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SOLUBILITY DATA SERIES

Volume 44

COPPER AND SILVER HALATES

SOLUBILITY DATA SERIES

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Volume 44

COPPER AND SILVER HALATES

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FOREWORD

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

The Solubility Data Series is a project of Commission V.8 (Solubility Data) of the International Union of Pure and Applied Chemistry (IUPAC). The project had its origins in 1973, when the Analytical Chemistry Division of IUPAC set up a Subcommission on Solubility Data under the chairmanship of the late Prof. A.S. Kertes. When publication of the Solubility Data Series began in 1979, the Committee became a full commission of IUPAC, again under the chairmanship of Prof. Kertes, who also became Editor-in-Chief of the Series. The Series as its goal the preparation of a comprehensive and critical compilation of data on solubilities in all physical systems, including gases, liquids and solids.

The motivation for the Series arose from the realization that, while solubility data are of importance in a wide range of fields in science and technology, the existing data had not been summarized in a form that was at the same time comprehensive and complete. Existing compilations of solubility data indeed existed, but they contained many errors, were in general uncritical, and were seriously out-of-date.

It was also realized that a new series of compilations of data gave educational opportunities, in that careful compilations of existing data could be used to demonstrate what constitutes data of high and lasting quality. As well, if the data were summarized in a sufficiently complete form, any individual could prepare his or her own evaluation, independently of the published evaluation. Thus, a special format was established for each volume, consisting of individual data sheets for each separate publication, and critical evaluations for each separate system, provided sufficient data from different sources were available for comparison. The compilations and, especially, the evaluations were to be prepared by active scientists who were either involved in producing new data, or were interested in using data of high quality. With minor modifications in format, this strategy has continued throughout the Series.

In the standard arrangement of each volume, the Critical Evaluation gives the following information:

- (i) A text which discusses the numerical solubility information which has been abstracted from the primary sources in the form of compilation sheets. The text concerns primarily the quality of the data, after consideration of the purity of the materials and their characterization, the experimental method used, the uncertainties in the experimental values, the reproducibility, the agreement with accepted test values, and, finally, the fitting of the data to suitable functions, along with statistical tests of the fitted data.
- (11) A set of recommended data, whenever possible, including weighted averages and estimated standard deviations. If applicable, one or more smoothing equations which have been computed or verified by the evaluator are also given.
- (iii) A graphical plot of the recommended data, in the form of phase diagrams where appropriate.

The Compilation part consists of data sheets which summarize the experimental data from the primary literature. Here much effort is put into obtaining complete coverage; many good data have appeared in publications from the late nineteenth and early twentieth centuries, or in obscure journals. Data of demonstrably low precision are not compiled, but are mentioned in the Critical Evaluation. Similarly, graphical data, given the uncertainty of accurate conversion to numerical values, are

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compiled only where no better data are available. The documentation of data of low precision can serve to alert researchers to areas where more work is needed.

A typical data sheet contains the following information:

- (i) list of components: names, formulas, Chemical Abstracts Registry Numbers;
- (ii) primary source of the data;

(iii) experimental variables;

(iv) compiler's name;

(v) experimental values as they appear in the primary source, in modern units with explanations if appropriate;

(vi) experimental methods used;

(vii) apparatus and procedure used;

(viii) source and purity of materials used;

- (ix) estimated error, either from the primary source or estimated by the compiler;
 - (x) references relevant to the generation of the data cited in the primary source.

Each volume also contains a general introduction to the particular type of system, such as solubility of gases, of solids in liquids, etc., which contains a discussion of the nomenclature used, the principles of accurate determination of solubilities, and related thermodynamic principles. This general introduction is followed by a specific introduction to the subject matter of the volume itself.

The Series embodies a new approach to the presentation of numerical data, and the details continue to be influenced strongly by the perceived needs of prospective users. The approach used will, it is hoped, encourage attention to the quality of new published work, as authors become more aware that their work will attain permanence only if it meets the standards set out in these volumes. If the Series succeeds in this respect, even partially, the Solubility Data Commission will have justified the labour expended by many scientists throughout the world in its production.

