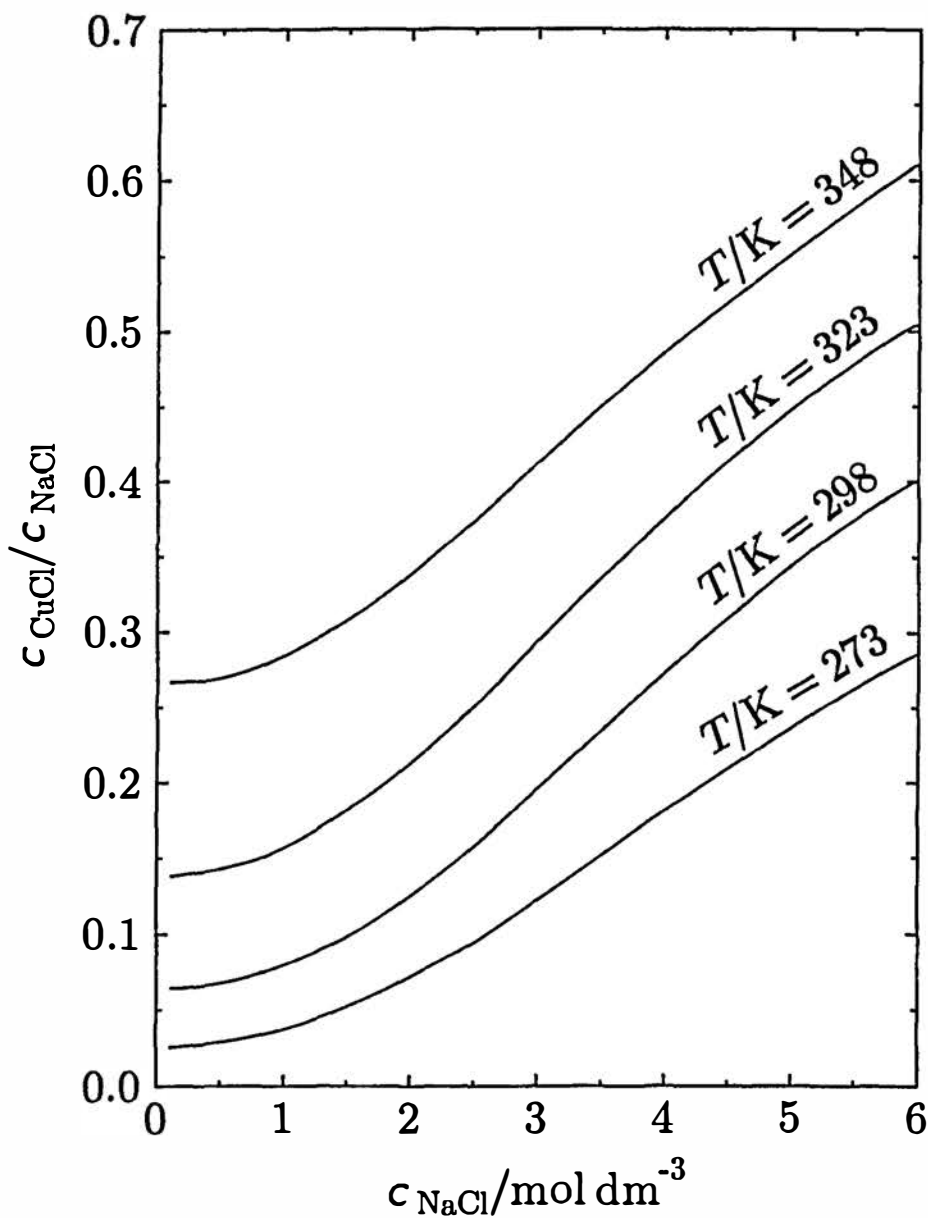


Fig. 3. Ratio of CuCl Solubility to NaCl Concentration Plotted Against Concentration of NaCl at 273, 298, 323 and 348 K

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Cha²⁴ 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

$c_{\text{HCl}}/\text{mol dm}^{-3}$	$c_{\text{CuCl}}/\text{mol dm}^{-3}$ 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; H₂O; [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 $c_{\text{CuCl}}/c_{\text{HCl}}$ 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

$c_{\text{HCl}}/\text{mol dm}^{-3}$	$c_{\text{CuCl}}/c_{\text{HCl}}$ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:**Solubility in Aqueous NaCl**

Tables 19A and 19B give recommended values of the solubility and of $c_{\text{CuCl}}/c_{\text{NaCl}}$ 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

$c_{\text{NaCl}}/\text{mol dm}^{-3}$	$c_{\text{CuCl}}/\text{mol dm}^{-3}$ 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:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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

$c_{\text{NaCl}}/\text{mol dm}^{-3}$	$c_{\text{CuCl}}/c_{\text{NaCl}}$ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:
Solubility of CuCl in Aqueous KCl

Table 20 gives values of the solubility and $m_{\text{CuCl}}/m_{\text{KCl}}$ 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

$m_{\text{KCl}}/\text{mol kg}^{-1}$	$m_{\text{CuCl}}/\text{mol kg}^{-1}$ at T/K of			$m_{\text{CuCl}}/m_{\text{KCl}}$ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:
Solubility of CuCl in Aqueous NH₄Cl

Tables 21A and 21B give values of the solubility and of $m_{\text{CuCl}}/m_{\text{NH}_4\text{Cl}}$ for solutions of CuCl in aqueous NH₄Cl 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 NH₄Cl 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 NH₄Cl from 273 to 373 K

$m_{\text{NH}_4\text{Cl}}/\text{mol kg}^{-1}$	$m_{\text{CuCl}}/\text{mol kg}^{-1}$ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

Table 21B. Ratio of CuCl Solubility to NH₄Cl Molality in Aqueous NH₄Cl from 273 to 373 K

$m_{\text{NH}_4\text{Cl}}/\text{mol kg}^{-1}$	$m_{\text{CuCl}}/m_{\text{NH}_4\text{Cl}}$ 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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:
Solubility of CuCl in Aqueous CaCl₂

Tables 22A and 22B give values of the solubility and of $m_{\text{CuCl}}/m_{\text{CaCl}_2}$ for solutions of CuCl in aqueous CaCl₂ at temperatures of 298, 323, 348 and 368 K and CaCl₂ 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 $m_{\text{CuCl}}/m_{\text{CaCl}_2}$ differ markedly from corresponding values for the other soluble chlorides, since each mole of CaCl₂ supplies two moles of chloride.

Table 22A. Solubility of CuCl in Aqueous CaCl₂ from 298 to 368 K

$m_{\text{CaCl}_2}/\text{mol kg}^{-1}$	$m_{\text{CuCl}}/\text{mol kg}^{-1}$ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

Table 22B. Ratio of CuCl Solubility to CaCl₂ Molality in Aqueous CaCl₂ from 298 to 368 K

$m_{\text{CaCl}_2}/\text{mol kg}^{-1}$	$m_{\text{CuCl}}/m_{\text{CaCl}_2}$ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>33. Chaltykyan, O. A. <i>Zh. Obshch. Khim.</i> <u>1948</u>, 18, 1626.</p> <p>34. Gokhale, S. D. <i>J. Univ. Bombay</i> <u>1953</u>, A20, 53.</p> <p>35. Malik, W. U.; Rahman, S. M. F.; Ali, S. A. <i>Z. Anorg. Allg. Chem.</i> <u>1959</u>, 299, 322.</p> <p>36. O'Connor, J. J.; Thomasian, A.; Armington, A. F. <i>J. Electrochem. Soc.</i> <u>1968</u>, 115, 931.</p> <p>37. Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u>, 3, K53.</p> <p>38. Novikov, G. I.; Voropaev, L. E.; Rud'ko, P. K.; Zharskii, I. M. <i>Zh. Neorg. Khim.</i> <u>1979</u>, 24, 811; <i>Russ. J. Inorg. Chem. (Engl. Trans.)</i> <u>1979</u>, 24, 452.</p> <p>39. Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Khim.-Tekh. Inst.</i> <u>1964</u>, 47, 111.</p> <p>40. Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1969</u>, 12, 706.</p> <p>41. Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1970</u>, 13, 437.</p> <p>42. Peters, M. A.; Johnson, R. K. <i>U. S. Patent No. 4,101,315</i>, July 18, <u>1978</u>.</p> <p>43. Fontana, A.; van Muylder, J.; Winand, R. <i>Hydrometallurgy</i> <u>1983</u>, 11, 297.</p> <p>44. Kosyakina, O. A. <i>Dokl. Nauchn. Konf. Jaroslavsk. Gos. Ped. Inst.</i> <u>1962</u> 1, 21.</p> <p>45. Brönsted, J. N. <i>Z. Phys. Chem.</i> <u>1912</u>, 80, 206.</p> <p>46. Valetton, J. J. P.; Frömel, W. <i>Z. Anorg. Allg. Chem.</i> <u>1924</u>, 137, 91.</p> <p>47. Iguchi, M.; Nakanishi, S. <i>J. Soc. Chem. Ind. Japan</i> <u>1941</u>, 44, S417.</p> <p>48. Shirokova, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Khim.-Tekh. Inst. Mendeleeva</i> <u>1965</u>, 49, 73.</p> <p>49. Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Nauchn. Trud. Giredmeta</i> <u>1974</u>, 62, 52.</p> <p>50. Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Zh. Prikl. Khim.</i> <u>1980</u>, 53, 2202; <i>Russ. J. Appl. Chem. (Engl. Trans.)</i> <u>1980</u>, 53, 1654.</p> <p>51. Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Zh. Prikl. Khim.</i> <u>1978</u>, 51, 1015; <i>Russ. J. Appl. Chem. (Engl. Trans.)</i> <u>1978</u>, 51, 977.</p> <p>52. Shutov, A. A., Utkina, I. N.; Lobkareva, V. L.; Reshetov, S. P. <i>Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1974</u>, 17, 1751.</p> <p>53. Shutov, A. A.; Shvedova, L. V.; Ermolaeva, T. G. <i>Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1977</u>, 20, 302.</p> <p>54. McConnell, H.; Davidson, N. <i>J. Am. Chem. Soc.</i> <u>1950</u>, 72, 3168.</p> <p>55. Vestin, R.; Somersalo, A.; Mueller, B. <i>Acta Chem. Scand.</i> <u>1953</u>, 7, 745.</p> <p>56. Winter, D. G.; Covington, J. W.; Muir, D. H. <i>Chloride Electrometall. Proc. Symp.</i> <u>1982</u>, 167.</p> <p>57. Berger, J. M.; Winand, R. <i>Hydrometallurgy</i>, <u>1984</u>, 12(1), 61.</p> <p>58. Gilliland, E. R.; Bliss, H. L.; Kip, C. E. <i>J. Am. Chem. Soc.</i> <u>1941</u>, 63, 2088.</p> <p>59. Ward, A. L.; Makin, E. C., Jr. <i>J. Am. Chem. Soc.</i> <u>1947</u>, 69, 657.</p> <p>60. Keefer, R. M.; Andrews, L. J. <i>J. Am. Chem. Soc.</i> <u>1949</u>, 71, 1723.</p> <p>61. Keefer, R. M.; Andrews, L. J.; Kepner, R. E. <i>J. Am. Chem. Soc.</i> <u>1949</u>, 71, 3906.</p> <p>62. Andrews, J. J., Keefer, R. M. <i>J. Am. Chem. Soc.</i> <u>1948</u>, 70, 3261.</p>	

<p>COMPONENTS:</p> <p>(1) Copper(I) Chloride; CuCl; [7758-89-6]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
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COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
CRITICAL EVALUATION: 95. Chaltykyan, O. A. <i>Dokl. Akad. Nauk Arm. SSR</i> 1948 , 8, 153. 96. Carlson, B.; Wettermark, G. <i>Z. Naturforsch.</i> 1976 , 31a, 297. 97. Braun, M.; Nobe, K. <i>J. Electrochem. Soc.</i> 1979 , 126, 1666. 98. Bodländer, G.; Storbeck, O. <i>Z. Anorg. Chem.</i> 1902 , 31, 458. 99. Sugasaka, K; Fujii, A. <i>Bull. Chem. Soc. (Japan)</i> 1976 , 49, 82. 100. Náray-Szabó, St. v.; Szabó, Z. <i>Z. Phys. Chem.</i> 1933 , A166, 228. 101. Sukhova, T. G.; Temkin, O. N.; Flid, R. M. <i>Zh. Neorg. Khim.</i> 1969 , 14, 928; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1969 , 14, 483. 102. Pestrikov, V. F.; Kranilov, U. P. <i>Koord. Khim.</i> 1978 , 4, 368. 103. Pitzer, K. S.; Kim, J. J. <i>J. Am. Chem. Soc.</i> 1974 , 96, 5701. 104. Fritz, J. J. <i>J. Chem. Eng. Data</i> 1982 , 27, 188. 105. Silvester, L. F.; Pitzer, K. S. <i>J. Solution Chem.</i> 1978 , 7, 327. 106. Kortim, G.; Vogel, W.; Andrussow, K. <i>Dissociation Constants of Organic Acids in Aqueous Solution</i> , Butterworths, London, 1961 . 107. Karimova, N. N.; Ksandrov, N. V.; Nikandrov, I. S. <i>Zh. Prikl. Khim.</i> 1988 , 61, 136. 108. Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J. <i>Afinidad</i> 1987 , 44 (408), 125.	

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Sosnitskii, V. N.; Fofanov, G. M. <i>Zh. Neorg. Khim.</i> 1979 , <i>24</i> , 1708-1710; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1979 , <i>24</i> (6), 947-949.
VARIABLES: Concentration of NaCl at 298 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Potentiometric Determination of the Solubility Product of Copper(I) Chloride</u></p> <p>ΔE at $25.0 \pm 0.3^\circ\text{C}$ of cell</p> <p>Pt CuCl_(s) CuSO₄ (0.1 mol dm⁻³), HClO₄ (0.1 mol dm⁻³), NaCl (x mol dm⁻³) salt bridge CuSO₄ (0.1 mol dm⁻³), HClO₄ (0.1 mol dm⁻³), NaCl (x mol dm⁻³) AgCl_(s) Ag</p> <p>as function of NaCl concentration from 0.1 to 10.4 mol dm⁻³.</p> <p>Slope of $\Delta E/\text{mV}$ vs. $\log c_{\text{NaCl}}/\text{mol dm}^{-3}$ interpreted to give $K_{\text{SO}} = (2.5 \pm 0.77) \cdot 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$ at zero ionic strength.</p>	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: Potential ($E_{\text{Cu}^{2+}/\text{Cu}^+}$) of platinum electrode taken to be $E_{\text{Cu}^{2+}/\text{Cu}^+}/V = 0.153 + 0.059 \log \frac{[\text{Cl}^-][\text{Cu}^{2+}]f_1f_2}{K_{\text{SO}}}$ with $[\text{Cl}^-]$ taken as $[\text{Cl}^-] = [\text{NaCl}]/(1 + \beta_2 K_{\text{SO}})$, giving $E_{\text{Cu}^{2+}/\text{Cu}^+}/V = 0.153 + 0.059 \log \frac{[\text{Cu}^{2+}][\text{NaCl}]f_1f_2}{K_{\text{SO}}(1 + \beta_2 K_{\text{SO}})}$ 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_{SO} .	
REFERENCES: 1. Butler, J. N. <i>Ionic Equilibrium</i> , Addison Wesley, Massachusetts, 1964 . 2. Vasil'ev, V. P.; Kunin, B. T. <i>Zh. Anal. Khim.</i> 1975 , <i>20</i> , 1881. 3. Karyakin, Yu. V.; Angelov, I. I. <i>Pure Chemical Substances</i> , Moscow, 1974 , p. 240.	

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Gavrish, M. L.; Galinker, I. S. <i>Dokl. Akad. Nauk SSSR</i> <u>1955</u> , 102, 89-91.
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VARIABLES: $T/K = 433$ to 633	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:					
<u>Solubility of CuCl in Water</u>					
$t/^{\circ}\text{C}$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/^{\circ}\text{C}$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/^{\circ}\text{C}$	$\frac{m_1}{\text{mol kg}^{-1}}$
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: 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 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Le Chatelier, H. <i>C. R. Hebd. Seances Acad. Sci.</i> <u>1884</u> , 98, 813-816.
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VARIABLES: Concentration of HCl at 290 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:Solubility of CuCl in Aqueous HCl at 17°C

$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{[\text{Cl}]_{\text{total}}^-}{\text{equiv. dm}^{-3}}$	$\frac{[\text{Cu}^+]}{\text{equiv. dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$\frac{c_1^a}{\text{mol dm}^{-3}}$
-	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. <i>Ann. Chim. Phys.</i> <u>1889</u> , 17, 347.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Engel, R. <i>Ann. Chim. Phys.</i> <u>1889</u> , 342-384.																		
VARIABLES: Concentration of HCl at undefined temperature (probably about 293 K)	PREPARED BY: J. J. FRITZ																		
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl at 20°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{\rho}{\text{g cm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">1.049</td> <td style="text-align: center;">1.75</td> <td style="text-align: center;">0.15</td> </tr> <tr> <td style="text-align: center;">1.065</td> <td style="text-align: center;">2.6</td> <td style="text-align: center;">0.29</td> </tr> <tr> <td style="text-align: center;">1.132</td> <td style="text-align: center;">4.475</td> <td style="text-align: center;">0.825</td> </tr> <tr> <td style="text-align: center;">1.261</td> <td style="text-align: center;">6.85</td> <td style="text-align: center;">1.55</td> </tr> <tr> <td style="text-align: center;">1.345</td> <td style="text-align: center;">10.40</td> <td style="text-align: center;">3.3</td> </tr> </tbody> </table> <p>^a Temperature estimated by compiler.</p>		$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	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
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Engel, R. <i>C. R. Hebd. Seances Acad. Sci.</i> <u>1895</u> , 121, 528-530.																		
VARIABLES: Concentration of HCl at 288 to 289 K	PREPARED BY: J. J. FRITZ																		
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl at 15 – 16°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{\rho}{\text{g cm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">–</td> <td style="text-align: center;">4.88</td> <td style="text-align: center;">0.61</td> </tr> <tr> <td style="text-align: center;">1.19</td> <td style="text-align: center;">5.44</td> <td style="text-align: center;">0.74</td> </tr> <tr> <td style="text-align: center;">1.27</td> <td style="text-align: center;">6.89</td> <td style="text-align: center;">1.08</td> </tr> <tr> <td style="text-align: center;">1.29</td> <td style="text-align: center;">7.50</td> <td style="text-align: center;">1.28</td> </tr> <tr> <td style="text-align: center;">1.38</td> <td style="text-align: center;">9.20</td> <td style="text-align: center;">1.60</td> </tr> </tbody> </table>		$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	–	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
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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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Abel, E. <i>Z. Anorg. Chem.</i> 1901 , 26, 361-437.																																
VARIABLES: Concentration of HCl at 288 K	PREPARED BY: J. J. FRITZ																																
EXPERIMENTAL VALUES: <u>Solubility of CuCl in Aqueous HCl at 15°C</u> <table border="1" style="margin: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.0422</td><td style="text-align: center;">0.0011</td></tr> <tr><td style="text-align: center;">0.052</td><td style="text-align: center;">0.00134</td></tr> <tr><td style="text-align: center;">0.063</td><td style="text-align: center;">0.00155</td></tr> <tr><td style="text-align: center;">0.0928</td><td style="text-align: center;">0.00455</td></tr> <tr><td style="text-align: center;">0.173</td><td style="text-align: center;">0.0077</td></tr> <tr><td style="text-align: center;">0.204</td><td style="text-align: center;">0.0103</td></tr> <tr><td style="text-align: center;">0.300</td><td style="text-align: center;">0.0162</td></tr> <tr><td style="text-align: center;">0.438</td><td style="text-align: center;">0.0221</td></tr> <tr><td style="text-align: center;">0.500</td><td style="text-align: center;">0.0270</td></tr> <tr><td style="text-align: center;">0.530</td><td style="text-align: center;">0.0275</td></tr> <tr><td style="text-align: center;">0.610</td><td style="text-align: center;">0.0337</td></tr> <tr><td style="text-align: center;">0.988</td><td style="text-align: center;">0.0671</td></tr> <tr><td style="text-align: center;">1.27</td><td style="text-align: center;">0.0937</td></tr> <tr><td style="text-align: center;">1.33</td><td style="text-align: center;">0.0963</td></tr> <tr><td style="text-align: center;">2.07</td><td style="text-align: center;">0.181</td></tr> </tbody> </table>		$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	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
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Noyes, A. A.; Chow, M. <i>J. Am. Chem. Soc.</i> <u>1918</u> , 40, 739-763.															
VARIABLES: Concentration of HCl at 298 K	PREPARED BY: J. J. FRITZ															
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl at 25°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{[\text{Cl}]_{\text{total}}^-}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">1.2815</td> <td style="text-align: center;">1.1650</td> <td style="text-align: center;">0.1165</td> </tr> <tr> <td style="text-align: center;">0.3364</td> <td style="text-align: center;">1.3165</td> <td style="text-align: center;">0.01988</td> </tr> <tr> <td style="text-align: center;">0.2290</td> <td style="text-align: center;">0.2156</td> <td style="text-align: center;">0.01340</td> </tr> <tr> <td style="text-align: center;">0.1038</td> <td style="text-align: center;">0.0978</td> <td style="text-align: center;">0.00596</td> </tr> </tbody> </table>		$\frac{[\text{Cl}]_{\text{total}}^-}{\text{mol dm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	1.2815	1.1650	0.1165	0.3364	1.3165	0.01988	0.2290	0.2156	0.01340	0.1038	0.0978	0.00596
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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 IINO ₃ .	<table border="1" style="width: 100%;"> <tbody> <tr> <td data-bbox="686 1692 1233 1780"> SOURCE AND PURITY OF MATERIALS: Not given. </td> </tr> <tr> <td data-bbox="686 1780 1233 1868"> ESTIMATED ERROR: Not stated. </td> </tr> <tr> <td data-bbox="686 1868 1233 1943"> REFERENCES: </td> </tr> </tbody> </table>	SOURCE AND PURITY OF MATERIALS: Not given.	ESTIMATED ERROR: Not stated.	REFERENCES:												
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VARIABLES: Concentration of HCl at 292 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:**Solubility of CuCl in Aqueous HCl at 19°C**

$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$\frac{c_1^a}{\text{mol dm}^{-3}}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Chang, K. S.; Cha, Y.-T. <i>J. Chin. Chem. Soc.</i> <u>1934</u> , 2, 293-306.																																																																														
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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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Morosov, I. C.; Ustanishkova, G. V. <i>Izv. Akad. Nauk. SSSR</i> <u>1944</u> , 451-456.
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VARIABLES: Molality of HCl at 293 to 373 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:					
Solubility of CuCl in Aqueous HCl					
(Note: All data presented graphically, numerical values below obtained from graphs by compiler.)					
$t/^{\circ}\text{C}$	$100w_2$	$100w_1$	$100w_3$	$\frac{m_2^a}{\text{mol kg}^{-1}}$	$\frac{m_1^a}{\text{mol kg}^{-1}}$
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: Not given.	SOURCE AND PURITY OF MATERIALS: Sources not given. CuCl 99.9%
	ESTIMATED ERROR: Not given; uncertainty in reading graphs app. 0.5 mass %.
	REFERENCES:

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Morosov, I. C.; Ustanishkova, G. V. <i>Izv. Akad. Nauk. SSSR</i> <u>1944</u> , 451-456.
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EXPERIMENTAL VALUES:

(continued)

$t/^\circ\text{C}$	$100w_2$	$100w_1$	$100w_3$	$\frac{m_2^a}{\text{mol kg}^{-1}}$	$\frac{m_1^a}{\text{mol kg}^{-1}}$
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

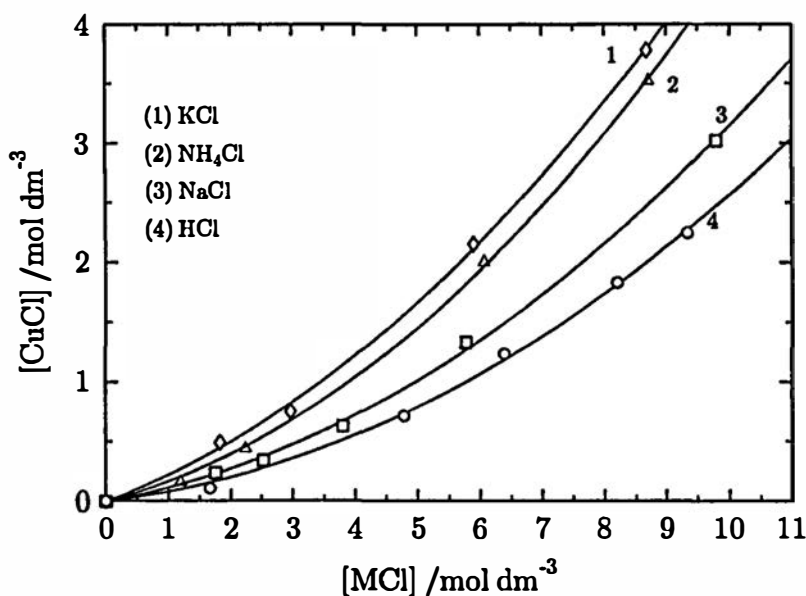
^a Calculated by compiler.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Chaltykyan O. A. <i>Zh. Obsch. Khim.</i> <u>1948</u> , 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 (NH₄Cl) quoted from the literature.

**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:

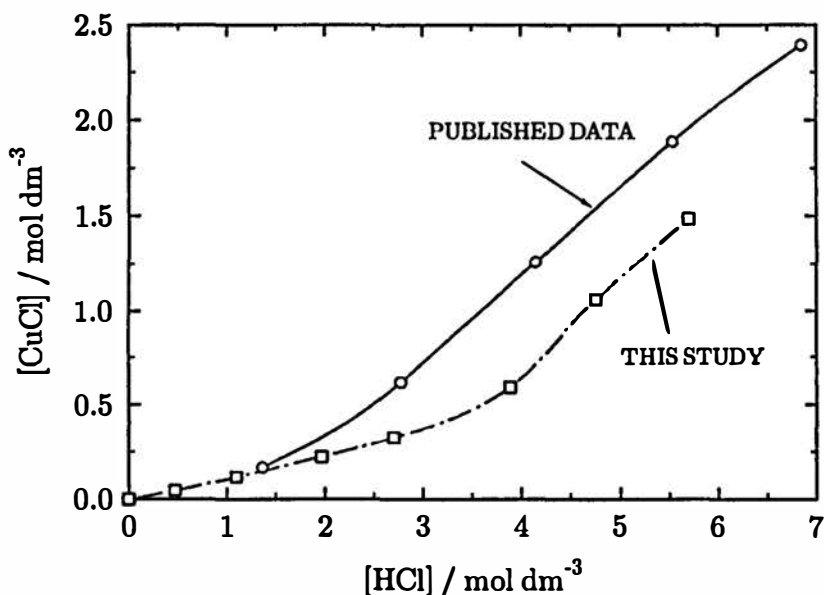
COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Malik, W. U.; Rahman, S. M. F.; Ali, S. A. <i>Z. Anorg. Chem.</i> 1959 , 299, 322-327.																																																																																				
VARIABLES: Concentration of HCl at unspecified temperature (probably about 300 K)	PREPARED BY: J. J. FRITZ																																																																																				
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{\rho_2}{\text{g dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2^a}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{\rho_1}{\text{g dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1^a}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr><td>4.68</td><td>0.128</td><td>3.9</td><td>0.039</td></tr> <tr><td>9.15</td><td>0.251</td><td>5.92</td><td>0.060</td></tr> <tr><td>14.05</td><td>0.385</td><td>8.92</td><td>0.090</td></tr> <tr><td>19.25</td><td>0.528</td><td>13.87</td><td>0.140</td></tr> <tr><td>23.36</td><td>0.641</td><td>16.85</td><td>0.170</td></tr> <tr><td>28.3</td><td>0.776</td><td>19.82</td><td>0.200</td></tr> <tr><td>33.81</td><td>0.927</td><td>27.75</td><td>0.280</td></tr> <tr><td>38.8</td><td>1.064</td><td>31.7</td><td>0.320</td></tr> <tr><td>45.3</td><td>1.242</td><td>35.7</td><td>0.360</td></tr> <tr><td>50.5</td><td>1.385</td><td>43.6</td><td>0.440</td></tr> <tr><td>55.3</td><td>1.517</td><td>51.53</td><td>0.520</td></tr> <tr><td>60.9</td><td>1.670</td><td>56.5</td><td>0.571</td></tr> <tr><td>65.0</td><td>1.783</td><td>63.0</td><td>0.636</td></tr> <tr><td>70.2</td><td>1.925</td><td>71.4</td><td>0.721</td></tr> <tr><td>75.4</td><td>2.068</td><td>77.5</td><td>0.783</td></tr> <tr><td>80.9</td><td>2.219</td><td>88.2</td><td>0.891</td></tr> <tr><td>84.9</td><td>2.329</td><td>98.1</td><td>0.991</td></tr> <tr><td>90.0</td><td>2.468</td><td>101.4</td><td>1.024</td></tr> <tr><td>100.4</td><td>2.754</td><td>107.0</td><td>1.080</td></tr> <tr><td>(109.00)^b</td><td>(2.990)^b</td><td>(132.80)^b</td><td>(1.341)^b</td></tr> </tbody> </table> <p>^a Calculated by compiler. ^b Original (slightly unsaturated) solution.</p>		$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{c_1^a}{\text{mol dm}^{-3}}$	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
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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 ₄ SCN 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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: O'Connor, J. J.; Thomasian, A.; Armington, A. F. <i>J. Electrochem. Soc.</i> 1968 , <i>115</i> , 931-932.
VARIABLES: Concentration of HCl at 295 K	PREPARED BY: 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:

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.

SOURCE AND PURITY OF MATERIALS:

Not stated.

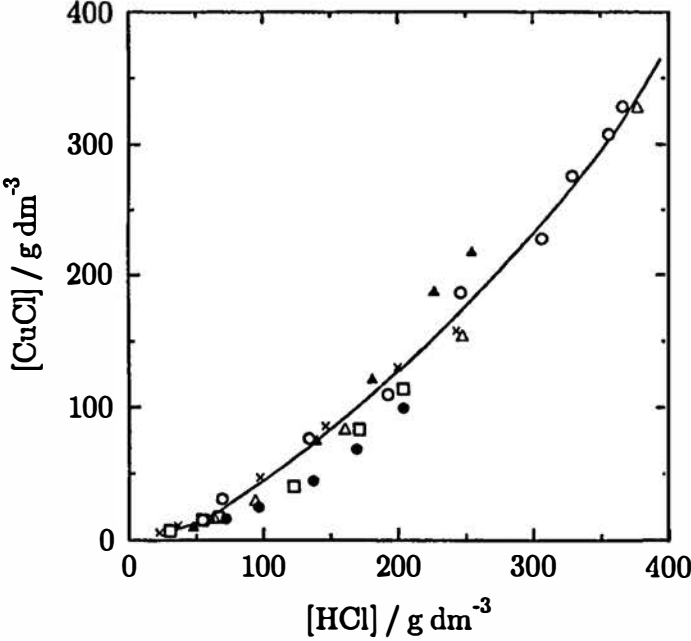
ESTIMATED ERROR:

Not given.

REFERENCES:

- Linke, W. F. *Solubility of Inorganic and Metal Organic Compounds*, Vol. 1, 4rd ed., Van Norstrand Co., Princeton, **1958**, p. 925.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.																													
VARIABLES: <i>T/K</i> = 298 to 328	PREPARED BY: J. J. FRITZ																													
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th rowspan="2"><i>t/°C</i></th> <th colspan="2">HCl in Solution^a</th> <th colspan="2">Solubility of CuCl^a</th> </tr> <tr> <th>g/100 ml H₂O</th> <th><i>m</i>₂/mol kg⁻¹</th> <th>g/100 ml H₂O</th> <th><i>m</i>₁/mol kg⁻¹</th> </tr> </thead> <tbody> <tr> <td>25</td> <td>22.0</td> <td>6.0</td> <td>17.2</td> <td>1.74</td> </tr> <tr> <td>35</td> <td>22.0</td> <td>6.0</td> <td>17.7</td> <td>1.79</td> </tr> <tr> <td>45</td> <td>22.0</td> <td>6.0</td> <td>18.6</td> <td>1.88</td> </tr> <tr> <td>55</td> <td>22.0</td> <td>6.0</td> <td>19.8</td> <td>2.00</td> </tr> </tbody> </table> <p>^a Molalities were calculated by the compiler, taking the author's "g/100 ml H₂O" to mean g/100 g H₂O within the precision of the data.</p>		<i>t/°C</i>	HCl in Solution ^a		Solubility of CuCl ^a		g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> 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
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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 ₂ O ₂ .	SOURCE AND PURITY OF MATERIALS: Not stated. ESTIMATED ERROR: Not given. REFERENCES:																													

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Glodzińska, W.; Zembura, Z. <i>Roczniki Chem.</i> <u>1974</u> , 48, 341-343.
VARIABLES: Concentration of HCl at 298 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl at 25°C</u></p> <p>Give graphical presentation of solubility of CuCl ($\rho_1/\text{g dm}^{-3}$) as a function of HCl mass concentration ($\rho_2/\text{g dm}^{-3} = 50$ to 370), with earlier results shown for comparison.</p> <p>Give equation for solubility of CuCl at $25 \pm 0.1^\circ\text{C}$</p> $\rho_1/\text{g dm}^{-3} = -22.2605 + 7.362 \cdot 10^{-1}(\rho_2/\text{g dm}^{-3}) - 7 \cdot 10^{-4}(\rho_2/\text{g dm}^{-3})^2 + 3.35 \cdot 10^{-6}(\rho_2/\text{g dm}^{-3})^3$ <p>Claimed validity from 55 to 370 g dm^{-3} HCl.</p> <div style="text-align: center;">  </div> <p>○ 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 <i>et al.</i> (1968) at 22°C. Curve calculated from equation given above.</p>	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: Copper(II) chloride in aqueous HCl reduced with excess metallic copper at $25 \pm 0.1^\circ\text{C}$. Copper oxidized to CuSO ₄ , then determined iodometrically. Chloride determined argentometrically.	SOURCE AND PURITY OF MATERIALS: Not stated. ESTIMATED ERROR: 4 to 8% REFERENCES:

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kale, S. S.; Tamhankar, S. S., and Chaudhari, R. V. <i>J. Chem. Eng. Data</i> 1979 , <i>24</i> (2), 110-111.
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VARIABLES: Concentration of HCl at 293 to 323 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous HCl</u></p> <hr/> <table style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th rowspan="2">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th colspan="4">$10^2 c_1/\text{mol dm}^{-3}$ at $t/^\circ\text{C}$ of</th> </tr> <tr> <th>20</th> <th>30</th> <th>40</th> <th>50</th> </tr> </thead> <tbody> <tr> <td>0.0</td> <td>0.295</td> <td>0.380</td> <td>0.519</td> <td>0.668</td> </tr> <tr> <td>0.129</td> <td>0.944</td> <td>1.175</td> <td>1.603</td> <td>1.927</td> </tr> <tr> <td>0.158</td> <td>1.122</td> <td>1.380</td> <td>1.884</td> <td>2.238</td> </tr> <tr> <td>0.266</td> <td>1.698</td> <td>2.113</td> <td>2.985</td> <td>3.467</td> </tr> <tr> <td>0.398</td> <td>2.398</td> <td>2.985</td> <td>4.121</td> <td>4.897</td> </tr> <tr> <td>0.603</td> <td>3.388</td> <td>4.168</td> <td>5.888</td> <td>6.839</td> </tr> </tbody> </table> <hr/> <p>Give equation $\ln c_1/\text{mol dm}^{-3} = A + BK/T + C \ln(1 + Dc_2/\text{mol dm}^{-3})$, where c_1 is solubility of CuCl and c_2 is concentration of HCl, and $A = 2.2265$, $B = -2.3480 \cdot 10^3$, $C = 1.0486$, $D = 15.0$.</p> <p>Quote $\sigma = 1.1513 \cdot 10^{-3}$</p> <p>Derive $\Delta H = 4.696 \text{ kcal mol}^{-1}$.</p>					$\frac{c_2}{\text{mol dm}^{-3}}$	$10^2 c_1/\text{mol dm}^{-3}$ at $t/^\circ\text{C}$ 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
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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. <i>Quantitative Inorganic Analysis</i> , 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kremann, R.; Noss, F. <i>Monatsh. Chem.</i> <u>1912</u> , 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-H₂O at 26.5°C**

$100\zeta_{2,3}$	$100\zeta_{1,3}$	Solid Phase	$m_2/\text{mol kg}^{-1}$ ^a	$m_1/\text{mol kg}^{-1}$ ^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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fedotieff, P. P. <i>Z. Anorg. Allg. Chem.</i> 1928 , 173, 81-91.
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VARIABLES: Composition at 292 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES: <u>Composition of Saturated Solutions in the System CuCl-NaCl-H₂O at 19°C</u>				
$\rho_2/g\ dm^{-3}$	$\rho_1/g\ dm^{-3}$	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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Chaltykyan O. A. <i>Zh. Obshch. Khim.</i> <u>1948</u> , 18, 1626-1638.														
VARIABLES: Concentration of NaCl at 298 K	PREPARED BY: J. J. FRITZ														
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous NaCl at 25°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">c_2^a</th> <th style="text-align: center;">c_1^a</th> </tr> <tr> <th style="text-align: center;">mol dm⁻³</th> <th style="text-align: center;">mol dm⁻³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">1.76</td> <td style="text-align: center;">0.24</td> </tr> <tr> <td style="text-align: center;">2.52</td> <td style="text-align: center;">0.34</td> </tr> <tr> <td style="text-align: center;">3.81</td> <td style="text-align: center;">0.63</td> </tr> <tr> <td style="text-align: center;">5.77</td> <td style="text-align: center;">1.33</td> </tr> <tr> <td style="text-align: center;">9.79</td> <td style="text-align: center;">3.02</td> </tr> </tbody> </table> <p>^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.</p>		c_2^a	c_1^a	mol dm ⁻³	mol dm ⁻³	1.76	0.24	2.52	0.34	3.81	0.63	5.77	1.33	9.79	3.02
c_2^a	c_1^a														
mol dm ⁻³	mol dm ⁻³														
1.76	0.24														
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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) Sodium Chloride; NaCl; [7647-14-5] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kosyakina, O. A. <i>Dokl. Nauchn. Konf. Jaroslavsk. Gos. Ped. Inst.</i> <u>1962</u> , 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–H₂O 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 KMnO₄, 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% alkalis.

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.
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VARIABLES: Molality of NaCl at 298 to 328 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:				
<u>Solubility of CuCl in Aqueous NaCl</u>				
<i>t</i> /°C	NaCl in Solution ^a		Solubility of CuCl ^a	
	g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> ₁ /mol kg ⁻¹
25	35.9 18.0 9.0	6.14 3.08 1.54	19.9 5.8 3.6	2.01 0.59 0.36
35	35.9 18.0 9.0	6.14 3.08 1.54	20.5 7.2 4.0	2.07 0.73 0.40
45	35.9 18.0 9.0	6.14 3.08 1.54	21.4 8.0 4.0	2.16 0.81 0.40
55	35.9 18.0 9.0	6.14 3.08 1.54	21.9 8.4 4.2	2.21 0.85 0.42

^a Molalities were calculated by the compiler, taking the author's "g/100 ml H₂O" to mean g/100 g H₂O 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 ₂ O 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Isv. Vysh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1969</u> , 12, 706-708.
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VARIABLES: Concentration of NaCl at 273 to 368 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:				
<u>Solubility of CuCl in Aqueous NaCl</u>				
$t/^{\circ}\text{C}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$	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; H₂O; [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)

$t/^\circ\text{C}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$	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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Isv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1970</u> , 13, 437-439.																																				
VARIABLES: Concentration of NaCl at 298 and 368 K	PREPARED BY: J. J. FRITZ																																				
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous NaCl</u></p> <hr/> <table style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;">$\frac{\rho_2}{\text{g dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2^a}{\text{mol dm}^{-3}}$</th> <th colspan="2" style="text-align: center;">$t/^{\circ}\text{C} = 25$</th> <th colspan="2" style="text-align: center;">$t/^{\circ}\text{C} = 95$</th> </tr> <tr> <th></th> <th></th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3\text{ a}}$</th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3\text{ a}}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">100</td> <td style="text-align: center;">1.71</td> <td style="text-align: center;">25</td> <td style="text-align: center;">0.25</td> <td style="text-align: center;">70</td> <td style="text-align: center;">0.71</td> </tr> <tr> <td style="text-align: center;">200</td> <td style="text-align: center;">3.42</td> <td style="text-align: center;">85</td> <td style="text-align: center;">0.86</td> <td style="text-align: center;">200</td> <td style="text-align: center;">2.02</td> </tr> <tr> <td style="text-align: center;">250</td> <td style="text-align: center;">4.28</td> <td style="text-align: center;">140</td> <td style="text-align: center;">1.41</td> <td style="text-align: center;">265</td> <td style="text-align: center;">2.68</td> </tr> <tr> <td style="text-align: center;">300</td> <td style="text-align: center;">5.13</td> <td style="text-align: center;">225</td> <td style="text-align: center;">2.27</td> <td style="text-align: center;">350</td> <td style="text-align: center;">3.53</td> </tr> </tbody> </table> <hr/> <p>^a Calculated by compiler.</p>		$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$t/^{\circ}\text{C} = 25$		$t/^{\circ}\text{C} = 95$				$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3\text{ a}}$	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3\text{ a}}$	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
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COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Chloride; KCl; [7447-40-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Le Chatelier, H. <i>C. R. Hebd. Seances Acad. Sci.</i> <u>1884</u> , 98, 813-816.
VARIABLES: Concentration of KCl at 290 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:**Solubility of CuCl in Aqueous KCl at 17°C**

$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{[\text{Cl}]_{\text{total}}^-}{\text{equiv. dm}^{-3}}$	$\frac{[\text{Cu}^+]}{\text{equiv. dm}^{-3}}$	$\frac{c_2^{\text{a}}}{\text{mol dm}^{-3}}$	$\frac{c_1^{\text{a}}}{\text{mol dm}^{-3}}$
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. <i>Ann. Chim. Phys.</i> <u>1889</u> , 17, 347.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Chloride; KCl; [7447-40-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Brönsted, J. N. <i>Z. Phys. Chem.</i> <u>1912</u> , 80, 206-234.																																																																																																																																										
VARIABLES: Composition at 295 K	PREPARED BY: J. J. FRITZ																																																																																																																																										
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Composition of Saturated Solutions in the System CuCl-KCl-H₂O at 22°C</u></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;">$\frac{m_2}{\text{mol kg}^{-1}}$</th> <th style="text-align: center;">$\frac{m_1}{\text{mol kg}^{-1}}$</th> <th style="text-align: center;">Solid Phase</th> <th style="text-align: center;">$\frac{m_2}{\text{mol kg}^{-1}}$</th> <th style="text-align: center;">$\frac{m_1}{\text{mol kg}^{-1}}$</th> <th style="text-align: center;">Solid Phase</th> </tr> </thead> <tbody> <tr><td>0.540</td><td>0.012</td><td>CuCl</td><td>5.139</td><td>2.411</td><td>A</td></tr> <tr><td>0.945</td><td>0.044</td><td>CuCl</td><td>5.061</td><td>2.261</td><td>A</td></tr> <tr><td>1.215</td><td>0.096</td><td>CuCl</td><td>5.189</td><td>2.353</td><td>A</td></tr> <tr><td>1.486</td><td>0.156</td><td>CuCl</td><td>5.122</td><td>2.367</td><td>A</td></tr> <tr><td>1.756</td><td>0.256</td><td>CuCl</td><td>4.767</td><td>1.786</td><td>A</td></tr> <tr><td>2.298</td><td>0.480</td><td>CuCl</td><td>4.838</td><td>1.765</td><td>A</td></tr> <tr><td>2.569</td><td>0.612</td><td>CuCl</td><td>4.728</td><td>1.438</td><td>A</td></tr> <tr><td>2.837</td><td>0.795</td><td>CuCl</td><td>4.553</td><td>1.072</td><td>A</td></tr> <tr><td>3.109</td><td>0.963</td><td>CuCl</td><td>4.539</td><td>0.794</td><td>A</td></tr> <tr><td>3.378</td><td>1.193</td><td>CuCl</td><td>4.511</td><td>0.640</td><td>A</td></tr> <tr><td>3.919</td><td>1.519</td><td>CuCl</td><td>4.529</td><td>0.513</td><td>A</td></tr> <tr><td>3.927</td><td>1.585</td><td>CuCl</td><td>4.671</td><td>0.441</td><td>A</td></tr> <tr><td>3.918</td><td>1.483</td><td>CuCl</td><td>4.643</td><td>0.399</td><td>A</td></tr> <tr><td>4.191</td><td>1.813</td><td>CuCl</td><td>4.689</td><td>0.371</td><td>A</td></tr> <tr><td>4.460</td><td>2.067</td><td>CuCl</td><td>4.926</td><td>0.310</td><td>A</td></tr> <tr><td>5.165</td><td>2.705</td><td>CuCl</td><td>5.059</td><td>0.274</td><td>A</td></tr> <tr><td>5.424</td><td>2.950</td><td>CuCl</td><td>5.075</td><td>0.249</td><td>A</td></tr> <tr><td>5.565</td><td>3.365</td><td>CuCl</td><td>5.101</td><td>0.274</td><td>A+KCl</td></tr> <tr><td>6.321</td><td>4.062</td><td>CuCl</td><td>5.085</td><td>0.226</td><td>KCl</td></tr> <tr><td>6.281</td><td>4.046</td><td>CuCl</td><td>4.963</td><td>0.174</td><td>KCl</td></tr> <tr><td>6.446</td><td>4.090</td><td>CuCl+A</td><td>4.827</td><td>0.080</td><td>KCl</td></tr> <tr><td>5.276</td><td>2.575</td><td>A</td><td>4.639</td><td>0.000</td><td>KCl</td></tr> </tbody> </table> <p>Solid phase: (A) CuCl·2KCl.</p>		$\frac{m_2}{\text{mol kg}^{-1}}$	$\frac{m_1}{\text{mol kg}^{-1}}$	Solid Phase	$\frac{m_2}{\text{mol kg}^{-1}}$	$\frac{m_1}{\text{mol kg}^{-1}}$	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
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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																																																																																																																																						
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Valeton, J. J. P.; Frömel, W. <i>Z. Anorg. Allg. Chem.</i> 1924 , <i>137</i> , 91-100.
VARIABLES: Composition at 298 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:
Composition of Saturated Solutions in the System CuCl-KCl-H₂O

$100x_2$	$100x_1$	$100x_3$	Solid Phase	$m_2/\text{mol kg}^{-1 a}$	$m_1/\text{mol kg}^{-1 a}$
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 cm³ specimens removed for analysis every 10 hours. Analyzed for copper electrolytically after oxidation to Cu(II) with concentrated HNO₃ and conversion to CuSO₄ with H₂SO₄. Analyzed for potassium as K₂SO₄ 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:

- Mitscherlich, E. *Berl. Akad. Ber.* **1840**, 8.
- 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Valetton, J. J. P.; Frömel, W. <i>Z. Anorg. Allg. Chem.</i> <u>1924</u> , 137, 91-100.
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EXPERIMENTAL VALUES:

(continued)

$100x_2$	$100x_1$	$100x_3$	Solid Phase	$m_2/\text{mol kg}^{-1 \text{ a}}$	$m_1/\text{mol kg}^{-1 \text{ a}}$
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·CuCl; (B) KCl·CuCl·H₂O.

^a Calculated by compiler.

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Chloride; KCl; [7447-40-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Chaltykyan O. A. <i>Zh. Obshch. Khim.</i> <u>1948</u> , 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Malik, W. U.; Rahman, S. M. F.; Ali, S. A. <i>Z. Anorg. Chem.</i> 1959 , 299, 322-327.																																																																
VARIABLES: Concentration of KCl at unspecified temperature (probably about 300 K)	PREPARED BY: J. J. FRITZ																																																																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous KCl</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$\frac{\rho_2}{\text{g dm}^{-3}}$</th> <th>$\frac{c_2^a}{\text{mol dm}^{-3}}$</th> <th>$\frac{\rho_1}{\text{g dm}^{-3}}$</th> <th>$\frac{c_1^a}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr><td>10.0</td><td>0.134</td><td>1.4</td><td>0.0141</td></tr> <tr><td>19.0</td><td>0.255</td><td>3.0</td><td>0.0303</td></tr> <tr><td>30.0</td><td>0.402</td><td>5.0</td><td>0.0504</td></tr> <tr><td>49.0</td><td>0.657</td><td>11.2</td><td>0.150</td></tr> <tr><td>60.0</td><td>0.804</td><td>18.2</td><td>0.184</td></tr> <tr><td>71.0</td><td>0.952</td><td>26.8</td><td>0.271</td></tr> <tr><td>80.0</td><td>1.073</td><td>35.7</td><td>0.360</td></tr> <tr><td>89.2</td><td>1.196</td><td>41.2</td><td>0.416</td></tr> <tr><td>100.0</td><td>1.341</td><td>50.6</td><td>0.511</td></tr> <tr><td>110.9</td><td>1.487</td><td>54.4</td><td>0.549</td></tr> <tr><td>124.0</td><td>1.663</td><td>73.4</td><td>0.741</td></tr> <tr><td>134.0</td><td>1.797</td><td>82.3</td><td>0.831</td></tr> <tr><td>146.6</td><td>1.966</td><td>99.1</td><td>1.001</td></tr> <tr><td>158.6</td><td>2.127</td><td>109.0</td><td>1.101</td></tr> <tr><td>(223.8)^b</td><td>(3.002)^b</td><td>(186.0)^b</td><td>(1.878)^b</td></tr> </tbody> </table> <p>^a Calculated by compiler. ^b Original unsaturated solutions.</p>		$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{c_1^a}{\text{mol dm}^{-3}}$	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
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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 ₄ SCN 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 ₄ Cl; [12125-02-9] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Morosov, I. C.; Ustaniskova, G. V. <i>Isv. Akad. Nauk SSSR</i> <u>1944</u> , 451-456.
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VARIABLES: Composition at 273 to 373 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System CuCl-NH₄Cl-H₂O

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

$t/^{\circ}\text{C}$	$100w_2$	$100w_1$	$100w_3$	Solid Phase	$\frac{m_2^a}{\text{mol kg}^{-1}}$	$\frac{m_1^a}{\text{mol kg}^{-1}}$
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 ₄ Cl	8.1	2.4
	26	11.5	62	NH ₄ Cl	7.8	2.3
	26	9	65	NH ₄ Cl	7.5	1.4
	22.5	0	67.5	NH ₄ Cl	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 ₄ Cl	17	10.1
	31	26.5	41.5	NH ₄ Cl	14	6.4
	30	15.5	54.5	NH ₄ Cl	10	2.9
	29	11	60	NH ₄ Cl	9.0	1.9
	28.5	5.5	66	NH ₄ Cl	8.1	0.8
	27	0	73	NH ₄ Cl	6.9	0

continued...

AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: Not given.	SOURCE AND PURITY OF MATERIALS: Sources not given CuCl 99.9% NH ₄ Cl 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]				Morosov, I. C.; Ustaniskova, G. V. <i>Isv. Akad. Nauk SSSR</i> 1944, 451-456.			
(2) Ammonium Chloride; NH ₄ Cl; [12125-02-9]							
(3) Water; H ₂ O; [7732-18-5]							
EXPERIMENTAL VALUES:							
(continued)							
$t/^{\circ}\text{C}$	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 ₄ Cl	28	24	
	32.5	46	21.5	NH ₄ Cl	28	22	
	34	40	26	NH ₄ Cl	24	16	
	35	35.5	29.8	NH ₄ Cl	22	12	
	35.5	29.5	35	NH ₄ Cl	19	8.5	
	35.5	20	44.5	NH ₄ Cl	15	4.5	
	35	16	49	NH ₄ Cl	13	3.3	
	35	10	55	NH ₄ Cl	12	1.8	
	34.5	5	60.5	NH ₄ Cl	11	0.8	
	34	0	66	NH ₄ Cl	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 ₄ Cl	b	b	
32		57	10.5	NH ₄ Cl	b	b	
38		43	19	NH ₄ Cl	37	22	
40		26.5	23.5	NH ₄ Cl	32	11	
39		14.5	46.5	NH ₄ Cl	16	3	
38.5		3.5	58	NH ₄ Cl	12	0.6	
38		0	62	NH ₄ Cl	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 ₄ Cl	b	b	
	40	46.5	13.5	NH ₄ Cl	b	b	
	42	34.5	23.5	NH ₄ Cl	33	15	
	42	31.5	26.5	NH ₄ Cl	30	12	
	43.5	17	39.5	NH ₄ Cl	21	4	
	42	0	58	NH ₄ Cl	13.5	0	
	Solid phases: (A) 2NH ₄ Cl·CuCl; (B) NH ₄ Cl·CuCl.						
	^a Calculated by compiler.						
^b Salt content too high for reasonable calculation of molality.							

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Ammonium Chloride; NH ₄ Cl; [12125-02-9] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.
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VARIABLES: Molality of NH ₄ Cl at 298 to 318 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:				
<u>Solubility of CuCl in Aqueous NH₄Cl</u>				
<i>t</i> /°C	NH ₄ Cl in Solution ^a		Solubility of CuCl ^a	
	g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> ₁ /mol kg ⁻¹
25	37.4 18.7 9.4	7.00 3.50 1.76	34.2 11.0 4.6	3.45 1.11 0.46
35	37.4 18.7 9.4	7.00 3.50 1.76	34.9 12.3 5.5	3.53 1.24 0.56
45	37.4 18.7 9.4	7.00 3.50 1.76	35.4 13.7 6.4	3.58 1.38 0.65
55	37.4 18.7 9.4	7.00 3.50 1.76	35.8 14.5 6.9	3.62 1.46 0.70
^a Molalities were calculated by the compiler, taking the author's "g/100 ml H ₂ O" to mean g/100 g H ₂ O 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 ₂ O ₂ .	SOURCE AND PURITY OF MATERIALS: Not stated.
	ESTIMATED ERROR: Not given.
	REFERENCES:

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Lithium Chloride; LiCl; [7447-41-8] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.																																																													
VARIABLES: Molality of LiCl at 298 to 328 K	PREPARED BY: J. J. FRITZ																																																													
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous LiCl</u></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th rowspan="2" style="text-align: center;"><i>t</i>/°C</th> <th colspan="2" style="text-align: center;">LiCl in Solution^a</th> <th colspan="2" style="text-align: center;">Solubility of CuCl^a</th> </tr> <tr> <th style="text-align: center;">g/100 ml H₂O</th> <th style="text-align: center;"><i>m</i>₂/mol kg⁻¹</th> <th style="text-align: center;">g/100 ml H₂O</th> <th style="text-align: center;"><i>m</i>₁/mol kg⁻¹</th> </tr> </thead> <tbody> <tr> <td rowspan="3" style="text-align: center;">25</td> <td style="text-align: center;">82.8</td> <td style="text-align: center;">19.5</td> <td style="text-align: center;">38.6</td> <td style="text-align: center;">3.90</td> </tr> <tr> <td style="text-align: center;">41.4</td> <td style="text-align: center;">9.8</td> <td style="text-align: center;">24.4</td> <td style="text-align: center;">2.46</td> </tr> <tr> <td style="text-align: center;">20.7</td> <td style="text-align: center;">4.9</td> <td style="text-align: center;">10.4</td> <td style="text-align: center;">1.05</td> </tr> <tr> <td rowspan="3" style="text-align: center;">35</td> <td style="text-align: center;">82.8</td> <td style="text-align: center;">19.5</td> <td style="text-align: center;">40.5</td> <td style="text-align: center;">4.09</td> </tr> <tr> <td style="text-align: center;">41.4</td> <td style="text-align: center;">9.8</td> <td style="text-align: center;">25.6</td> <td style="text-align: center;">2.59</td> </tr> <tr> <td style="text-align: center;">20.7</td> <td style="text-align: center;">4.9</td> <td style="text-align: center;">11.3</td> <td style="text-align: center;">1.14</td> </tr> <tr> <td rowspan="3" style="text-align: center;">45</td> <td style="text-align: center;">82.8</td> <td style="text-align: center;">19.5</td> <td style="text-align: center;">42.4</td> <td style="text-align: center;">4.28</td> </tr> <tr> <td style="text-align: center;">41.4</td> <td style="text-align: center;">9.8</td> <td style="text-align: center;">26.9</td> <td style="text-align: center;">2.72</td> </tr> <tr> <td style="text-align: center;">20.7</td> <td style="text-align: center;">4.9</td> <td style="text-align: center;">11.8</td> <td style="text-align: center;">1.19</td> </tr> <tr> <td rowspan="3" style="text-align: center;">55</td> <td style="text-align: center;">82.8</td> <td style="text-align: center;">19.5</td> <td style="text-align: center;">44.1</td> <td style="text-align: center;">4.45</td> </tr> <tr> <td style="text-align: center;">41.4</td> <td style="text-align: center;">9.8</td> <td style="text-align: center;">28.1</td> <td style="text-align: center;">2.92</td> </tr> <tr> <td style="text-align: center;">20.7</td> <td style="text-align: center;">4.9</td> <td style="text-align: center;">12.7</td> <td style="text-align: center;">1.28</td> </tr> </tbody> </table> <p>^a Molalities were calculated by the compiler, taking the author's "g/100 ml H₂O" to mean g/100 g H₂O within the precision of the data.</p>		<i>t</i> /°C	LiCl in Solution ^a		Solubility of CuCl ^a		g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> 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
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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 ₂ O 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Shirokova, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Inst. Khim.-Tekh. Inst. Mendeleeva</i> <u>1965</u> , 49, 73-77.																																																																																																
VARIABLES: Molality of CaCl ₂ at 303 to 363 K	PREPARED BY: J. J. FRITZ																																																																																																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous CaCl₂^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th><i>T/K</i></th> <th><i>100w₂</i></th> <th><i>100w₁</i></th> <th><i>100w₃</i></th> <th><i>m₂/mol kg⁻¹</i></th> <th><i>m₁/mol kg⁻¹</i></th> </tr> </thead> <tbody> <tr><td>303</td><td>5.2</td><td>0.9</td><td>93.9</td><td>0.5</td><td>0.1</td></tr> <tr><td></td><td>10.8</td><td>3.2</td><td>86.0</td><td>1.1</td><td>0.4</td></tr> <tr><td></td><td>23.6</td><td>14.6</td><td>61.8</td><td>3.4</td><td>0.4</td></tr> <tr><td></td><td>24.8</td><td>14.6</td><td>60.6</td><td>3.7</td><td>2.4</td></tr> <tr><td></td><td>28.0</td><td>18.6</td><td>53.4</td><td>4.7</td><td>3.5</td></tr> <tr><td></td><td>28.3</td><td>19.6</td><td>52.1</td><td>4.9</td><td>3.8</td></tr> <tr><td></td><td>30.6</td><td>22.4</td><td>47.0</td><td>5.9</td><td>4.8</td></tr> <tr><td></td><td>32.0</td><td>22.4</td><td>47.6</td><td>6.1</td><td>4.8</td></tr> <tr><td></td><td>33.7</td><td>22.5</td><td>39.8</td><td>7.6</td><td>5.7</td></tr> <tr><td></td><td>37.1</td><td>22.0</td><td>40.9</td><td>8.2</td><td>5.4</td></tr> <tr><td></td><td>37.9</td><td>21.4</td><td>40.7</td><td>8.4</td><td>5.3</td></tr> <tr><td></td><td>38.6</td><td>21.4</td><td>40.0</td><td>8.7</td><td>5.4</td></tr> <tr><td></td><td>39.4</td><td>19.6</td><td>41.0</td><td>8.7</td><td>4.8</td></tr> <tr><td></td><td>39.6</td><td>18.7</td><td>41.7</td><td>8.6</td><td>4.5</td></tr> <tr><td></td><td>46.8^b</td><td>16.8^b</td><td>36.4^b</td><td>11.6^b</td><td>4.7^b</td></tr> </tbody> </table> <p style="text-align: right;">continued...</p>		<i>T/K</i>	<i>100w₂</i>	<i>100w₁</i>	<i>100w₃</i>	<i>m₂/mol kg⁻¹</i>	<i>m₁/mol kg⁻¹</i>	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
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Shirokova, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Inst. Khim.-Tekh. Inst. Mendeleeva</i> <u>1965</u> , 49, 73-77.
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EXPERIMENTAL VALUES:

(continued)

T/K	$100w_2$	$100w_1$	$100w_3$	$m_2/\text{mol kg}^{-1}$	$m_1/\text{mol kg}^{-1}$
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
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
	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 CaCl₂ — at 303 K, CaCl₂·6H₂O; at other temperatures, CaCl₂·2H₂O. 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.
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VARIABLES: Molality of CaCl ₂ at 298 to 328 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:

Solubility of CuCl in Aqueous CaCl₂

<i>t</i> /°C	CaCl ₂ in Solution ^a		Solubility of CuCl ^a	
	g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> 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 H₂O" to mean g/100 g H₂O 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 ₂ O 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Isv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1970</u> , 13, 437-439.																																														
VARIABLES: Concentration of CaCl ₂ at 298 and 368 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																														
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous CaCl₂</u></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th rowspan="2" style="text-align: center;">$\frac{\rho_2}{\text{g dm}^{-3}}$</th> <th rowspan="2" style="text-align: center;">$\frac{c_2^a}{\text{mol dm}^{-3}}$</th> <th colspan="2" style="text-align: center;">$t/^{\circ}\text{C} = 25$</th> <th colspan="2" style="text-align: center;">$t/^{\circ}\text{C} = 95$</th> </tr> <tr> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3\text{a}}$</th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3\text{a}}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">100</td> <td style="text-align: center;">0.90</td> <td style="text-align: center;">25</td> <td style="text-align: center;">0.25</td> <td style="text-align: center;">60</td> <td style="text-align: center;">0.61</td> </tr> <tr> <td style="text-align: center;">200</td> <td style="text-align: center;">1.80</td> <td style="text-align: center;">70</td> <td style="text-align: center;">0.71</td> <td style="text-align: center;">150</td> <td style="text-align: center;">1.52</td> </tr> <tr> <td style="text-align: center;">300</td> <td style="text-align: center;">2.70</td> <td style="text-align: center;">130</td> <td style="text-align: center;">1.31</td> <td style="text-align: center;">275</td> <td style="text-align: center;">2.78</td> </tr> <tr> <td style="text-align: center;">400</td> <td style="text-align: center;">3.60</td> <td style="text-align: center;">250</td> <td style="text-align: center;">2.53</td> <td style="text-align: center;">395</td> <td style="text-align: center;">3.99</td> </tr> <tr> <td style="text-align: center;">450</td> <td style="text-align: center;">4.05</td> <td style="text-align: center;">305</td> <td style="text-align: center;">3.08</td> <td style="text-align: center;">415</td> <td style="text-align: center;">4.19</td> </tr> <tr> <td style="text-align: center;">500</td> <td style="text-align: center;">4.51</td> <td style="text-align: center;">345</td> <td style="text-align: center;">3.48</td> <td style="text-align: center;">430</td> <td style="text-align: center;">4.34</td> </tr> </tbody> </table> <p>^a Calculated by compiler.</p>		$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$t/^{\circ}\text{C} = 25$		$t/^{\circ}\text{C} = 95$		$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3\text{a}}$	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3\text{a}}$	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
$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$			$t/^{\circ}\text{C} = 25$		$t/^{\circ}\text{C} = 95$																																									
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COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Iron(II) Chloride; FeCl ₂ ; [7758-94-3] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kremann, R.; Noss, F. <i>Monatsh. Chem.</i> 1912 , <i>33</i> , 1205-1215.
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VARIABLES: Composition at 294.7 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:

Composition of Saturated Solutions in the System CuCl-FeCl₂-H₂O at 21.5°C

$100\zeta_{2,3}^a$	$100\zeta_{1,3}^a$	Solid Phase	$m_2/\text{mol kg}^{-1b}$	$m_1/\text{mol kg}^{-1b}$
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 ·4H ₂ O	5.775	2.343
71.90	21.66	FeCl ₂ ·4H ₂ O	5.673	2.187
69.34	11.90	FeCl ₂ ·4H ₂ O	5.471	1.202
65.10	0	FeCl ₂ ·4H ₂ O	5.136	0

^a Nearly identical duplicates averaged by compiler.

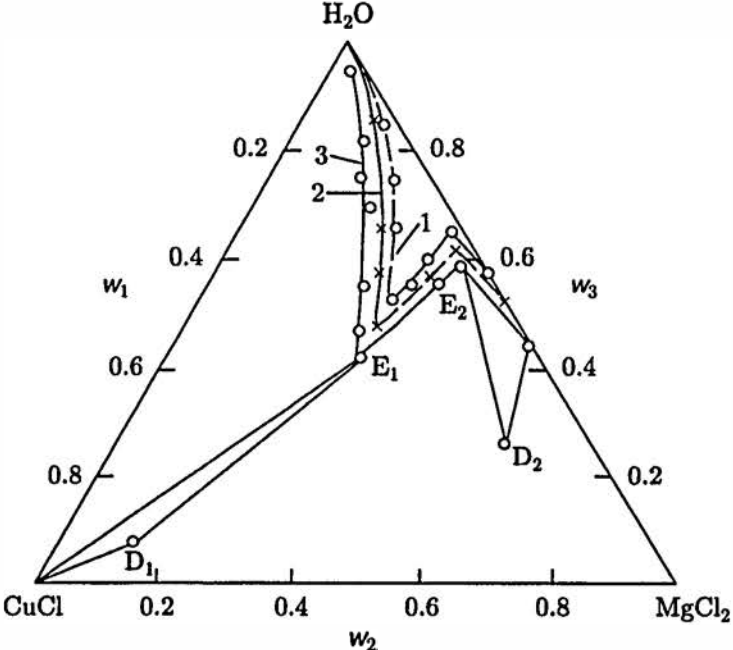
^b Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Shook mixtures in thermostat, analyzed solutions — methods not stated.	SOURCE AND PURITY OF MATERIALS: FeCl ₂ ·4H ₂ O 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fedotieff, P. P. <i>Z. Anorg. Allg. Chem.</i> 1928 , 173, 81-91.																								
VARIABLES: Concentration of CuCl ₂ at 292 K	PREPARED BY: J. J. FRITZ																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous CuCl₂ at 22°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$\rho_2/\text{g dm}^{-3}$</th> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$\rho_1/\text{g dm}^{-3 \text{ a}}$</th> <th>$c_1/\text{mol dm}^{-3 \text{ a}}$</th> </tr> </thead> <tbody> <tr> <td>134.5</td> <td>1.00</td> <td>15.8</td> <td>0.160</td> </tr> <tr> <td>260.0</td> <td>1.93</td> <td>40.7</td> <td>0.411</td> </tr> <tr> <td>435.7</td> <td>3.24</td> <td>63.8</td> <td>0.644</td> </tr> <tr> <td>536.5</td> <td>3.99</td> <td>78.7</td> <td>0.795</td> </tr> <tr> <td>661.9^b</td> <td>4.92^b</td> <td>87.4^b</td> <td>0.883^b</td> </tr> </tbody> </table> <p>^a Calculated by compiler. ^b This solution saturated with both CuCl and CuCl₂.</p>		$\rho_2/\text{g dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$\rho_1/\text{g dm}^{-3 \text{ a}}$	$c_1/\text{mol dm}^{-3 \text{ a}}$	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
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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) Copper(II) Chloride; CuCl ₂ ; [7447-39-4] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Isv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.</i> <u>1970</u> , 13, 437-439.																																								
VARIABLES: Concentration of CuCl ₂ at 298 and 368 K	PREPARED BY: J. J. FRITZ																																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous CuCl₂</u></p> <hr/> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th rowspan="2" style="text-align: center;">$\frac{\rho_2}{\text{g dm}^{-3}}$</th> <th rowspan="2" style="text-align: center;">$\frac{c_2^a}{\text{mol dm}^{-3}}$</th> <th colspan="2" style="text-align: center;">$t/^{\circ}\text{C} = 25$</th> <th colspan="2" style="text-align: center;">$t/^{\circ}\text{C} = 95$</th> </tr> <tr> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$ ^a</th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$ ^a</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">200</td> <td style="text-align: center;">1.49</td> <td style="text-align: center;">30</td> <td style="text-align: center;">0.30</td> <td style="text-align: center;">50</td> <td style="text-align: center;">0.50</td> </tr> <tr> <td style="text-align: center;">300</td> <td style="text-align: center;">2.23</td> <td style="text-align: center;">50</td> <td style="text-align: center;">0.50</td> <td style="text-align: center;">72</td> <td style="text-align: center;">0.73</td> </tr> <tr> <td style="text-align: center;">400</td> <td style="text-align: center;">2.97</td> <td style="text-align: center;">68</td> <td style="text-align: center;">0.69</td> <td style="text-align: center;">90</td> <td style="text-align: center;">0.91</td> </tr> <tr> <td style="text-align: center;">500</td> <td style="text-align: center;">3.72</td> <td style="text-align: center;">80</td> <td style="text-align: center;">0.81</td> <td style="text-align: center;">103</td> <td style="text-align: center;">1.04</td> </tr> <tr> <td style="text-align: center;">600</td> <td style="text-align: center;">4.46</td> <td style="text-align: center;">90</td> <td style="text-align: center;">0.91</td> <td style="text-align: center;">115</td> <td style="text-align: center;">1.16</td> </tr> </tbody> </table> <hr/> <p>^a Calculated by compiler.</p> <p>Also gives small scale graph of solubilities at 0, 25, 50, 75 and 95°C as a function of $c_{\text{CuCl}_2}/\text{mol dm}^{-3}$, covering slightly wider range of CuCl₂ concentrations (app. 0.2 to 4.7 mol dm⁻³).</p>		$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$t/^{\circ}\text{C} = 25$		$t/^{\circ}\text{C} = 95$		$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3}$ ^a	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3}$ ^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
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AUXILIARY INFORMATION																																									
METHOD/APPARATUS/PROCEDURE: Not given.	SOURCE AND PURITY OF MATERIALS: Not given. ESTIMATED ERROR: Not evident. REFERENCES: Utkina, I. N.; Kunin, T. I.; Shutov, A. A. <i>Isv. Vyssh. Ucheb. Zaved., Khim. Khim. Tekhnol.</i> <u>1969</u> , 12, 706.																																								

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Magnesium Chloride; CuCl ₂ ; [7786-30-3] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Karimova, N. N.; Ksandrov, N. V.; Nikandrov, I. S. <i>Zh. Prikl. Khim.</i> 1988 , <i>61</i> , 136-138.
VARIABLES: Composition at 273, 283 and 313 K	PREPARED BY: E. KÖNIGSBERGER
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Phase Diagram of the System CuCl-MgCl₂-H₂O</u></p>  <p>Temperatures: (1) 273 K, (2) 283 K, (3) 313 K. Solid phases: D₁: 12CuCl·MgCl₂·12H₂O, D₂: CuCl·5MgCl₂·12H₂O. Eutonic points: E₁: Solution at equilibrium with CuCl and D₁, E₂: Solution at equilibrium with MgCl₂·6H₂O and D₂.</p>	
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 diffractometry 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Vestin, R.; Somersalo, A.; Mueller, B. <i>Acta Chem. Scand.</i> <u>1953</u> , 7, 745-763.																										
VARIABLES: Molality of HCl at 298 K	PREPARED BY: J. J. FRITZ																										
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in HCl-HClO₄ Solutions at 25°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$m_2/\text{mol kg}^{-1}$</th> <th style="text-align: center;">$m_1/\text{mol kg}^{-1}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.1000</td><td style="text-align: center;">0.00468</td></tr> <tr><td style="text-align: center;">0.1500</td><td style="text-align: center;">0.00708</td></tr> <tr><td style="text-align: center;">0.199</td><td style="text-align: center;">0.00977</td></tr> <tr><td style="text-align: center;">0.415</td><td style="text-align: center;">0.0230</td></tr> <tr><td style="text-align: center;">0.500</td><td style="text-align: center;">0.0293</td></tr> <tr><td style="text-align: center;">0.600</td><td style="text-align: center;">0.0368</td></tr> <tr><td style="text-align: center;">0.800</td><td style="text-align: center;">0.0531</td></tr> <tr><td style="text-align: center;">1.000</td><td style="text-align: center;">0.0729</td></tr> <tr><td style="text-align: center;">1.500</td><td style="text-align: center;">0.1318</td></tr> <tr><td style="text-align: center;">2.00</td><td style="text-align: center;">0.210</td></tr> <tr><td style="text-align: center;">3.00</td><td style="text-align: center;">0.427</td></tr> <tr><td style="text-align: center;">4.00</td><td style="text-align: center;">0.735</td></tr> </tbody> </table> <p>^a All solutions made up to constant nominal ionic strength $I_m = 4.0 \text{ mol kg}^{-1}$, using HClO₄ as "inert" electrolyte.</p>		$m_2/\text{mol kg}^{-1}$	$m_1/\text{mol kg}^{-1}$	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
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Hikita, H.; Ishikawa, H.; Esaka, N. <i>Nippon Kagaku Kaiishi</i> <u>1973</u> , (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-HClO₄ 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. <i>Ind. Eng. Chem. Anal. Ed.</i> <u>1940</u> , 12, 155. 2. Fritz, J. J. <i>J. Phys. Chem.</i> <u>1980</u> , 94, 2241.

COMPONENTS:			ORIGINAL MEASUREMENTS:		
(1) Copper(I) Chloride; CuCl; [7758-89-6]			Hikita, H.; Ishikawa, H.; Esaka, N.		
(2) Hydrogen Chloride; HCl; [7647-01-0]			Nippon Kagaku Kaiishi <u>1973</u> , (1), 13-18.		
(3) Hydrogen Perchlorate; HClO ₄ ; [7601-90-3]					
(4) Water; H ₂ O; [7732-18-5]					
EXPERIMENTAL VALUES:					
(continued)					
I_c	c_2	c_3	$c_1/\text{mol dm}^{-3}$ at T/K of		
			288	298	308
mol dm^{-3}	mol dm^{-3}	mol dm^{-3}			
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	
5.0	1.23	2.28		0.105	
	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	
6.5	1.24	3.75		0.0927	
	1.49	3.50		0.126	
	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; HClO₄; [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

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

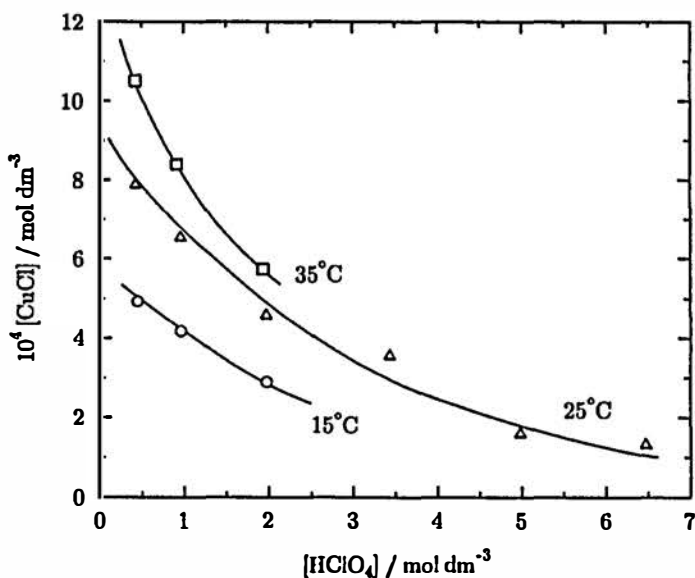
EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in HCl Solutions at 298 K

$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$
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 HClO₄ 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.



$c_3 / \text{mol dm}^{-3}$	$10^4 c_1 / \text{mol dm}^{-3}$ 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Ahrland, S.; and Rawsthorne, J. <i>Acta Chem. Scand.</i> 1970 , <i>24</i> (1), 157-172.
VARIABLES: Concentration of NaCl at 298 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:
Solubility of CuCl in NaCl-NaClO₄-(HClO₄) Solutions at 25°C^a

$\frac{10^3 c_2}{\text{mol dm}^{-3}}$	$\frac{10^3 c_1}{\text{mol dm}^{-3}}$	$\frac{10^3 c_2}{\text{mol dm}^{-3}}$	$\frac{10^3 c_1}{\text{mol dm}^{-3}}$	$\frac{10^3 c_2}{\text{mol dm}^{-3}}$	$\frac{10^3 c_1}{\text{mol dm}^{-3}}$
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 HClO₄ and at constant nominal ionic strength $I_c = 5.0$ mol dm⁻³, using NaClO₄ 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Gokhale, S. D. <i>Journal of the University of Bombay</i> <u>1953</u> , 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

$t/^{\circ}\text{C}$	$c_1/\text{mol dm}^{-3}$ at $c_2/\text{mol dm}^{-3}$ 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 K₂Cr₂O₇.

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:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
 (2) Sodium Chloride; NaCl; [7647-14-5]
 (3) Hydrogen Chloride; HCl; [7647-01-0]
 (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

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 cm³ of aqueous NaCl (4.0 mol dm⁻³).

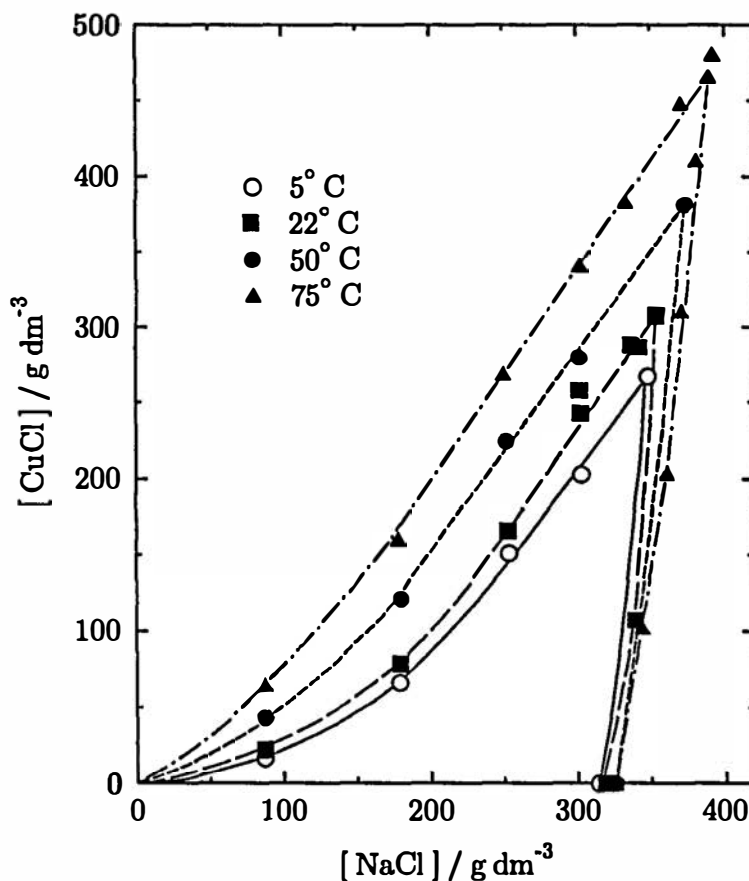
^b Calculated by compiler.