January, 1989

J.W. Lorimer, London, Canada

PREFACE

The present volume is the third in a series of four volumes on inorganic metal halates. The first volume on Alkaline Earth Metal Halates was published in 1983 (1), and the second volume on Alkali Metal Halates, Ammonium Iodate and Iodic Acid was published in 1987 (2). A fourth volume on Transition Metal, Lanthanide and Other Metal Halates is presently in course of preparation.

This volume includes critical evaluations and compilations for halate solubilities of the Group 11 metals, and the literature was searched up to 1987. The evaluators and compilers were not able to locate solubility data for gold halates or for copper bromate. Thus the solubility data included in this volume are those for the five compounds copper chlorate and iodate, and silver chlorate, bromate and iodate.

To arrive at either recommended or tentative solubilities, we generally appplied a statistical treatment similar to that recommended by Cohen-Adad (3) based on the thermodynamic treatment of saturated solutions and their equilibrated solid phases as discussed in the Introduction to the Solubility of Solids in Liquids found in this volume. These thermodynamic treatments allow one to describe the polytherm for a binary system over the complete range of ice as the solid phase to the melting point of the pure solute by the general expression

$$Y = \frac{A}{T/K} + B \ln(T/K) + C + D(T/K)$$

For convenience of the users, the solubilities can be extracted from the complex Y term in the above equation with the simple computer programs (written in BASIC) listed in the Preface of IUPAC Solubility Data Series, Vol. 30 (2). In several instances involving the solubility of a halate in the presence of a non-saturating component such as a salt or an acid, the data were critically evaluated using a simple power series fitting equation. Generally, data were evaluated when two or more independent studies were available, but there are a few exceptions: e.g. in instances where comparisons were not possible due to differences in units and/or temperature, and where the data were judged to result in averages with large standard deviations such as data for the solubilities of various halates in several organic solvent systems.

We believe the literature search through 1987 is complete, and an incomplete survey of Chemical Abstracts was made through the first half of 1988. In a few instances, relevant papers were not compiled as it was not possible to obtain either reprints or other reproductions of the original publications. For example, we were unable to obtain the papers in references (4) and (5).

The editors would like to acknowledge the cooperation of the American Chemical Society and VAAP, the copyright agency of the USSR, for permission to reproduce figures from their publications.

The editors gratefully acknowledge the advice and comments from members and associates of IUPAC Commission V.8, and in particular to Professors H.L. Clever, R. Cohen-Adad, J.W. Lorimer and C.L. Young. We are also grateful to K. Loening of the Chemical Abstracts Service for providing Registry Numbers for numerous compounds.

One of us (H. M.) would also like to acknowledge the hospitality of Prof. H.L. Clever during his stay at the Solubility Research Center at Emory University (1981-1982), and to Dr. Nobuyuki Tanaka (Professor Emeritus of Tohoku University and President of Nippon Jimuki Co., Ltd.), Profs. H. Akaiwa (Gunma University) and M. Fujii (Niigata University) for their valuable comments and suggestions. This work was partially supported by a Grant-in-Aid of Scientific Research from the Japan Association of Chemistry in 1979 and 1984.

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December, 1989

PREFACE (continued)

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INTRODUCTION TO THE SOLUBILITY OF SOLIDS IN LIQUIDS

Nature of the Project

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

Definitions

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

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

The solubility of a substance B is the relative proportion of B (or a substance related chemically to B) in a mixture which is saturated with respect to solid B at a specified temperature and pressure. Saturated implies the existence of equilibrium with respect to the processes of dissolution and precipitation; the equilibrium may be stable or metastable. The solubility of a substance in metastable equilibrium is usually greater than that of the corresponding 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 quantities used as measures of solubility and in the reference states used for definition of activities, activity coefficients and osmotic coefficients.

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

Quantities Used as Measures of Solubility

1. Mole fraction of substance B, xB:

$$x_B = n_B / \sum_{s=1}^{C} n_s$$
 [1]

where n_8 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 B is 100 x_B .

2. Mass fraction of substance B, was

$$w_B = m_B' / \sum_{s=1}^C m_s'$$
 [2]

where m_8 is the mass of substance s. Mass per cent is 100 wg. The equivalent terms weight fraction and weight per cent are not used.