^c In all cases, specified amounts of aqueous HCl (12 mol dm⁻³) were added to 40 cm³ 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Peters, M. A.; Johnson, R. K; <i>U. S. Patent No. 4,101,315, July 18, 1978.</i>
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)-H₂O

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:
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Peters, M. A.; Johnson, R. K; <i>U. S. Patent No. 4,101,315, July 18, 1978.</i>
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EXPERIMENTAL VALUES:

(continued)

$t/^\circ\text{C}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_3^a}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fontana, A.; van Muylder, J.; Winand, R. <i>Hydrometallurgy</i> 1983 , <i>11</i> , 297-314.																																																
VARIABLES: Composition at 298 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in NaCl-HCl Solutions at 25°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{c_2 + c_3}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.90^b</td><td style="text-align: center;">0.00</td><td style="text-align: center;">0.069</td></tr> <tr><td style="text-align: center;">1.00</td><td style="text-align: center;">0.00</td><td style="text-align: center;">0.096</td></tr> <tr><td style="text-align: center;">1.50</td><td style="text-align: center;">0.50</td><td style="text-align: center;">0.208</td></tr> <tr><td style="text-align: center;">1.63^b</td><td style="text-align: center;">0.63</td><td style="text-align: center;">0.233</td></tr> <tr><td style="text-align: center;">2.00</td><td style="text-align: center;">1.00</td><td style="text-align: center;">0.351</td></tr> <tr><td colspan="3" style="text-align: center;"> </td></tr> <tr><td style="text-align: center;">2.50</td><td style="text-align: center;">1.50</td><td style="text-align: center;">0.490</td></tr> <tr><td style="text-align: center;">2.62^b</td><td style="text-align: center;">1.62</td><td style="text-align: center;">0.527</td></tr> <tr><td style="text-align: center;">3.00</td><td style="text-align: center;">2.00</td><td style="text-align: center;">0.684</td></tr> <tr><td style="text-align: center;">3.50</td><td style="text-align: center;">2.50</td><td style="text-align: center;">0.892</td></tr> <tr><td style="text-align: center;">3.78^b</td><td style="text-align: center;">2.78</td><td style="text-align: center;">1.021</td></tr> <tr><td colspan="3" style="text-align: center;"> </td></tr> <tr><td style="text-align: center;">4.00</td><td style="text-align: center;">3.00</td><td style="text-align: center;">1.174</td></tr> <tr><td style="text-align: center;">4.50</td><td style="text-align: center;">3.50</td><td style="text-align: center;">1.556</td></tr> <tr><td style="text-align: center;">4.64^b</td><td style="text-align: center;">3.64</td><td style="text-align: center;">1.634</td></tr> </tbody> </table> <p>^a Data read from the graph reproduced on the following page, which includes a phase diagram for the system.</p> <p>^b These data given as points on the graph; all others read from the smooth curve shown.</p> <p style="text-align: right;">continued...</p>		$\frac{c_2 + c_3}{\text{mol dm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	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
$\frac{c_2 + c_3}{\text{mol dm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$																																															
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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 ₂ Cl 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; H₂O; [7732-18-5]

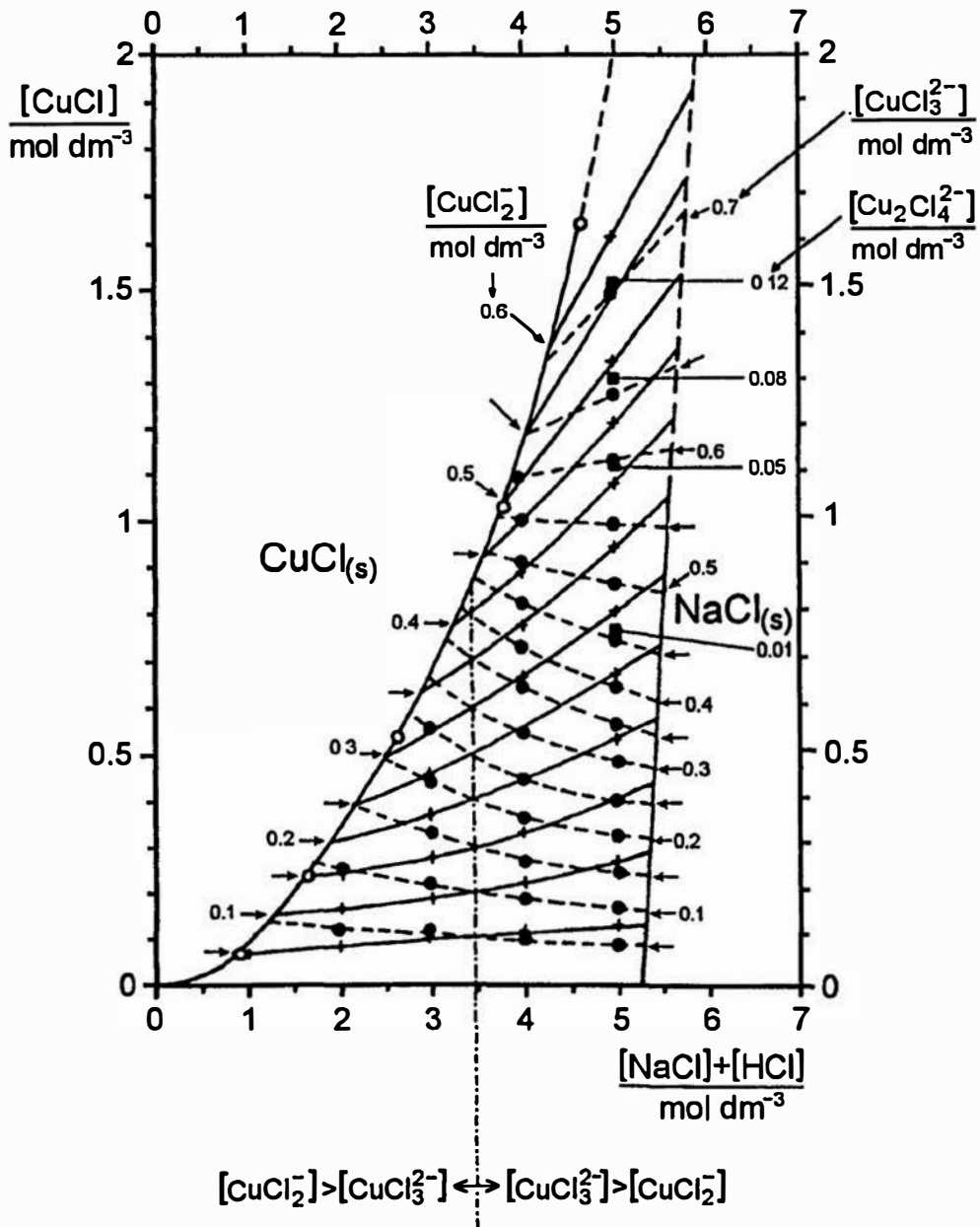
ORIGINAL MEASUREMENTS:

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 $\text{Cu}_2\text{Cl}_4^{2-}$ (■) 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 ₄ Cl; [12125-02-9] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Iguchi, M.; Nakanishi, G. <i>J. Soc. Chem. Ind. Japan</i> <u>1941</u> , <i>44</i> , S417-420.																																													
VARIABLES: Concentrations of NH ₄ Cl and HCl at 343 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																													
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous NH₄Cl at 70°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$100w_2$</th> <th>$100w_1$</th> <th>$100w_4$</th> <th>$m_2/\text{mol kg}^{-1\text{ a}}$</th> <th>$m_1/\text{mol kg}^{-1\text{ a}}$</th> </tr> </thead> <tbody> <tr><td>8.9</td><td>6.7</td><td>84.4</td><td>1.97</td><td>0.80</td></tr> <tr><td>17.5</td><td>15.5</td><td>67.0</td><td>4.88</td><td>2.34</td></tr> <tr><td>22.6</td><td>29.2</td><td>48.2</td><td>8.77</td><td>6.12</td></tr> <tr><td>25.0</td><td>39.0</td><td>36.0</td><td>12.98</td><td>10.94</td></tr> <tr><td>27.1</td><td>48.9</td><td>24.0</td><td>21.11</td><td>20.58</td></tr> <tr><td>27.6</td><td>52.7</td><td>19.7</td><td>26.2</td><td>27.0</td></tr> <tr><td>28.2</td><td>54.5</td><td>17.3</td><td>30.5</td><td>31.8</td></tr> <tr><td>28.6</td><td>55.4</td><td>16.0</td><td>33.4</td><td>35.0</td></tr> </tbody> </table> <p style="text-align: right;">continued...</p>		$100w_2$	$100w_1$	$100w_4$	$m_2/\text{mol kg}^{-1\text{ a}}$	$m_1/\text{mol kg}^{-1\text{ a}}$	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
$100w_2$	$100w_1$	$100w_4$	$m_2/\text{mol kg}^{-1\text{ a}}$	$m_1/\text{mol kg}^{-1\text{ a}}$																																										
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AUXILIARY INFORMATION																																														
METHOD/APPARATUS/PROCEDURE: Dissolved NH ₄ Cl 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 ₄ Cl 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 ₄ Cl; [12125-02-9] (3) Hydrogen Chloride; HCl; [7647-01-0] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Iguchi, M.; Nakanishi, G. <i>J. Soc. Chem. Ind. Japan</i> 1941 , <i>44</i> , S417-420.
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EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in NH₄Cl-HCl Solutions at 70°C

$100w_3^b$	$100w_2$	$100w_1$	$100(w_3 + w_4)$	$m_3/\text{mol kg}^{-1 a}$	$m_2/\text{mol kg}^{-1 a}$	$m_1/\text{mol kg}^{-1 a}$
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 NH₄Cl (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 ₂ O; [7732-18-15]	ORIGINAL MEASUREMENTS: Poma, G. <i>Atti. Accad. Naz. Lincei</i> <u>1909</u> , 18-1, 133-138.																																																																						
VARIABLES: Concentrations of CuCl ₂ and HCl at 298 K	PREPARED BY: J. J. FRITZ																																																																						
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in CuCl₂-HCl Solutions at 25°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{c_3}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{[\text{Cu}^+]+[\text{Cu}^{2+}]}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1^b}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr> <td rowspan="6" style="text-align: center; vertical-align: middle;">1</td> <td style="text-align: center;">0</td> <td style="text-align: center;">0.0862</td> <td style="text-align: center;">0.0862</td> </tr> <tr> <td style="text-align: center;">0.1001</td> <td style="text-align: center;">0.2017</td> <td style="text-align: center;">0.1016</td> </tr> <tr> <td style="text-align: center;">0.2002</td> <td style="text-align: center;">0.3256</td> <td style="text-align: center;">0.1254</td> </tr> <tr> <td style="text-align: center;">0.3003</td> <td style="text-align: center;">0.4452</td> <td style="text-align: center;">0.1449</td> </tr> <tr> <td style="text-align: center;">0.4004</td> <td style="text-align: center;">0.5707</td> <td style="text-align: center;">0.1703</td> </tr> <tr> <td style="text-align: center;">0.5005</td> <td style="text-align: center;">0.6924</td> <td style="text-align: center;">0.1919</td> </tr> <tr> <td rowspan="6" style="text-align: center; vertical-align: middle;">2</td> <td style="text-align: center;">0</td> <td style="text-align: center;">0.2365</td> <td style="text-align: center;">0.2365</td> </tr> <tr> <td style="text-align: center;">0.0940</td> <td style="text-align: center;">0.3528</td> <td style="text-align: center;">0.2588</td> </tr> <tr> <td style="text-align: center;">0.1410</td> <td style="text-align: center;">0.4160</td> <td style="text-align: center;">0.2750</td> </tr> <tr> <td style="text-align: center;">0.1880</td> <td style="text-align: center;">0.4766</td> <td style="text-align: center;">0.2886</td> </tr> <tr> <td style="text-align: center;">0.2350</td> <td style="text-align: center;">0.5385</td> <td style="text-align: center;">0.3035</td> </tr> <tr> <td style="text-align: center;">0.2820</td> <td style="text-align: center;">0.6038</td> <td style="text-align: center;">0.3218</td> </tr> <tr> <td rowspan="9" style="text-align: center; vertical-align: middle;">4</td> <td style="text-align: center;">0</td> <td style="text-align: center;">0.7704</td> <td style="text-align: center;">0.7704</td> </tr> <tr> <td style="text-align: center;">0.0473</td> <td style="text-align: center;">0.8357</td> <td style="text-align: center;">0.7884</td> </tr> <tr> <td style="text-align: center;">0.0946</td> <td style="text-align: center;">0.9044</td> <td style="text-align: center;">0.8098</td> </tr> <tr> <td style="text-align: center;">0.1420</td> <td style="text-align: center;">0.9701</td> <td style="text-align: center;">0.8281</td> </tr> <tr> <td style="text-align: center;">0.1894</td> <td style="text-align: center;">1.0370</td> <td style="text-align: center;">0.8476</td> </tr> <tr> <td style="text-align: center;">0.2367</td> <td style="text-align: center;">1.1040</td> <td style="text-align: center;">0.8673</td> </tr> <tr> <td style="text-align: center;">0.3768</td> <td style="text-align: center;">1.3040</td> <td style="text-align: center;">0.9272</td> </tr> <tr> <td style="text-align: center;">0.4261</td> <td style="text-align: center;">1.3700</td> <td style="text-align: center;">0.9439</td> </tr> <tr> <td style="text-align: center;">0.4734</td> <td style="text-align: center;">1.4380</td> <td style="text-align: center;">0.9646</td> </tr> </tbody> </table> <p>^a The identical data are also presented in Ref. 1. ^b Calculated by compiler.</p>		$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{[\text{Cu}^+]+[\text{Cu}^{2+}]}{\text{mol dm}^{-3}}$	$\frac{c_1^b}{\text{mol dm}^{-3}}$	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
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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. <i>Gazz. Chim. Ital.</i> <u>1910</u> , 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Edgar, G.; Cannon, L. S. <i>J. Am. Chem. Soc.</i> 1922 , <i>44</i> , 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 CuCl₂-HCl Solutions^a

$t/^\circ\text{C}$	$\frac{10^3[\text{Cu}^{2+}]}{\text{mol kg}^{-1}}$	$\frac{10^3[\text{H}^+]}{\text{mol kg}^{-1}}$	$\frac{10^3[\text{Cl}^-]_{\text{total}}}{\text{mol kg}^{-1}}$	$\frac{10^3m_1}{\text{mol kg}^{-1}}$
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 $\text{CuCl}_{(s)} + \text{AgCl}_{(s)} \rightleftharpoons \text{Cu}^{2+} + 2\text{Cl}^- + \text{Ag}_{(s)}$ in dilute aqueous HCl, approaching from both sides. Mixtures kept in dark amber bottles in thermostat at either 25 or 40°C ($\pm 0.02^\circ\text{C}$) 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: (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Nauchn. Trud. Giredmeta</i> <u>1974</u> , 62, 52-56.																																								
VARIABLES: Composition at 293 to 353 K	PREPARED BY: S. V. PETRENKO and E. KÖNIGSBERGER																																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility Isotherm of the System CuCl-CuCl₂-H₂O^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$t/^\circ\text{C}$</th> <th>$\rho_2/\text{g dm}^{-3}$</th> <th>$\rho_1/\text{g dm}^{-3}$</th> <th>Solid Phase</th> </tr> </thead> <tbody> <tr> <td rowspan="3">20</td> <td>593</td> <td>21.6</td> <td>CuCl</td> </tr> <tr> <td>621</td> <td>37.3</td> <td>CuCl</td> </tr> <tr> <td>652</td> <td>51.0</td> <td>CuCl</td> </tr> </tbody> </table> <p style="text-align: center;"><u>Solubility Isotherms of the System CuCl-CuCl₂-HCl-H₂O</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$t/^\circ\text{C}$</th> <th>$\rho_2/\text{g dm}^{-3}$</th> <th>$\rho_3/\text{g dm}^{-3}$</th> <th>$\rho_1/\text{g dm}^{-3}$</th> <th>Solid Phase</th> </tr> </thead> <tbody> <tr> <td rowspan="5">20</td> <td>150</td> <td>297.5</td> <td>232</td> <td>CuCl^b</td> </tr> <tr> <td>170</td> <td>273.0</td> <td>208</td> <td>CuCl^b</td> </tr> <tr> <td>194</td> <td>275.5</td> <td>191</td> <td>CuCl^b</td> </tr> <tr> <td>199</td> <td>258.9</td> <td>206</td> <td>CuCl^b</td> </tr> <tr> <td>212</td> <td>249.3</td> <td>176</td> <td>CuCl^b</td> </tr> </tbody> </table> <p style="text-align: right;">continued...</p>		$t/^\circ\text{C}$	$\rho_2/\text{g dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	Solid Phase	20	593	21.6	CuCl	621	37.3	CuCl	652	51.0	CuCl	$t/^\circ\text{C}$	$\rho_2/\text{g dm}^{-3}$	$\rho_3/\text{g dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	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
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METHOD/APPARATUS/PROCEDURE: Solubility studied with saturation method. CuCl ₂ , CuCl, H ₂ O 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. <i>Spravochnik po Rastvorimosty Solevyh Sistem</i> , T. III., Nauka, <u>1970</u> . 2. Mel'nik, P. M.; Morgart, R. M.; Vatamanyuk, V. I.; Podlesnyak, O. Z. <i>Khim. Prom.</i> <u>1972</u> , (7), 517.																																								

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Nauchn. Trud. Giredmeta</i> <u>1974</u> , 62, 52-56.
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EXPERIMENTAL VALUES:

(continued)

Solubility Isotherms of the System CuCl-CuCl₂-HCl-H₂O^c

$t/^{\circ}\text{C}$	$\rho_2/\text{g dm}^{-3}$	$\rho_3/\text{g dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Novikov, G. I.; Voropaev, L. E.; Rud'ko, P. K.; Zharskii, I. M. <i>Zh. Neorg. Khim.</i> <u>1979</u> , <i>24</i> , 811-813; <i>Russ J. Inorg. Chem. (Engl. Transl.)</i> <u>1979</u> , <i>24</i> , 452-454.																																																																																																																										
VARIABLES: Composition at 283 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																																																																																																										
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubilities in the System CuCl-CuCl₂-HCl-H₂O at 10°C</u></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th rowspan="2"></th> <th colspan="3">Composition of Solution</th> <th colspan="3">Composition of Solid</th> <th rowspan="2">Solid Phase</th> </tr> <tr> <th>100w_{3,initial}</th> <th>100w₂</th> <th>100w₁</th> <th>100w₃</th> <th>100w₂</th> <th>100w₁</th> </tr> </thead> <tbody> <tr> <td rowspan="7" style="text-align: center; vertical-align: middle;">2.5</td> <td>37.13</td> <td>0.00</td> <td>2.44</td> <td>-</td> <td>-</td> <td>-</td> <td>A</td> </tr> <tr> <td>36.95</td> <td>3.54</td> <td>2.42</td> <td>74.38</td> <td>0.87</td> <td>0.59</td> <td>A</td> </tr> <tr> <td>36.51</td> <td>4.78</td> <td>2.49</td> <td>69.75</td> <td>1.72</td> <td>0.57</td> <td>A</td> </tr> <tr> <td>36.18</td> <td>5.47</td> <td>2.46</td> <td>43.40</td> <td>37.56</td> <td>0.62</td> <td>A+B</td> </tr> <tr> <td>28.05</td> <td>4.83</td> <td>2.83</td> <td>6.52</td> <td>79.30</td> <td>0.65</td> <td>B</td> </tr> <tr> <td>16.19</td> <td>3.39</td> <td>3.10</td> <td>4.15</td> <td>81.23</td> <td>0.79</td> <td>B</td> </tr> <tr> <td>0.14</td> <td>2.26</td> <td>3.39</td> <td>2.48</td> <td>76.87</td> <td>0.82</td> <td>B</td> </tr> <tr> <td></td> <td>0.00</td> <td>0.66</td> <td>3.62</td> <td>-</td> <td>-</td> <td>-</td> <td>B</td> </tr> <tr> <td rowspan="7" style="text-align: center; vertical-align: middle;">10.0</td> <td>26.29</td> <td>0.00</td> <td>9.18</td> <td>-</td> <td>-</td> <td>-</td> <td>A</td> </tr> <tr> <td>26.28</td> <td>2.50</td> <td>9.06</td> <td>66.53</td> <td>1.65</td> <td>5.97</td> <td>A</td> </tr> <tr> <td>25.46</td> <td>5.91</td> <td>8.52</td> <td>70.13</td> <td>1.28</td> <td>1.79</td> <td>A</td> </tr> <tr> <td>25.98</td> <td>7.70</td> <td>8.23</td> <td>50.50</td> <td>32.72</td> <td>1.72</td> <td>A+B</td> </tr> <tr> <td>21.21</td> <td>7.37</td> <td>9.23</td> <td>7.05</td> <td>70.58</td> <td>3.06</td> <td>B</td> </tr> <tr> <td>11.87</td> <td>7.42</td> <td>10.48</td> <td>3.49</td> <td>72.50</td> <td>3.02</td> <td>B</td> </tr> <tr> <td>0.00</td> <td>7.20</td> <td>11.07</td> <td>-</td> <td>-</td> <td>-</td> <td>B</td> </tr> </tbody> </table> <p style="text-align: right;">continued...</p>			Composition of Solution			Composition of Solid			Solid Phase	100w _{3,initial}	100w ₂	100w ₁	100w ₃	100w ₂	100w ₁	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
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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																																																																																																																				
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. <i>Osnovy Analiticheskoi Khimii</i> , Izd. Khimiya, Moscow, <u>1970</u> , Part II, p. 326. 2. Mel'nik, P. M.; Morgart, R. M.; Vatamanyuk, V. I. <i>Khim. Prom.</i> <u>1972</u> , (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Novikov, G. I.; Voropaev, L. E.; Rud'ko, P. K.; Zharskii, I. M. <i>Zh. Neorg. Khim.</i> <u>1979</u> , <i>24</i> , 811-813; <i>Russ J. Inorg. Chem. (Engl. Transl.)</i> <u>1979</u> , <i>24</i> , 452-454.
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EXPERIMENTAL VALUES:

(continued)

	Composition of Solution			Composition of Solid			Solid Phase	
	100w _{3,initial}	100w ₂	100w ₁	100w ₂	100w ₁	100w ₃		
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: CuCl₂·2H₂O; B: CuCl.

The authors also give equations for mass percentages of CuCl (1) and CuCl₂ (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Zh. Prikl. Khim.</i> <u>1980</u> , <i>53</i> , 2202-2206; <i>Russ. J. Appl. Chem. (Engl. Transl.)</i> <u>1980</u> , <i>53</i> , 1654-1658.																																																																																													
VARIABLES: Composition at 293 to 353 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																																																																													
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<table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;">$t/^{\circ}\text{C}$</th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$\rho_2/\text{g dm}^{-3}$</th> <th style="text-align: center;">$\rho_3/\text{g dm}^{-3}$</th> <th style="text-align: center;">$\rho/\text{g cm}^{-3}$</th> </tr> </thead> <tbody> <tr> <td rowspan="8" style="text-align: center; vertical-align: middle;">20</td> <td style="text-align: center;">84.15</td> <td style="text-align: center;">545.1</td> <td style="text-align: center;">29.68</td> <td style="text-align: center;">1.42</td> </tr> <tr> <td style="text-align: center;">97.85</td> <td style="text-align: center;">480.97</td> <td style="text-align: center;">65.96</td> <td style="text-align: center;">1.41</td> </tr> <tr> <td style="text-align: center;">88.2</td> <td style="text-align: center;">414.0</td> <td style="text-align: center;">76.7</td> <td style="text-align: center;">1.37</td> </tr> <tr> <td style="text-align: center;">108.0</td> <td style="text-align: center;">372.0</td> <td style="text-align: center;">131.5</td> <td style="text-align: center;">1.39</td> </tr> <tr> <td style="text-align: center;">96.0</td> <td style="text-align: center;">367.0</td> <td style="text-align: center;">164.1</td> <td style="text-align: center;">1.40</td> </tr> <tr> <td style="text-align: center;">78.28</td> <td style="text-align: center;">351.9</td> <td style="text-align: center;">187.7</td> <td style="text-align: center;">1.40</td> </tr> <tr> <td style="text-align: center;">73.3</td> <td style="text-align: center;">329.0</td> <td style="text-align: center;">214.0</td> <td style="text-align: center;">1.40</td> </tr> <tr> <td style="text-align: center;">97.85</td> <td style="text-align: center;">332.1</td> <td style="text-align: center;">277.02</td> <td style="text-align: center;">1.45</td> </tr> <tr> <td rowspan="6" style="text-align: center; vertical-align: middle;">40</td> <td style="text-align: center;">144.0</td> <td style="text-align: center;">310.0</td> <td style="text-align: center;">307.0</td> <td style="text-align: center;">1.49</td> </tr> <tr> <td style="text-align: center;">88.07</td> <td style="text-align: center;">571.0</td> <td style="text-align: center;">51.12</td> <td style="text-align: center;">1.45</td> </tr> <tr> <td style="text-align: center;">137.0</td> <td style="text-align: center;">428.0</td> <td style="text-align: center;">146.76</td> <td style="text-align: center;">1.45</td> </tr> <tr> <td style="text-align: center;">113.0</td> <td style="text-align: center;">389.0</td> <td style="text-align: center;">160.0</td> <td style="text-align: center;">1.42</td> </tr> <tr> <td style="text-align: center;">96.2</td> <td style="text-align: center;">400.5</td> <td style="text-align: center;">206.0</td> <td style="text-align: center;">1.45</td> </tr> <tr> <td style="text-align: center;">166.32</td> <td style="text-align: center;">411.68</td> <td style="text-align: center;">344.97</td> <td style="text-align: center;">1.59</td> </tr> <tr> <td rowspan="4" style="text-align: center; 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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. <i>et al.</i> <i>Nauchn. Trud. Giredmeta</i> <u>1974</u> , <i>62</i> , 52.																																																																																													

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Zh. Prikl. Khim.</i> 1980 , <i>53</i> , 2202-2206; <i>Russ. J. Appl. Chem. (Engl. Transl.)</i> 1980 , <i>53</i> , 1654-1658.
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EXPERIMENTAL VALUES:

(continued)

Composition of Solutions Saturated with CuCl Only ($t = 20^{\circ}\text{C}$)

$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{\rho_3}{\text{g dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$	$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{\rho_3}{\text{g dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$
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-CuCl₂-H₂O
(Solid Phases: CuCl and CuCl₂)

$t/^{\circ}\text{C}$	$\rho_1/\text{g dm}^{-3}$	$\rho_2/\text{g dm}^{-3}$	$\rho/\text{g cm}^{-3}$
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-CuCl₂-HCl-H₂O
(Solid Phases: CuCl₂ and CuCl)

$t/^{\circ}\text{C}$	$\rho_1/\text{g dm}^{-3}$	$\rho_2/\text{g dm}^{-3}$	$\rho_3/\text{g dm}^{-3}$	$\rho/\text{g cm}^{-3}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J. <i>Afinidad</i> 1987 , <i>44</i> (408), 125-128.
VARIABLES: Composition at 293 to 323 K	PREPARED BY: E. KÖNIGSBERGER

EXPERIMENTAL VALUES:
Solubility of CuCl in HCl-HClO₄ Solutions of $I_c = 1.0, 1.5$ and 2.0 mol dm^{-3} ^a

c_2 mol dm ⁻³	$c_1/\text{mol dm}^{-3}$ at $t/^\circ\text{C}$ 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%

$$c_{\text{CuCl}}/c_{\text{HCl}} = 331 \exp(-2628 \text{ K}/T) + 1.36 \exp(-1109 \text{ K}/T) c_{\text{HCl}}/\text{mol dm}^{-3} \quad (4)$$

continued...

AUXILIARY INFORMATION
METHOD/APPARATUS/PROCEDURE:

All experiments were carried out in a 250 cm³ 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 FeCl₃ solution and the Fe(II) formed titrated with standard K₂Cr₂O₇ solution using barium diphenylaminosulfonate as an indicator.

SOURCE AND PURITY OF MATERIALS:

Not stated.

ESTIMATED ERROR:

Not stated.

REFERENCES:

- 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; HClO₄; [7601-90-3]
- (4) Copper(II) Chloride; CuCl₂; [7447-39-4]
- (5) Water; H₂O; [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-HClO₄-CuCl₂ solutions:

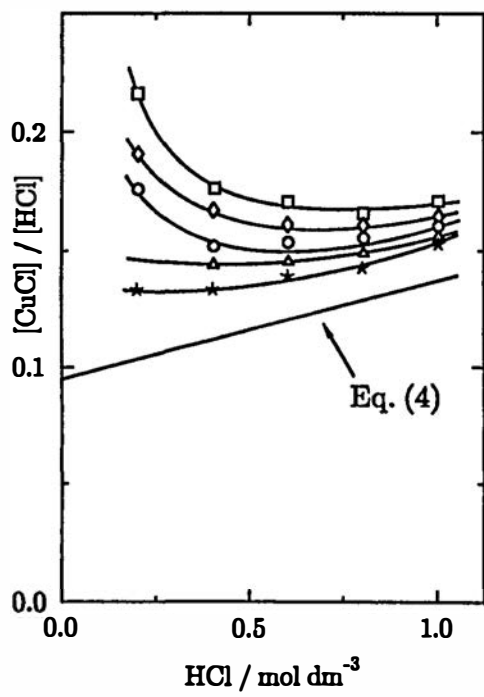


Figure 2

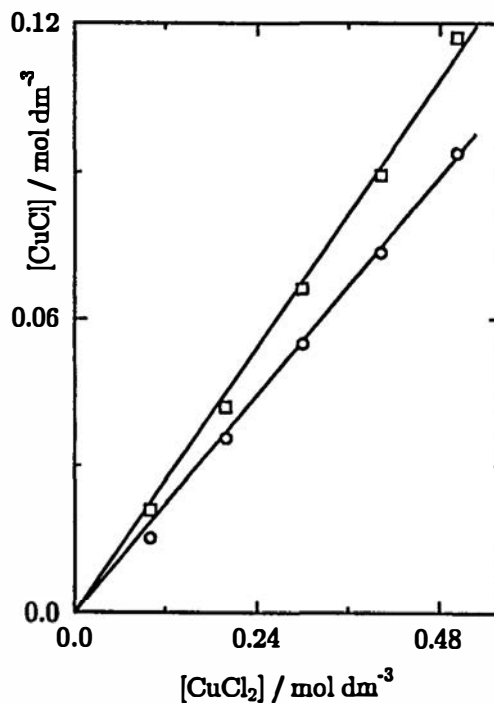


Figure 3

$$[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$$

$$t = 50^\circ\text{C}$$

$$\left. \begin{array}{l} \square \ 0.10 \\ \diamond \ 0.08 \\ \circ \ 0.06 \\ \triangle \ 0.04 \\ * \ 0.02 \end{array} \right\} \frac{[\text{CuCl}_2]}{\text{mol dm}^{-3}}$$

$$2 [\text{CuCl}_2] + [\text{HClO}_4] = 1.0 \text{ mol dm}^{-3}$$

$$\left. \begin{array}{l} \square \ 50 \\ \circ \ 40 \end{array} \right\} t/^\circ\text{C}$$

The following equation represents CuCl solubilities in HCl-CuCl₂ solutions of ionic strength 1.0 to 2.0 mol dm⁻³ in the temperature range of 20 to 50°C within 10%:

$$c_{\text{CuCl}}/\text{mol dm}^{-3} = 331 \exp(-2628 \text{ K}/T) c_{\text{HCl}}/\text{mol dm}^{-3} \\ + 1.36 \exp(-1109 \text{ K}/T) (c_{\text{HCl}}/\text{mol dm}^{-3})^2 \\ + 119.6 \exp(-2008 \text{ K}/T) c_{\text{CuCl}_2}/\text{mol dm}^{-3}$$

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Sodium Sulfate; Na ₂ SO ₄ ; [7757-82-6] (4) Copper(II) Chloride; CuCl ₂ ; [7447-39-4] (5) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Khim.-Tekh. Inst.</i> <u>1964</u> , 47, 111-114.																																																																																																								
VARIABLES: Composition at 293 to 363 K	PREPARED BY: J. J. FRITZ																																																																																																								
EXPERIMENTAL VALUES: <u>Solubility of CuCl in Aqueous NaCl</u> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;"><i>t</i>/°C</th> <th style="text-align: left;">100<i>w</i>₂</th> <th style="text-align: left;"><i>m</i>₂/mol kg^{-1 a}</th> <th style="text-align: left;">100<i>w</i>₁</th> <th style="text-align: left;"><i>m</i>₁/mol kg^{-1 a}</th> </tr> </thead> <tbody> <tr> <td rowspan="4">20</td> <td>3.96</td> <td>0.708</td> <td>0.41</td> <td>0.043</td> </tr> <tr> <td>4.04</td> <td>0.724</td> <td>0.45</td> <td>0.048</td> </tr> <tr> <td>15.10</td> <td>3.25</td> <td>5.44</td> <td>0.691</td> </tr> <tr> <td>15.30</td> <td>3.30</td> <td>5.48</td> <td>0.699</td> </tr> <tr> <td rowspan="12">30</td> <td>5.35</td> <td>0.977</td> <td>0.95</td> <td>0.102</td> </tr> <tr> <td>5.40</td> <td>0.988</td> <td>1.07</td> <td>0.116</td> </tr> <tr> <td>10.00</td> <td>1.958</td> <td>2.60</td> <td>0.300</td> </tr> <tr> <td>10.12</td> <td>1.984</td> <td>2.62</td> <td>0.303</td> </tr> <tr> <td>15.80</td> <td>3.47</td> <td>6.24</td> <td>0.808</td> </tr> <tr> <td>16.72</td> <td>3.71</td> <td>6.24</td> <td>0.818</td> </tr> <tr> <td>22.00</td> <td>5.94</td> <td>14.61</td> <td>2.328</td> </tr> <tr> <td>22.60</td> <td>6.16</td> <td>14.62</td> <td>2.352</td> </tr> <tr> <td>22.60</td> <td>6.16</td> <td>14.66</td> <td>2.360</td> </tr> <tr> <td>23.00</td> <td>6.31</td> <td>14.64</td> <td>2.371</td> </tr> <tr> <td>23.30</td> <td>6.58</td> <td>16.11</td> <td>2.685</td> </tr> <tr> <td>24.60</td> <td>7.37</td> <td>18.31</td> <td>3.239</td> </tr> <tr> <td rowspan="8">50</td> <td>5.70</td> <td>1.051</td> <td>1.52</td> <td>0.165</td> </tr> <tr> <td>5.70</td> <td>1.056</td> <td>1.91</td> <td>0.209</td> </tr> <tr> <td>10.00</td> <td>1.993</td> <td>4.15</td> <td>0.488</td> </tr> <tr> <td>10.20</td> <td>2.029</td> <td>3.78</td> <td>0.444</td> </tr> <tr> <td>15.70</td> <td>3.51</td> <td>7.85</td> <td>1.037</td> </tr> <tr> <td>15.70</td> <td>3.52</td> <td>7.96</td> <td>1.053</td> </tr> <tr> <td>22.70</td> <td>6.45</td> <td>17.09</td> <td>2.866</td> </tr> <tr> <td>23.00</td> <td>6.54</td> <td>16.80</td> <td>2.818</td> </tr> </tbody> </table> <p style="text-align: right;">continued...</p>		<i>t</i> /°C	100 <i>w</i> ₂	<i>m</i> ₂ /mol kg ^{-1 a}	100 <i>w</i> ₁	<i>m</i> 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
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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 ₂ SO ₄ ; [7757-82-6] (4) Copper(II) Chloride; CuCl ₂ ; [7447-39-4] (5) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Khim.-Tekh. Inst.</i> <u>1964</u> , <i>47</i> , 111-114.
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EXPERIMENTAL VALUES:

(continued)

$t/^{\circ}\text{C}$	$100w_2$	$m_2/\text{mol kg}^{-1\text{ a}}$	$100w_1$	$m_1/\text{mol kg}^{-1\text{ a}}$
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
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-CuCl₂ Solutions at 80°C

$100w_2$	$m_2/\text{mol kg}^{-1\text{ a}}$	$100w_4$	$m_4/\text{mol kg}^{-1\text{ a}}$	$100w_1$	$m_1/\text{mol kg}^{-1\text{ a}}$
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 ₂ SO ₄ ; [7757-82-6] (4) Copper(II) Chloride; CuCl ₂ ; [7447-39-4] (5) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Sin, G. N.; Shokin, I. N.; Kuznetsova, A. G. <i>Tr. Mosk. Khim.-Tekh. Inst.</i> 1964 , <i>47</i> , 111-114.
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EXPERIMENTAL VALUES:

(continued)

Solubility of CuCl in NaCl-Na₂SO₄ Solutions at 20°C

$100w_2$	$m_2/\text{mol kg}^{-1 \text{ a}}$	$100w_3$	$m_3/\text{mol kg}^{-1 \text{ a}}$	$100w_1$	$m_1/\text{mol kg}^{-1 \text{ a}}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Zh. Prikl. Khim.</i> 1978 , <i>51</i> , 1015-1019; <i>Russ. J. Appl. Chem. (Engl. Transl.)</i> 1978 , <i>51</i> , 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

$\rho_3/\text{g dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	$\rho_2/\text{g dm}^{-3}$	$\rho/\text{g cm}^{-3}$
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

$\rho_3/\text{g dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	$\rho_2/\text{g dm}^{-3}$	$\rho/\text{g cm}^{-3}$
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: (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Pochtarev, A. N.; Petrova, I. Yu.; Kozhemyakin, V. A. <i>Zh. Prikl. Khim.</i> <u>1978</u> , <i>51</i> , 1015-1019; <i>Russ. J. Appl. Chem. (Engl. Transl.)</i> <u>1978</u> , <i>51</i> , 977-980.
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EXPERIMENTAL VALUES:

(continued)

Composition of Solutions Saturated with CuCl_(s) at 26.5°C

Section	app. ρ_3/ρ_2	$\rho_3/\text{g dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	$\rho_2/\text{g dm}^{-3}$	$\rho/\text{g cm}^{-3}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Bodländer, G.; Storbeck, O. <i>Z. Anorg. Chem.</i> <u>1902</u> , 31, 1-41.																																																																
VARIABLES: Concentration of KCl at 289 to 293 K	PREPARED BY: J. J. FRITZ																																																																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous KCl</u></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: left;"><u>T/K</u></th> <th style="text-align: left;"><u>10³ c₂/mol dm⁻³</u></th> <th style="text-align: left;"><u>10³ [Cu²⁺]/mol dm⁻³</u></th> <th style="text-align: left;"><u>10³ c₁/mol dm⁻³</u></th> </tr> </thead> <tbody> <tr><td>293</td><td>0</td><td>2.222</td><td>0.629</td></tr> <tr><td>292</td><td>1</td><td>1.901</td><td>0.484</td></tr> <tr><td>292</td><td>2</td><td>1.571</td><td>0.589</td></tr> <tr><td>292</td><td>2.5</td><td>1.421</td><td>0.534</td></tr> <tr><td>292</td><td>3</td><td>1.523</td><td>0.460</td></tr> <tr><td>289</td><td>5</td><td>1.008</td><td>0.514</td></tr> <tr><td>291</td><td>10</td><td>0.475</td><td>0.761</td></tr> <tr><td>293</td><td>15</td><td>0.322</td><td>1.022</td></tr> <tr><td>292</td><td>20</td><td>0.324</td><td>1.122</td></tr> <tr><td>292</td><td>30</td><td>0.1308</td><td>1.630</td></tr> <tr><td>291</td><td>50</td><td>0.1088</td><td>2.302</td></tr> <tr><td>289</td><td>100</td><td>0</td><td>4.702</td></tr> <tr><td>289</td><td>200</td><td>0</td><td>9.485</td></tr> <tr><td>292</td><td>1000</td><td>0</td><td>97.0</td></tr> <tr><td>289</td><td>2000</td><td>0</td><td>384.0</td></tr> </tbody> </table> <p>Note: Cu²⁺ (and metallic copper) formed by disproportionation of Cu⁺ at low chloride concentrations.</p>		<u>T/K</u>	<u>10³ c₂/mol dm⁻³</u>	<u>10³ [Cu²⁺]/mol dm⁻³</u>	<u>10³ c₁/mol dm⁻³</u>	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
<u>T/K</u>	<u>10³ c₂/mol dm⁻³</u>	<u>10³ [Cu²⁺]/mol dm⁻³</u>	<u>10³ c₁/mol dm⁻³</u>																																																														
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Camacho Rubio, F.; Paez Dueñas, M. P.; Moreno Carretero, J. <i>An. Quim.</i> <u>1985</u> , A81, 121-128.
VARIABLES: Composition at 293 to 323 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous Mixtures</u></p> <p>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.</p> <p>Fig. 1. Solubility in aqueous HCl at 298 K vs. concentration of HCl.</p> <p>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.</p> <p>Fig. 6. S/C vs. chloride concentration for four NaCl-HCl mixtures of ionic strength 2 mol dm⁻³ at 303 K.</p> <p>Fig. 7. S/C vs. chloride concentration for equimolar NaCl-HCl mixtures of 4 different ionic strengths at 303 K.</p> <p>Fig. 10. S/C vs. total chloride concentration for four CuCl₂-HCl mixtures of ionic strength 2 mol dm⁻³ at 303 K.</p> <p>Fig. 11. S/C vs. HCl concentration along for the same mixtures as in Fig. 10.</p> <p style="text-align: right;">continued...</p>	
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 ₂ Cr ₂ O 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. <i>Ind. Eng. Chem. Anal. Ed.</i> <u>1946</u> , 18, 136.

COMPONENTS:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
- (2) Sodium Chloride; NaCl; [7647-14-5]
- (3) Sodium Perchlorate; NaClO₄; [7601-89-0]
- (4) Copper(II) Chloride; CuCl₂; [7447-39-4]
- (5) Hydrogen Chloride; HCl; [7647-01-0]
- (6) Hydrogen Perchlorate; HClO₄; [7601-90-3]
- (7) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.;
Moreno Carretero, J.
An. Quim. **1985**, *A81*, 121-128.

EXPERIMENTAL VALUES:

(continued)

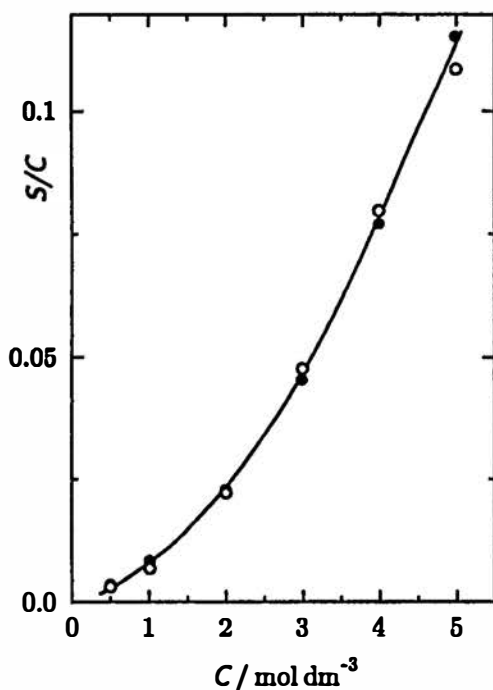


Figure 1

Solubility in HCl Solutions

 $t = 25^{\circ}\text{C}$

- Hikita *et al.* (1973)
- This work

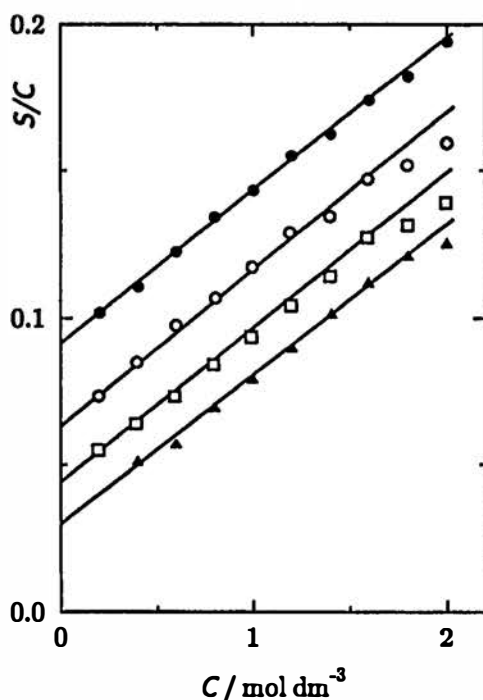


Figure 4

 $I = 2 \text{ mol dm}^{-3}$ $[\text{Na}^+]/[\text{H}^+] = 1$

- ▲ 20
 - 30
 - 40
 - 50
- } $t/^{\circ}\text{C}$

continued ...

COMPONENTS:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
- (2) Sodium Chloride; NaCl; [7647-14-5]
- (3) Sodium Perchlorate; NaClO₄; [7601-89-0]
- (4) Copper(II) Chloride; CuCl₂; [7447-39-4]
- (5) Hydrogen Chloride; HCl; [7647-01-0]
- (6) Hydrogen Perchlorate; HClO₄; [7601-90-3]
- (7) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.;
Moreno Carretero, J.
An. Quim. **1985**, *A81*, 121-128.

EXPERIMENTAL VALUES:

(continued)

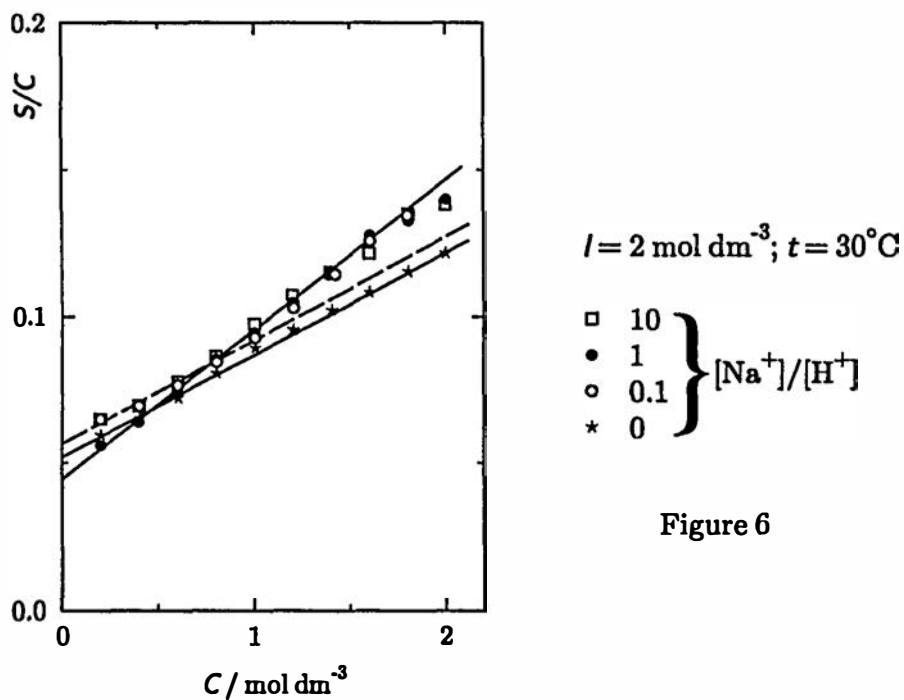


Figure 6

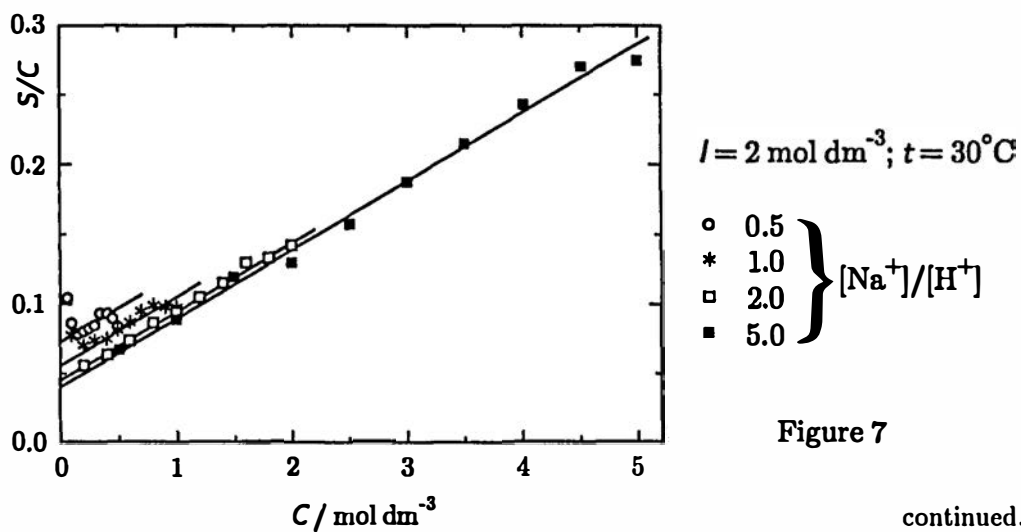


Figure 7

continued...

COMPONENTS:

- (1) Copper(I) Chloride; CuCl; [7758-89-6]
- (2) Sodium Chloride; NaCl; [7647-14-5]
- (3) Sodium Perchlorate; NaClO₄; [7601-89-0]
- (4) Copper(II) Chloride; CuCl₂; [7447-39-4]
- (5) Hydrogen Chloride; HCl; [7647-01-0]
- (6) Hydrogen Perchlorate; HClO₄; [7601-90-3]
- (7) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Camacho Rubio, F.; Paez Dueñas, M. P.;
Moreno Carretero, J.
An. Quim. **1985**, *A81*, 121-128.

EXPERIMENTAL VALUES:

(continued)

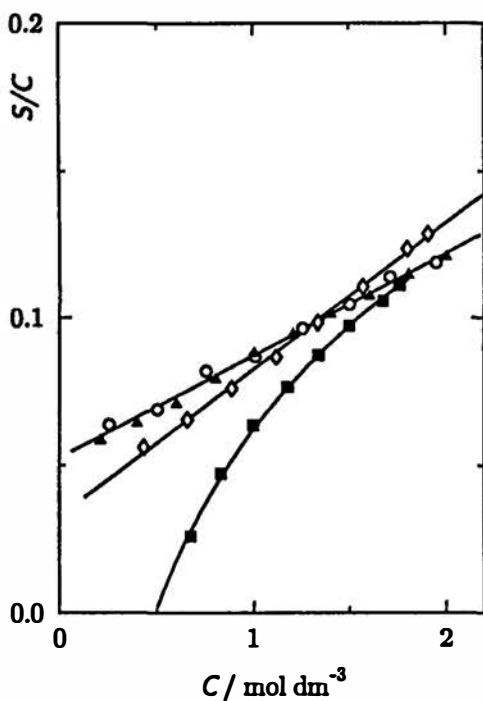


Figure 10

$$I = 2 \text{ mol dm}^{-3}; t = 30^\circ\text{C}$$

$$[\text{Na}^+]/[\text{H}^+] = 0$$

○ 0.00	}	[Cu(II)]
▲ 0.05		
◇ 0.10		
■ 0.25		
		mol dm ⁻³

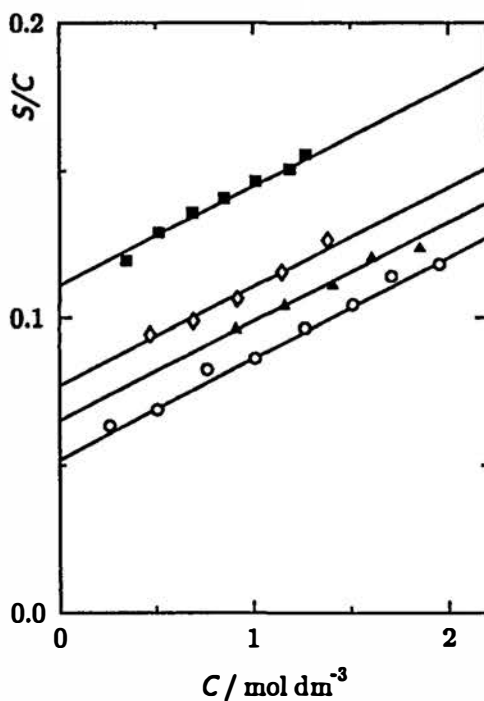


Figure 11

$$I = 2 \text{ mol dm}^{-3}; t = 30^\circ\text{C}$$

$$[\text{Na}^+]/[\text{H}^+] = 0$$

■ 0.25	}	[Cu(II)]
◇ 0.10		
▲ 0.05		
○ 0.00		
		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 ₂ O; [7732-18-5]		ORIGINAL MEASUREMENTS: Berger, J. M.; Winand, R. <i>Hydrometallurgy</i> <u>1984</u> , 12 (1), 61-81.					
VARIABLES: Composition at 298, 303 and 363 K		PREPARED BY: J. J. FRITZ					
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubilities in the System CuCl-NaCl-FeCl₂-ZnCl₂-HCl-H₂O</u></p>							
<i>t</i> /°C	Solid Phase	$\frac{m_2}{\text{mol kg}^{-1}}$	$\frac{m_5}{\text{mol kg}^{-1}}$	$\frac{m_3}{\text{mol kg}^{-1}}$	$\frac{m_4}{\text{mol kg}^{-1}}$	$\frac{m_1}{\text{mol kg}^{-1}}$	$\frac{\rho}{\text{kg m}^{-3}}$
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 reagents of Riedel-de Haen trade mark; purity not specified.			
				ESTIMATED ERROR:			
				REFERENCES:			

COMPONENTS:		ORIGINAL MEASUREMENTS:					
(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 ₂ O; [7732-18-5]		Berger, J. M.; Winand, R. <i>Hydrometallurgy</i> 1984 , <i>12</i> (1), 61-81.					
EXPERIMENTAL VALUES:							
(continued)							
$t/^\circ\text{C}$	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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Winter, D. G.; Covington, J. W.; Muir, D. M. <i>Chloride Electrometall., Proc. Symp. 1982,</i> 167-188.																																																																																																																													
VARIABLES: Composition at 293 to 343 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																																																																																																													
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Aqueous Mixtures at 50°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$\frac{c_2}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_3}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_4}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_5}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr><td></td><td></td><td></td><td>4.0</td><td>1.90</td></tr> <tr><td>1.0</td><td></td><td></td><td>4.0</td><td>1.62</td></tr> <tr><td>1.0</td><td></td><td></td><td>4.0</td><td>1.61</td></tr> <tr><td>1.5</td><td></td><td></td><td>4.0</td><td>1.80</td></tr> <tr><td>2.0</td><td></td><td></td><td>3.0</td><td>1.75</td></tr> <tr><td>2.0</td><td>1.0</td><td></td><td>1.0</td><td>1.53</td></tr> <tr><td>2.0</td><td>1.0</td><td></td><td>2.0</td><td>1.96</td></tr> <tr><td>2.0</td><td>1.0</td><td>1.0</td><td>1.0</td><td>1.76</td></tr> <tr><td>2.0</td><td>1.0</td><td>1.0</td><td>2.0</td><td>1.99</td></tr> <tr><td>3.0</td><td></td><td></td><td>2.0</td><td>1.86</td></tr> <tr><td>3.0</td><td></td><td></td><td>2.0</td><td>1.83</td></tr> <tr><td>3.0</td><td>1.0</td><td></td><td></td><td>1.59</td></tr> <tr><td>3.0</td><td>1.0</td><td></td><td>1.0</td><td>2.14</td></tr> <tr><td>3.0</td><td>1.0</td><td></td><td>2.0</td><td>2.40</td></tr> <tr><td>3.0</td><td>1.0</td><td></td><td></td><td>1.59</td></tr> <tr><td>3.0</td><td>2.0</td><td></td><td></td><td>2.40</td></tr> <tr><td>4.0</td><td></td><td></td><td>0.5</td><td>1.62</td></tr> <tr><td>4.0</td><td></td><td></td><td>1.0</td><td>1.92</td></tr> <tr><td>4.0</td><td></td><td></td><td>1.0</td><td>1.93</td></tr> <tr><td>4.0</td><td></td><td></td><td>2.0</td><td>1.83</td></tr> <tr><td>4.0</td><td>1.0</td><td></td><td></td><td>2.16</td></tr> <tr><td>4.0</td><td>2.0</td><td></td><td></td><td>2.84</td></tr> <tr><td>5.0</td><td></td><td></td><td></td><td>2.30</td></tr> <tr><td>5.0</td><td>1.0</td><td></td><td></td><td>3.00</td></tr> </tbody> </table> <p style="text-align: right;">continued...</p>		$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_4}{\text{mol dm}^{-3}}$	$\frac{c_5}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$				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
$\frac{c_2}{\text{mol dm}^{-3}}$	$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_4}{\text{mol dm}^{-3}}$	$\frac{c_5}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$																																																																																																																										
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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]
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- (4) Copper(II) Chloride; CuCl₂; [7447-39-4]
- (5) Hydrogen Chloride; HCl; [7647-01-0]
- (6) Water; H₂O; [7732-18-5]

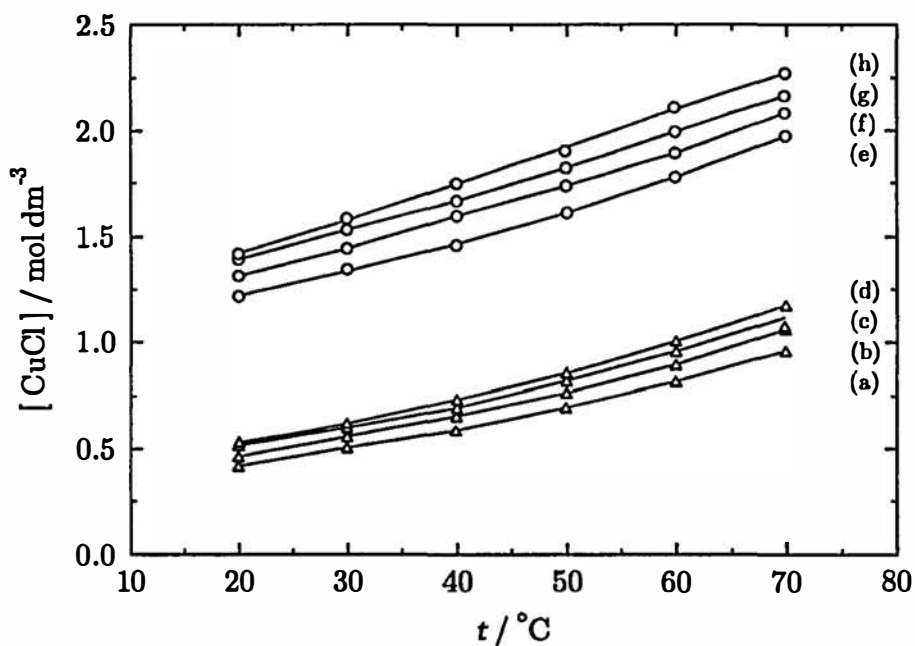
ORIGINAL MEASUREMENTS:

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

^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 ₃ H ₆ O; [107-18-6] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kepner, R. E.; Andrews, L. J. <i>J. Org. Chem.</i> 1948 , <i>13</i> , 208-213.																																																			
VARIABLES: Concentrations of HCl and allyl alcohol at 298 K	PREPARED BY: J. J. FRITZ																																																			
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VARIABLES: Composition at 298 K	PREPARED BY: J. J. FRITZ
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<u>Solubility of CuCl in Aqueous γ, γ-Dimethylallyl Alcohol at 25°C</u>			
$c_4/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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
<u>Solubility of CuCl in Aqueous β-Chloroallyl Alcohol at 25°C</u>			
$c_5/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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.
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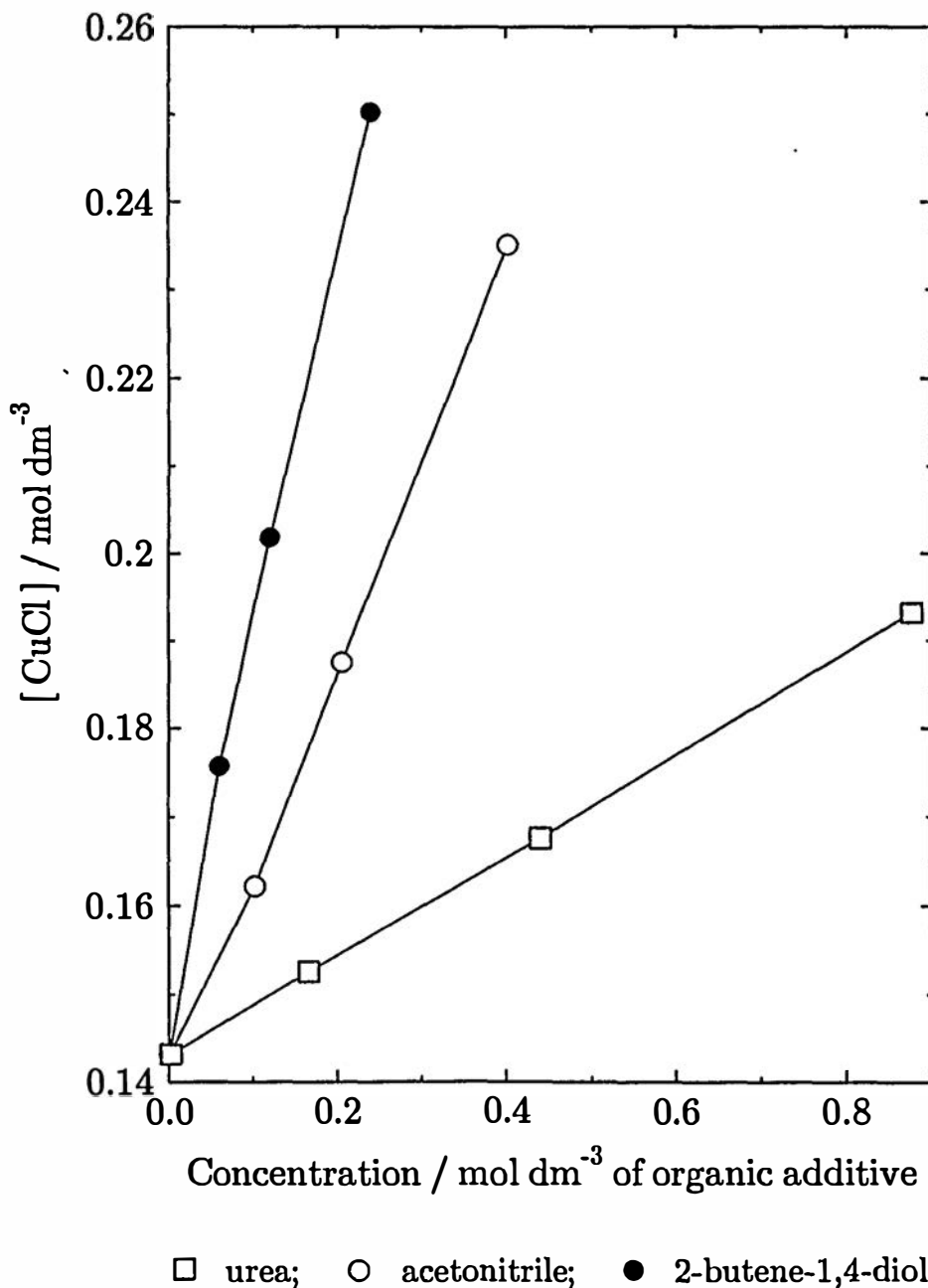
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- (5) Water; H₂O; [7732-18-5]

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Flerov, V. N.
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EXPERIMENTAL VALUES:

(continued)



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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
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CRITICAL EVALUATION:
BINARY SYSTEMS

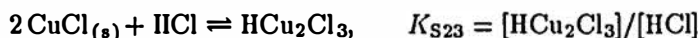
Only a few sets of data are available for the solubility of CuCl in organic solvents. Heines and Yntema¹ report the solubility in dioxane as 0.031 g cm⁻³ solution (0.31 mol dm⁻³) at 300 K. Naumann and Schier² and Pleshkov³ reported the solubility in acetonitrile. Naumann and Schier² gave 11.76 g CuCl per 100 g saturated solution (1.35 mol kg⁻¹) at 291 K. Pleshkov³ 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 [(CH₃)₂SO₂] at 400 K as 10^{-12.7} (2 · 10⁻¹³) mol² 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 · 10⁻⁷ mol kg⁻¹ in the molten dimethyl sulfone.

TERNARY SYSTEMS
CuCl-HCl-Ethanol

In 1934 Chang and Liu⁵ 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 Cha⁶ in a similar investigation of the system CuCl-HCl-H₂O.

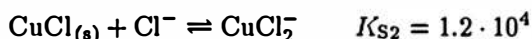
Their data can be fitted following the equation



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 HCuCl₂ 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 CuCl₂⁻ in molten dimethyl sulfone [(C₂H₅)₄NCl] at 400 K, using chloride ion between 0.008 and 0.7 mol kg⁻¹ supplied by tetraethylammonium chloride [(C₂H₅)₄NCl]. They give a value of 10^{16.8} (6.3 · 10¹⁶) mol⁻² kg². 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.*:



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: <u>CuCl-KSeCN-Acetone</u> 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 $\text{CuCl}_{(s)} + \text{SeCN}^- \rightleftharpoons \text{Cu}(\text{SeCN})\text{Cl}^-, \quad K = [\text{Cu}(\text{SeCN})\text{Cl}^-]/[\text{Cl}^-]$ 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. <p style="text-align: center;">REFERENCES</p> <ol style="list-style-type: none"> 1. Heines, V.; Yntema, L. F. <i>Trans. Kentucky Acad. Sci.</i> <u>1938</u>, 7, 85. 2. Naumann, A.; Schier, A. <i>Ber. Dtsch. Chem. Ges.</i> <u>1914</u>, 47, 247. 3. Pleshkov, V. A. <i>Zh. Fiz. Khim.</i> <u>1948</u>, 22, 351. 4. Machtinger, M.; Vuaille, M. J.; Tremillon, B. <i>J. Electroanal. Chem. Interfacial Electrochem.</i> <u>1977</u>, 83, 273. 5. Chang, K. S.; Liu, Y.-M. <i>J. Chin. Chem. Soc.</i> <u>1934</u>, 2, 307. 6. Chang, K. S.; Cha, Y.-T. <i>J. Chin. Chem. Soc.</i> <u>1934</u>, 2, 293. 7. Golub, A. M.; Skopenko, V. V. <i>Zh. Neorg. Khim.</i> <u>1960</u>, 5, 1973; <i>Russ J. Inorg. Chem. (Engl. Trans.)</i> <u>1960</u>, 5, 961. 	

COMPONENTS: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Hydrogen Chloride; HCl; [7647-01-0] (3) Ethanol; C ₂ H ₆ O; [64-17-5]	ORIGINAL MEASUREMENTS: Chang, K. S.; Liu, Y.-M. <i>J. Chin. Chem. Soc.</i> <u>1934</u> , 2, 307-310.																										
VARIABLES: Concentration of HCl at 298 K	PREPARED BY: J. J. FRITZ																										
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Ethanolic HCl Solutions at 25°C</u></p> <table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <thead> <tr> <th style="border-top: 1px solid black; border-bottom: 1px solid black;">$c_2/\text{mol dm}^{-3}$</th> <th style="border-top: 1px solid black; border-bottom: 1px solid black;">$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.07839</td><td>0.06078</td></tr> <tr><td>0.1524</td><td>0.1281</td></tr> <tr><td>0.2775</td><td>0.2336</td></tr> <tr><td>0.3223</td><td>0.2766</td></tr> <tr><td>0.3953</td><td>0.3338</td></tr> <tr><td>0.4304</td><td>0.3660</td></tr> <tr><td>0.4356</td><td>0.3660</td></tr> <tr><td>0.4676</td><td>0.4035</td></tr> <tr><td>0.5368</td><td>0.4663</td></tr> <tr><td>0.6108</td><td>0.5230</td></tr> <tr><td>0.6479</td><td>0.5538</td></tr> <tr><td>0.7254</td><td>0.6299</td></tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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: (1) Copper(I) Chloride; CuCl; [7758-89-6] (2) Potassium Selenocyanate; KSeCN; [3425-46-5] (3) Acetone; C ₂ H ₆ O; [67-64-1]	ORIGINAL MEASUREMENTS: Golub, A. M.; Skopenko, V. V. <i>Zh. Neorg. Khim.</i> 1960 , <i>5</i> , 1973; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1960 , <i>5</i> , 961-963.														
VARIABLES: Concentration of KSeCN at unspecified temperature (probably 293 K)	PREPARED BY: J. J. FRITZ														
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCl in Acetone Solution of KSeCN</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$c_2/\text{mol dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.51</td><td style="text-align: center;">0.0980</td></tr> <tr><td style="text-align: center;">0.55</td><td style="text-align: center;">0.1050</td></tr> <tr><td style="text-align: center;">0.59</td><td style="text-align: center;">0.1171</td></tr> <tr><td style="text-align: center;">0.61</td><td style="text-align: center;">0.1227</td></tr> <tr><td style="text-align: center;">0.81</td><td style="text-align: center;">0.1520</td></tr> <tr><td style="text-align: center;">0.86</td><td style="text-align: center;">0.1621</td></tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	0.51	0.0980	0.55	0.1050	0.59	0.1171	0.61	0.1227	0.81	0.1520	0.86	0.1621
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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. <i>Nauchn. Dokl. Vys. Shkoly, Khim. Khim. Tekhnol.</i> 1958 , <i>III (4)</i> , 685. 2. Karyakin, Yu. V.; Angelov, I. I. <i>Pure Chemical Reagents</i> , 1955 , p. 345.														

COMPONENTS: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:**THE BINARY SYSTEM**

There are only a few data on the solubility of cuprous bromide in pure water. In 1902, Bodländer and Storbeck¹ gave a value of $4.15 \cdot 10^{-8} \text{ mol dm}^{-3}$, presumably at about 293 K. This value was quoted in 1931 by Kolthoff and Furman². 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 500³ (1952) yields a value of $5.8 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$. Zhuk⁴ (1954) quotes a value of $5.3 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$, and Chaltykyan⁶ (1966) reported it without giving any source of information. Latimer⁵ (1952) gives a value of $5.9 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ 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 $(5.5 \pm 0.5) \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ 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 CuBr⁰ and the reaction $2\text{CuBr}_{(s)} \rightleftharpoons \text{Cu}^+ + \text{CuBr}_2^-$. Finally Ahrlund and Tagesson⁸ obtained a value of $(1.3 \pm 0.06) \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ at 298 K in $5.0 \text{ mol dm}^{-3} \text{ NaClO}_4$.

Gavrish and Galinker⁹ 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, $\ln(m_{\text{CuBr}}/\text{mol kg}^{-1})$, 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

$$\ln(m_{\text{CuBr}}/\text{mol kg}^{-1}) = -4457 \text{ K}/T + 7.605$$

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-H₂O**

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 Storbeck¹, who measured the solubility at a temperature of $292 \pm 1 \text{ K}$ for seven concentrations of KBr from 0.025 to $0.500 \text{ mol dm}^{-3}$; at concentrations below 0.1 mol dm^{-3} , their solutions contained minor amounts of Cu²⁺ 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 Wilke¹¹ 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 Malik¹² 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 Luzik¹³ 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 KNO₃.

The data of Bodländer and Storbeck¹ and those of Fritz and Luzik¹³ can be represented to a few per cent by a model using equilibrium constants for the formation of complexes and

COMPONENTS:

- (1) Copper(I) Bromide; CuBr; [7787-70-4]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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 Luzik¹³ to a standard deviation of 3 per cent and those of Bodländer and Storbeck¹ 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 an approximate idea of the solubility of CuBr in aqueous KBr at 323 K. The data of Khan and Malik¹² 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 Wilke¹¹ 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 Luzik¹³ are recommended for use at 298 K, with an estimated uncertainty of 3 per cent, and those of Bodländer and Storbeck¹ 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–H₂O

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 Caldwell¹⁴ 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 NaNO₃. In 1968 Wilke¹¹ 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 Tagesson⁸ 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 NaClO₄ with 0.1 mol dm⁻³ of HClO₄ present.

Of the three sets of data, those of Peters and Caldwell¹⁴ 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 Tagesson⁸ 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 NaClO₄). The solubility values given by Wilke¹¹ were low by at least a factor of 10 and have been Rejected.

CuBr–HBr–H₂O

The only data reported for the solubility of CuBr in aqueous HBr are those of Wilke¹¹ (1968) and those of Khan and Malik¹² (1970). Wilke¹¹ gave the solubility for one concentration of HBr at four temperatures (298, 308, 318 and 328 K). Khan and Malik¹² 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 Wilke¹² are exceedingly low and have also been Rejected.

COMPONENTS: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:
CuBr-MgBr₂-H₂O

The only data reported for the solubility of CuBr in aqueous MgBr₂ are those of Khan and Malik¹² (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

Wilke¹¹ reported values for the solubility of CuBr in aqueous LiBr and aqueous NiI₄Br 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·2KBr, CuBr·3KBr and CuBr·4KBr were formed at 323 K in their solubility study of the system CuBr-KBr-H₂O, 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 Hurlburt¹⁵ prepared the double salts CuBr·2NiI₄Br and CuBr·NH₄Br·H₂O. The crystal structure of the first of these was determined by Brink and van Arkel¹⁶. Mellor¹⁷ discusses a variety of early work on compounds containing CuBr combined with ammonia. In a series of papers, Harris¹⁸⁻²⁰ reported a number of compounds involving CuBr with ammoniacal ligands, as follows: (a) 3 mixed compounds containing both CuBr and CuBr₂, *viz.* Cu(NH₃)₄Br₂·CuBr, Cu(en)₂Br₂·CuBr and Cu(en)₂Br₂·CuBr·2.5H₂O (en = ethylene diamine); (b) 3 compounds containing CuBr and CuI, *viz.* [Cu^{II}(NH₃)₄][Cu^IBr]₂, [Cu^{II}(en)₂][Cu^IBr]₂, and pyridinium bromiodocuprate [C₅H₅NH][CuBr]. In all cases the compounds were verified by chemical analysis. Rosenheim and Steinhauser²¹ prepared the salt CuBr·NiI₄Br·(NH₄)₂S₂O₃. They verified its composition by chemical analysis and described its crystal structure. Canneri and Luchini²² prepared CuBr·Cu₂S₂O₃·9Na₂S₂O₃, verifying the composition by chemical analysis.

Gilliland *et al.*²³ prepared the compound CuBr·C₂H₄ and measured its (large) vapor pressure between 273 and 290 K. Somewhat later Gilliland and coworkers²⁴ prepared CuBr·C₄H₆ and CuBr·C₂H₂ 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 thio-sulfates, 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 CuBr⁰, CuBr₂⁻, CuBr₃²⁻ and Cu₃Br₆³⁻. Virial parameters for the ion pairs Na⁺-Br⁻, K⁺-Br⁻ and K⁺-NO₃⁻ were taken from Pitzer and Mayorga²⁵, 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: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Luzik¹³ to 3 per cent (r.m.s.) and those of Bodländer and Storbeck¹ 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 Caldwell¹⁴ 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	$\frac{K_{S_{mn}}}{(\text{mol dm}^{-3})^{(1-m-n)}}$	$\frac{\Delta_r H^\ominus}{\text{kJ mol}^{-1}}$
CuBr ⁰	$1.8 \cdot 10^{-5}$	-
CuBr ₂ ⁻	0.00389	32.1
CuBr ₃ ²⁻	0.01429	22.0
Cu ₃ Br ₆ ³⁻	$3.21 \cdot 10^{-4}$	43.9

^a The equilibrium constants, $K_{S_{mn}}$, and enthalpies of reaction, $\Delta_r H^\ominus$, are for the reactions $m \text{ CuBr}_{(s)} + (n - m) \text{ Br}^- \rightleftharpoons \text{Cu}_m \text{ Br}_n^{m-n}$ with standard state in mol dm⁻³.

Table 24. Virial Parameters for Ion Pairs of Bromide Species with K⁺ and Na⁺ at 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 ₃ Br 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 Latimer⁵ for CuBr₂⁻ at 298.15 K, zero ionic strength (obviously based on K_{S0} and β_2 of Bodländer and Storbeck¹), and a set of values given for CuBr⁰, CuBr₂⁻ and CuBr₃²⁻ given by Peters and Caldwell¹⁴ 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 Tagesson⁸ 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 $c_{\text{CuBr}}/c_{\text{KBr}}$ is given to facilitate

COMPONENTS: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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

$\frac{c_{\text{KBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{c_{\text{KBr}}}$	$\frac{c_{\text{KBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{c_{\text{KBr}}}$
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 Caldwell¹⁴ 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

$\frac{c_{\text{NaBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{c_{\text{NaBr}}}$	$\frac{c_{\text{NaBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{\text{mol dm}^{-3}}$	$\frac{c_{\text{CuBr}}}{c_{\text{NaBr}}}$
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:

- (1) Copper(I) Bromide; CuBr; [7787-70-4]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

J. J. FRITZ
 Department of Chemistry
 The Pennsylvania State University
 June, 1991

CRITICAL EVALUATION:

The values of $c_{\text{CuBr}}/c_{\text{MBr}}$ 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.

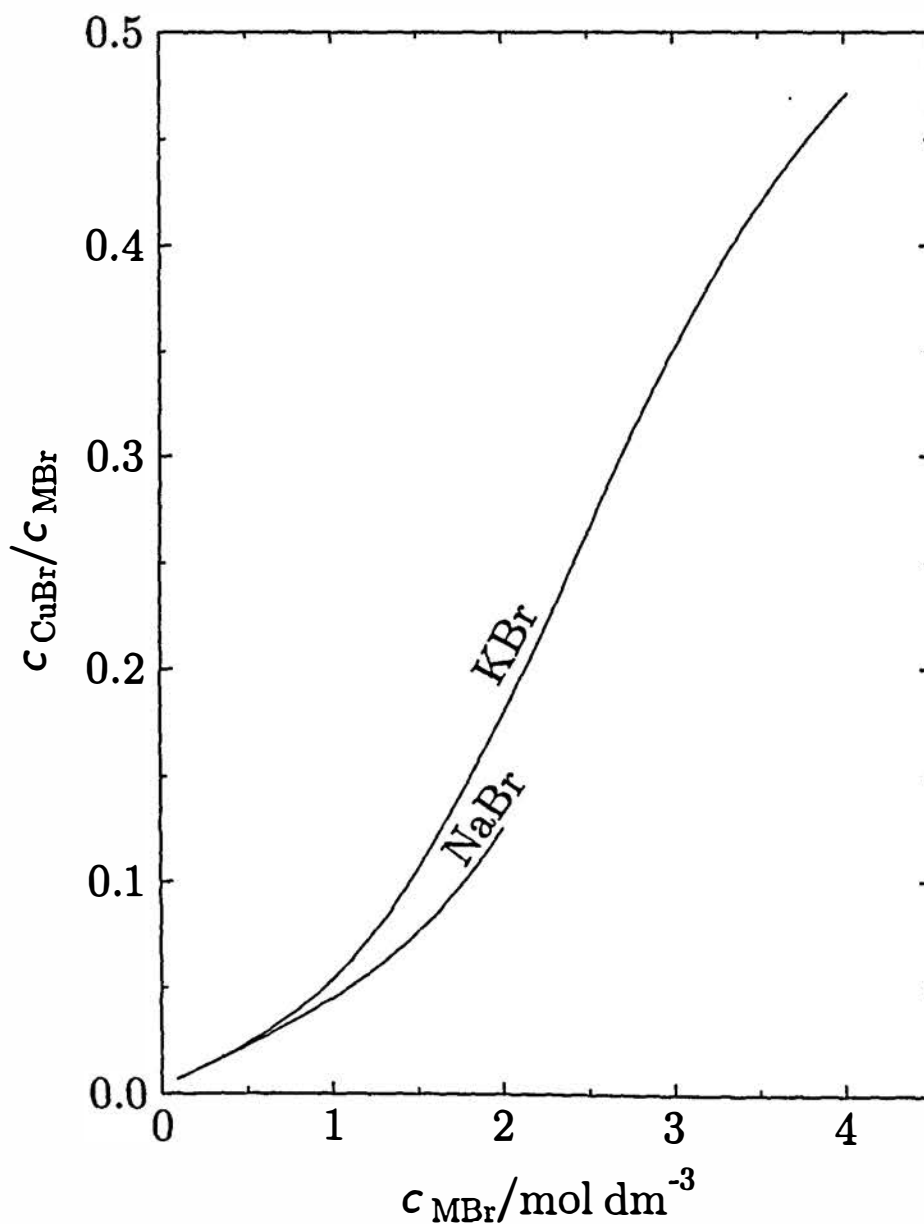


Fig. 4. Ratio of CuBr Solubility to Initial Concentration of Aqueous Bromide Plotted Against Concentration for KBr and NaBr at 298 K

COMPONENTS:

- (1) Copper(I) Bromide; CuBr; [7787-70-4]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

J. J. FRITZ
 Department of Chemistry
 The Pennsylvania State University
 June, 1991

CRITICAL EVALUATION:

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COMPONENTS: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Gavrish, M. L.; Galinker, I. S. <i>Dokl. Akad. Nauk SSSR</i> <u>1955</u> , 102, 89-91.																																				
VARIABLES: <i>T/K</i> = 473 to 603	PREPARED BY: J. J. FRITZ																																				
EXPERIMENTAL VALUES: <u>Solubility of CuBr in Water</u> <table border="1" style="margin: auto;"> <thead> <tr> <th><i>t/°C</i></th> <th>$\frac{m_1}{\text{mol kg}^{-1}}$</th> <th><i>t/°C</i></th> <th>$\frac{m_1}{\text{mol kg}^{-1}}$</th> <th><i>t/°C</i></th> <th>$\frac{m_1}{\text{mol kg}^{-1}}$</th> </tr> </thead> <tbody> <tr> <td>200</td> <td>0.149</td> <td>260</td> <td>0.49</td> <td>300</td> <td>0.820</td> </tr> <tr> <td>220</td> <td>0.217</td> <td>270</td> <td>0.66</td> <td>310</td> <td>0.930</td> </tr> <tr> <td>230</td> <td>0.286</td> <td>280</td> <td>0.716</td> <td>320</td> <td>1.01</td> </tr> <tr> <td>240</td> <td>0.369</td> <td>290</td> <td>0.790</td> <td>330</td> <td>1.07</td> </tr> <tr> <td>250</td> <td>0.411</td> <td></td> <td></td> <td></td> <td></td> </tr> </tbody> </table>		<i>t/°C</i>	$\frac{m_1}{\text{mol kg}^{-1}}$	<i>t/°C</i>	$\frac{m_1}{\text{mol kg}^{-1}}$	<i>t/°C</i>	$\frac{m_1}{\text{mol kg}^{-1}}$	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				
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Bodländer, G.; Storbeck, O. <i>Z. Anorg. Chem.</i> 1902 , <i>31</i> , 458-476.
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VARIABLES: Composition at 291 to 293 K ^a	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:
Solubility of CuBr in Aqueous KBr

$10^3 c_2/\text{mol dm}^{-3}$	$10^3 [\text{Cu}^{2+}]/\text{mol dm}^{-3}$ ^b	$10^3 c_1/\text{mol dm}^{-3}$
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 Cu²⁺ given arose through disproportionation of dissolved Cu⁺ to produce metallic Cu and Cu²⁺.