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

$$x_{S,B} = m_B / \sum_{s=1}^{C'} m_S = x_B / \sum_{s=1}^{C'} x_s$$
 [3]

$$w_{S,B} = m_{B'} / \sum_{S=1}^{C'} m_{S'} = w_{B} / \sum_{S=1}^{C'} w_{S}$$
 [3a]

where the summation is over the solutes only. For the solvent A, $x_{S,A} = x_A/(1-x_A)$, $w_{S,A} = w_A/(1-w_A)$. These quantities are called Jänecke mole (mass) fractions in many papers.

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

$$m_B = n_B/n_A M_A$$
 SI base units: mol kg⁻¹ [4]

where M_A is the molar mass of the solvent.

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

$$c_B = [B] = n_B/V$$
 SI base units: mol m⁻³ [5]

The symbol c_B is preferred to [B], but both are used. The terms molarity and molar are not used.

Mole and mass fractions 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 among these quantities can be carried out using the equations given in Table I-1 following this Introduction. Other useful quantities will be defined in the prefaces to individual volumes or on specific data sheets.

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

- 6. Density: $\rho = m/V$ SI base units: kg m⁻³ [6]
- 7. Relative density: d; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol d_t will be used for the density of a mixture at t°C, 1 bar divided by the density of water at t°C, 1 bar. (In some cases 1 atm = 101.325 kPa is used instead of 1 bar = 100 kPa.)
- 8. A note on nomenclature. The above definitions use the nomenclature of the IUPAC Green Book (1), in which a solute is called B and a solvent 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 nomenclature and theoretical equations given in this Introduction with equations and nomenclature used on the evaluation and compilation sheets.

Thermodynamics of Solubility

The principal aims of the Solubility Data Project are the tabulation and evaluation of: (a) solubilities as defined above; (b) the nature of the saturating phase. Thermodynamic analysis of solubility phenomena has two aims: (a) to provide a rational basis for the construction of functions to represent solubility data; (b) to enable thermodynamic quantities to be extracted from solubility data. Both these are difficult to achieve in many cases because of a lack of experimental or theoretical information concerning activity coefficients. Where thermodynamic quantities can be found, they are not evaluated critically, since this task would involve critical evaluation of a large body of data that is not directly relevant to solubility. The following is an outline of the principal thermodynamic relations encountered in discussions of solubility. For more extensive discussions and references, see books on thermodynamics, e.g., (5-12).

Activity Coefficients (1)

(a) Mixtures. The activity coefficient f_{B} of a substance B is given by

RT in
$$(f_B x_B) = \mu_B - \mu_B^*$$
 [7]

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

$$\lim_{x_{B}\to 1} f_{B} - 1$$
 [8]

(b) Solutions.

(1) Solute B. The molal activity coefficient γ_B is given by RT $\ln(\gamma_B m_B) = \mu_B - (\mu_B - RT \ln m_B)^{\infty}$ [9]

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

$$\gamma_{B}^{\infty} = 1$$
 [10]

Activity coefficients y_B connected with concentrations c_B , and $f_{X,B}$ (called the rational activity coefficient) connected with mole fractions x_B are defined in analogous ways. The relations among them are (1, 9), where ρ^* is the density of the pure solvent:

$$f_B = (1 + M_A \Sigma m_S) \gamma_B = [\rho + \Sigma (M_A - M_S) c_S] y_B / \rho^*$$
 [11]

$$\gamma_B = (1 - \sum_{s} x_s) f_{X,B} = (\rho - \sum_{s} M_s c_s) y_B / \rho^*$$
 [12]

$$y_B = \rho^* f_{X,B} [1 + \sum_{S} (M_S/M_A - 1) x_B] / \rho = \rho^* (1 + \sum_{S} M_S m_S) \gamma_B / \rho$$
 [13]