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Malik, W. U.; Rahman, S. M. F.; Malik, A. <i>Z. Anorg. Allg. Chem.</i> 1962 , <i>314</i> , 276-280.																																																																								
VARIABLES: Concentration of KBr at 323 K	PREPARED BY: J. J. FRITZ																																																																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuBr in Aqueous KBr at 50°C</u></p> <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="text-align: center;">$\rho_2/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_2/\text{mol dm}^{-3\text{a}}$</th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3\text{a}}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">185.39</td><td style="text-align: center;">1.558</td><td style="text-align: center;">65.4</td><td style="text-align: center;">0.524</td></tr> <tr><td style="text-align: center;">170.31</td><td style="text-align: center;">1.431</td><td style="text-align: center;">58.2</td><td style="text-align: center;">0.406</td></tr> <tr><td style="text-align: center;">164.3</td><td style="text-align: center;">1.381</td><td style="text-align: center;">41.5</td><td style="text-align: center;">0.289</td></tr> <tr><td style="text-align: center;">152.6</td><td style="text-align: center;">1.282</td><td style="text-align: center;">33.3</td><td style="text-align: center;">0.232</td></tr> <tr><td style="text-align: center;">140.9</td><td style="text-align: center;">1.184</td><td style="text-align: center;">31.6</td><td style="text-align: center;">0.220</td></tr> <tr><td colspan="4" style="text-align: center;"> </td></tr> <tr><td style="text-align: center;">134.6</td><td style="text-align: center;">1.131</td><td style="text-align: center;">26.4</td><td style="text-align: center;">0.184</td></tr> <tr><td style="text-align: center;">128.9</td><td style="text-align: center;">1.083</td><td style="text-align: center;">20.3</td><td style="text-align: center;">0.142</td></tr> <tr><td style="text-align: center;">120.3</td><td style="text-align: center;">1.011</td><td style="text-align: center;">15.87</td><td style="text-align: center;">0.111</td></tr> <tr><td style="text-align: center;">73.03</td><td style="text-align: center;">0.614</td><td style="text-align: center;">8.71</td><td style="text-align: center;">0.061</td></tr> <tr><td style="text-align: center;">70.98</td><td style="text-align: center;">0.596</td><td style="text-align: center;">6.88</td><td style="text-align: center;">0.048</td></tr> <tr><td colspan="4" style="text-align: center;"> </td></tr> <tr><td style="text-align: center;">69.1</td><td style="text-align: center;">0.581</td><td style="text-align: center;">4.9</td><td style="text-align: center;">0.034</td></tr> <tr><td style="text-align: center;">63.4</td><td style="text-align: center;">0.533</td><td style="text-align: center;">3.9</td><td style="text-align: center;">0.027</td></tr> <tr><td style="text-align: center;">62.6</td><td style="text-align: center;">0.526</td><td style="text-align: center;">3.6</td><td style="text-align: center;">0.025</td></tr> <tr><td style="text-align: center;">61.2</td><td style="text-align: center;">0.514</td><td style="text-align: center;">3.2</td><td style="text-align: center;">0.023</td></tr> <tr><td style="text-align: center;">54.8</td><td style="text-align: center;">0.461</td><td style="text-align: center;">2.8</td><td style="text-align: center;">0.020</td></tr> </tbody> </table> <p>^a Calculated by compiler.</p>		$\rho_2/\text{g dm}^{-3}$	$c_2/\text{mol dm}^{-3\text{a}}$	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3\text{a}}$	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
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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 ₄ SCN 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:																																																																								

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COMPONENTS: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Sodium Bromide; NaBr; [7647-15-6] (3) Water; H ₂ O; [7732-18-5]			ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.		
VARIABLES: Molality of NaBr at 298 to 328 K			PREPARED BY: J. J. FRITZ		
EXPERIMENTAL VALUES:					
<u>Solubility of CuBr in Aqueous NaBr</u>					
<i>t</i> /°C	NaBr in Solution ^a		Solubility of CuBr ^a		
	g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> ₁ /mol kg ⁻¹	
25	90.5 45.3 22.6	8.79 4.40 2.20	2.5 0.6 0.1	0.17 0.04 0.007	
35	90.5 45.3 22.6	8.79 4.40 2.20	2.6 0.7 0.1	0.18 0.05 0.007	
45	90.5 45.3 22.6	8.79 4.40 2.20	2.8 0.7 0.1	0.20 0.05 0.007	
55	90.5 45.3 22.6	8.79 4.40 2.20	2.8 0.8 0.2	0.20 0.06 0.014	
^a Molalities were calculated by the compiler, taking the author's "g/100 ml H ₂ O" to mean g/100 g H ₂ O 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.
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VARIABLES: <i>T/K</i> = 298 to 328	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuBr in Aqueous HBr</u></p>				
<i>t/°C</i>	HBr in Solution ^a		Solubility of CuBr ^a	
	<i>g/100 ml H₂O</i>	<i>m₂/mol kg⁻¹</i>	<i>g/100 ml H₂O</i>	<i>m₁/mol kg⁻¹</i>
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 ₂ O" to mean g/100 g H ₂ O 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) Lithium Bromide; LiBr; [7550-35-8] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.
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VARIABLES: Molality of LiBr at 298 to 328 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:

Solubility of CuBr in Aqueous LiBr

$t/^{\circ}\text{C}$	LiBr in Solution ^a		Solubility of CuBr ^a	
	g/100 ml H ₂ O	$m_2/\text{mol kg}^{-1}$	g/100 ml H ₂ O	$m_1/\text{mol kg}^{-1}$
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 H₂O" to mean g/100 g H₂O 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) Ammonium Bromide; NH ₄ Br; [12124-97-9] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Wilke, K.-Th. <i>Krist. Tech.</i> <u>1968</u> , 3, K53-K55.
VARIABLES: Molality of NH ₄ Br at 298 to 328 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:
Solubility of CuBr in Aqueous NH₄Br

<i>t</i> /°C	NH ₄ Br in Solution ^a		Solubility of CuBr ^a	
	g/100 ml H ₂ O	<i>m</i> ₂ /mol kg ⁻¹	g/100 ml H ₂ O	<i>m</i> 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 H₂O" to mean g/100 g H₂O 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fritz, J. J.; Luzik, E. <i>J. Solution Chem.</i> 1987 , <i>16</i> , 79-85.																																
VARIABLES: Concentrations of KBr and KNO ₃ at 298.0 K	PREPARED BY: J. J. FRITZ																																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuBr in Aqueous KBr at 24.8°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$c_2/\text{mol dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.0989</td><td style="text-align: center;">0.00064</td></tr> <tr><td style="text-align: center;">0.1978</td><td style="text-align: center;">0.00185</td></tr> <tr><td style="text-align: center;">0.3955</td><td style="text-align: center;">0.00633</td></tr> <tr><td style="text-align: center;">0.4738</td><td style="text-align: center;">0.00959</td></tr> <tr><td style="text-align: center;">0.5933</td><td style="text-align: center;">0.01539</td></tr> <tr><td colspan="2" style="text-align: center;"> </td></tr> <tr><td style="text-align: center;">0.7910</td><td style="text-align: center;">0.0289</td></tr> <tr><td style="text-align: center;">0.9888</td><td style="text-align: center;">0.0496</td></tr> <tr><td style="text-align: center;">1.483</td><td style="text-align: center;">0.1511</td></tr> <tr><td style="text-align: center;">1.978</td><td style="text-align: center;">0.334</td></tr> <tr><td style="text-align: center;">2.472</td><td style="text-align: center;">0.647</td></tr> <tr><td colspan="2" style="text-align: center;"> </td></tr> <tr><td style="text-align: center;">2.966</td><td style="text-align: center;">1.005</td></tr> <tr><td style="text-align: center;">3.461</td><td style="text-align: center;">1.418</td></tr> <tr><td style="text-align: center;">3.955</td><td style="text-align: center;">1.860</td></tr> </tbody> </table> <p style="text-align: right;">continued...</p>		$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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 ₂ SO 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. <i>Inorganic Syntheses</i> , 1942 , <i>2</i> , 1.																																

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fritz, J. J.; Luzik, E. <i>J. Solution Chem.</i> <u>1987</u> , <i>16</i> , 79-85.
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EXPERIMENTAL VALUES:

(continued)

Solubility of CuBr in KBr-KNO₃ Solutions at 24.8°C

$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Peters, D. G.; Caldwell, R. L. <i>Inorg. Chem.</i> 1967 , <i>6</i> , 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: <p style="text-align: center;"><u>Solubility of CuBr in NaBr-NaNO₃ Solutions at 25°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">[Br⁻]/mol dm⁻³</th> <th style="text-align: center;">c₁/mol dm⁻³</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">0.051</td> <td style="text-align: center;">0.00035 ± 0.00002</td> </tr> <tr> <td style="text-align: center;">0.102</td> <td style="text-align: center;">0.00079 ± 0.00001</td> </tr> <tr> <td style="text-align: center;">0.206</td> <td style="text-align: center;">0.00223 ± 0.00001</td> </tr> <tr> <td style="text-align: center;">0.495</td> <td style="text-align: center;">0.0104 ± 0.0001</td> </tr> <tr> <td style="text-align: center;">0.595</td> <td style="text-align: center;">0.0151 ± 0.0001</td> </tr> <tr> <td style="text-align: center;">0.798</td> <td style="text-align: center;">0.0282 ± 0.0002</td> </tr> <tr> <td style="text-align: center;">1.01</td> <td style="text-align: center;">0.0456 ± 0.0018</td> </tr> <tr> <td style="text-align: center;">1.52</td> <td style="text-align: center;">0.118 ± 0.008</td> </tr> </tbody> </table> <p>^a Ionic strength maintained using NaNO₃.</p>		[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
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Ahrlund, S.; Tagesson, B. <i>Acta Chem. Scand.</i> <u>1977</u> , <i>A31</i> , 615-624.																														
VARIABLES: Concentration of NaBr at 298 K	PREPARED BY: J. J. FRITZ																														
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuBr in NaBr-NaClO₄-(HClO₄) Solutions at 25° C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$\frac{[\text{Br}^-]_{\text{free}}}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_3}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_4}{\text{mol dm}^{-3}}$</th> <th>$\frac{[\text{Br}^-]_{\text{total}}^{\text{a}}}{\text{mol dm}^{-3}}$</th> <th>$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr> <td>0.113</td> <td>0.10</td> <td>4.887</td> <td>0.113</td> <td>0.00039</td> </tr> <tr> <td>0.201</td> <td>0.10</td> <td>4.698</td> <td>0.202</td> <td>0.00156</td> </tr> <tr> <td>0.226</td> <td>0.10</td> <td>4.673</td> <td>0.227</td> <td>0.00218</td> </tr> <tr> <td>0.283</td> <td>0.10</td> <td>4.616</td> <td>0.284</td> <td>0.00367</td> </tr> <tr> <td>0.429</td> <td>0.10</td> <td>4.469</td> <td>0.431</td> <td>0.00743</td> </tr> </tbody> </table> <p>^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.</p>		$\frac{[\text{Br}^-]_{\text{free}}}{\text{mol dm}^{-3}}$	$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_4}{\text{mol dm}^{-3}}$	$\frac{[\text{Br}^-]_{\text{total}}^{\text{a}}}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	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
$\frac{[\text{Br}^-]_{\text{free}}}{\text{mol dm}^{-3}}$	$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_4}{\text{mol dm}^{-3}}$	$\frac{[\text{Br}^-]_{\text{total}}^{\text{a}}}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$																											
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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 recrystallization; NaBr (<i>Mallinckrodt p. a.</i>) used without further purification. ESTIMATED ERROR: Not given. REFERENCES:																														

COMPONENTS: (1) Copper(I) Bromide; CuBr; [7787-70-4] (2) Organic Solvents	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
CRITICAL EVALUATION: <p style="text-align: center;">BINARY SYSTEMS</p> <p>There have been two reports of the solubility of CuBr in an organic solvent without any added salt. In 1914 Naumann and Schier¹ reported that the solubility of CuBr in acetonitrile at 291 K was approximately 0.0386 g CuBr per g acetonitrile.</p> <p>In 1977 Machtinger <i>et al.</i>² gave a value of the solubility product of CuBr in molten dimethyl sulfone [(CH₃)₂SO₂] at 400 K as 10^{-12.4} (4 · 10⁻¹³) mol² kg⁻² from cell measurements in which the potential of a copper electrode 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 <i>K</i>_{S0} would correspond to a solubility of about 6.3 · 10⁻⁷ mol kg⁻¹ in the molten dimethyl sulfone.</p> <p style="text-align: center;">TERNARY SYSTEMS</p> <p>Machtinger <i>et al.</i>² also used titration curves to evaluate a stability constant for the ion CuBr₂⁻ in molten dimethyl sulfone [(CH₃)₂SO₂] 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 · 10¹⁵) mol⁻² kg². Using this value with their value for the solubility product of CuBr in their medium gives a value of <i>K</i>_{S2} for addition of Br⁻ to CuBr_(s), viz.:</p> $\text{CuBr}_{(s)} + \text{Br}^- \rightleftharpoons \text{CuBr}_2^- \quad K_{S2} = 520$ <p>This value of <i>K</i>_{S2} would correspond to essentially complete absorption of Br⁻ by solid cuprous bromide. Machtinger <i>et al.</i>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⁻!</p> <p style="text-align: center;">REFERENCES</p> <ol style="list-style-type: none"> 1. Naumann, A.; Schier, A. <i>Ber. Dtsch. Chem. Ges.</i> <u>1914</u>, <i>47</i>, 247. 2. Machtinger, M.; Vuaille, M. J.; Tremillon, B. <i>J. Electroanal. Chem. Interfacial Electrochem.</i> <u>1977</u>, <i>83</i>, 273. 	

COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:**THE BINARY SYSTEM**

There are very few data on the solubility of cuprous iodide in pure water. In 1902 Bodländer and Storbeck¹ reported a value of $5.06 \cdot 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$ 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 Furman². 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 500³ (1952) yields a value of $1.2 \cdot 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$; Zhuk⁴ (1954) quotes a value of $1.1 \cdot 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$, as do Latimer⁵ (1952) and Chaltykyan⁶ (1966); Krestov *et al.*⁷ (1977) quote a value of $1.3 \cdot 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$. A value of $(1.2 \pm 0.1) \cdot 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$ 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 CuI⁰ and the reaction $2\text{CuI}_{(s)} \rightleftharpoons \text{Cu}^+ + \text{CuI}_2^-$.) Ahrland and Tagesson⁸ reported a value of $(1.92 \pm 0.06) \cdot 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$ at 298.16 K, 5.0 mol dm⁻³ ionic strength maintained by acidified NaClO₄. This value is surprisingly low, but could be valid for the high ionic strength they used. Golub, Sazhienko and Romanenko⁹ (1962) reported a value of $9.4 \cdot 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$ at 20°C (293 K); this is not unreasonable for that temperature.

Gavrish and Galinker¹⁰ 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

$$\ln(m_{\text{CuI}}/\text{mol kg}^{-1}) = -5692 \text{ K}/T + 6.920$$

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 Yakhkind¹¹ made 13 measurements at 293 K in a nominal ionic strength of 3.9 mol dm⁻³, using NaNO₃ 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 Tagesson⁸ (1977) measured the solubility at 298.16 K, 5.0 mol dm⁻³ ionic strength maintained by NaClO₄ with 0.1 mol dm⁻³ HClO₄ 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 Sarbaev¹² 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 NaNO₃. 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

<p>COMPONENTS:</p> <p>(1) Copper(I) Iodide; CuI; [7681-65-4]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>of 4.0 mol dm⁻³, with KI from 0.5 to 3.3 mol dm⁻³. In 1964 Gavrish and Galinker¹³ 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[CuI₂⁻], where [I⁻] is the equilibrium concentration of iodide ion in mol dm⁻³ and [CuI₂⁻] 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 CuI₂⁻ from CuI_(s) and I⁻.</p> <p>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.</p> <p>Only one set of measurements has been reported for the solubility of CuI in aqueous hydrogen iodide. These were made by Popolitov <i>et al.</i>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.</p> <p>No solubility data were found for the system CuI-NH₄I-H₂O, but Wells and Hurlburt¹⁵ were able to prepare a double salt CuI·NH₄I from a solution of the two salts in aqueous HI. The solubility of CuI in aqueous NH₄I should be at least as large as in corresponding concentrations of aqueous KI.</p> <p><u>CuI-NaI-H₂O</u></p> <p>The results of Gyunner and Yakhkind¹¹ 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 Tagesson⁸ are consistent with data for other conditions to about 6 per cent, and should be suitable for their conditions within this uncertainty.</p> <p><u>CuI-KI-H₂O</u></p> <p>The data of Fridman and Sarbaev¹² for systems containing only KI agreed with other data to about 6 per cent. The data they obtained using NaNO₃ 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 <i>et al.</i>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.</p> <p>The data given by Gavrish and Galinker¹³ 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.</p>	

COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:
CuI-HI-H₂O

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⁻, NO₃⁻ and ClO₄⁻ from Pitzer and Mayorga¹⁶; 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 CuI⁰, CuI₂⁻, CuI₃²⁻ and Cu₃I₆³⁻. 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 · 10 ⁻⁵	—
CuI ₂ ⁻	7.9 · 10 ⁻⁵	33.9
CuI ₃ ²⁻	7.8 · 10 ⁻⁴	58.6
Cu ₃ I ₆ ³⁻	4.4 · 10 ⁻⁶	32.2

^a The neutral complex CuI⁰ did not contribute significantly to the solubilities and a value near that for CuBr⁰ 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 $m \text{ CuI}_{(s)} + (n - m) \text{ I}^- \rightleftharpoons \text{Cu}_m \text{ I}_n^{m-n}$, 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 Storbeck¹ gave a value of 1.55 · 10⁸ for the stability constant of CuI₂⁻ at about 293 K, corresponding to a value of 7.8 · 10⁻⁴ for the formation constant K_{S2} . In 1952 Latimer⁵ gave a value of 6.3 · 10⁻⁴ for K_{S2} at 298 K; he did not specify his source, but quoted Bodländer and Storbeck¹, apparently modifying their result somewhat. In 1964 Gavrish and Galinker¹³ 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: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Tagesson⁸ gave a set of stability constants at 298.15 K for a medium maintained at ionic strength 5.0 mol dm⁻³. They considered CuI₂⁻ and CuI₃²⁻, 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 ⁺		
	$\beta^{(0)}$	$\beta^{(1)}$	<i>C</i>	$\beta^{(0)}$	$\beta^{(1)}$	<i>C</i>
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 ₃ I ₆ ³⁻	0.2467	3.547	-0.003098	0.123	3.37	-0.00732

^a The parameters for the 'salting out' effect for CuI⁰ 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 $c_{\text{CuI}}/c_{\text{MI}}$, the ratio of solubility to iodide concentration, is given for each concentration, to somewhat greater precision than the solubility itself. $c_{\text{CuI}}/c_{\text{MI}}$ 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: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

Table 29. Solubility and Ratio of Solubility to Initial Iodide Concentration for CuI in Aqueous NaI

$\frac{c_{\text{NaI}}}{\text{mol dm}^{-3}}$	$T = 293 \text{ K}$		$T = 298 \text{ K}$	
	$c_{\text{CuI}}/\text{mol dm}^{-3}$	$c_{\text{CuI}}/c_{\text{NaI}}$	$c_{\text{CuI}}/\text{mol dm}^{-3}$	$c_{\text{CuI}}/c_{\text{NaI}}$
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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

Table 30. Solubility and Ratio of Solubility to Initial Iodide Concentration for CuI in Aqueous KI

c_{KI} mol dm ⁻³	$T = 293 \text{ K}$		$T = 298 \text{ K}$	
	$c_{CuI}/\text{mol dm}^{-3}$	c_{CuI}/c_{KI}	$c_{CuI}/\text{mol dm}^{-3}$	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:

- (1) Copper(I) Iodide; CuI; [7681-18-5]
- (2) Water; H₂O; [7732-18-5]

EVALUATOR:

J. J. FRITZ
Department of Chemistry
The Pennsylvania State University
June, 1991

CRITICAL EVALUATION:

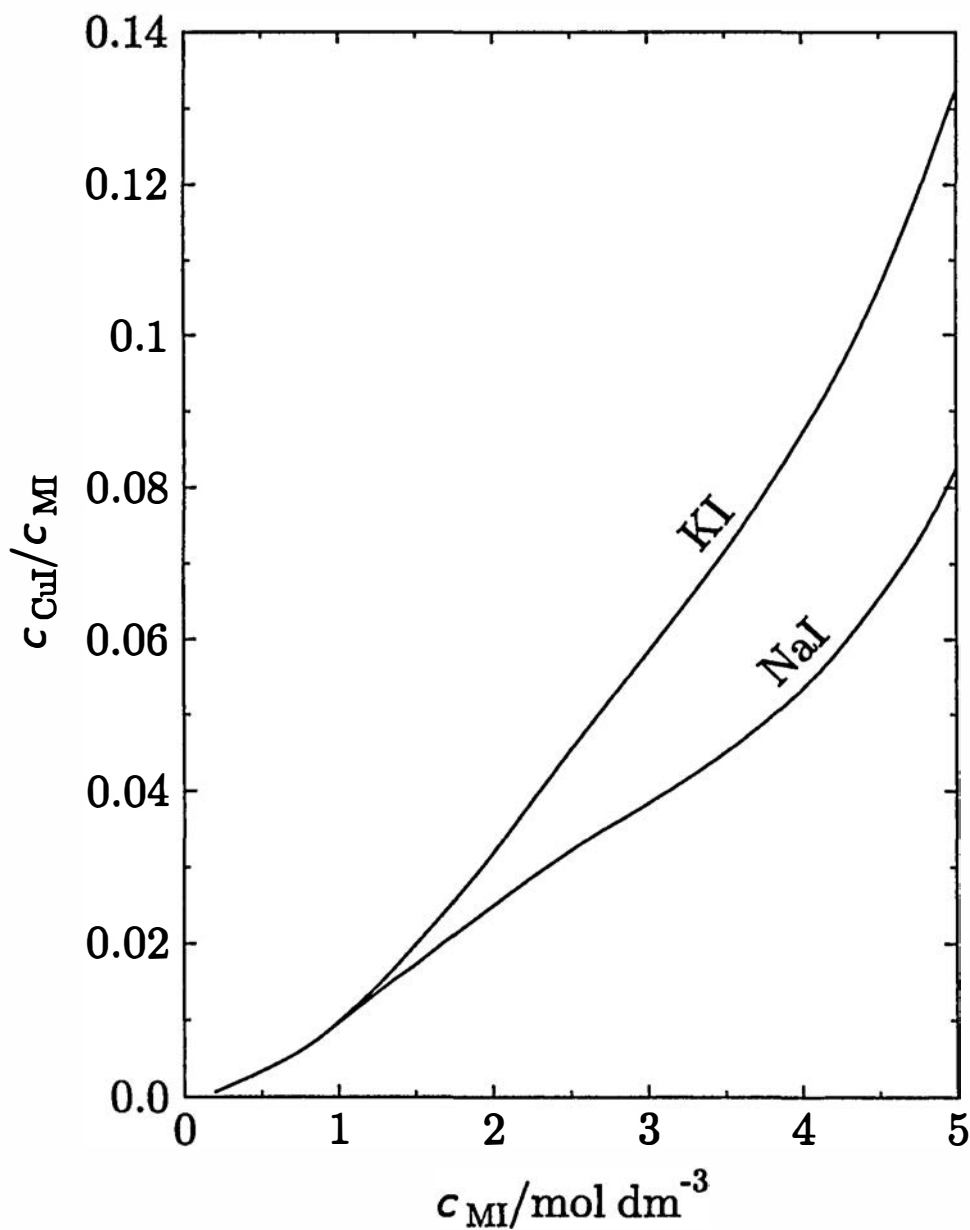


Fig. 5. Ratio of CuI Solubility to Initial Concentration of Aqueous Iodide Plotted Against Concentration for NaI and KI at 298.15 K

<p>COMPONENTS:</p> <p>(1) Copper(I) Iodide; CuI; [7681-65-4]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p style="text-align: center;">DOUBLE SALTS INVOLVING CuI</p> <p>Mellor¹⁷ describes early studies of compounds containing ammonia and/or NH₄I along with CuI. In a series of papers, Harris¹⁸⁻²¹ 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 CuI₂ 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.</p> <p style="text-align: center;">SYSTEMS INVOLVING OTHER SOLUBLE HALIDES</p> <p>There are four reports of the solubility of cuprous iodide in aqueous solutions of salts other than iodides. In 1909 Kohn²² 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 Klein²³ gave results for the solubility in 2 to 4 mol dm⁻³ NH₄Br at 294 K. Finally, in 1959 Fridman and Sarbaev¹² 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 NaNO₃. The data given by Fridman and Sarbaev¹² are the most extensive (10 points).</p> <p>Of the two sets of data for aqueous KBr, the solubilities given by Fridman and Sarbaev¹² are larger than those of Kohn²² 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 Klein²³ for aqueous NH₄Br are roughly the same as those of Kohn²¹ for aqueous KBr. The solubilities given by Fridman and Sarbaev¹² 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 NH₄Br is equal to or less than in aqueous KI, and its solubility in aqueous KCl is much smaller than in aqueous KI.</p> <p>For all of the data, the ratio of solubility to halide concentration ($c_{\text{CuI}}/c_{\text{L}^-}$) increases with increasing concentration of the soluble halide. Fridman and Sarbaev¹² attribute the solubility to the formation of mixed complexes CuIL⁻ and CuIL₂²⁻, where L is either Br or Cl, with the increase in $c_{\text{CuI}}/c_{\text{L}^-}$ due to formation of the second complex with increasing ligand concentration. They give stability constants for these complexes based on their measurements.</p> <p style="text-align: center;">SYSTEMS INVOLVING THIOSULFATES</p> <p>Three sets of measurements have been reported for the solubility of cuprous iodide in aqueous Na₂S₂O₃ and one for the solubility of CuI in aqueous K₂S₂O₃. In 1952, Yatsimirskii and Panova²⁴ gave values for the solubility at 298 K in aqueous solutions of Na₂S₂O₃ from 0.02 to 0.54 mol kg⁻¹ (10 points). In 1968 Gyunner and Yakhkind¹¹ published 8 values of solubility for CuI in aqueous Na₂S₂O₃ from 0.2 to 1.0 mol dm⁻³ at 20°C. In 1975 Golub, Butsko and Dobryanskaya²⁵ published results for aqueous Na₂S₂O₃ 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 Yakhkind¹¹ measured solubility by changes in the refractive index of the</p>	

COMPONENTS:

- (1) Copper(I) Iodide; CuI; [7681-65-4]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

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 June, 1991

CRITICAL EVALUATION:

solution. Finally, in 1976 a second paper by Golub and coworkers²⁶ gave values for the solubility in aqueous K₂S₂O₃ 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:



Independent least-squares analysis of the data confirmed that such a treatment worked, and also that the formation of a complex Cu(S₂O₃)⁻ by the reaction CuI_(s) + S₂O₃²⁻ ⇌ Cu(S₂O₃)⁻ + 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 Panova²⁴ give a value of 3.5 ± 0.5 for the constant K₁ 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 K₁ = 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 K₁ = 3.45, with average deviation of 2.7%. Yatsimirskii and Panova²⁴ 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



Their value corresponds to β = 3.2 · 10¹² mol⁻² kg².

Gyunner and Yakhkind¹¹ give a value for K₁ 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 K₁ = 2.61, with a standard deviation of 0.005 mol dm⁻³; that on percentage deviations gave K₁ = 2.66, with fit to 1.4 per cent. They calculated the reciprocal of β, corresponding to β = 2.4 · 10¹² mol⁻² dm⁶ at 293 K. They also made four solubility measurements on systems in which the concentration of Na₂S₂O₃ was between 0.56 and 0.67 mol dm⁻³, with NaI concentrations from 0.15 (highest [S₂O₃²⁻]) to 0.6 mol dm⁻³ (lowest [S₂O₃²⁻]). The solubilities observed in these cases were not significantly different from those observed for the same concentration of S₂O₃²⁻ 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 Na₂S₂O₃ gives a value of 3.3 for K₁ 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 deviation 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/β corresponds to β of 3.48 · 10¹² mol⁻² dm⁶. 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 Romaneko⁹ 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 K₁ 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/β.

<p>COMPONENTS:</p> <p>(1) Copper(I) Iodide; CuI; [7681-65-4]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>In connection with their solubility measurements Golub <i>et al.</i>²⁵ isolated two salts, whose chemical composition corresponded to Na₂[CuIS₂O₃] · 2H₂O and Na₄[CuI(S₂O₃)₂] · 2H₂O, and described their solubility properties. Their potentiometric measurements were made with Cu(I) concentrations of 0.005 mol dm⁻³ and Na₂S₂O₃ concentrations of 0.2 to 1.44 mol dm⁻³, with Na₂SO₄ added to maintain constant nominal ionic strength (value not specified).</p> <p>These measurements indicated formation under these conditions of a series of complexes of Cu⁺ with S₂O₃²⁻ but without iodide. They gave values for stability constants of four such; these were, with S₂O₃²⁻ represented as L⁻², CuL⁻, CuL₂³⁻, CuL₃⁵⁻ and CuL₄⁷⁻, the last of these predominant. They also isolated a series of salts whose chemical compositions corresponded to Na₃CuL₂ · 2H₂O, Na₅CuL₃ · 6H₂O and Na₇CuL₄ · 7H₂O and described their solubility properties.</p> <p>The measurements of Golub <i>et al.</i>²⁶ on the solubility of CuI in aqueous K₂S₂O₃ (temperature unspecified) were interpreted to give a <i>K</i>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 <i>K</i>₁ of 10.72, with standard deviation of 0.2 per cent. The authors give a value of 1.1 · 10¹³ for the stability constant of CuIS₂O₃²⁻. 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⁻, CuL₂³⁻, CuL₃⁵⁻ and CuL₄⁷⁻, where L represents the ion S₂O₃²⁻. 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 K₂CuIL, K₄CuIL₂, K₆CuIL₃, K₃CuL₂, K₄Cu₂L₃, K₅CuL₃ and K₇CuL₄. Rosenheim and Steinhauser²⁷ prepared the double salt CuI · NH₄I · 4(NH₄)₂S₂O₃ and verified its composition by chemical analysis.</p> <p><i>Summary.</i> All of the measurements reported for the solubility of CuI in aqueous Na₂S₂O₃ or K₂S₂O₃ can be interpreted in terms of the formation of a mixed complex CuIS₂O₃²⁻ by the reaction:</p> $\text{CuI}_{(s)} + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{CuIS}_2\text{O}_3^{2-} \quad K_1 = [\text{CuIS}_2\text{O}_3^{2-}]/[\text{S}_2\text{O}_3^{2-}]$ <p>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 <i>et al.</i>^{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 Panova²⁴ and those of Gyunner and Yakhkind¹¹ are Accepted for their respective conditions. The results of Golub <i>et al.</i>^{25,26} for solubility of CuI in aqueous Na₂S₂O₃ and in aqueous K₂S₂O₃ 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.</p> <p>The isolation of a variety of salts, both with and without iodide content, by Golub <i>et al.</i>^{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 <i>β</i> 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 <i>β</i> from the experimentally determined <i>K</i>₁.</p>	

COMPONENTS:

- (1) Copper(I) Iodide; CuI; [7681-65-4]
 (2) Water; H₂O; [7732-18-5]

EVALUATOR:

J. J. FRITZ
 Department of Chemistry
 The Pennsylvania State University
 June, 1991

CRITICAL EVALUATION:

CuI-KNbO₃-H₂O

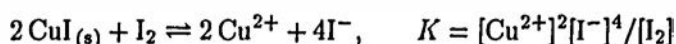
Tanirbergenov²⁸ measured the solubility of CuI in aqueous potassium metaniobate (KNbO₃) at 293 K, using concentrations of KNbO₃ from 0.05 to 0.33 mol dm⁻³ (10 points), with ionic strength held constant at 0.33 mol dm⁻³ by use of KNO₃. He also made a series of potentiometric measurements with a Cu(I) concentration of 0.0027 mol dm⁻³ and KNbO₃ 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 NbO₃⁻.

Tanirbergenov²⁸ attributed the solubility of CuI to formation of the mixed complex CuINbO₃⁻ by the reaction $\text{CuI}_{(s)} + \text{NbO}_3^- \rightleftharpoons \text{CuINbO}_3^-$, 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-I₂-H₂O

In 1910 Fedotieff²⁹ 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 · 10⁻³ mol dm⁻³, with iodine concentrations in solution varying from 4.6 to 59.9 · 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 I₂ 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



with the subsequent reaction



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 $10.7 \cdot 10^{-9} \text{ mol}^5 \text{ dm}^{-15}$. 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 Kapler³⁰ made a series of measurements on the solubility of CuI in solutions of iodine in 7 polar solvents at 20°C. Kapler³⁰ found that his results can be correlated by the equation

$$\log c_{\text{CuI}} / \text{mol dm}^{-3} = a \log c_{\text{I}_2} / \text{mol dm}^{-3} + \log b.$$

He did not report actual solubility data for water as solvent, however, the constants $a = 0.56$ and $b = 0.14$ provided represent Fedotieff's²⁹ data within a few per cent. Kapler³⁰ confirmed the existence of Cu²⁺ by ESR spectroscopy and also detected higher polyiodide anions I_{2n+1}⁻ ($n = 1 - 4$) by UV-VIS spectroscopy.

COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
CRITICAL EVALUATION: <p style="text-align: center;">REFERENCES</p> <ol style="list-style-type: none"> 1. Bodländer, G.; Storbeck, O. <i>Z. Anorg. Chem.</i> <u>1902</u>, 31, 458. 2. Kolthoff, I.M.; Furman, N.H. <i>Potentiometric Titrations</i>, Wiley, New York, <u>1931</u>, p. 453. 3. U. S. National Bureau of Standards Circular 500, <i>Selected Values of Chemical Thermodynamics</i>, U. S. Government, Washington, <u>1952</u>. 4. Zhuk, H. P. <i>Zh. Fiz. Khim.</i> <u>1954</u>, 28, 1523. 5. Latimer, W. M.; <i>Oxidation Potentials</i>, Prentice Hall, New York, <u>1952</u>, p. 186. 6. Chaltykyan, O. A. <i>Copper Catalytic Reactions</i>, Consultants Bureau, New York, <u>1966</u>, p. 4. 7. Krestov, G. A.; Kobenin, V. A.; Sokolov, V. N. <i>Zh. Neorg. Khim.</i> <u>1977</u>, 22, 2864; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1977</u>, 22, 1556. 8. Ahrland, S.; Tagesson, B. <i>Acta Chem. Scand.</i> <u>1977</u>, A31, 615. 9. Golub, A. M.; Sazhienko, S. M.; Romanenko, L. I. <i>Ukr. Khim. Zh.</i> <u>1962</u>, 28, 561. 10. Gavrish, M. L.; Galinker, I. S. <i>Dokl. Akad. Nauk SSSR</i> <u>1955</u>, 102, 89. 11. Gyunner, E. A.; Yakhkind, N. D.; <i>Zh. Neorg. Khim.</i> <u>1968</u>, 13, 2758; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1968</u>, 13, 1420. 12. Fridman, Ya. D.; Sarbaev, Dzh. S. <i>Zh. Neorg. Khim.</i> <u>1959</u>, 4, 1849; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1959</u>, 4, 535. 13. Gavrish, M. L.; Galinker, I. S. <i>Zh. Neorg. Khim.</i> <u>1964</u>, 9, 1289; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1964</u>, 9, 702. 14. Popolitov, V. I.; Minizon, Yu. M.; Nikitenko, V. A.; Stoyukhin, S. G. <i>Kristallografiya</i> <u>1984</u>, 29, 779; <i>Sov. Phys. Crystallogr. (Engl. Transl.)</i> <u>1984</u>, 29, 460. 15. Wells, H. L.; Hurlburt, E. B. <i>Z. Anorg. Chem.</i> <u>1895</u>, 16, 157. 16. Pitzer, K. S.; Mayorga, G. <i>J. Phys. Chem.</i> <u>1973</u>, 77, 2300. 17. Mellor, J. W. <i>A Comprehensive Treatise on Inorganic and Theoretical Chemistry</i>, vol. III, Wiley, New York, <u>1961</u>. 18. Harris, C. M. <i>J. Proc. Roy. Soc. New South Wales</i> <u>1948</u>, 82, 218. 19. Harris, C. M. <i>J. Proc. Roy. Soc. New South Wales</i> <u>1951</u>, 84, 111. 20. Harris, C. M. <i>J. Proc. Roy. Soc. New South Wales</i> <u>1952</u>, 85, 138. 21. Harris, C. M.; Schafer, H. N. S. <i>Proc. Roy. Soc. New South Wales</i> <u>1952</u>, 85, 145. 22. Kohn, M. <i>Z. Anorg. Chem.</i> <u>1909</u>, 63, 337. 23. Kohn, M.; Klein, A. <i>Z. Anorg. Chem.</i> <u>1912</u>, 77, 252. 24. Yatsimirskii, K. B.; Panova, V. E. <i>Zh. Obshch. Khim.</i> <u>1952</u>, 22, 1284. 25. Golub, A. M.; Butsko, S. S.; Dobryanskaya, L. P. <i>Zh. Neorg. Khim.</i> <u>1975</u>, 20, 2728; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1975</u>, 20, 1510. 26. Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. <i>Ukr. Khim. Zh.</i> <u>1976</u>, 42, 343. 27. Rosenheim, A.; Steinhauser, S. <i>Z. Anorg. Chem.</i> <u>1900</u>, 25, 103. 28. Tanirbergenov, B. <i>Ukr. Khim. Zh.</i> <u>1980</u>, 46, 262; <i>Sov. Prog. Chem. (Engl. Transl.)</i> <u>1980</u>, 46, 39. 29. Fedotieff, P. P. <i>Z. Anorg. Chem.</i> <u>1910-11</u>, 69, 22. 30. Kapler, R. <i>Z. Chem. (Leipzig)</i> <u>1990</u>, 30, 226. 	

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VARIABLES: T/K = 453 to 613	PREPARED BY: J. J. FRITZ																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in Water</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$t/^{\circ}\text{C}$</th> <th>$\frac{m_1}{\text{mol kg}^{-1}}$</th> <th>$t/^{\circ}\text{C}$</th> <th>$\frac{m_1}{\text{mol kg}^{-1}}$</th> <th>$t/^{\circ}\text{C}$</th> <th>$\frac{m_1}{\text{mol kg}^{-1}}$</th> </tr> </thead> <tbody> <tr> <td>180</td> <td>0.003621</td> <td>240</td> <td>0.01323</td> <td>300</td> <td>0.04945</td> </tr> <tr> <td>200</td> <td>0.0065</td> <td>260</td> <td>0.029</td> <td>320</td> <td>0.06239</td> </tr> <tr> <td>220</td> <td>0.008299</td> <td>280</td> <td>0.040</td> <td>340</td> <td>0.08993</td> </tr> </tbody> </table>		$t/^{\circ}\text{C}$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/^{\circ}\text{C}$	$\frac{m_1}{\text{mol kg}^{-1}}$	$t/^{\circ}\text{C}$	$\frac{m_1}{\text{mol kg}^{-1}}$	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
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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:																								

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VARIABLES: Concentrations of NaI and NaNO ₃ at 293 K	PREPARED BY: J. J. FRITZ																																							
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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. <i>Russ. J. Inorg. Chem.</i> <u>1968</u> , 13, 128. 2. Karyakin, Yu. V.; Angelov, I. I. <i>Pure Chemical Reagents</i> , <u>1955</u> , p. 348.																																							

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VARIABLES: Concentration of NaI at 298 K	PREPARED BY: J. J. FRITZ																									
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in NaI-NaClO₄-(HClO₄) Solutions at 25°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$\frac{[I^-]_{free}}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_3}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_4}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{[I^-]_{total}^a}{\text{mol dm}^{-3}}$</th> <th style="text-align: center;">$\frac{c_1}{\text{mol dm}^{-3}}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">0.201</td> <td style="text-align: center;">0.10</td> <td style="text-align: center;">4.699</td> <td style="text-align: center;">0.201</td> <td style="text-align: center;">0.00019</td> </tr> <tr> <td style="text-align: center;">0.343</td> <td style="text-align: center;">0.10</td> <td style="text-align: center;">4.556</td> <td style="text-align: center;">0.344</td> <td style="text-align: center;">0.00062</td> </tr> <tr> <td style="text-align: center;">0.490</td> <td style="text-align: center;">0.10</td> <td style="text-align: center;">4.409</td> <td style="text-align: center;">0.491</td> <td style="text-align: center;">0.00136</td> </tr> <tr> <td style="text-align: center;">0.733</td> <td style="text-align: center;">0.10</td> <td style="text-align: center;">4.167</td> <td style="text-align: center;">0.736</td> <td style="text-align: center;">0.00316</td> </tr> </tbody> </table> <p>^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.</p>		$\frac{[I^-]_{free}}{\text{mol dm}^{-3}}$	$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_4}{\text{mol dm}^{-3}}$	$\frac{[I^-]_{total}^a}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$	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
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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 BDII 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fridman, Ya. D.; Sarbaev, Dzh. S. <i>Zh. Neorg. Khim.</i> 1959 , <i>4</i> , 1849-1859; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1959 , <i>4</i> , 835-841.																														
VARIABLES: Concentrations of KI and NaNO ₃ at 298 K	PREPARED BY: J. J. FRITZ																														
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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: <p style="text-align: center;"><u>Solubility of CuI in KI-NaNO₃ Solutions of $I_c = 0.6$ mol dm⁻³ at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>c_2/mol dm⁻³</th> <th>c_3/mol dm⁻³</th> <th>c_1/mol dm⁻³</th> </tr> </thead> <tbody> <tr><td>0.104</td><td>0.496</td><td>$9.44 \cdot 10^{-5}$</td></tr> <tr><td>0.150</td><td>0.450</td><td>$1.37 \cdot 10^{-4}$</td></tr> <tr><td>0.199</td><td>0.401</td><td>$2.25 \cdot 10^{-4}$</td></tr> <tr><td>0.250</td><td>0.350</td><td>$3.38 \cdot 10^{-4}$</td></tr> <tr><td>0.300</td><td>0.300</td><td>$4.83 \cdot 10^{-4}$</td></tr> <tr><td>0.349</td><td>0.251</td><td>$5.25 \cdot 10^{-4}$</td></tr> <tr><td>0.499</td><td>0.151</td><td>$9.23 \cdot 10^{-4}$</td></tr> <tr><td>0.626</td><td>-</td><td>$2.28 \cdot 10^{-3}$</td></tr> </tbody> </table> <p style="text-align: center;"><u>Solubility of CuI in KI-NaNO₃ Solutions of $I_c = 4.0$ mol dm⁻³ at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>c_2/mol dm⁻³</th> <th>c_3/mol dm⁻³</th> <th>c_1/mol dm⁻³</th> </tr> </thead> <tbody> <tr><td>0.521</td><td>3.479</td><td>0.0009</td></tr> <tr><td>0.728</td><td>3.272</td><td>0.0031</td></tr> <tr><td>0.834</td><td>3.166</td><td>0.0032</td></tr> <tr><td>1.034</td><td>2.966</td><td>0.0075</td></tr> <tr><td>1.252</td><td>2.748</td><td>0.0102</td></tr> <tr><td>1.293</td><td>2.707</td><td>0.0124</td></tr> <tr><td>1.758</td><td>2.242</td><td>0.0269</td></tr> <tr><td>2.177</td><td>1.823</td><td>0.0492</td></tr> <tr><td>2.585</td><td>1.415</td><td>0.0804</td></tr> <tr><td>2.608</td><td>1.392</td><td>0.0766</td></tr> <tr><td>2.895</td><td>1.105</td><td>0.1103</td></tr> <tr><td>2.921</td><td>1.079</td><td>0.1092</td></tr> <tr><td>3.309</td><td>0.691</td><td>0.1718</td></tr> </tbody> </table>		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	-	$2.28 \cdot 10^{-3}$	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
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Popolitov, V. I.; Mininon, Yu. M.; Nikitenko, V. A.; Stoyukhin, S. G. <i>Kristallografiya</i> 1984, 29, 779-784; <i>Sov. Phys. Crystallogr. (Engl. Transl.)</i> 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.