For an electrolyte solute $B = C_{\nu+}A_{\nu-}$, the activity on the molality scale is replaced by (9)

$$\gamma_{B}m_{B} = \gamma_{\pm}^{\nu}m_{B}^{\nu}Q^{\nu} \tag{14}$$

where $\nu = \nu_+ + \nu_-$, $Q = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu}$, and γ_\pm is the mean ionic activity coefficient on the molality scale. A similar relation holds for the concentration activity, $y_{\rm RCR}$. For the mole fractional activity,

$$f_{X,B}x_{B} = Q^{\nu}f_{\pm}^{\nu}x_{\pm}^{\nu}$$
 [15]

where $x_{\pm} = (x_{+}x_{-})^{1/\nu}$. The quantities x_{+} and x_{-} are the ionic mole fractions (9), which are

$$x_{+} = \nu_{+}x_{B}/[1 + \sum_{s}(\nu_{s} - 1)x_{s}]; \quad x_{-} = \nu_{-}x_{B}[1 + \sum_{s}(\nu_{s} - 1)x_{s}]$$
 [16]

where $\nu_{\rm S}$ is the sum of the stoichiometric coefficients for the ions in a salt with mole fraction $x_{\rm S}$. Note that the mole fraction of solvent is now

$$x_A' = (1 - \sum_{S} v_S x_S) / [1 + \sum_{S} (v_S - 1) x_S]$$
 [17]

so that

$$x_{A}' + \sum_{s} v_{s} x_{s} - 1$$
 [18]

The relations among the various mean ionic activity coefficients are:

$$f_{\pm} = (1 + M_A \sum_{S} v_S m_S) \gamma_{\pm} = [\rho + \sum_{S} (v_S M_A - M_S) c_S] y_{\pm} / \rho^*$$
 [19]

$$\gamma_{\pm} = \frac{(1 - \sum_{S} x_{S}) f_{\pm}}{1 + \sum_{S} (v_{S} - 1) x_{S}} = (\rho - \sum_{S} M_{S} c_{S}) y_{\pm} / \rho^{*}$$
 [20]

$$y_{\pm} = \frac{\rho^{*}[1 + \sum_{S}(M_{S}/M_{A} - 1)x_{S}]f_{\pm}}{\rho[1 + \sum_{S}(\nu_{S} - 1)x_{S}]} = \rho^{*}(1 + \sum_{S}M_{S}m_{S})^{\gamma}_{\pm}/\rho$$
 [21]

(i1) Solvent, A:

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

$$\phi = (\mu_A^* - \mu_A)/RT M_A \sum_{S} m_S$$
 [22]

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

The rational osmotic coefficient, ϕ_{X} , is defined as (1):

$$\phi_{X} = (\mu_{A} - \mu_{A}^{*})/RT \ln x_{A} = \phi M_{A} \sum_{S} m_{S} / \ln(1 + M_{A} \sum_{S} m_{S})$$
 [23]

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

For a mixed solvent, the molar mass in the above equations is replaced by the average molar mass; i.e., for a two-component solvent with components $J,\ K,\ M_A$ becomes

$$M_A = M_J + (M_K - M_J) x_{V,K}$$
 [24]

where $x_{V,K}$ is the solvent mole fraction of component K.

The osmotic coefficient is related directly to the vapor pressure, p, of a solution in equilibrium with vapor containing A only by (12, p.306):

$$\phi M_{A} \sum_{S} v_{S} m_{S} = -\ln(p/p_{A}^{*}) + (V_{m,A}^{*} - B_{AA})(p - p_{A}^{*})/RT$$
 [25]

where $p_A^{\,\star}$, $V_{m,\,A}^{\,\star}$ are the vapor pressure and molar volume of pure solvent A, and B_{AA} is the second virial coefficient of the vapor.

The Liquid Phase

A general thermodynamic differential equation which gives solubility as a function of temperature, pressure and composition can be derived. The approach is similar to that of Kirkwood and Oppenheim (7); see also (11, 12). Consider a solid mixture containing c thermodynamic components i. The Gibbs-Duhem equation for this mixture is:

$$\sum_{i=1}^{C} x_{i}'(S_{i}'dT - V_{i}'dp + d\mu_{i}') = 0$$
 [26]

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

$$\sum_{i=1}^{C} x_{i}(S_{i}dT - V_{i}dp + d\mu_{i}') + \sum_{i=C+1}^{C} x_{i}(S_{i}dT - V_{i}dp + d\mu_{i}) = 0$$
 [27]

Subtract [26] from [27] and use the equation

$$d\mu_i = (d\mu_i)_{T,D} - S_i dT + V_i dp$$
 [28]

and the Gibbs-Duhem equation at constant temperature and pressure:

$$\sum_{i=1}^{C} x_{i} (d\mu_{i}')_{T,p} + \sum_{i=C+1}^{C'} x_{i} (d\mu_{i})_{T,p} = 0$$
 [29]

The resulting equation is:

$$RT \int_{1}^{C} x_{i}' (dlna_{i})_{T,p} = \int_{1}^{C} x_{i}' (H_{i} - H_{i}') dT/T - \int_{1}^{C} x_{i}' (V_{i} - V_{i}') dp$$
 [30]

where

$$H_i - H_i' = T(S_i - S_i')$$
 [31]

is the enthalpy of transfer of component i from the solid to the liquid phase at a given temperature, pressure and composition, with H_i and S_i the partial molar enthalpy and entropy of component 1.

Use of the equations

$$H_i - H_i^0 = -RT^2(\partial \ln a_i/\partial T)_{X,p}$$
 [32]

and

$$V_i - V_i^0 = RT(\partial \ln a_i/\partial p)_{X,T}$$
 [33]

where superscript o indicates an arbitrary reference state gives:

$$RT_{i=1}^{C} x_{i}' dlna_{i} = \sum_{i=1}^{C} x_{i}' (H_{i}^{0} - H_{i}') dT/T - \sum_{i=1}^{C} x_{i}' (V_{i}^{0} - V_{i}') dp$$
 [34]

Where

$$dlna_i = (dlna_i)_{T,p} + (dlna_i/\partial T)_{X,p} + (dlna_i/\partial p)_{X,T}$$
[35]

The terms involving enthalpies and volumes in the solid phase can be written as:

$$\sum_{i=1}^{C} x_{i}' H_{i}' = H_{s}^{*} \qquad \sum_{i=1}^{C} x_{i}' V_{i}' = V_{s}^{*}$$
 [36]

With eqn [36], the final general solubility equation may then be written:

$$R_{i=1}^{C} x_{i}' d \ln a_{i} = (H_{S}^{*} - \sum_{i=1}^{C} x_{i}' H_{i}^{0}) d(1/T) - (V_{S}^{*} - \sum_{i=1}^{C} x_{i}' V_{i}^{0}) dp/T$$
[37]

Note that those components which are not present in both phases do not appear in the solubility equation. However, they do affect the solubility through their effect on the activities of the solutes.

Several applications of eqn [37] (all with pressure held constant) will be discussed below. Other cases will be discussed in individual evaluations.

(a) Solubility as a function of temperature.

Consider a binary solid compound AnB in a single solvent A. There is

no fundamental thermodynamic distinction between a binary compound of A and B which dissociates completely or partially on melting and a solid mixture of A and B; the binary compound can be regarded as a solid mixture of constant composition. Thus, with c = 2, $x_A = n/(n + 1)$, $x_B = 1/(n + 1)$, eqn [37] becomes:

$$dln(a_A^n a_B) = -\Delta H_{AB}^{\circ} d(1/RT)$$
 [38]

where

$$\Delta H_{AB}^{0} = nH_{A} + H_{B} - (n+1)H_{S}^{*}$$
 [39]

is the molar enthalpy of melting and dissociation of pure solid $A_{\rm B}B$ to form A and B in their reference states. Integration between T and $T_{\rm U}$, the melting point of the pure binary compound $A_{\rm D}B$, gives:

$$\ln(a_A^{\Pi}a_B) = \ln(a_A^{\Pi}a_B)_{T=T_0} - \int_{T_0}^{T} \Delta H_{AB} d(1/RT)$$
 [40]