$c_2/\text{mol dm}^{-3}$	$100w_1$ at $t/^\circ\text{C}$ 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

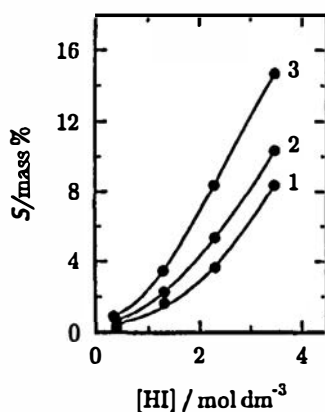


FIG. 1. Solubility of CuI vs. HI concentration.
 $t/^\circ\text{C} = (1) 200; (2) 250; (3) 300$.

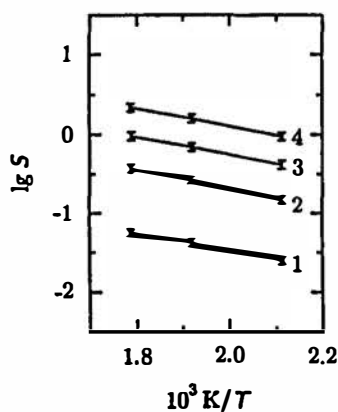


FIG. 2. Graphs of $\log S$ vs. reciprocal of temperature^a.
 Mass percentage of HI: (1) 5; (2) 15; (3) 25; (4) 35.

^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: (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fridman, Ya. D.; Sarbaev, Dzh. S. <i>Zh. Neorg. Khim.</i> <u>1959</u> , 4, 1849-1859; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1959</u> , 4, 835-841.																		
VARIABLES: Concentrations of KCl and NaNO ₃ at 298 K	PREPARED BY: J. J. FRITZ																		
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COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Potassium Bromide; KBr; [7758-02-3] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kohn, M. <i>Z. Anorg. Chem.</i> <u>1909</u> , 63, 337-339.																																								
VARIABLES: Concentration of KBr at 291 to 297 K	PREPARED BY: J. J. FRITZ																																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in Aqueous KBr</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$t/^{\circ}\text{C}$</th> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$\rho_1/\text{g dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$ ^a</th> </tr> </thead> <tbody> <tr><td>18</td><td>2.0</td><td>1.4653</td><td>0.0077</td></tr> <tr><td>19.5</td><td>2.0</td><td>1.4666</td><td>0.0077</td></tr> <tr><td>24</td><td>2.0</td><td>1.5576</td><td>0.0082</td></tr> <tr><td>19.5</td><td>3.0</td><td>3.4094</td><td>0.0179</td></tr> <tr><td>20</td><td>3.0</td><td>3.4656</td><td>0.0182</td></tr> <tr><td>23</td><td>3.0</td><td>3.5949</td><td>0.0189</td></tr> <tr><td>22</td><td>4.0</td><td>7.1263</td><td>0.0374</td></tr> <tr><td>22</td><td>4.0</td><td>6.9768</td><td>0.0366</td></tr> <tr><td>23</td><td>4.0</td><td>7.0581</td><td>0.0371</td></tr> </tbody> </table>		$t/^{\circ}\text{C}$	$c_2/\text{mol dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3}$ ^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
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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:																																								

^a Calculated by compiler.

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fridman, Ya. D.; Sarbaev, Dzh. S. <i>Zh. Neorg. Khim.</i> 1959, 4, 1849-1859; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1959, 4, 835-841.																																	
VARIABLES: Concentrations of KBr and NaNO ₃ at 298 K	PREPARED BY: J. J. FRITZ																																	
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in KBr-NaNO₃ Solutions at 25° C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_3/\text{mol dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.505</td><td>4.5</td><td>0.0098</td></tr> <tr><td>1.010</td><td>4.0</td><td>0.0118</td></tr> <tr><td>1.535</td><td>3.5</td><td>0.0141</td></tr> <tr><td>2.02</td><td>3.0</td><td>0.0211</td></tr> <tr><td>2.545</td><td>2.5</td><td>0.0276</td></tr> <tr><td>3.05</td><td>2.0</td><td>0.0317</td></tr> <tr><td>3.575</td><td>1.4</td><td>0.0392</td></tr> <tr><td>4.121</td><td>0.9</td><td>0.0523</td></tr> <tr><td>4.767</td><td>0.2</td><td>0.0666</td></tr> <tr><td>5.050</td><td>-</td><td>0.0771</td></tr> </tbody> </table> <p>^a Constant ionic strength of 5 mol dm⁻³.</p>		$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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 argentometrically. 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 ₄ I. 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 ₄ Br; [12124-97-9] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kohn, M.; Klein, A. <i>Z. Anorg. Chem.</i> <u>1912</u> , <i>77</i> , 252-254.												
VARIABLES: Concentration of NH ₄ Br at 291 K	PREPARED BY: J. J. FRITZ												
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in Aqueous NH₄Br at 18°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$c_2/\text{mol dm}^{-3}$</th> <th style="text-align: center;">$\rho_1/\text{g dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$ ^a</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">2.0</td> <td style="text-align: center;">1.9068</td> <td style="text-align: center;">0.0100</td> </tr> <tr> <td style="text-align: center;">3.0</td> <td style="text-align: center;">3.6540</td> <td style="text-align: center;">0.0192</td> </tr> <tr> <td style="text-align: center;">4.0</td> <td style="text-align: center;">6.0588</td> <td style="text-align: center;">0.0318</td> </tr> </tbody> </table> <p>^a Calculated by compiler.</p>		$c_2/\text{mol dm}^{-3}$	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3}$ ^a	2.0	1.9068	0.0100	3.0	3.6540	0.0192	4.0	6.0588	0.0318
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METHOD/APPARATUS/PROCEDURE: Shook CuI with NH ₄ Br solutions at 293 K. Heated with HNO ₃ to drive out bromine and iodine while oxidizing copper to Cu ²⁺ . Precipitated copper as Cu ₂ S 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 ₂ S ₂ O ₃ ; [7772-98-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Yatsimirskii, K. B.; Panova, V. E. <i>Zh. Obshch. Khim.</i> <u>1952</u> , 22, 1284-1289.																						
VARIABLES: Molality of Na ₂ S ₂ O ₃ at 298 K	PREPARED BY: J. J. FRITZ																						
EXPERIMENTAL VALUES: <u>Solubility of CuI in Aqueous Na₂S₂O₃ at 25°C</u> <table border="1" style="margin: auto;"> <thead> <tr> <th style="text-align: center;">$10^2 m_2 / \text{mol kg}^{-1}$</th> <th style="text-align: center;">$10^2 m_1 / \text{mol kg}^{-1}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">1.927</td><td style="text-align: center;">1.555</td></tr> <tr><td style="text-align: center;">3.624</td><td style="text-align: center;">2.780</td></tr> <tr><td style="text-align: center;">4.210</td><td style="text-align: center;">3.446</td></tr> <tr><td style="text-align: center;">7.029</td><td style="text-align: center;">5.270</td></tr> <tr><td style="text-align: center;">7.940</td><td style="text-align: center;">6.084</td></tr> <tr><td style="text-align: center;">8.708</td><td style="text-align: center;">6.654</td></tr> <tr><td style="text-align: center;">18.05</td><td style="text-align: center;">13.85</td></tr> <tr><td style="text-align: center;">32.54</td><td style="text-align: center;">25.03</td></tr> <tr><td style="text-align: center;">44.20</td><td style="text-align: center;">33.55</td></tr> <tr><td style="text-align: center;">53.76</td><td style="text-align: center;">42.82</td></tr> </tbody> </table>		$10^2 m_2 / \text{mol kg}^{-1}$	$10^2 m_1 / \text{mol kg}^{-1}$	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
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METHOD/APPARATUS/PROCEDURE: Held solid CuI in contact with Na ₂ S ₂ O ₃ solution in thermostat at 25 ± 0.1°C for several days, with continuous shaking. Analyzed for total S ₂ O 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 ·5H ₂ O. Source of materials not given. ESTIMATED ERROR: Not given; internal consistency app. 3%. REFERENCES:																						

COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Sodium Thiosulfate; Na ₂ S ₂ O ₃ ; [7772-98-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Golub, A. M.; Butsko, S. S.; Dobryanskaya, L. P. <i>Zh. Neorg. Khim.</i> 1975, 20, 2728-2732; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1975, 20, 1510-1512.																																		
VARIABLES: Concentration of Na ₂ S ₂ O ₃ at unspecified temperature (probably about 298 K)	PREPARED BY: J. J. FRITZ																																		
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METHOD/APPARATUS/PROCEDURE: Added dry CuI to solutions of Na ₂ S ₂ O ₃ , shook mixture in the dark until equilibrium was attained. Analyzed solutions for copper iodometrically.	SOURCE AND PURITY OF MATERIALS: Prepared CuI by treating aqueous CuSO ₄ with KI, washed and dried it before use. Used "C.P." Na ₂ S ₂ O ₃ .																																		
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VARIABLES: Composition at 293 K	PREPARED BY: J. J. FRITZ																																															
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in Na₂S₂O₃-Na₂SO₄ Solutions at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_4/\text{mol dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.200</td><td>0.8</td><td>0.148</td></tr> <tr><td>0.400</td><td>0.6</td><td>0.288</td></tr> <tr><td>0.500</td><td>0.5</td><td>0.374</td></tr> <tr><td>0.600</td><td>0.4</td><td>0.431</td></tr> <tr><td>0.700</td><td>0.3</td><td>0.506</td></tr> <tr><td>0.800</td><td>0.2</td><td>0.580</td></tr> <tr><td>0.900</td><td>0.1</td><td>0.645</td></tr> <tr><td>1.000</td><td>-</td><td>0.723</td></tr> </tbody> </table> <p style="text-align: center;"><u>Solubility of CuI in NaI-Na₂S₂O₃-Na₂SO₄ Solutions at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_3/\text{mol dm}^{-3}$</th> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_4/\text{mol dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.150</td><td>0.665</td><td>0.285</td><td>0.483</td></tr> <tr><td>0.300</td><td>0.630</td><td>0.270</td><td>0.456</td></tr> <tr><td>0.450</td><td>0.595</td><td>0.255</td><td>0.427</td></tr> <tr><td>0.600</td><td>0.560</td><td>0.240</td><td>0.403</td></tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_4/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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	$c_3/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_4/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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. <i>Russ. J. Inorg. Chem.</i> <u>1968</u> , <i>13</i> , 1005. 2. Karyakin, Yu. V.; Angelov, I. I. <i>Pure Chemical Reagents</i> , <u>1955</u> , p. 348.																																															

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VARIABLES: Concentration of K ₂ S ₂ O ₃ at unspecified temperature (probably 298 K)	PREPARED BY: J. J. FRITZ																				
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in Aqueous K₂S₂O₃</u></p> <table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <thead> <tr> <th style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 5px;"><i>c</i>₂/mol dm⁻³</th> <th style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 5px;"><i>c</i>₁/mol dm⁻³</th> </tr> </thead> <tbody> <tr><td style="padding: 2px 10px;">0.0124</td><td style="padding: 2px 10px;">0.0113</td></tr> <tr><td style="padding: 2px 10px;">0.0485</td><td style="padding: 2px 10px;">0.0442</td></tr> <tr><td style="padding: 2px 10px;">0.0997</td><td style="padding: 2px 10px;">0.0913</td></tr> <tr><td style="padding: 2px 10px;">0.1454</td><td style="padding: 2px 10px;">0.1332</td></tr> <tr><td style="padding: 2px 10px;">0.1952</td><td style="padding: 2px 10px;">0.1788</td></tr> <tr><td style="padding: 2px 10px;">0.2408</td><td style="padding: 2px 10px;">0.2204</td></tr> <tr><td style="padding: 2px 10px;">0.2969</td><td style="padding: 2px 10px;">0.2720</td></tr> <tr><td style="padding: 2px 10px;">0.3421</td><td style="padding: 2px 10px;">0.3133</td></tr> <tr><td style="padding: 2px 10px;">0.3983</td><td style="padding: 2px 10px;">0.3645</td></tr> </tbody> </table>		<i>c</i> ₂ /mol dm ⁻³	<i>c</i> 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
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METHOD/APPARATUS/PROCEDURE: Maintained solid CuI in contact with K ₂ S ₂ O 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 ₂ S ₂ O ₃ . No other information given.																				
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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Tanirbergenov, B. <i>Ukr. Khim. Zh.</i> <u>1980</u> , 46 (3), 262-264; <i>Sov. Prog. Chem. (Engl. Transl.)</i> <u>1980</u> , 46 (3), 39-41.																																	
VARIABLES: Concentrations of KNbO ₃ and KNO ₃ at 293 K	PREPARED BY: J. J. FRITZ																																	
EXPERIMENTAL VALUES: <u>Solubility of CuI in KNbO₃-KNO₃ Solutions at 20°C</u> <table border="1" style="margin: auto;"> <thead> <tr> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_3/\text{mol dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.05</td><td>0.28</td><td>0.006</td></tr> <tr><td>0.08</td><td>0.25</td><td>0.009</td></tr> <tr><td>0.11</td><td>0.22</td><td>0.013</td></tr> <tr><td>0.14</td><td>0.19</td><td>0.017</td></tr> <tr><td>0.17</td><td>0.16</td><td>0.020</td></tr> <tr><td>0.21</td><td>0.12</td><td>0.025</td></tr> <tr><td>0.24</td><td>0.09</td><td>0.029</td></tr> <tr><td>0.27</td><td>0.06</td><td>0.033</td></tr> <tr><td>0.30</td><td>0.03</td><td>0.036</td></tr> <tr><td>0.33</td><td>0.00</td><td>0.039</td></tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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. <i>et. al.</i> , <i>Volumetric Analysis (Russ. Transl.)</i> <u>1961</u> , 3, 430.																																	

COMPONENTS: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Iodine; I ₂ ; [7553-56-2] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fedotieff, P. P. <i>Z. Anorg. Chem.</i> <u>1910-11</u> , 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
$\rho_2/g\ dm^{-3}$	$10^3c_2/mol\ dm^{-3}$	$\rho_1/g\ dm^{-3}$	$10^3c_1/mol\ dm^{-3}$	$10^3c_2/mol\ dm^{-3}$
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 I₂

$t/^\circ C$	I ₂ Supplied		Solubility of CuI ^a		Total I ₂ ^b
	$\rho_2/g\ dm^{-3}$	$10^3c_2/mol\ dm^{-3}$	$\rho_1/g\ dm^{-3}$	$10^3c_1/mol\ dm^{-3}$	$10^3c_2/mol\ dm^{-3}$
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 Cu²⁺.^b Total includes iodine derived from dissolved CuI.^c This solution is in equilibrium with both CuI and I₂.

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 ₂ S ₂ O ₈ . 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: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Organic Solvents	EVALUATORS: J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996
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CRITICAL EVALUATION:**BINARY SYSTEMS**

In 1914 Naumann and Schier¹ 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 [(CH₃)₂SO₂] at 400 K as 10^{-13.3} (5 · 10⁻¹⁴) mol² 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 · 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 CuI₂⁻ 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 · 10¹⁴) 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.:



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 Romanenko³ 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 Malik⁴ 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 CuI₂⁻ 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 Cu₂I₃⁻. For NaI-ethanol, they give the reaction



for NaI-acetone, they find a better fit for the reaction



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: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Organic Solvents	EVALUATORS: J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996
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CRITICAL EVALUATION:

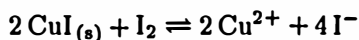
In 1990 Kapler⁵ made an interesting series of measurements on the solubility of CuI in solutions of iodine in 7 polar solvents at 20°C. Kapler⁵ found that his results can be correlated by the equation

$$\log c_{\text{CuI}}/\text{mol dm}^{-3} = a \log c_{\text{I}_2}/\text{mol dm}^{-3} + \log b.$$

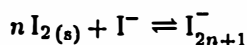
He reported actual solubility data in graphical form only for two systems (See Compilations) but provided the following set of a and b values:

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

Kapler⁵ attributed solution of CuI to the reaction



with the subsequent reaction



increasing the total iodine present in solution and driving the first reaction to the right.

Kapler⁵ 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.

Kapler's⁵ 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 $\text{CuI}-\text{I}_2-\text{H}_2\text{O}$ with the data of Fedotieff⁶.

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.
3. Golub, A.M; Sazhienko, S. M.; Romanenko, L. I. *Ukr. Khim. Zh.* 1962, *28*, 561.
4. Khan, M. M.; Zaidi, S. A. A.; Malik, A. U. *Z. Anorg. Allg. Chem.*, 1970, *375*, 291.
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 ₂ H ₆ O; [67-64-1]	ORIGINAL MEASUREMENTS: Golub, A. M.; Sazhienko, S. M.; Romanenko, L. I. <i>Ukr. Khim. Zh.</i> <u>1962</u> , 28, 561-565.																		
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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.																		
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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:																								

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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																																				
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: (1) Copper(I) Iodide; CuI; [7681-65-4] (2) Iodine; I ₂ ; [7553-56-2] (3) Methanol; CH ₄ O; [67-56-1] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kapler, R. <i>Z. Chem. (Leipzig)</i> <u>1990</u> , 30, 226-227.																												
VARIABLES: Concentration of I ₂ at 293 K	PREPARED BY: E. KÖNIGSBERGER																												
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuI in Solutions of I₂ in Methanol-Water (1:1) at 20°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$c_2/\text{mol dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.110</td><td style="text-align: center;">0.033</td></tr> <tr><td style="text-align: center;">0.140</td><td style="text-align: center;">0.046</td></tr> <tr><td style="text-align: center;">0.170</td><td style="text-align: center;">0.047</td></tr> <tr><td style="text-align: center;">0.220</td><td style="text-align: center;">0.061</td></tr> <tr><td style="text-align: center;">0.251</td><td style="text-align: center;">0.069</td></tr> <tr><td style="text-align: center;">0.290</td><td style="text-align: center;">0.077</td></tr> <tr><td style="text-align: center;">0.327</td><td style="text-align: center;">0.091</td></tr> <tr><td style="text-align: center;">0.389</td><td style="text-align: center;">0.098</td></tr> <tr><td style="text-align: center;">0.424</td><td style="text-align: center;">0.109</td></tr> <tr><td style="text-align: center;">0.470</td><td style="text-align: center;">0.121</td></tr> <tr><td style="text-align: center;">0.527</td><td style="text-align: center;">0.127</td></tr> <tr><td style="text-align: center;">0.595</td><td style="text-align: center;">0.140</td></tr> <tr><td style="text-align: center;">0.648</td><td style="text-align: center;">0.149</td></tr> </tbody> </table> <p>^a The values given in the table were digitized from the graph presented by the author.</p>		$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Rose¹ 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 Ragg² 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 Furman³ gave a value for the solubility product at 298 K of $1.6 \cdot 10^{-11}$ mol² dm⁻⁶ without stating its source, though it would appear to have been derived from the result of Kohlrausch and Rose¹ cited above. In 1950 Vladimirova and Kakovsky⁴ reported a value of $4.8 \cdot 10^{-15}$ mol² dm⁻⁶ at the same temperature, based on some potentiometric measurements and a study of equilibria involving CuSCN and CN⁻. In 1952 Latimer⁵ gave value of $4 \cdot 10^{-14}$ mol² dm⁻⁶ at 298.15 K, zero ionic strength, based on admittedly approximate values of cell potentials involving Cu⁺ and SCN⁻. In 1956 Golub⁶ gave a value of $1.85 \cdot 10^{-13}$ mol² 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 NaNO₃; 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 $4.82 \cdot 10^{-12}$ mol² dm⁻⁶ in 2 mol dm⁻³ NaNO₃ and $7.08 \cdot 10^{-12}$ mol² dm⁻⁶ in 4 mol dm⁻³ NaNO₃. Also in 1966, Chaltykyan⁸ gave a value of $4.0 \cdot 10^{-14}$ mol² dm⁻⁶ without stating its source (probably Latimer⁵). In 1977, Ahrland and Tagesson⁹ give a value (based on solubility and potentiometric measurements of solutions of CuSCN in aqueous NaSCN) of $(1.71 \pm 0.16) \cdot 10^{-15}$ mol² dm⁻⁶ at 298.16 K and a constant ionic strength of 5.0 mol dm⁻³ maintained by NaClO₄ with 0.1 mol dm⁻³ of HClO₄ added. Finally, in 1982 Mazo *et al.*¹⁰ published a value of $(5 \pm 1) \cdot 10^{-15}$ mol² dm⁻⁶ for the solubility product at 298 K in a solution of ionic strength 4 mol dm⁻³ maintained by use of NaClO₄.

Of the values given for the solubility product, the value given by Kolthoff and Furman³ is almost certainly too high. The values given by Golub⁶, Ahrland and Tagesson⁹ 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 CuSCN⁰; 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 Latimer⁵ and of Vladimirova and Kakovsky⁴, both subject to some uncertainty. Latimer⁵ considered the cell potentials used in his calculation as approximate only, without indicating the degree of uncertainty. The approach used by Vladimirova and Kakovsky⁴ 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 $4 \cdot 10^{-14}$ mol² dm⁻⁶ (order of magnitude 10^{-15} mol² dm⁻⁶).

The value given for 298.16 K by Ahrland and Tagesson⁹ was determined from a combination of solubility and potentiometric methods in solutions of 5 mol dm⁻³ ionic strength maintained by acidified NaClO₄, and is probably reliable to their quoted uncertainty for such a medium. That given by Golub⁶ at 293 K was obtained by similar procedures in a medium of ionic strength 4.5 mol dm⁻³ maintained by use of NaNO₃; 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 NaClO₄. It lies between the values given by the other two sets of investigators, much closer to that of Ahrland and Tagesson⁹. It would appear that

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

the values given by Ahrland and Tagesson⁹ 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 Golub⁶ made a series of measurements at 293 K in aqueous KSCN-NaNO₃ 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 NaNO₃. In 1958 Fridman and Sarbaev¹¹ 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 NaNO₃. In 1968 Gyunner and Yakhkind¹² made observations of the solubility at 293 K in aqueous NH₄SCN-NH₄NO₃ 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 NH₄NO₃. In 1977 Ahrland and Tagesson⁹ 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 NaClO₄ with 0.1 mol dm⁻³ of HClO₄ 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 NaClO₄ (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 supply 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 Golub⁶ 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 (NaNO₃)]. The data of Fridman and Sarbaev¹¹ 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-NaClO₄.

Ahrland and Tagesson⁹ 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 ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Tagesson⁹ 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 NH₄SCN

The data of Gyunner and Yakhkind¹² 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 CuSCN⁰, Cu(SCN)₂⁻, Cu(SCN)₃²⁻ and Cu₃(SCN)₆³⁻. 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	$\frac{K_{Smn}^b}{(\text{mol dm}^{-3})^{(1-m-n)}}$	$\frac{\Delta_r H^{\ominus b}}{\text{kJ mol}^{-1}}$	$\beta^{(0)}$	$\beta^{(1)}$	C
CuSCN ⁰	2 · 10 ⁻⁶	-	0.235	0.322	-0.031 ^c
Cu(SCN) ₂ ⁻	6.8 · 10 ⁻⁶	23	0.003	-1.373	0.0182
Cu(SCN) ₃ ²⁻	1.02 · 10 ⁻³	19	0.263	-0.404	0.0027
Cu ₃ (SCN) ₆ ³⁻	4.0 · 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 conjunction with the parameters given for this and other soluble salts by Pitzer and Mayorga¹³.

^b The equilibrium constants and enthalpy changes are for the reaction
 $m \text{CuSCN}_{(s)} + (n - m)\text{SCN}^- \rightleftharpoons \text{Cu}_m(\text{SCN})_n^{m-n}$.

^c There was not sufficient data to evaluate parameters for CuSCN⁰. 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 CuSCN⁰ 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 Tagesson⁹, Fridman and Sarbaev¹¹, Golub⁶, Gyunner and Yakhkind¹² and Korshunov and Malyugina¹⁴. 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: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 $\text{Cu}_m(\text{SCN})_n^{m-n}$ from $\text{CuSCN}_{(s)}$ 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 Malyugina¹⁴ give a value for the dissociation constant of $\text{Cu}(\text{SCN})_4^{3-}$ of $7 \cdot 10^{-10} \text{ mol}^4 \text{ dm}^{-12}$, but this is at least an order of magnitude low.]

Table 32. Solubility Product and Formation Constants for Complexes of CuSCN

Constant ^b	Reference No. ^a				
	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: $T = 293 \text{ K}$, KSCN , $I_c = 4.5 \text{ mol dm}^{-3}$ (NaNO_3); values are also given for K_{14} at 313 and 333 K

Ref. 9: $T = 298 \text{ K}$, NaSCN , $I_c = 5.0 \text{ mol dm}^{-3}$ ($\text{NaClO}_4\text{-HClO}_4$)

Ref. 10: $T = 298 \text{ K}$, NaSCN , $I_c = 4.0 \text{ mol dm}^{-3}$ (NaClO_4)

Ref. 11: $T = 298 \text{ K}$, KSCN , $I_c = 1 \text{ to } 4 \text{ mol dm}^{-3}$

Ref. 12: $T = 293 \text{ K}$, NH_4SCN , $I_c = 4.4 \text{ mol dm}^{-3}$ (NH_4NO_3)

^b Units of K_{Smn} are $(\text{mol dm}^{-3})^{(1-m-n)}$.

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 Sarbaev¹¹ are certainly much too large. The values for K_{S5} given by Golub⁶ and by Mazo *et al.*¹⁰, and the value for K_{S6} given by Golub⁶ 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 $\text{CuSCN}_{(s)}$ 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: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 $c_{\text{CuSCN}}/c_{\text{KSCN}}$. The values of $c_{\text{CuSCN}}/c_{\text{KSCN}}$ are plotted against KSCN concentration in Fig. 6. The values in the table agree with the results of Fridman and Sarbaev¹¹ 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

$c_{\text{KSCN}}/\text{mol dm}^{-3}$	$c_{\text{CuSCN}}/\text{mol dm}^{-3}$	$c_{\text{CuSCN}}/c_{\text{KSCN}}$
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:

- (1) Copper(I) Thiocyanate; CuSCN;
[1111-67-7]
(2) Water; H₂O; [7732-18-5]

EVALUATOR:

J. J. FRITZ
Department of Chemistry
The Pennsylvania State University
June, 1991

CRITICAL EVALUATION:

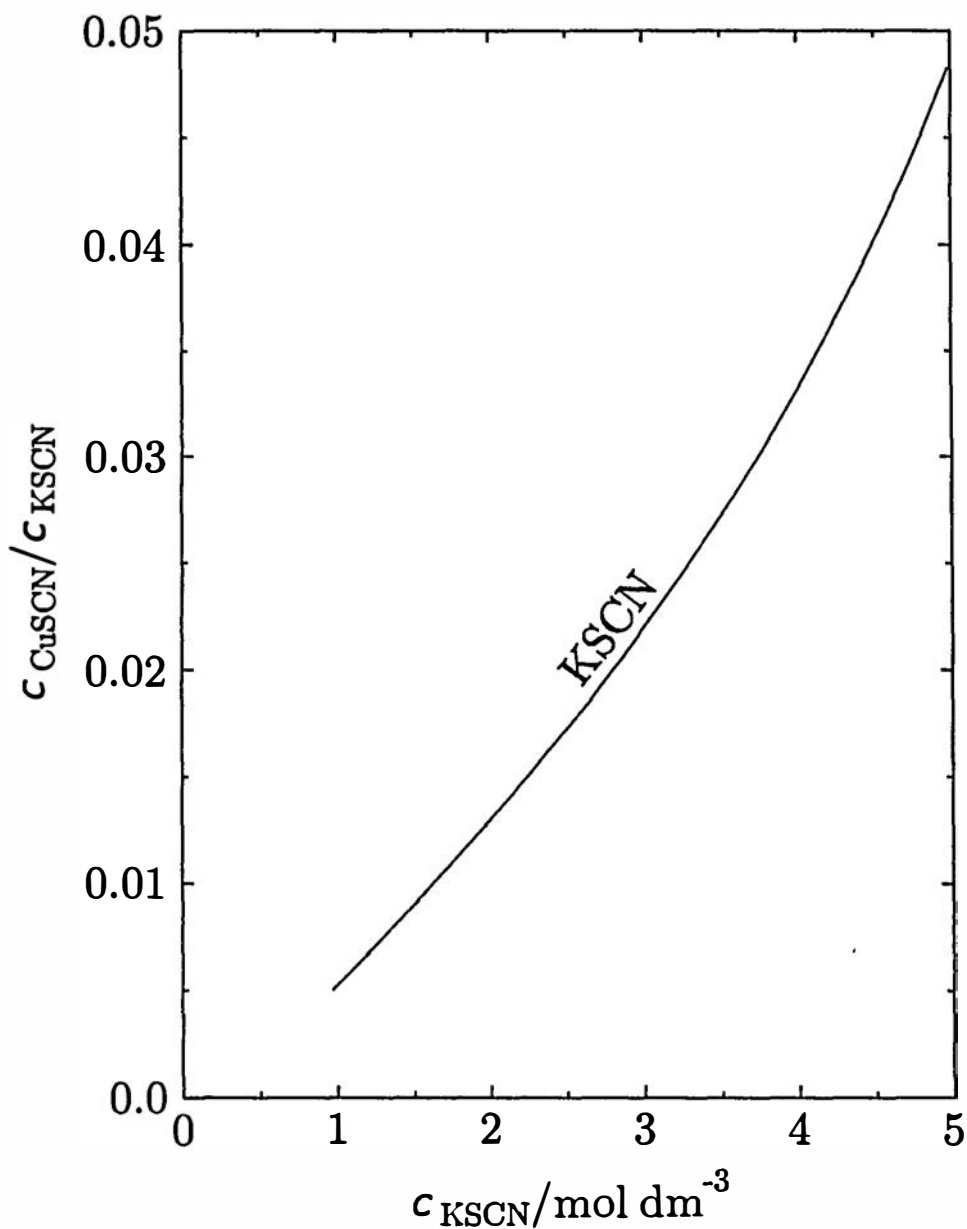


Fig. 6. Ratio of CuSCN Solubility to KSCN Concentration Plotted Against Concentration of KSCN at 298.15 K

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:**SOLUBILITY IN AQUEOUS SOLUTIONS OF SOLUBLE HALIDES**

Fridman and Sarbaev¹¹ 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 NaNO₃. 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 Sarbaev¹¹ 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 Sarbaev¹¹ attribute the solubility in aqueous KI to the formation of addition products Cu(SCN)I⁻, Cu(SCN)I₂²⁻ and Cu(SCN)I₃³⁻. 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)₃I₂⁴⁻.

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⁻ ⇌ CuI₂⁻ + SCN⁻ or 2CuSCN + 2I⁻ ⇌ CuI₂⁻ + 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 Sarbaev¹¹ 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 NaNO₃; 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 (NaNO₃). The solubilities they report are indeed smaller than those given by Fridman and Sarbaev¹¹ 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 Sarbaev¹¹ 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

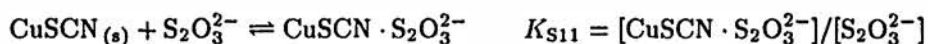
<p>COMPONENTS:</p> <p>(1) Copper(I) Thiocyanate; CuSCN; [1111-67-7]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>case of NaBr solutions. Their measurements should be of the correct order of magnitude, but there is strong suspicion that they are too high.</p> <p>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 NaNO₃ 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 <i>et al.</i>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.</p> <p style="text-align: center;">SOLUBILITY IN AQUEOUS Na₂S₂O₃ AND K₂S₂O₃</p> <p>Three sets of measurements have been reported on the solubility of CuSCN in aqueous solutions of Na₂S₂O₃ and one set in aqueous K₂S₂O₃. In 1952, Yatsimirski and Panova¹⁵ reported a set of solubility measurements at 298 K for Na₂S₂O₃ solutions from 0.017 to 0.83 mol kg⁻¹ (13 points). In 1968 Gyunner and Yakhkind¹² reported solubility measurements at 293 K for Na₂S₂O₃ 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 Na₂SO₄; they also reported four measurements with Na₂S₂O₃ concentrations from 0.45 to 0.81 mol dm⁻³, with NaSCN added as well. In 1976 Golub <i>et al.</i>¹⁶ reported both solubility and potentiometric measurements on CuSCN in both aqueous Na₂S₂O₃ and aqueous K₂S₂O₃ at 298 K with ionic strength maintained at 2.4 mol dm⁻³ by use of the corresponding alkali sulfate. For Na₂S₂O₃ they reported solubilities for 16 concentrations of thiosulfate from 0.22 to 1.4 mol dm⁻³; for K₂S₂O₃ 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 Yakhkind¹² 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.</p> <p>The solubilities determined by Gyunner and Yakhkind¹² and by Golub <i>et al.</i>¹⁶ on aqueous Na₂S₂O₃ 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 <i>et al.</i>, 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.</p> <p>The measurements of Yatsimirski and Panova¹⁵ were apparently made at whatever ionic strength was provided by the concentration of Na₂S₂O₃ 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 Panova¹⁵ 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.</p> <p>The results of Golub <i>et al.</i>¹⁶ on aqueous K₂S₂O₃ are consistent to a per cent or less, but are nearly three times as large as for Na₂S₂O₃ solutions; this is in line with the generally</p>	

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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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 Na₂S₂O₃ solutions.

All of the investigators agreed that the observed solubilities were produced by the formation of an addition complex by a reaction such as $\text{CuSCN}_{(s)} + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{CuSCN} \cdot \text{S}_2\text{O}_3^{2-}$ rather than a replacement reaction such as $\text{CuSCN}_{(s)} + \text{S}_2\text{O}_3^{2-} \rightleftharpoons \text{Cu}(\text{S}_2\text{O}_3)^- + \text{SCN}^-$. 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 Yakhkind¹² 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



and stability constants for formation of the complex from the three ions. In Na₂S₂O₃ 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 $8 \cdot 10^{13} \text{ mol}^{-2} \text{ dm}^6$ (Gyunner); these differences come mainly from the choice for the (uncertain) value of the solubility product of CuSCN. For solutions in aqueous K₂S₂O₃ Golub *et al.*¹⁶ obtained a K_{S11} of 1.95 ± 0.13 and a stability constant of $1.05 \cdot 10^{13} \text{ mol}^{-2} \text{ dm}^6$. (Note: It is possible that other addition complexes may also be formed, but the experimental results provide no basis for identifying any.)

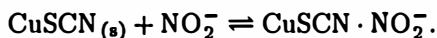
Golub *et al.*¹⁶ used their potentiometric measurements on unsaturated solutions to evaluate stability constants for complexes formed between Cu⁺ and S₂O₃²⁻; they considered complexes CuL⁻, CuL₂³⁻, CuL₃⁵⁻ and CuL₄⁷⁻, where L represents S₂O₃. For Na₂S₂O₃ solutions they gave values ranging from $8 \cdot 10^8 \text{ mol}^{-1} \text{ dm}^3$ for the first complex to $3.2 \cdot 10^{11} \text{ mol}^{-4} \text{ dm}^{12}$ for the last, and values about 10 times higher for K₂S₂O₃ 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 NaNO₂

Swinarski *et al.*⁷ reported the solubility of CuSCN in aqueous NaNO₂ at 293 K, in solutions maintained at a constant ionic strength of 2.0 mol dm^{-3} by use of NaNO₃. They give 9 measurements at NaNO₂ concentrations ranging from 0.4 to 2.02 mol dm^{-3} , with solubility nearly proportional to the concentration of NO₂⁻. Above 0.6 mol dm^{-3} the ratio S/C_L of solubility to NO₂⁻ 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 NaNO₃ without added NaNO₂. 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·NO₂⁻, and this is consistent with their observations. They give a value of $2.37 \cdot 10^8 \text{ mol}^{-2} \text{ dm}^6$ for the stability constant of this ion, based on their value of $4.8 \cdot 10^{-12} \text{ mol}^2 \text{ dm}^{-6}$ for the solubility product at 293 K, $I = 2.0 \text{ mol dm}^{-3}$. This corresponds to an equilibrium constant of $1.14 \cdot 10^{-3}$ for the equilibrium

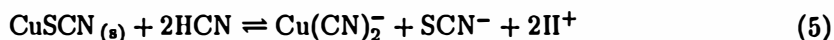
COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:


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 Kakovsky⁴ (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



with an equilibrium constant $K = [\text{Cu}(\text{CN})_2^-][\text{SCN}^-][\text{H}^+]^2/[\text{HCN}]^2$. They report a value for this equilibrium constant of $1.31 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$, 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 Kakovsky⁴ 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: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Water; H ₂ O; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:**REFERENCES**

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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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Golub, A. M. <i>Zh. Neorg. Khim.</i> <u>1956</u> , 1, 2517-2531; <i>J. Inorg. Chem. USSR (Engl. Transl.)</i> <u>1956</u> , 1, 87-100.																																										
VARIABLES: Concentrations of KSCN and NaNO ₃ at 293 K	PREPARED BY: J. J. FRITZ																																										
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuSCN in KSCN-NaNO₃ Solutions at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_3/\text{mol dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.7508</td><td>3.75</td><td>0.006150</td></tr> <tr><td>0.7674</td><td>3.73</td><td>0.00122</td></tr> <tr><td>1.2788</td><td>3.22</td><td>0.004516</td></tr> <tr><td>1.3642</td><td>3.14</td><td>0.00569</td></tr> <tr><td>1.5017</td><td>3.00</td><td>0.005936</td></tr> <tr><td>2.0463</td><td>2.45</td><td>0.01626</td></tr> <tr><td>2.2525</td><td>2.25</td><td>0.02046</td></tr> <tr><td>2.7284</td><td>1.78</td><td>0.03780</td></tr> <tr><td>2.8156</td><td>1.68</td><td>0.04096</td></tr> <tr><td>3.0695</td><td>1.53</td><td>0.07259</td></tr> <tr><td>3.3788</td><td>1.12</td><td>0.07373</td></tr> <tr><td>3.9429</td><td>0.56</td><td>0.1082</td></tr> <tr><td>4.505</td><td>-</td><td>0.1775</td></tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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 ₂ O in concentrated NH ₄ SCN 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 ₄ SCN; [1762-95-4] (3) Ammonium Nitrate; NH ₄ NO ₃ ; [6484-52-2] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Gyunner, E. A.; Yakhkind, N. D. <i>Zh. Neorg. Khim.</i> <u>1968</u> , <i>13</i> , 2758-2763; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1968</u> , <i>13</i> , 1420-1422.																																	
VARIABLES: Concentrations of NH ₄ SCN and NH ₄ NO ₃ at 293 K	PREPARED BY: J. J. FRITZ																																	
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METHOD/APPARATUS/PROCEDURE: Method described in Ref. 1	SOURCE AND PURITY OF MATERIALS: Prepared CuSCN by dissolving Cu ₂ O in concentrated NH ₄ SCN solution; Washed, recrystallized and dried the product. Used "C.P." NH ₄ SCN and NH ₄ NO ₃ . ESTIMATED ERROR: Not given. REFERENCES: 1. Gyunner, E. A.; Yakhkind, N. D. <i>Russ.</i> <i>J. Inorg. Chem</i> <u>1968</u> , <i>13</i> , 128.																																	

COMPONENTS: (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Mazo, L. H.; Neves, E. de A.; De Azevedo, L. A. <i>An. Simp. Bras. Eletroquim. Eletroanal.</i> 3rd, 1982, 1, 333-338.																
VARIABLES: Concentration of NaSCN at 298 K	PREPARED BY: J. J. FRITZ																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuSCN in NaSCN–NaClO₄ Solutions at 25°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$c_2/\text{mol dm}^{-3}$</th> <th style="text-align: center;">$10^3 c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.238</td><td style="text-align: center;">0.125</td></tr> <tr><td style="text-align: center;">0.358</td><td style="text-align: center;">0.463</td></tr> <tr><td style="text-align: center;">0.528</td><td style="text-align: center;">1.06</td></tr> <tr><td style="text-align: center;">0.763</td><td style="text-align: center;">2.55</td></tr> <tr><td style="text-align: center;">1.000</td><td style="text-align: center;">4.94</td></tr> <tr><td style="text-align: center;">1.250</td><td style="text-align: center;">6.66</td></tr> <tr><td style="text-align: center;">1.53</td><td style="text-align: center;">10.10</td></tr> </tbody> </table> <p>^a The table gives the data read from the graph of Mazo <i>et al.</i> by the compiler. Nominal ionic strength of 4.0 mol dm⁻³ maintained by addition of NaClO₄.</p>		$c_2/\text{mol dm}^{-3}$	$10^3 c_1/\text{mol dm}^{-3}$	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
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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. <i>Quantitative Inorganic Analysis</i> , Longman, London, 1955, p. 431.																