(1) Non-electrolytes

In eqn [32], introduce the pure liquids as reference states. Then, using a simple first-order dependence of ΔH_{AB}^{\star} on temperature, and assuming that the activitity coefficients conform to those for a simple mixture (6):

$$RT \ln f_A = wx_B^2 \qquad RT \ln f_B = wx_A^2 \qquad [41]$$

then, if w is independent of temperature, eqn [32] and [33] give:

$$\ln\{x_B(1-x_B)^n\} + \ln\left\{\frac{n^n}{(1+n)^{n+1}}\right\} = G(T)$$
 [42]

where

$$G(T) = -\left[\frac{\Delta H_{AB}^{*} - T^{*}\Delta C_{p}^{*}}{R}\right]\left\{\frac{1}{T} - \frac{1}{T^{*}}\right\} + \frac{\Delta C_{p}^{*}}{R}\ln(T/T^{*}) - \frac{w}{R}\left\{\frac{x_{A}^{2} + nx_{B}^{2}}{T} - \frac{n}{(n+1)T^{*}}\right\}$$
[43]

where ΔC_p^* is the change in molar heat capacity accompanying fusion plus decomposition of the pure compound to pure liquid A and B at temperature T^* , (assumed here to be independent of temperature and composition), and ΔH_{AB}^* is the corresponding change in enthalpy at $T = T^*$. Equation [42] has the general form:

$$\ln\{x_B(1-x_B)^n\} = A_1 + A_2/(T/K) + A_3\ln(T/K) + A_4(x_A^2 + nx_B^2)/(T/K)$$
[44]

If the solid contains only component B, then n = 0 in eqn [42] to [44].

If the infinite dilution reference state is used, then:

RT
$$\ln f_{X,B} = w(x_A^2 - 1)$$
 [45]

and [39] becomes

$$\Delta H_{AB}^{\infty} = nH_{A}^{*} + H_{B}^{\infty} - (n+1)H_{S}^{*}$$
 [46]

where ΔH_{AB}^{∞} is the enthalpy of melting and dissociation of solid compound $A_{n}B$ to the infinitely dilute reference state of solute B in solvent A; H_{A}^{\star} and H_{B}^{∞} are the partial molar enthalpies of the solute and solvent at infinite dilution. Clearly, the integral of eqn [32] will have the same form as eqn [35], with ΔH_{AB}^{∞} replacing ΔH_{AB}^{\star} , ΔC_{p}^{∞} replacing ΔC_{p}^{\star} , and x_{A}^{2} - 1 replacing x_{A}^{2} in the last term.

See (5) and (11) for applications of these equations to experimental data.

(1i) Electrolytes

(a) Mole fraction scale

If the liquid phase is an aqueous electrolyte solution, and the solid is a salt hydrate, the above treatment needs slight modification. Using rational mean activity coefficients, eqn [34] becomes:

$$\ln\left[\frac{x_{B}^{\nu}(1-x_{B})^{n}}{(1+(\nu-1)x_{B})^{n+\nu}}\right] - \ln\left[\frac{n^{n}}{(n+\nu)^{n+\nu}}\right] + \ln\left[\left[\frac{f_{B}}{f_{B}^{\star}}\right]^{\nu}\left[\frac{f_{A}}{f_{A}^{\star}}\right]^{n}\right]$$

$$= -\left[\frac{\Delta H_{AB}^{\star} - T^{\star}\Delta C_{D}^{\star}}{R}\right]\left[\frac{1}{T} - \frac{1}{T^{\star}}\right] + \frac{\Delta C_{D}^{\star}}{R} \ln(T/T^{\star})$$
[47]

where superscript * indicates the pure salt hydrate. If it is assumed that the activity coefficients follow the same temperature dependence as the right-hand side of eqn [47] (13-16), the thermochemical quantities on the right-hand side of eqn [47] are not rigorous thermodynamic enthalpies and heat capacities, but are apparent quantities only. Data on activity coefficients (9) in concentrated solutions indicate that the terms involving these quantities are not negligible, and their dependence on temperature and composition along the solubility-temperature curve is a subject of current research.

A similar equation (with $\nu=2$ and without the heat capacity terms or activity coefficients) has been used to fit solubility data for some MOH-H₂O systems, where M is an alkali metal (13); enthalpy values obtained agreed well with known values. The full equation has been deduced by another method in (14) and applied to MCl₂-H₂O systems in (14) and (15). For a summary of the use of equation [47] and similar equations, see (14).