COMPONENTS: (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Ahrland, S.; Tagesson, B. <i>Acta Chem. Scand.</i> 1977 , A31, 615-624.
VARIABLES: Concentration of Thiocyanate at 298 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in NaSCN-NaClO₄-(HClO₄) Solutions at 25°C

$\frac{[\text{SCN}^-]_{\text{free}}}{\text{mol dm}^{-3}}$	$\frac{c_3}{\text{mol dm}^{-3}}$	$\frac{c_4}{\text{mol dm}^{-3}}$	$\frac{[\text{SCN}^-]_{\text{total}}^{\text{a}}}{\text{mol dm}^{-3}}$	$\frac{c_1}{\text{mol dm}^{-3}}$
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 (<i>Mallinckrodt p. a.</i>) used without further purification.
	ESTIMATED ERROR: Not given.
	REFERENCES:

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [11 11-67-7] (2) Sodium Chloride; NaCl; [7647-14-5] (3) Sodium Nitrate; NaNO ₃ ; [7631-99-4] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Swinarski, A.; Danilczuk, E.; Gogolin, R. <i>Roczniki Chem.</i> <u>1966</u> , 40, 737-741.																														
VARIABLES: Concentrations of NaCl and NaNO ₃ at 293 K	PREPARED BY: J. J. FRITZ																														
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuSCN in NaCl-NaNO₃ Solutions at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_3/\text{mol dm}^{-3}$</th> <th>$10^4 c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>4.0</td><td>-</td><td>5.36</td></tr> <tr><td>3.8</td><td>0.2</td><td>5.12</td></tr> <tr><td>3.4</td><td>0.6</td><td>4.80</td></tr> <tr><td>3.0</td><td>1.0</td><td>4.26</td></tr> <tr><td>2.8</td><td>1.2</td><td>4.16</td></tr> <tr><td>2.6</td><td>1.4</td><td>3.84</td></tr> <tr><td>2.4</td><td>1.6</td><td>3.65</td></tr> <tr><td>2.2</td><td>1.8</td><td>3.39</td></tr> <tr><td>2.0</td><td>2.0</td><td>3.21</td></tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$10^4 c_1/\text{mol dm}^{-3}$	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
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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: (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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Swinarski, A.; Danilczuk, E.; Gogolin, R. <i>Roczniki Chem.</i> <u>1966</u> , <i>40</i> , 737-741.
VARIABLES: Concentrations of NaBr and NaNO ₃ at 293 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuSCN in NaBr-NaNO₃ Solutions at 20°C

$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	$10^4 c_1/\text{mol dm}^{-3}$
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 ₂ S ₂ O ₃ ; [7772-98-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Yatsimirskii, K. B.; Panova, V. E. <i>Zh. Obshch. Khim.</i> <u>1952</u> , 22, 1284-1289.																																
VARIABLES: Molality of Na ₂ S ₂ O ₃ at 298 K	PREPARED BY: J. J. FRITZ																																
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuSCN in Aqueous Na₂S₂O₃ at 25° C</u></p> <table style="margin-left: auto; margin-right: auto; border-collapse: collapse;"> <thead> <tr> <th style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 5px;">$10^2 m_2 / \text{mol kg}^{-1}$</th> <th style="border-top: 1px solid black; border-bottom: 1px solid black; padding: 5px;">$10^2 m_1 / \text{mol kg}^{-1}$</th> </tr> </thead> <tbody> <tr><td style="padding: 5px;">1.720</td><td style="padding: 5px;">0.3368</td></tr> <tr><td style="padding: 5px;">2.109</td><td style="padding: 5px;">0.4194</td></tr> <tr><td style="padding: 5px;">3.542</td><td style="padding: 5px;">0.7705</td></tr> <tr><td style="padding: 5px;">4.900</td><td style="padding: 5px;">0.9652</td></tr> <tr><td style="padding: 5px;">6.370</td><td style="padding: 5px;">1.305</td></tr> <tr><td colspan="2" style="padding: 5px 5px 10px 5px;"> </td></tr> <tr><td style="padding: 5px;">7.750</td><td style="padding: 5px;">1.748</td></tr> <tr><td style="padding: 5px;">11.94</td><td style="padding: 5px;">2.822</td></tr> <tr><td style="padding: 5px;">18.41</td><td style="padding: 5px;">4.304</td></tr> <tr><td style="padding: 5px;">24.32</td><td style="padding: 5px;">6.127</td></tr> <tr><td style="padding: 5px;">33.72</td><td style="padding: 5px;">8.645</td></tr> <tr><td colspan="2" style="padding: 5px 5px 10px 5px;"> </td></tr> <tr><td style="padding: 5px;">42.46</td><td style="padding: 5px;">11.01</td></tr> <tr><td style="padding: 5px;">52.16</td><td style="padding: 5px;">13.54</td></tr> <tr><td style="padding: 5px;">83.23</td><td style="padding: 5px;">23.98</td></tr> </tbody> </table>		$10^2 m_2 / \text{mol kg}^{-1}$	$10^2 m_1 / \text{mol kg}^{-1}$	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
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METHOD/APPARATUS/PROCEDURE: Held solid CuSCN in contact with Na ₂ S ₂ O ₃ solution in thermostat at 25 ± 0.1° C for several days, with continuous shaking. Analyzed for total S ₂ O 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 · 5H ₂ O and KSCN. Source of materials not given.																																
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COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Sodium Thiosulfate; Na ₂ S ₂ O ₃ ; [7772-98-7] (3) Sodium Sulfate; Na ₂ SO ₄ ; [7757-82-6] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. <i>Zh. Neorg. Khim.</i> 1976 , <i>21</i> , 2733-2737; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1976 , <i>21</i> , 1504-1506.																																		
VARIABLES: Concentration of Na ₂ S ₂ O ₃ at 298 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER																																		
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuSCN in Na₂S₂O₃-Na₂SO₄ Solutions at 25°C^a</u></p> <table style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;"><u>c₂/mol dm⁻³</u></th> <th style="text-align: center;"><u>c₁/mol dm⁻³</u></th> </tr> </thead> <tbody> <tr><td style="text-align: center;">0.219</td><td style="text-align: center;">0.0524</td></tr> <tr><td style="text-align: center;">0.257</td><td style="text-align: center;">0.0602</td></tr> <tr><td style="text-align: center;">0.299</td><td style="text-align: center;">0.0704</td></tr> <tr><td style="text-align: center;">0.333</td><td style="text-align: center;">0.0794</td></tr> <tr><td style="text-align: center;">0.445</td><td style="text-align: center;">0.1050</td></tr> <tr><td style="text-align: center;">0.500</td><td style="text-align: center;">0.1170</td></tr> <tr><td style="text-align: center;">0.527</td><td style="text-align: center;">0.1280</td></tr> <tr><td style="text-align: center;">0.555</td><td style="text-align: center;">0.1340</td></tr> <tr><td style="text-align: center;">0.667</td><td style="text-align: center;">0.1580</td></tr> <tr><td style="text-align: center;">0.713</td><td style="text-align: center;">0.1680</td></tr> <tr><td style="text-align: center;">0.833</td><td style="text-align: center;">0.1990</td></tr> <tr><td style="text-align: center;">0.984</td><td style="text-align: center;">0.2260</td></tr> <tr><td style="text-align: center;">1.020</td><td style="text-align: center;">0.2320</td></tr> <tr><td style="text-align: center;">1.140</td><td style="text-align: center;">0.2620</td></tr> <tr><td style="text-align: center;">1.250</td><td style="text-align: center;">0.2850</td></tr> <tr><td style="text-align: center;">1.428</td><td style="text-align: center;">0.3230</td></tr> </tbody> </table> <p>^a Nominal ionic strength of 2.4 mol dm⁻³ maintained by addition of Na₂SO₄.</p>		<u>c₂/mol dm⁻³</u>	<u>c₁/mol dm⁻³</u>	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
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AUXILIARY INFORMATION																																			
METHOD/APPARATUS/PROCEDURE: Shook solid CuSCN with Na ₂ S ₂ O 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: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Potassium Thiosulfate; K ₂ S ₂ O ₃ ; [10294-66-3] (3) Potassium Sulfate; K ₂ SO ₄ ; [7778-80-5] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Golub, A. M.; Dobryanskaya, L. P.; Butsko, S. S. <i>Zh. Neorg. Khim.</i> 1976 , <i>21</i> , 2733-2737; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1976 , <i>21</i> , 1504-1506.
VARIABLES: Concentration of K ₂ S ₂ O ₃ at 298 K	PREPARED BY: J. J. FRITZ and E. KÖNIGSBERGER

EXPERIMENTAL VALUES:

Solubility of CuSCN in K₂S₂O₃-K₂SO₄ Solutions at 25°C^a

$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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 K₂SO₄.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Shook solid CuSCN with K ₂ S ₂ O 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: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Sodium Thiosulfate; Na ₂ S ₂ O ₃ ; [7772-98-7] (3) Sodium Thiocyanate; NaSCN; [540-72-7] (4) Sodium Sulfate; Na ₂ SO ₄ ; [7757-82-6] (5) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Gyunner, E. A.; Yakhkind, N. D. <i>Zh. Neorg. Khim.</i> <u>1968</u> , <i>13</i> , 2758-2763; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1968</u> , <i>13</i> , 1420-1422.
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VARIABLES: Concentrations of Na ₂ S ₂ O ₃ , NaSCN and Na ₂ SO ₄ at 293 K	PREPARED BY: J. J. FRITZ
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EXPERIMENTAL VALUES:

Solubility of CuSCN in Na₂S₂O₃-Na₂SO₄ Solutions at 20°C

$c_2/\text{mol dm}^{-3}$	$c_4/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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-Na₂S₂O₃-Na₂SO₄ Solutions at 20°C

$c_3/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_4/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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 ₂ O in concentrated NH ₄ SCN 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. <i>Russ. J. Inorg. Chem.</i> <u>1968</u> , <i>13</i> , 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fridman, Ya D.; Sarbaev, Dzh. S. <i>Zh. Neorg. Khim.</i> 1959 , 4, 1849-1859; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> 1959 , 4, 835-841.																																				
VARIABLES: Concentrations of KSCN, KI and NaNO ₃ at 298 K	PREPARED BY: J. J. FRITZ																																				
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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 ₄ SCN. Sources and purities of materials not given. ESTIMATED ERROR: Not given. REFERENCES:																																				

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EXPERIMENTAL VALUES:

(continued)

Solubility of CuSCN in KI-NaNO₃ Solutions at 25°C

$c_3/\text{mol dm}^{-3}$	$c_4/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Fridman, Ya D.; Sarbaev, Dzh. S. <i>Zh. Neorg. Khim.</i> <u>1959</u> , 4, 1849-1859; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1959</u> , 4, 835-841.
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EXPERIMENTAL VALUES:

(continued)

Solubility of CuSCN in KI-KSCN Solutions at 25°C

$c_3/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Swinarski, A.; Danilczuk, E.; Gogolin, R. <i>Roczniki Chem.</i> 1966 , <i>40</i> , 737-741.
VARIABLES: Concentrations of NaNO ₂ and NaNO ₃ at 293 K	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:
Solubility of CuSCN in NaNO₂-NaNO₃ Solutions at 20°C

$c_2/\text{mol dm}^{-3}$	$c_3/\text{mol dm}^{-3}$	pH	$10^4 c_1/\text{mol dm}^{-3}$
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 NaNO₂-NaNO₃ 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 Cu²⁺.

SOURCE AND PURITY OF MATERIALS:

Prepared CuSCN by reduction of aqueous mixtures of CuSO₄ 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Vladimirova, M. G.; Kakovsky, I. A. <i>Zh. Prikl. Khim.</i> <u>1950</u> , 23 , 580-598; <i>J. Appl. Chem. (USSR) (Engl. Transl.)</i> <u>1950</u> , 23 , 615-632.																																																
VARIABLES: Concentration of HCN at 298 K	PREPARED BY: J. J. FRITZ																																																
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COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-7] (2) Organic Solvents	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

No measurements were found on any binary systems involving CuSCN and an organic solvent. The results on ternary systems are given below.

Golub¹ 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)₃²⁻, 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 dm³, respectively, for formation of the singly and doubly charged complexes from solid CuSCN.

Golub¹ 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 CuSCN⁰ 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.

Golub¹ 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 Kilimnik² succeeded in preparing a compound K₂Cu(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. Harris³ succeeded in preparing the pyridinium compounds (C₅H₅NH)Cu^I(SCN)₂ and (C₅H₅NH)Cu^IISCN, also from acetone solution. Rosenheim and Steinhäuser⁴ prepared the salt CuSCN · NH₄SCN · 4(NH₄)₂S₂O₃ and verified its composition by chemical analysis. Canneri and Luchini⁵ prepared the salt 2CuSCN · 5Na₂S₂O₃ and verified its composition by chemical analysis.

REFERENCES

1. Golub, A. M. *Zh. Neorg. Khim.* **1956**, *1*, 2517; *J. Inorg. Chem. USSR (Engl. Trans.)* **1956**, *1*, 87.
2. Golub, A. M.; Kilimnik, G. M. *Zh. Neorg. Khim.* **1959**, *4*, 1352; *Russ. J. Inorg. Chem.* **1959**, *4*, 608.
3. Harris, C. M. *J. Proc. Roy. Soc. New South Wales* **1951**, *84*, 111.
4. Rosenheim, A.; Steinhäuser, S. *Z. Anorg. Chem.* **1900**, *25*, 103.
5. Canneri, G.; Luchini, R. *Gazz. Chim. Ital.* **1922**, *52(II)*, 261.

COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-3] (2) Potassium Thiocyanate; KSCN; [333-20-0] (3) Ethanol; C ₂ H ₆ O; [64-17-5]	ORIGINAL MEASUREMENTS: Golub, A. M. <i>Zh. Neorg. Khim.</i> <u>1956</u> , 1, 2517-2531; <i>J. Inorg. Chem. USSR</i> <u>1956</u> , 1, 87-100.												
VARIABLES: Concentration of KSCN at 293 K	PREPARED BY: J. J. FRITZ												
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuSCN in Ethanolic KSCN at 20°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th style="text-align: center;">$c_2/\text{mol dm}^{-3}$</th> <th style="text-align: center;">$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr> <td style="text-align: center;">0.06768</td> <td style="text-align: center;">0.9678</td> </tr> <tr> <td style="text-align: center;">0.1160</td> <td style="text-align: center;">2.2258</td> </tr> <tr> <td style="text-align: center;">0.2031</td> <td style="text-align: center;">4.516</td> </tr> <tr> <td style="text-align: center;">0.2901</td> <td style="text-align: center;">7.42</td> </tr> <tr> <td style="text-align: center;">0.4061</td> <td style="text-align: center;">11.61</td> </tr> </tbody> </table>		$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	0.06768	0.9678	0.1160	2.2258	0.2031	4.516	0.2901	7.42	0.4061	11.61
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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 ₂ O in concentrated, purified NH ₄ SCN. Thereafter the precipitate was reprecipitated, washed and dried. Recrystallized KSCN and redistilled absolute ethanol were used.												
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COMPONENTS: (1) Copper(I) Thiocyanate; CuSCN; [1111-67-3] (2) Potassium Thiocyanate; KSCN; [333-20-0] (3) Acetone; C ₂ H ₆ O; [67-64-1]	ORIGINAL MEASUREMENTS: Golub, A. M. <i>Zh. Neorg. Khim.</i> <u>1956</u> , <i>1</i> , 2517-2531; <i>J. Inorg. Chem. USSR</i> <u>1956</u> , <i>1</i> , 87-100.																						
VARIABLES: Concentration of KSCN at 293 K	PREPARED BY: J. J. FRITZ																						
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COMPONENTS: (1) Copper(I) Selenocyanate; CuSeCN; [no registry number known] (2) Water; H ₂ O; [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. <i>Zh. Neorg. Khim.</i> <u>1960</u> , 5, 1973; <i>Russ J. Inorg. Chem. (Engl. Transl.)</i> <u>1960</u> , 5, 961.	

<p>COMPONENTS:</p> <p>(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATORS:</p> <p>J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996</p>
<p>CRITICAL EVALUATION:</p> <p style="text-align: center;">THE BINARY SYSTEM</p> <p>The only measurement of the solubility of cuprous cyanide in pure water found in the literature was that of Ragg¹ (1950), who gave a value of $2.6 \cdot 10^{-3} \text{ g dm}^{-3}$ at 288 K; he also gave a value of $6.0 \cdot 10^{-3} \text{ g dm}^{-3}$ in sea water. Vladimirova and Kakovsky² (1950) give a value for the solubility product at 298 K of $3.2 \cdot 10^{-20} \text{ mol}^2 \text{ dm}^{-6}$. Their value was obtained indirectly by measurement of the equilibrium constants of the reactions $\text{CuCN}_{(s)} + \text{HCN} \rightleftharpoons \text{Cu}(\text{CN})_2^- + \text{H}^+$ and $\text{CuSCN}_{(s)} + 2 \text{HCN} \rightleftharpoons \text{Cu}(\text{CN})_2^- + \text{SCN}^- + 2 \text{H}^+$. Butler³ reported the same value for the solubility product in 1964, without attribution.</p> <p>The value given by Ragg¹ for the solubility of CuCN in pure water corresponds to a concentration of $2.9 \cdot 10^{-5} \text{ mol dm}^{-3}$, much higher than would result from dissociative solution of CuCN. Another possibility is the reaction $2 \text{CuCN}_{(s)} \rightleftharpoons \text{Cu}^+ + \text{Cu}(\text{CN})_2^-$, for which the results of Vladimirova and Kakovsky² give an equilibrium constant of $5.1 \cdot 10^{-16} \text{ mol}^2 \text{ dm}^{-6}$. However, this would yield a solubility of only about $2 \cdot 10^{-8} \text{ mol dm}^{-3}$. The additional solubility observed by Ragg¹ could have been due to the production of neutral CuCN^0 (properties unknown) or possibly to acidity in the water used.</p> <p>The value of $3.2 \cdot 10^{-20} \text{ mol}^2 \text{ dm}^{-6}$ given by Vladimirova and Kakovsky² 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 Ragg¹ and could be as low as the value $2 \cdot 10^{-8} \text{ mol dm}^{-3}$ derived from the measurements of Vladimirova and Kakovsky².</p> <p style="text-align: center;">SOLUBILITY IN AQUEOUS SOLUTIONS OF ALKALI CYANIDES AND HCN</p> <p>There have been three investigations of the solubility of CuCN in aqueous solutions of alkali cyanides. In 1924 Bassett and Corbet⁴ published a complete phase diagram for the system CuCN-KCN-H₂O at 298 K. In 1938 Plaksin and Fishkova⁵ made similar measurements on this system and the system CuCN-NaCN-H₂O at 288, 298 and 308 K. In 1950 Vladimirova and Kakovsky² measured the solubility of CuCN in 7 concentrations of aqueous HCN at 298 K.</p> <p>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.</p> <p>Results with Aqueous KCN</p> <p>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 Corbet⁴ and Plaksin and Fishkova⁵. 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. $\text{KCu}_2(\text{CN})_3 \cdot \text{H}_2\text{O}$, $\text{KCu}(\text{CN})_2$, $\text{K}_3\text{Cu}(\text{CN})_4 \cdot \text{H}_2\text{O}$ and $\text{K}_3\text{Cu}(\text{CN})_4$, 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. $\text{KCu}(\text{CN})_2$ 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. $\text{K}_3\text{Cu}(\text{CN})_4$ and its hydrate were found at KCN molalities between 10.2 and 12.8 and cuprous molalities from 1.23 to 6.0. [Note that they report the <u>equilibrium</u> 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.]</p>	

<p>COMPONENTS:</p> <p>(1) Copper(I) Cyanide; CuCN; [544-92-3]</p> <p>(2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATORS:</p> <p>J. J. FRITZ, Department of Chemistry The Pennsylvania State University</p> <p>E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben</p> <p>June, 1996</p>
<p>CRITICAL EVALUATION:</p> <p>Plaksin and Fishkova⁵ 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 K₂Cu(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 Corbet³ 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 Corbet³ observed that conversion of CuCN to double salt was incomplete, even after 2 days equilibration.)</p> <p>The two sets of solubilities at 298 K can be compared after conversion of the data of Plaksin and Fishkova⁵ to mol kg⁻¹ using the densities they report for their solutions. In the range where both groups reported values, those of Plaksin and Fishkova⁵ are 5 to 10 per cent higher than those of Bassett and Corbet⁴. The latter would appear to be the more reliable and are Recommended for use. The data of Plaksin and Fishkova⁵ at 288 and 308 K are Accepted tentatively, subject to an uncertainty of 10 per cent on the high side.</p> <p>The question of the double salts produced between KCN and CuCN has been the subject of many past investigations. For example, in 1902 Itzig⁶ reported salts corresponding to KCu₂(CN)₃·H₂O, KCu(CN)₂, K₂Cu₃(CN)₅ and K₃Cu(CN)₄ at room temperature. In 1904 Kunschert⁷ reported observation of three of these (excepting K₂Cu₃(CN)₅). In 1912 Truthe⁸ identified KCu₂(CN)₃, KCu(CN)₂ and K₃Cu(CN)₄ in his study of the phase diagram of the system CuCN-KCN in the temperature range 500 to 900 K. Bassett and Corbet⁴ (1924) confirmed the presence of KCu₂(CN)₃·H₂O, KCu(CN)₂ and K₃Cu(CN)₄·H₂O by chemical analysis. Finally, Staritsky and coworkers described the preparation and crystal structure of KCu(CN)₂·9H₂O, KCu₂(CN)₃·H₂O¹⁰ and K₃Cu(CN)₄¹¹. Thus the three compounds KCu₂(CN)₃, KCu(CN)₂ and K₃Cu(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.</p> <p>Results with Aqueous NaCN</p> <p>Plaksin and Fishkova⁵ 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.</p> <p>There is some information in the literature about double salt formation between CuCN and NaCN. Truthe⁸ identified compounds corresponding to NaCu(CN)₂, Na₂Cu(CN)₃ and Na₃Cu(CN)₄ in his study of the phase behaviour of the system CuCN-NaCN between 550 and 820 K. Plaksin and Fishkova⁵ claimed to find the first two of these in equilibrium with NaCN solutions, along with two pentacyano salts, Na₃Cu₂(CN)₅ and (at their lowest temperature) Na₄Cu(CN)₅. The three salts found by Truthe⁸ 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.</p>	

COMPONENTS:

- (1) Copper(I) Cyanide; CuCN; [544-92-3]
 (2) Water; H₂O; [7732-18-5]

EVALUATORS:

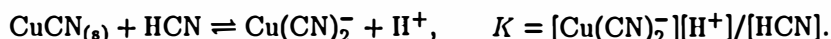
J. J. FRITZ, Department of Chemistry
 The Pennsylvania State University
 E. KÖNIGSBERGER, Department of Physical
 Chemistry, Montanuniversität Leoben
 June, 1996

CRITICAL EVALUATION:

Results with Aqueous HCN

The only results reported for the solubility of CuCN in aqueous HCN are those of Vladimirova and Kakovsky². 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 H₂SO₄ 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 H₂SO₄ to the medium reduces the solubility for a given HCN concentration.

Vladimirova and Kakovsky² interpreted their solubility data in terms of the reaction



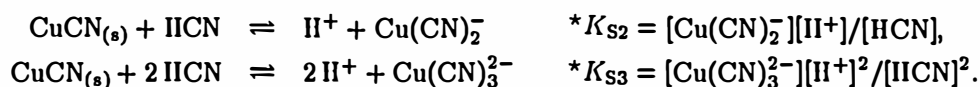
They derived a value of $1.22 \cdot 10^{-5}$ mol dm⁻³ for this equilibrium constant. With estimated corrections for ionic strength effects, this fitted their data for "pure" aqueous HCN within a few per cent and the data for solutions containing strong acid to a poorer precision of 10 to 20 per cent, apparently because of difficulty in determination of the final concentration of H⁺.

Vladimirova and Kakovsky² 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 H₂O 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⁺]/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[II] 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)₃²⁻ as predominant species while the initial concentration of HCN remains virtually unchanged. Thus the results were interpreted in terms of the equilibria



<p>COMPONENTS:</p> <p>(1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H₂O; [7732-18-5]</p>	<p>EVALUATORS:</p> <p>J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996</p>
<p>CRITICAL EVALUATION:</p> <p>The neutral complex CuCN⁰ became important only at the lowest CN⁻ concentrations used. By taking the Cu(I) speciation into account, Königsberger <i>et al.</i>¹⁵ derived log *K_{S2} values for the 4 ionic strengths investigated and obtained log *K_{S2}/mol dm⁻³ = -4.9 ± 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 <i>et al.</i>¹⁵ agrees perfectly with that of Vladimirova and Kakovsky², however, Königsberger <i>et al.</i>¹⁵ investigated a well-buffered system and were able to measure p[H] values very precisely.</p> <p><u>Equilibrium Constants for Complex Formation</u></p> <p>In the course of their measurements Vladimirova and Kakovsky² obtained a value of 5 · 10⁻⁵ for the equilibrium constant of the reaction CuCN_(s) + CN⁻ ⇌ Cu(CN)₂⁻. This can be compared with a value of 3.2 · 10⁻⁴ derived from their solubility product and a value of 1 · 10⁻¹⁶ mol² dm⁻⁶ for the dissociation constant of Cu(CN)₂⁻ given by Latimer¹². They also give values for the Gibbs energy changes involved in formation of Cu(CN)₃²⁻ and Cu(CN)₄³⁻ from the singly charged complex ion, but the meaning of their numbers is unclear. [In 1931 Kolthoff and Furman¹³ had given a value of 5 · 10⁻²⁸ mol⁴ dm⁻¹² for the dissociation constant of Cu(CN)₄³⁻ (source not given).] In 1964 Butler³ gave values for the equilibrium constants for formation of Cu(CN)₂⁻, Cu(CN)₃²⁻ and Cu(CN)₄³⁻ from CuCN_(s) and CN⁻, supposedly corrected to zero ionic strength; he did not give the source of his information.</p> <p>In 1993 Hefter <i>et al.</i>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 β₁/mol⁻¹ dm³ = 16.33, log β₂/mol⁻² dm⁶ = 23.97, log β₃/mol⁻³ dm⁹ = 29.40 and log β₄/mol⁻⁴ dm¹² = 31.87, are valid for I_c = 1 mol dm⁻³ NaCl and 25°C. Hefter <i>et al.</i>¹⁶ present a table where their results are compared with data given in a comprehensive review¹⁷. It should be noted that CuCN⁰ is not normally detected in this type of measurement; the value given by Hefter <i>et al.</i>¹⁶ was estimated. In fact, the results of the CuCN solubility study of Königsberger <i>et al.</i>¹⁵ suggest that log β₁ may actually be lower by about half an order of magnitude.</p> <p><u>Other Double Salts Containing CuCN</u></p> <p>In 1891 Fleurent¹⁴ reported a compound NiH₄Cu₂(CN)₃·3NH₃ with its composition verified by chemical analysis. Itzig⁶ isolated a mixed compound K₃Cu(CN)₃SCN·H₂O when CuCN was dissolved in an aqueous mixture of KCN and KSCN.</p> <p><u>Other Information</u></p> <p>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.</p>	

COMPONENTS: (1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Water; H ₂ O; [7732-18-5]	EVALUATORS: J. J. FRITZ, Department of Chemistry The Pennsylvania State University E. KÖNIGSBERGER, Department of Physical Chemistry, Montanuniversität Leoben June, 1996
CRITICAL EVALUATION: <p style="text-align: center;">REFERENCES</p> <ol style="list-style-type: none"> 1. Ragg, M. <i>Farbe und Lack</i> <u>1950</u>, <i>56</i>, 435. 2. Vladimirova, M. G.; Kakovsky, I. A. <i>Zh. Prikl. Khim.</i> <u>1950</u>, <i>23</i>, 590; <i>J. Appl. Chem. USSR (Engl. Transl.)</i> <u>1950</u>, <i>23</i>, 615. 3. Butler, J. N. <i>Ionic Equilibrium</i>, Addison Wesley, Massachusetts, <u>1964</u>, p. 275. 4. Bassett, H.; Corbet, A. S. <i>J. Chem. Soc.</i> 1924, <i>125</i>, 1660. 5. Plaksin, I. N.; Fishkova, Ts. E. <i>Izv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim. Akad. Nauk SSSR</i> <u>1938</u>, <i>10</i>, 229. 6. Itzig, H. <i>Ber. Dtsch. Chem. Ges.</i> <u>1902</u>, <i>35</i>, 106. 7. Kunschert, F. <i>Z. Anorg. Chem.</i> <u>1904</u>, <i>41</i>, 359. 8. Truthe, W. <i>Z. Anorg. Chem.</i> <u>1912</u>, <i>76</i>, 129. 9. Staritsky, E.; Walker, D. I. <i>Anal. Chem.</i> <u>1956</u>, <i>28</i>, 419. 10. Walker, D. I.; Staritsky, E. <i>Anal. Chem.</i> <u>1956</u>, <i>28</i>, 421. 11. Staritsky, E.; Ellinger, F. H. <i>Anal. Chem.</i> <u>1956</u>, <i>28</i>, 422. 12. Latimer, W. M. <i>Oxidation Potentials</i>, Prentice Hall, New York, <u>1952</u>, p. 186. 13. Kolthoff, I. M.; Furman, N. H. <i>Potentiometric Titrations</i>, Wiley, New York, <u>1931</u>, p. 453. 14. Fleurent, M. E. <i>C. R. Hebd. Seances Acad. Sci.</i> <u>1891</u>, <i>113</i>, 1045. 15. Königsberger, E.; Solis, J. S.; May, P. M.; Hefter, G. T. <i>6th International Symposium on Solubility Phenomena</i> <u>1994</u>, Buenos Aires, Argentina. 16. Hefter, G. T.; May, P. M.; Sipos, P. <i>J. Chem. Soc., Chem. Commun.</i> <u>1993</u>, 1704. 17. Beck, M. T. <i>Pure Appl. Chem.</i> <u>1987</u>, <i>59</i>, 1703. 	

COMPONENTS: (1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Potassium Cyanide; KCN; [151-50-8] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Bassett, H.; Corbet, A. S. <i>J. Chem. Soc.</i> 1924 , 125, 1660-1675.																																																																																																									
VARIABLES: Composition at 298 K	PREPARED BY: J. J. FRITZ																																																																																																									
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B: KCu(CN)₂; C: K₃Cu(CN)₄ · H₂O; D: K₃Cu(CN)₄; E: KCN.</p>		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
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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 ₂ SO ₄ ; dried at 293-393 K and weighed. To determine KCN content, the liquid was distilled with H ₂ SO 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 ₂ SO 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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Plaksin, I. N.; Fishkova, Ts. E. <i>Isv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim., Akad. Nauk SSSR</i> <u>1938</u> , <i>10</i> , 229-244.																																																																																																		
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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 ₂ SO ₄ . Used Kahlbaum KCN of 99 to 99.8% purity; other chemicals "C. P.", purity not given.																																																																																																		
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EXPERIMENTAL VALUES:						
(continued)						
$t/^{\circ}\text{C}$	$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{c_1^a}{\text{mol dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$	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 $\text{KCu}(\text{CN})_2$ at low concentrations and $\text{K}_2\text{Cu}(\text{CN})_3$ at higher concentrations (not precisely identified)]; C: KCN.

COMPONENTS: (1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Sodium Cyanide; NaCN; [143-33-9] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Plaksin, I. N.; Fishkova, Ts. E. <i>Isv. Sekt. Fiz.-Khim. Anal. Obshch. Ne-org. Khim., Akad. Nauk SSSR</i> <u>1938</u> , 10, 229-244.																																																																																																		
VARIABLES: Concentration of NaCN at 288 to 308 K	PREPARED BY: J. J. FRITZ																																																																																																		
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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.	SOURCE AND PURITY OF MATERIALS: To obtain CuCN, produced cyano-complexes by adding NaCN to CuSO ₄ solutions, then precipitated CuCN by adding H ₂ SO ₄ . Used Kahlbaum NaCN of 99 to 99.8% purity; other chemicals "C. P.", purity not given.																																																																																																		
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COMPONENTS: (1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Sodium Cyanide; NaCN; [143-33-9] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Plaksin, I. N.; Fishkova, Ts. E. <i>Isv. Sekt. Fiz.-Khim. Anal. Obshch. Neorg. Khim., Akad. Nauk SSSR</i> 1938 , <i>10</i> , 229-244.
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EXPERIMENTAL VALUES:

(continued)

$t/^{\circ}\text{C}$	$\frac{\rho_2}{\text{g dm}^{-3}}$	$\frac{c_2^a}{\text{mol dm}^{-3}}$	$\frac{\rho_1}{\text{g dm}^{-3}}$	$\frac{c_1^a}{\text{mol dm}^{-3}}$	$\frac{\rho}{\text{g cm}^{-3}}$	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 Na₂Cu(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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Vladimirova, M. G.; Kakovsky, I. A. <i>Zh. Prikl. Khim.</i> <u>1950</u> , 23, 580; <i>J. Appl. Chem. USSR (Engl. Transl.)</i> <u>1950</u> , 23, 615-632.																								
VARIABLES: Concentration of HCN at 298 K	PREPARED BY: J. J. FRITZ																								
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of CuCN in Aqueous HCN at 25°C</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_2^{\text{initial}}/\text{mol dm}^{-3\text{a}}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr><td>0.138</td><td>0.1394</td><td>0.00136</td></tr> <tr><td>0.200</td><td>0.2017</td><td>0.00166</td></tr> <tr><td>0.374</td><td>0.3763</td><td>0.00228</td></tr> <tr><td>0.381</td><td>0.3834</td><td>0.00235</td></tr> <tr><td>0.726</td><td>0.7293</td><td>0.00326</td></tr> <tr><td>1.086</td><td>1.090</td><td>0.00400</td></tr> <tr><td>1.444</td><td>1.449</td><td>0.00468</td></tr> </tbody> </table> <p>^a Calculated by compiler.</p>		$c_2/\text{mol dm}^{-3}$	$c_2^{\text{initial}}/\text{mol dm}^{-3\text{a}}$	$c_1/\text{mol dm}^{-3}$	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
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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. <i>Volumetric Analysis (Russ. Ed.)</i> <u>1950</u> . 2. Karyakin, Yu. V. <i>Pure Chemical Reagents</i> <u>1936</u> .																								

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 ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Vladimirova, M. G.; Kakovsky, I. A. <i>Zh. Prikl. Khim.</i> <u>1950</u> , 23, 580; <i>J. Appl. Chem. USSR (Engl. Transl.)</i> <u>1950</u> , 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

$c_2/\text{mol dm}^{-3}$	$c_2^{\text{initial}}/\text{mol dm}^{-3\text{a}}$	$c_3/\text{mol dm}^{-3\text{a}}$	$c_1/\text{mol dm}^{-3}$	$I_c/\text{mol dm}^{-3}$
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 AgNO₃, copper by method of Kolthoff (Ref. 1).

SOURCE AND PURITY OF MATERIALS:
 Prepared HCN by method of Karyakin (Ref. 2), CuCN by reducing CuSO₄ solution (with cyanide 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: (1) Copper(I) Cyanide; CuCN; [544-92-3] (2) Hydrogen Cyanide; HCN; [420-05-3] (3) Sulfuric Acid; H ₂ SO ₄ ; [7664-93-9] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Vladimirova, M. G.; Kakovsky, I. A. <i>Zh. Prikl. Khim.</i> <u>1950</u> , 23, 580; <i>J. Appl. Chem. USSR (Engl. Transl.)</i> <u>1950</u> , 23, 615-632.																																																		
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style="text-align: center;">0.50</td> <td style="text-align: center;">0.010</td> <td style="text-align: center;">0.010</td> <td style="text-align: center;">8.959</td> <td style="text-align: center;">4.508</td> <td style="text-align: center;">9.38</td> </tr> <tr> <td style="text-align: center;">0.010</td> <td style="text-align: center;">0.040</td> <td style="text-align: center;">8.342</td> <td style="text-align: center;">3.877</td> <td style="text-align: center;">9.29</td> </tr> <tr> <td style="text-align: center;">0.010</td> <td style="text-align: center;">0.0025</td> <td style="text-align: center;">9.516</td> <td style="text-align: center;">5.064</td> <td style="text-align: center;">9.30</td> </tr> <tr> <td rowspan="8" style="text-align: center;">1.00</td> <td style="text-align: center;">0.010</td> <td style="text-align: center;">0.010</td> <td style="text-align: center;">8.985</td> <td style="text-align: center;">4.450</td> <td style="text-align: center;">(9.15)</td> </tr> <tr> <td style="text-align: center;">0.010</td> <td style="text-align: center;">0.020</td> <td style="text-align: center;">8.690</td> <td style="text-align: center;">4.144</td> <td style="text-align: center;">9.67</td> </tr> <tr> <td style="text-align: center;">0.010</td> <td style="text-align: center;">0.005</td> <td style="text-align: center;">9.281</td> <td style="text-align: center;">4.748</td> <td style="text-align: center;">9.69</td> </tr> <tr> <td style="text-align: center;">0.050</td> <td style="text-align: center;">0.050</td> <td style="text-align: center;">9.000</td> <td style="text-align: center;">4.250</td> <td style="text-align: center;">41.18</td> </tr> <tr> <td style="text-align: center;">0.040</td> <td style="text-align: center;">0.040</td> <td style="text-align: center;">9.005</td> <td style="text-align: center;">4.294</td> <td style="text-align: center;">34.38</td> </tr> <tr> <td style="text-align: center;">0.030</td> <td style="text-align: center;">0.030</td> <td 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⁻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
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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:																																																																																															

<p>COMPONENTS:</p> <p>(1) Copper(I) Cyanamide; Cu_2CN_2; [35380-03-1]</p> <p>(2) Water; H_2O; [7732-18-5]</p>	<p>EVALUATOR:</p> <p>J. J. FRITZ</p> <p>Department of Chemistry The Pennsylvania State University</p> <p>June, 1991</p>
<p>CRITICAL EVALUATION:</p> <p>The only data found on the solubility of cuprous cyanamide were those of Kitaev <i>et al.</i>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 $\log(\text{solubility})$ 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 $1.6 \cdot 10^{-24} \text{ mol}^3 \text{ dm}^{-9}$.</p> <p>The values obtained for the solubility of copper(I) cyanamide in nitric acid vary as $[\text{H}^+]^{0.64}$ (see Compilations). This is consistent with the interpretation that most of the solubility occurs mainly as a result of the reaction $\text{Cu}_2\text{CN}_2 + \text{H}^+ \rightleftharpoons \text{HCN}_2^- + 2\text{Cu}^+$ (which would give solubility varying approximately as the square root of hydrogen ion concentration), with part of it occurring due to the reaction $\text{Cu}_2\text{CN}_2 + 2\text{H}^+ \rightleftharpoons \text{H}_2\text{CN}_2 + 2\text{Cu}^+$, which would give solubility varying with the first power of $[\text{H}^+]$. The results over the wide range of $[\text{H}^+]$ 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.</p> <p style="text-align: center;">REFERENCE</p> <p>1. Kitaev, G. A.; Bol'shchikova, T. P.; Yatlova, L. E. <i>Zh. Neorg. Khim.</i> 1971, <i>16</i>, 3173; <i>Russ J. Inorg. Chem. (Engl. Transl.)</i> 1971, <i>16</i>, 1683.</p>	

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. <i>Zh. Neorg. Khim.</i> <u>1971</u> , 16, 3173; <i>Russ. J. Inorg. Chem. (Engl. Transl.)</i> <u>1971</u> , 16, 1683-1684.																		
VARIABLES: Concentration of HNO_3 at 298 K, ionic strength 1 mol dm^{-3}	PREPARED BY: J. J. FRITZ																		
EXPERIMENTAL VALUES: <p style="text-align: center;"><u>Solubility of Cu_2CN_2 in HNO_3-NaNO_3 Solutions at 25°C^a</u></p> <table border="1" style="margin-left: auto; margin-right: auto;"> <thead> <tr> <th>$c_3/\text{mol dm}^{-3}$</th> <th>$c_2/\text{mol dm}^{-3}$</th> <th>$c_1/\text{mol dm}^{-3}$</th> </tr> </thead> <tbody> <tr> <td>0.100</td> <td>0.9</td> <td>0.0537</td> </tr> <tr> <td>0.0107</td> <td>0.99</td> <td>0.0166</td> </tr> <tr> <td>0.0055</td> <td>0.99</td> <td>0.0100</td> </tr> <tr> <td>0.00112</td> <td>1.0</td> <td>0.00355</td> </tr> <tr> <td>0.00026</td> <td>1.0</td> <td>0.00135</td> </tr> </tbody> </table> <p>^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 $10^{-23.8}$ ($1.6 \cdot 10^{-24}$) $\text{mol}^2 \text{ dm}^{-6}$.</p>		$c_3/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	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
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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: (1) Copper(I) Azide; CuN_3 ; [14215-30-6] (2) Water; H_2O ; [7732-18-5]	EVALUATOR: J. J. FRITZ Department of Chemistry The Pennsylvania State University June, 1991
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CRITICAL EVALUATION:

Two rather fragmentary investigations of the solubility properties of copper(I) azide have been reported. In 1943 Straumanis and Círulis¹ 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 Suzuki² carried out a potentiometric investigation of the system $\text{CuN}_3\text{-NaN}_3\text{-H}_2\text{O}$ 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 Círulis¹ was $5 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ and that obtained by Suzuki² was $4.9 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$. 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 Círulis¹ 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: (1) Copper(I) Azide; CuN_3 ; [14215-30-6] (2) Hydrogen Azide; HN_3 ; [7782-79-8] (3) Water; H_2O ; [7732-18-5]	ORIGINAL MEASUREMENTS: Straumanis, M.; Círulis, A. <i>Z. Anorg. Allg. Chem.</i> 1943 , 251, 315-331.
VARIABLES: Concentration of HN_3 at room temperature (probably about 293 K)	PREPARED BY: J. J. FRITZ

EXPERIMENTAL VALUES:

Solubility of CuN_3 in Aqueous HN_3

$\rho_2/\text{g dm}^{-3}$	$c_2/\text{mol dm}^{-3 \text{ a}}$	$\rho_1/\text{g dm}^{-3}$	$c_1/\text{mol dm}^{-3 \text{ a}}$
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 $5 \cdot 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$, which is the square of $7.1 \cdot 10^{-5} \text{ mol dm}^{-3}$.

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.

CuCl	+ H ₂ O				E1-E3, 66	
	+ HCl	+ H ₂ O			E3-E6, E27, E28, E38, E39, E49, E52, E53, 67-81, 111, 114, 138	
	+ NaCl	+ H ₂ O			E6-E8, E28, E38, E39, E49, E51, E54, E55, 82-89, 113, 131, 132	
	+ KCl	+ H ₂ O			E8, E9, E26, E28, E29, E40, E50, E56, 90-95	
	+ NH ₄ Cl	+ H ₂ O			E9, E26, E29, E30, E40, E41, E50, E57, E58, 96-98, 119	
	+ LiCl	+ H ₂ O			E10, 99	
	+ CaCl ₂	+ H ₂ O			E10, E31, E32, E41, E42, E50, E59, E60, 100-103	
	+ FeCl ₂	+ H ₂ O			E11, E31, E32, 104	
	+ CuCl ₂	+ H ₂ O			E11, E30, E31, 105, 106, 123, 128	
	+ MgCl ₂	+ H ₂ O			E11, E26, 107	
	+ AlCl ₃	+ H ₂ O			E11	
	+ HClO ₄	+ H ₂ O			111	
	+ HCl	+ HClO ₄	+ H ₂ O		E12, E13, E38, E39, 108-110, 129, 139	
	+ NaCl	+ NaClO ₄	+ H ₂ O		E12, 112	
	+ NaCl	+ Na ₂ SO ₄	+ H ₂ O		E12, E13, 133	
	+ NaCl	+ HCl	+ H ₂ O		E13-E16, E38, E39, 113, 115-118, 141-144	
	+ NH ₄ Cl	+ HCl	+ H ₂ O		E16, 120	
	+ CuCl ₂	+ HCl	+ H ₂ O		E16, E17, E30, E31, 121-128	
	+ CuCl ₂	+ NaCl	+ H ₂ O		E18, E30, E31, 132, 134, 135	
	+ CuCl ₂	+ KCl	+ H ₂ O		E18, 136	
	+ CuCl ₂	+ CaCl ₂	+ H ₂ O		E18, E19	
	+ CuCl ₂	+ HClO ₄	+ H ₂ O		130	
	+ FeCl ₂	+ NaCl	+ H ₂ O		E18, E19, 143	
	+ NaCl	+ NaClO ₄	+ HClO ₄	+ H ₂ O	E12, 112	
	+ CuCl ₂	+ HCl	+ HClO ₄	+ H ₂ O	130, 140	
	+ FeCl ₂	+ NaCl	+ HCl	+ H ₂ O	E18, E19, 141, 143	
	+ ZnCl ₂	+ NaCl	+ HCl	+ H ₂ O	E18, E19, 141, 142	
	+ CuSO ₄	+ NaCl	+ HClO ₄	+ H ₂ O	65	
	+ ZnCl ₂	+ FeCl ₂	+ NaCl	+ HCl	+ H ₂ O	E18, E19, E32, 141, 142
	+ CuCl ₂	+ FeCl ₂	+ NaCl	+ HCl	+ H ₂ O	E18, E19, 143
	+ NaCl	+ HCl	+ NaClO ₄	+ HClO ₄	+ H ₂ O	E39, E40, 138, 139
	+ Allyl alcohol		+ H ₂ O		E20, E43, E44, 145	
	+ Crotyl alcohol		+ H ₂ O		E43, E44	
	+ β -Methylallyl alcohol		+ H ₂ O		E43, E44	
	+ Methylvinylcarbinol		+ H ₂ O		E43, E44	
	+ Ethylvinylcarbinol		+ H ₂ O		E43, E44	

CuCl	+ α, α -Dimethylallyl alcohol	+ H ₂ O	E43, E44
	+ γ, γ -Dimethylallyl alcohol	+ H ₂ O	E43, E44
	+ β -Chloroallyl alcohol	+ H ₂ O	E43, E44
	+ 3-Methyl-3-buten-2-ol	+ H ₂ O	E43, E44
	+ 2-Methyl-2-buten-1-ol	+ H ₂ O	E43, E44
	+ 4-Methyl-4-penten-2-ol	+ H ₂ O	E43, E44
	+ Allyl alcohol	+ HCl + H ₂ O	E20, E21, 145
	+ Allyl alcohol	+ HClO ₄ + H ₂ O	E20, E21, 146
	+ Crotyl alcohol	+ HCl + H ₂ O	E21, 147
	+ Crotyl alcohol	+ HClO ₄ + H ₂ O	E21, 147
	+ β -Methylallyl alcohol	+ HCl + H ₂ O	E21, 148
	+ β -Methylallyl alcohol	+ HClO ₄ + H ₂ O	E21, 148
	+ Methylvinylcarbinol	+ HCl + H ₂ O	E21, 149
	+ Methylvinylcarbinol	+ HClO ₄ + H ₂ O	E21, 149
	+ Ethylvinylcarbinol	+ HCl + H ₂ O	E21, 150
	+ Ethylvinylcarbinol	+ HClO ₄ + H ₂ O	E21, 150
	+ α, α -Dimethylallyl alcohol	+ HCl + H ₂ O	E21, 151
	+ α, α -Dimethylallyl alcohol	+ HClO ₄ + H ₂ O	E21, 151
	+ γ, γ -Dimethylallyl alcohol	+ HCl + H ₂ O	E21, 152
	+ γ, γ -Dimethylallyl alcohol	+ HClO ₄ + H ₂ O	E21, 152
	+ β -Chloroallyl alcohol	+ HCl + H ₂ O	E20, E21, 152
	+ β -Chloroallyl alcohol	+ HClO ₄ + H ₂ O	E20, E21, 152
	+ 3-Methyl-3-buten-2-ol	+ HCl + H ₂ O	E21, 153
	+ 3-Methyl-3-buten-2-ol	+ HClO ₄ + H ₂ O	E21, 153
	+ 2-Methyl-2-buten-1-ol	+ HCl + H ₂ O	E21, 153
	+ 2-Methyl-2-buten-1-ol	+ HClO ₄ + H ₂ O	E21, 153
	+ 4-Methyl-4-penten-2-ol	+ HCl + H ₂ O	E21, 154
	+ 4-Methyl-4-penten-3-ol	+ HClO ₄ + H ₂ O	E21, 154
	+ Allyl alcohol	+ HCl + HClO ₄ + H ₂ O	E20, E21, 146
	+ Allyl alcohol	+ HClO ₄ + NaClO ₄ + H ₂ O	E20, E21, 146
	+ Crotyl alcohol	+ HCl + HClO ₄ + H ₂ O	E21, 147
	+ β -Methylallyl alcohol	+ HCl + HClO ₄ + H ₂ O	E21, 148
	+ Methylvinylcarbinol	+ HCl + HClO ₄ + H ₂ O	E21, 149
	+ Ethylvinylcarbinol	+ HCl + HClO ₄ + H ₂ O	E21, 150
	+ α, α -Dimethylallyl alcohol	+ HCl + HClO ₄ + H ₂ O	E21, 151
	+ γ, γ -Dimethylallyl alcohol	+ HCl + HClO ₄ + H ₂ O	E21, 152
	+ β -Chloroallyl alcohol	+ HCl + HClO ₄ + H ₂ O	E20, E21, 152
	+ 3-Methyl-3-buten-2-ol	+ HCl + HClO ₄ + H ₂ O	E21, 153
	+ 2-Methyl-2-buten-1-ol	+ HCl + HClO ₄ + H ₂ O	E21, 153
	+ 4-Methyl-4-penten-2-ol	+ HCl + HClO ₄ + H ₂ O	E21, 154
	+ Maleic acid	+ H ₂ O	E45-E47
	+ Fumaric acid	+ H ₂ O	E22, E45-E47, 159
	+ Crotonic acid	+ H ₂ O	E45-E47
	+ Vinylacetic acid	+ H ₂ O	E45-E47
	+ Itaconic acid	+ H ₂ O	E45-E47
	+ Mesaconic acid	+ H ₂ O	E45-E47
	+ Citraconic acid	+ H ₂ O	E45-E47
	+ β, β -Dimethylacrylic acid	+ H ₂ O	E45-E47
	+ Tiglic acid	+ H ₂ O	E45-E47
	+ Maleic acid	+ HCl + H ₂ O	E22, E23, E45, 157
	+ Maleic acid	+ KCl + H ₂ O	E22, E45, 158
	+ Maleic acid	+ HClO ₄ + H ₂ O	E21-E23, E45, 155, 157
	+ Maleic acid	+ NaClO ₄ + H ₂ O	E22, E45, 158
	+ Maleic acid	+ H ₂ SO ₄ + H ₂ O	E21, E22, E45, 156
	+ Fumaric acid	+ HClO ₄ + H ₂ O	E22, E23, E45, 160
	+ Fumaric acid	+ H ₂ SO ₄ + H ₂ O	E22, E45, 159
	+ Crotonic acid	+ HClO ₄ + H ₂ O	E23, E45, 161
	+ Vinylacetic acid	+ HCl + H ₂ O	E23, E45, 162
	+ Vinylacetic acid	+ HClO ₄ + H ₂ O	E23, E45, 162
	+ Itaconic acid	+ HCl + H ₂ O	E23, E45, 163
	+ Itaconic acid	+ HClO ₄ + H ₂ O	E23, E45, 163

CuCl	+ Mesaconic acid	+ HClO ₄	+ H ₂ O	E23, E45, 164	
	+ Citraconic acid	+ HCl	+ H ₂ O	E23, E45, 164	
	+ Citraconic acid	+ HClO ₄	+ H ₂ O	E23, E45, 164	
	+ β, β -Dimethylacrylic acid	+ HCl	+ H ₂ O	E23, E45, 165	
	+ β, β -Dimethylacrylic acid	+ HClO ₄	+ H ₂ O	E23, E45, 165	
	+ Tiglic acid	+ HCl	+ H ₂ O	E23, E45, 166	
	+ Tiglic acid	+ HClO ₄	+ H ₂ O	E23, E45, 166	
	+ Maleic acid	+ HCl	+ HClO ₄	+ H ₂ O	E22, E23, E45, 157
	+ Maleic acid	+ KCl	+ NaClO ₄	+ H ₂ O	E22, E45, 158
	+ Fumaric acid	+ HCl	+ HClO ₄	+ H ₂ O	E22, E23, E45, 160
	+ Crotonic acid	+ HCl	+ HClO ₄	+ H ₂ O	E23, E45, 161
	+ Vinylacetic acid	+ HCl	+ HClO ₄	+ H ₂ O	E23, E45, 162
	+ Itaconic acid	+ HCl	+ HClO ₄	+ H ₂ O	E23, E45, 163
	+ Mesaconic acid	+ HCl	+ HClO ₄	+ H ₂ O	E23, E45, 164
	+ β, β -Dimethylacrylic acid	+ HCl	+ HClO ₄	+ H ₂ O	E23, E45, 165
	+ Tiglic acid	+ HCl	+ HClO ₄	+ H ₂ O	E23, E45, 166
	+ Urea	+ HCl	+ KCl	+ H ₂ O	E23, 167, 168
	+ 2-Butene-1,4-diol	+ HCl	+ KCl	+ H ₂ O	E23, 168, 169
	+ Acetonitrile	+ HCl	+ KCl	+ H ₂ O	E23, 168, 170
	+ Acetonitrile				E171
	+ Dioxane				E171
	+ Dimethyl sulfone				E171
	+ HCl + Ethanol				E171, 173
+ KSeCN + Acetone				E172, 174	
+ Tetraethylammonium chloride + Dimethyl sulfone				E171	
CuBr	+ H ₂ O			E175, 182	
	+ KBr	+ H ₂ O		E175-E180, 183-185, 190	
	+ NaBr	+ H ₂ O		E176-E180, 186	
	+ HBr	+ H ₂ O		E176, 187	
	+ MgBr ₂	+ H ₂ O		E177	
	+ LiBr	+ H ₂ O		E177, 188	
	+ NH ₄ Br	+ H ₂ O		E177, 189	
	+ KBr	+ KNO ₃	+ H ₂ O	E175-E177, 191	
	+ NaBr	+ NaNO ₃	+ H ₂ O	E176, 192	
	+ NaBr	+ NaClO ₄	+ H ₂ O	E175, 193	
	+ NaBr	+ NaClO ₄	+ HClO ₄	+ H ₂ O	E175, 193
	+ Acetonitrile			E194	
	+ Dimethyl sulfone			E194	
CuI	+ H ₂ O			E195, 207	
	+ NaI	+ H ₂ O		E195-E199, E201, 208	
	+ KI	+ H ₂ O		E195-E198, E200, E201, 210, 211	
	+ HI	+ H ₂ O		E196, E197, 212	
	+ KBr	+ H ₂ O		E202, 214, 215	
	+ NH ₄ Br	+ H ₂ O		E202, 216	
	+ Na ₂ S ₂ O ₃	+ H ₂ O		E202-E204, 217, 218, 219	
	+ K ₂ S ₂ O ₃	+ H ₂ O		E202-E204, 220	
	+ KNbO ₃	+ H ₂ O		E205, 221	
	+ I ₂	+ H ₂ O		E205, 222	
	+ NaI	+ NaNO ₃	+ H ₂ O	E195-E197, 208	
	+ NaI	+ NaClO ₄	+ H ₂ O	E195-E197, 209	
	+ KI	+ NaNO ₃	+ H ₂ O	E195-E197, 210, 211	
	+ KBr	+ NaNO ₃	+ H ₂ O	E202, 215	
	+ KCl	+ NaNO ₃	+ H ₂ O	E202, 213	
	+ Na ₂ S ₂ O ₃	+ Na ₂ SO ₄	+ H ₂ O	E203, 219	
	+ KNbO ₃	+ KNO ₃	+ H ₂ O	221	
	+ NaI	+ NaClO ₄	+ HClO ₄	+ H ₂ O	E195-E197, 209
	+ NaI	+ Na ₂ S ₂ O ₃	+ Na ₂ SO ₄	+ H ₂ O	E203, 219

CuI	+ Acetonitrile			E223
	+ Dimethyl sulfone			E223
	+ NaI	+ Acetone		E223, 225
	+ NaI	+ Ethanol		E223, 226
	+ KI	+ Acetone		E223, 227
	+ I ₂	+ Methanol		E224
	+ I ₂	+ Ethanol		E224, 228
	+ I ₂	+ Acetonitrile		E224
	+ I ₂	+ H ₂ O	+ Methanol	E224, 229
	+ I ₂	+ H ₂ O	+ Ethanol	E224
	+ I ₂	+ H ₂ O	+ Dioxane	E224
CuSCN	+ H ₂ O			E230, E231
	+ KSCN	+ H ₂ O		E231-E235, 241, 251
	+ NH ₄ SCN	+ H ₂ O		E231-E233, 242
	+ NaCl	+ H ₂ O		E236, 245
	+ NaBr	+ H ₂ O		E236, 246
	+ KI	+ H ₂ O		E236, 252
	+ Na ₂ S ₂ O ₃	+ H ₂ O		E237, E238, 247, 250
	+ NaNO ₂	+ H ₂ O		E238, E239, 254
	+ HCN	+ H ₂ O		E239, 255
	+ KSCN	+ NaNO ₃	+ H ₂ O	E231-E233, 241, 251
	+ KSCN	+ KI	+ H ₂ O	E236, 253
	+ NH ₄ SCN	+ NH ₄ NO ₃	+ H ₂ O	E231-E233, 242
	+ NaSCN	+ NaClO ₄	+ H ₂ O	E231-E233, 243, 244
	+ NaCl	+ NaNO ₃	+ H ₂ O	E236, 245
	+ NaBr	+ NaNO ₃	+ H ₂ O	E236, 246
	+ KI	+ NaNO ₃	+ H ₂ O	E236, 252
	+ Na ₂ S ₂ O ₃	+ Na ₂ SO ₄	+ H ₂ O	E237, E238, 248, 250
	+ K ₂ S ₂ O ₃	+ K ₂ SO ₄	+ H ₂ O	E237, E238, 249
	+ NaNO ₂	+ NaNO ₃	+ H ₂ O	E238, E239, 254
	+ HCN	+ HCl	+ H ₂ O	E239, 256
	+ NaSCN	+ Na ₂ S ₂ O ₃	+ Na ₂ SO ₄ + H ₂ O	E237, E238, 250
	+ NaSCN	+ NaClO ₄	+ HClO ₄ + H ₂ O	E231-E233, 244
	+ KSCN	+ Ethanol		E257, 258
	+ KSCN	+ Acetone		E257, 259
CuSeCN	+ H ₂ O			E260
CuCN	+ H ₂ O			E261
	+ KCN	+ H ₂ O		E261, E262, 266-268
	+ NaCN	+ H ₂ O		E261, E262, 269, 270
	+ HCN	+ H ₂ O		E261, E263, 271
	+ HCN	+ HCl	+ H ₂ O	E263, 272
	+ IICN	+ H ₂ SO ₄	+ H ₂ O	E263, 273
	+ NaCN	+ HCN	+ H ₂ O	E263, E264
	+ NaCN	+ HCN	+ NaCl + H ₂ O	E263, E264, 274
Cu ₂ CN ₂	+ H ₂ O			E275
	+ HNO ₃	+ H ₂ O		E275
	+ HNO ₃	+ NaNO ₃	+ H ₂ O	E275, 276
CuN ₃	+ H ₂ O			E277, 278
	+ NaN ₃	+ H ₂ O		E277
	+ HN ₃	+ H ₂ O		E277, 278

REGISTRY NUMBER INDEX

Page numbers preceded by E refer to evaluation text whereas those not preceded by E refer to compiled tables.

[57-13-6]	CH ₄ N ₂ O	Urea	167, 168
[64-17-5]	C ₂ H ₆ O	Ethanol	173, 226, 228, 258
[67-56-1]	CH ₄ O	Methanol	229
[67-64-1]	C ₂ H ₆ O	Acetone	174, 225, 227, 259
[75-05-8]	C ₂ H ₃ N	Acetonitrile	170
[80-59-1]	C ₅ H ₈ O ₂	Tiglic acid	166
[97-65-4]	C ₄ H ₆ O ₂	Itaconic acid	163
[107-18-6]	C ₃ H ₆ O	Allyl alcohol	145, 146
[107-93-7]	C ₄ H ₆ O ₂	Crotonic acid	161
[110-16-7]	C ₄ H ₄ O ₄	Maleic acid	155-158
[110-17-8]	C ₄ H ₄ O ₄	Fumaric acid	159, 160
[110-64-5]	C ₄ H ₈ O ₂	2-Butene-1,4-diol	169
[115-18-4]	C ₅ H ₁₀ O	α , α -Dimethylallyl alcohol	151
[143-33-9]	NaCN	Sodium cyanide	269, 270, 274
[151-50-8]	KCN	Potassium cyanide	266-268
[333-20-0]	KSCN	Potassium thiocyanate	241, 251-253, 258, 259
[420-05-3]	HCN	Hydrogen cyanide	255, 256, 271-274
[479-02-9]	C ₅ H ₁₀ O	2-Methyl-2-buten-1-ol	153
[498-23-7]	C ₅ H ₆ O ₄	Citraconic acid	164
[498-24-8]	C ₅ H ₆ O ₄	Mesaconic acid	164
[513-42-8]	C ₄ H ₈ O	β -Methylallyl alcohol	148
[540-72-7]	NaSCN	Sodium thiocyanate	243, 244, 250
[541-47-9]	C ₅ H ₈ O ₂	β , β -Dimethylacrylic acid	165
[544-92-3]	CuCN	Copper(I) cyanide	E261-E265, 266-274
[556-82-1]	C ₅ H ₁₀ O	γ , γ -Dimethylallyl alcohol	152
[598-32-3]	C ₄ H ₈ O	Methylvinylcarbinol	149
[616-25-1]	C ₅ H ₁₀ O	Ethylvinylcarbinol	150
[625-38-7]	C ₄ H ₆ O ₂	Vinylacetic acid	162
[1111-67-7]	CuSCN	Copper(I) thiocyanate	E230-E240, 241-256, E257, 258, 259
[1762-95-4]	NH ₄ SCN	Ammonium thiocyanate	242
[2004-67-3]	C ₆ H ₁₂ O	4-Methyl-4-penten-2-ol	154
[3425-46-5]	KSeCN	Potassium selenocyanate	174
[5976-47-6]	C ₃ H ₅ ClO	β -Chloroallyl alcohol	152
[6117-91-5]	C ₄ H ₈ O	Crotyl alcohol	147
[6484-52-2]	NH ₄ NO ₃	Ammonium nitrate	242
[7447-39-4]	CuCl ₂	Copper(II) chloride	105, 106, 121-140, 143, 144
[7447-40-7]	KCl	Potassium chloride	90-95, 136, 158, 167-170, 213
[7447-41-8]	LiCl	Lithium chloride	99
[7550-35-8]	LiBr	Lithium bromide	188
[7553-56-2]	I ₂	Iodine	222, 228, 229
[7601-89-0]	NaClO ₄	Sodium perchlorate	112, 137-140, 146, 158, 193, 209, 243, 244
[7601-90-3]	HClO ₄	Hydrogen perchlorate	65, 108-112, 129, 130, 137-140, 146-155, 157, 160-166, 193, 209, 244
[7631-99-4]	NaNO ₃	Sodium nitrate	192, 208, 210, 211, 213, 215, 241, 245, 246, 251-254
[7632-00-0]	NaNO ₂	Sodium nitrite	254
[7646-85-7]	ZnCl ₂	Zinc chloride	141, 142
[7647-01-0]	HCl	Hydrogen chloride	67-81, 108-111, 113-130, 137-154, 157, 160-170, 173, 256, 272, 274
[7647-14-5]	NaCl	Sodium chloride	65, 82-89, 112-118, 131-135, 137-144, 245, 274
[7647-15-6]	NaBr	Sodium bromide	186, 192, 193, 246
[7664-93-9]	H ₂ SO ₄	Sulfuric acid	156, 159, 273
[7681-11-0]	KI	Potassium iodide	210, 211, 227, 251-253

[7681-65-4]	CuI	Copper(I) iodide	E195-E206, 207-222, E223, E224, 225-229
[7681-82-5]	NaI	Sodium iodide	208, 209, 219, 225, 226
[7697-37-2]	HNO ₃	Nitric acid	276
[7732-18-5]	H ₂ O	Water	E1-E64, 65-170, E175-E181, 182-193, E195-E206, 207-222, 229, E230-E240, 241-256, E260-E265, 266-274, E275, 276, E277, 278
[7757-79-1]	KNO ₃	Potassium nitrate	190, 191, 221, 276
[7757-82-6]	Na ₂ SO ₄	Sodium sulfate	131-133, 219, 248, 250
[7758-02-3]	KBr	Potassium bromide	183-185, 190, 191, 214, 215
[7758-89-6]	CuCl	Copper(I) chloride	E1-E64, 65-170, E171, E172, 173, 174
[7758-94-3]	FeCl ₂	Iron(II) chloride	104, 141-144
[7758-98-7]	CuSO ₄	Copper(II) sulfate	65
[7772-98-7]	Na ₂ S ₂ O ₃	Sodium thiosulfate	217-219, 247, 248, 250
[7778-80-5]	K ₂ SO ₄	Potassium sulfate	249
[7782-79-8]	HN ₃	Hydrogen azide	278
[7786-30-3]	MgCl ₂	Magnesium chloride	107
[7787-70-4]	CuBr	Copper(I) bromide	E175-E181, 182-193, E194
[10034-85-2]	HI	Hydrogen iodide	212
[10035-10-6]	HBr	Hydrogen bromide	187
[10043-52-4]	CaCl ₂	Calcium chloride	100-103
[10294-66-3]	K ₂ S ₂ O ₃	Potassium thiosulfate	220, 249
[10473-14-0]	C ₅ H ₁₀ O	3-Methyl-3-buten-2-ol	153
[12030-85-2]	KNbO ₃	Potassium metaniobate	221
[12124-97-9]	NH ₄ Br	Ammonium bromide	189, 216
[12125-02-9]	NH ₄ Cl	Ammonium chloride	96-98, 119, 120
[14215-30-6]	CuN ₃	Copper(I) azide	E277, 278
[35380-03-1]	Cu ₂ CN ₂	Copper(I) cyanamide	E275, 276

AUTHOR INDEX

Page numbers preceded by E refer to evaluation text whereas those not preceded by E refer to compiled tables.

- Abel, E. E4, E61, 70
 Ahrland, S. E1, E2, E6, E8, E12-E15, E35-E37, E39, E61, E63, 112, E175, E176, E178, E181, 193, E195, E196, E198, E206, 209, E230-E232, E240, 244
- Ali, S. A. E5, E62, 77, 95
 Andrews, L. J. E1, E2, E20-E23, E43-E46, E61-E63, 145-166
 Andrussov, K. E46, E64
 Angelov, I. I. 65, 174, 208, 219, 220
 Armington, A. F. E5, E62, 78
 Bassett, H. E261, E262, E265, 266
 Beck, M. T. E265
 Berger, J. M. E18, E19, E32, E62, 141, 142
 Binnendijk, N. F. E63
 Birnbaum, N. 109
 Bliss, H. L. E26, E62, E181
 Bodländer, G. E1, E2, E8, E9, E18, E36, E37, E61, E64, 136, E175, E176, E178, E181, 183, E195, E197, E206
 E275, 276
- Bol'shchikova, T. P. E63
 Borshch, N. Ya. E36, E37, E64
 Braun, M. E24, E25, E63, E177, E181
 Brink, C. E8, E9, E24, E25, E28, E29, E40, E62, 91
 Brönsted, J. N. E202, E206, 218, 220, E240, 248, 249
 Butsko, S. S. E1, E2, E36, E61, 65, E261, E264, E265
 Butler, J. N. E176, E178, E179, E181, 192
 Caldwell, R. L. E3, E5, E6, E11-E17, E38, E40, E61, E64, 129, 130, 137-140
 Camacho Rubio, F. E25, E63, E177, E181, E257
 Canneri, G. E4, E6, E11, E16, E17, E61, 122
 Cannon, L. S. E36, E64
 Carlson, B. E3, E4, E6, E36-E38, E52, E61, 73, E171, E172
 Cha, Y.-T. E1, E2, E5-E8, E26-E29, E31, E36, E37, E61, E62, E64, 76, 84, 94, E175, E181, E195, E206, E230, E240
 Chaltskyan, O. A. E3, E4, E6, E36-E38, E52, E61, 73, E171, E172, 173
 Chang, K. S. E24, E63
 Chassevant, M. A. E5, E61, 81
 Chaudhari, R. V. E4, E35, E36, E61, 71
 Chow, M. E277, 278
 Círulis, A. E261, E262, E265, 266
 Corbet, A. S. E62, 143, 144
 Covington, J. W. E240, 245, 246, 254
 Danilczuk, E. E12, E36, E62
 Davidson, N. E240, 243
 De Azevedo, L. A. E24, E25, E63
 Deherain, P. P. E202, E206, 218, 220, E240, 248, 249
 Dobryanskaya, L. P. E4, E6, E11, E16, E17, E61, 122
 Edgar, G. 109
 Edwards, S. M. E1-E3, E61
 Egorov, A. M. E265
 Ellinger, F. H. E3, E61, 67-69, 80, 90
 Engler, R. E62
 Ermolaeva, T. G. E5, E61, 109-111
 Esaka, N. 129, 137, 145, 155, 156, 159
 Estes, R. R. E4, E7, E11, E28, E30, E31, E61, 72, 80, 83, 105, E205, E206, 222, E224
 Fedotieff, P. P.

- Flerov, V. N. E63, 167-170
 Fishkova, Ts. E. E261, E262, E265, 267-270
 Fitzhugh, J. R. E26, E63, E181
 Fleurent, M. E. E264, E265
 Flid, R. M. E63, E64
 Fofanov, G. M. E1, E2, E34, E61, 65
 Fontana, A. E6, E13, E15, E16, E28, E36, E62, 117, 118
 Fridman, Ya D. E195, E196, E202, E206, 210, 213, 215, E231-E234, E236, E240, 251-253
 Fritz, J. J. E61, E63, E64, 109, E175, E176, E178, E181, 190, 191
 Frömel, W. E8, E9, E24, E25, E28, E29, E62, 92, 93
 Fujii, A. E36, E37, E64
 Furman, N. H. E1, E2, E61, E175, E181, E195, E206, E230, E240, E264, E265
 Galinker, I. S. E1, E3, E61, 66, E175, E181, 182, E195-E197, E206, 207
 Gavrish, M. L. E1, E3, E61, 66, E175, E181, 182, E195-E197, E206, 207
 Gilliland, E. R. E26, E62, E63, E177, E181
 Glodzińska, W. E4, E5, E61, 80
 Gogolin, R. E240, 245, 246, 254
 Gokhale, S. D. E5-E7, E13-E15, E62, 113, 114
 Golub, A. M. E172, 174, E195, E196, E202-E204, E206, 211, 218, 220, E223, E224, 225, 226, E230-E233, E237, E238, E240, 241, 248, 249, E257, 258, 259, E260
 Gyunner, E. A. E195, E196, E202-E204, E206, 208, 219, E231, E232, E237, E238, E240, 242, 250
 Harris, C. M. E26, E63, E177, E181, E202, E206, E257
 Hatch, L. F. 129, 137, 145, 155, 156, 159
 Hefter, G. T. E263-E265, 274
 Heines, V. E171, E172
 Hikita, H. E1-E6, E12-E15, E33-E36, E38, E52, E61, 109-111
 Hurlburt, E. B. E25, E63, E177, E181, E196, E206
 Ishikawa, H. E5, E61, 109-111
 Itzig, H. E262, E264, E265
 Johnson, R. K. E6, E13, E15, E28, E62, 115, 116
 Kafarov, V. V. 123
 Kakovsky, I. A. E230, E239, E240, 255, 256, E261, E263-E265, 271-273
 Kale, S. S. E1, E2, E5, E6, E61, 81
 Kapler, R. E205, E206, E224, 228, 229
 Karimova, N. N. E11, E25, E64, 110
 Karyakin, Yu. V. 65, 174, 208, 219, 220, 255, 256, 271-273
 Keefer, R. M. E20-E23, E45, E62, E63, 146-166
 Keller, R. N. 145-166, 190
 Kelley, K. K. E3, E61
 Kepner, R. E. E1, E2, E20, E21, E23, E45, E61-E63, 145, 147-154, 160-166
 Khan, M. M. E175-E177, E181, E223, E224, 227
 Khodakovskii, I. L. E61
 Kilimnik, G. M. E257
 Kim, J. J. E37, E38, E42, E64
 Kip, C. E. E26, E62, E181
 Kitaev, G. A. E275, 276
 Klein, A. E202, E206, 216
 Kobenin, V. A. E61, E181, E206
 Koblyanskii, G. G. E26, E63
 Kohn, M. E202, E206, 214, 216
 Königsberger, E. E263-E265, 274
 Kogan, V. B. 123
 Kohlrausch, F. E230, E240
 Kolthoff, I. M. E1, E2, E61, E175, E181, E195, E206, 221, E230, E240, 255, 256, E264, E265, 271-273
 Korreng, E. E24, E25, E63
 Korshunov, I. A. E232, E233, E240

- Kortim, G. E46, E64
 Kosyakina, O. A. E7, E28, E62, 85
 Kozhemyakin, V. A. E62, 123, 124, 127, 128, 134, 135
 Kranilov, U. P. E37, E64
 Kremann, R. E1, E2, E7, E11, E28, E31, E32, E61, 82, 104
 Kreshkov, A. P. 125
 Krestov, G. A. E1-E3, E61, E175, E181, E195, E206
 Ksandrov, N. V. E11, E25, E64, 110
 Kuchirenko, V. I. E63, 167-170
 Kunin, B. T. E33, E35-E37, E63, 65
 Kunin, T. I. E62, 87-89, 103, 106, 107
 Kunschert, F. E262, E265
 Kutsnetsova, A. G. E6, E62, 100, 101, 131-133
 Latimer, W. M. E1-E3, E36, E61, E175, E178, E181, E195, E197, E206,
 E230, E240, E264, E265
 Laves, G. E25, E26, E63
 Le Chatelier, H. E3, E8, E9, E25, E40, E61, 67, 80, 90
 Linke, W. F. 78, 80
 Liu, Y.-M. E171, E172, 173
 Lobkareva, V. L. E62
 Luchini, R. E25, E63, E177, E181, E257
 Luzik, E. E175, E176, E178, E181, 190, 191
 MacGillavry, C. H. E24, E63
 Machtinger, M. E171, E172, E194, E223, E224
 Makin, E. C., Jr. E26, E62
 Malik, A. E181, 184
 Malik, W. U. E5, E6, E9, E24, E25, E62, 77, 95, E175-E178, E181, E184,
 E223, E224, 227
 Malyugina, N. I. E232, E233, E240
 Martell, A. E. E36, E63
 Marykian, D. O. E25, E63
 May, P. M. E265, 274
 Mayorga, G. E37, E39-E42, E61, E177, E181, E197, E206, E232, E240
 Mazo, L. H. E230-E233, E240, 243
 McConnel, H. E12, E36, E62
 Mellor, J. W. E24-E26, E63, E177, E181, E202, E206
 Mel'nik, P. M. 123, 125
 Mininzon, Yu. M. E206, 212
 Mitscherlich, E. E24, E25, E63, 92
 Moreno Carretero, J. E5, E61, E64, 129, 130, 137-140
 Morgan, P. S. E26, E63, E181
 Morgart, R. M. 123, 125
 Morosov, I. C. E4-E6, E9, E16, E25, E27, E29, E30, E40, E41, E61, 74, 75,
 96, 97
 Mueller, B. E62, 108
 Muir, D. H. E62, 143, 144
 Nakanishi, S. E9, E16, E62, 119, 120
 Náray-Szabó, St. v. E37, E64
 Naumann, A. E171, E172, E194, E223, E224
 Naumov, G. B. E3, E61
 Neumann, G. E24, E63
 Neves, E. de A. E240, 243
 Nikandrov, I. S. E11, E25, E64, 110
 Nikitenko, V. A. E206, 212
 Nobe, K. E36, E37, E64
 Noss, F. E1, E2, E7, E11, E28, E31, E32, E61, 82, 104
 Novikov, G. I. E5, E6, E11, E16, E17, E30, E31, E62, 125, 126
 Noyes, A. A. E4, E35, E36, E61, 71
 O'Connor, J. J. E5, E62, 78, 80
 Ogorodnikov, S. K. 123
 Paez Dueñas, M. P. E5, E61, E64, 129, 130, 137-140
 Panova, V. E. E202,-E204, E206, 217, E237, E240, 247

- Pestrikov, V. F. E37, E64
 Peters, D. G. E176, E178, E179, E181, 192
 Peters, M. A. E6, E13, E15, E28, E62, 115, 116
 Petrova, I. Yu. E62, 123, 124, 127, 128, 134, 135
 Pitzer, K. S. E37-E42, E61, E64, E177, E181, E197, E206, E232, E240
 Piotrovskii, K. B. E63
 Plaksin, I. N. E261, E262, E265, 267-270
 Pleshkov, V. A. E171, E172
 Pochtarev, A. N. E11, E16-E18, E30, E31, E62, 123, 124, 127, 128, 134, 135
 Podlesnyak, O. Z. 123
 Poma, G. E4, E11, E16, E17, E61, 121
 Popolitov, V. I. E196, E197, E206, 212
 Ragg, M. E230, E240, E261, E265
 Rahman, S. M. F. E5, E62, 77, 95, E181, 184
 Rawsthorne, J. E1, E2, E6, E8, E12-E15, E36, E37, E39, E61, 112
 Remy, H. E25, E26, E63
 Reshetov, S. P. E62
 Ritthausen, H. E25, E26, E63
 Robertson, G. R. 155-160
 Romanenko, L. I. E195, E203, E206, 211, E223, E224, 225, 226
 Rose, F. E230, E240
 Rosenheim, A. E25, E63, E177, E181, E204, E206, E257
 Rud'ko, P. K. E5, E62, 125, 126
 Ryzhenko, V. N. E61
 Sarbaev, Dzh. S. E195, E196, E202, E206, 210, 213, 215, E231-E234, E236, E240, 251,-253
 Sazhienko, S. M. E195, E203, E206, 211, E223, E224, 225, 226
 Schafer, H. N. S. E63, E181, E206
 Schier, A. E171, E172, E194, E223, E224
 Schiff, A. E25, E63, 92
 Seabold, J. E. E26, E63, E181
 Shirokova, G. N. E10, E11, E18, E19, E31, E32, E44, E62, 100, 101
 Shokin, I. N. E6, E62, 100, 101, 131-133
 Shul'ts, A. A. E26, E63
 Shutov, A. A. E11, E62, 87-89, 103-106
 Shvedova, L. V. E62
 Sigal, L. N. E23, E63, 167-170
 Sillén, L. G. E36, E63
 Silvester, L. F. E39, E42, E64
 Sin, G. N. E6-E8, E11-E13, E15, E18, E39, E62, 131-133
 Sipos, P. E265
 Skopenko, V. V. E172, 174, E260
 Smith, R. M. E36, E63
 Sokolov, V. N. E61, E181, E206
 Solis, J. S. E265, 274
 Somersalo, A. E62, 108
 Sosnitskii, V. N. E1, E2, E34, E61, 65
 Staritsky, E. E262, E265
 Steinhäuser, S. E25, E63, E177, E181, E204, E206, E257
 Storbeck, O. E1, E2, E8, E9, E18, E36, E37, E61, E64, 136, E175, E176, E178, E181, 183, E195, E197, E206
 Stoyukhin, S. G. E206, 212
 Straumanis, M. E277, 278
 Sugasaka, K. E36, E37, E64
 Sukhova, T. G. E36, E63
 Suzuki, K. E277
 Swinarski, A. E230, E236-E238, E240, 245, 246, 254
 Szabó, Z. E37, E64
 Tagesson, B. E35, E63, E175, E176, E178, E181, 193, E195, E196, E198, E206, 209, E230-E232, E240, 244
 Tamhankar, S. S. E5, E61, 81
 Tanirbergenov, B. E205, E206, 221

- Temkin, O. N. E63, E64
 Thomasian, A. E5, E62, 78
 Tremillon, B. E172, E194, E224
 Truthe, W. E262, E265
 Tuhtar, D. E35, E63
 Ustaniskova, G. V. E4-E6, E9, E16, E25, E27, E29, E30, E40, E41, E61, 74, 75, 96, 97
 Utkina, I. N. E6-E8, E10, E11, E15, E28, E39, E41, E62, 87-89, 103, 106
 Valetton, J. J. P. E8, E9, E24, E25, E28, E29, E62, 92, 93
 van Arkel, A. E. E25, E63, E177, E181
 Van de Linde, J. E63
 van Muylder, J. E62, 117, 118
 Vasil'ev, V. P. E33, E35-E37, E63, 65
 Vatamanyuk, V. I. 123, 125
 Vestin, R. E12, E62, 108
 Vladimirova, M. G. E230, E239, E240, 255, 256, E261, E263-E265, 271-273
 Vogel, A. I. 81, 243
 Vogel, W. E46, E64
 Voropaev, L. E. E5, E62, 125, 126
 Vuaille, M. J. E172, E194, E224
 Wagman, D. D. E34, E63
 Walker, D. I. E265
 Ward, A. L. E26, E62
 Wells, H. L. E25, E63, E177, E181, E196, E206
 Wettermark, G. E36, E64
 Wilke, K.-Th. E5, E7, E9, E10, E62, 79, 86, 98, 99, 102, E175-E177, E181, 185-189
 Winand, R. E18, E19, E32, E62, 117, 118, 141, 142
 Winter, D. G. E13-E15, E18, E19, E40, E62, 143, 144
 Wycoff, H. O. 145-166, 190
 Yakhkind, N. D. E195, E196, E202-E204, E206, 208, 219, E231, E232, E237, E238, E240, 242, 250
 Yatlova, L. E. E275, 276
 Yatsimirskii, K. B. E202,-E204, E206, 217, E237, E238, E240, 247
 Yntema, L. F. E171, E172
 Zaidi, S. A. A. E223, E224, 227
 Zembura, Z. E4, E5, E61, 80
 Zharskii, I. M. E5, E62, 125, 126
 Zhuk, H. P. E1, E2, E61, E175, E181, E195, E206
 Zvorkina, G. I. 167, 169, 170

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