(2) Molality scale

Substitution of the mean activities on the molality scale in eqn [40] gives:

$$\nu \ln \left[\frac{\gamma_{\pm} m_{\rm B}}{\gamma_{\pm}^* m_{\rm B}^*} \right] - \nu (m_{\rm B}/m_{\rm B}^* - 1) - \nu \{m_{\rm B}(\phi - 1)/m_{\rm B}^* - \phi^* + 1\}$$

$$= G(T)$$
[48]

where G(T) is the same as in eqn [47], $m_B^* = 1/nM_A$ is the molality of the anhydrous salt in the pure salt hydrate and γ_\pm and ϕ are the mean activity coefficient and the osmotic coefficient, respectively. Use of the osmotic coefficient for the activity of the solvent leads, therefore, to an equation that has a different appearance to [47]; the content is identical. However, while eqn [47] can be used over the whole range of composition (0 \le $x_B \le$ 1), the molality in eqn [48] becomes infinite at $x_B = 1$; use of eqn [48] is therefore confined to solutions sufficiently dilute that the molality is a useful measure of composition. The essentials of eqn [48] were deduced by Williamson (17); however, the form used here appears first in the Solubility Data Series. For typical applications (where activity and osmotic coefficients are not considered explicitly, so that the enthalpies and heat capacities are apparent values, as explained above), see (18).

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

(b) Solubility as a function of composition.

At constant temperature and pressure, the chemical potential of a saturating solid phase is constant:

$$\mu_{A_{n}B}^{*} = \mu_{A_{n}B}(\sin) = n\mu_{A} + \mu_{B}$$
 [49]
= $(n\mu_{A}^{*} + \nu_{+}\mu_{+}^{\infty} + \nu_{-}\mu_{-}^{\infty}) + nRT \ln f_{A}x_{A}$
+ $\nu_{R}T \ln (\gamma_{\pm}m_{\pm}Q)$

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

$$\Delta G^{\infty} = (\nu_{+}\mu_{+}^{\infty} + \nu_{-}\mu_{-}^{\infty} + n\mu_{A}^{*} - \mu_{AB}^{*})$$

$$= -RT \ln K_{B}$$

- -νRT ln(Qγ±mB)

[50]

is called the solubility product of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of $K_{\rm S}$ can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt $C_{\rm P}A_{\rm P}\cdot {\rm nH_2O}$ in the presence of other solutes is given by eqn [50] as

 $\nu \ln(m_{\rm H}/m_{\rm H}(0)) \sim -\nu \ln(\gamma_{\pm}/\gamma_{\pm}(0)) - n \ln(a_{\rm A}/a_{\rm A}(0))$

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

Consideration of complex mixed ligand equilibria in the solution phase are also frequently of importance in the interpretation of solubility equilibria. For nomenclature connected with these equilibria (and solubility equilibria as well), see (19, 20).

The Solid Phase

The definition of solubility permits the occurrence of a single solid phase which may be a pure anhydrous compound, a salt hydrate, a non-stoichiometric compound, or a solid mixture (or solid solution, or "mixed crystals"), and may be stable or metastable. As well, any number of solid phases consistent with the requirements of the phase rule may be present. Metastable solid phases are of widespread occurrence, and may appear as polymorphic (or allotropic) forms or crystal solvates whose rate of transition to more stable forms is very slow. Surface heterogeneity may also give rise to metastability, either when one solid precipitates on the surface of another, or if the size of the solid particles is sufficiently small that surface effects become important. In either case, the solid is not in stable equilibrium with the solution. See (21) for the modern formulation of the effect of particle size on solubility. The stability of a solid may also be affected by the atmosphere in which the system is equilibrated.

Many of these phenomena require very careful, and often prolonged, equilibration for their investigation and elimination. A very general analytical method, the "wet residues" method of Schreinemakers (22), is often used to investigate the composition of solid phases in equilibrium with salt solutions. This method has been reviewed in (23), where [see also (24)] least-squares methods for evaluating the composition of the solid phase from wet residue data (or initial composition data) and solubilities are described. In principle, the same method can be used with systems of other types. Many other techniques for examination of solids, in particular X-ray, optical, and thermal analysis methods, are used in conjunction with chemical analyses (including the wet residues method).

COMPILATIONS AND EVALUATIONS

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

Guide to the Compilations

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

Components. Each component is listed according to IUPAC name, formula, and Chemical Abstracts (CA) Registry Number. The formula is given either in terms of the IUPAC or Hill (25) system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

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

The saturating components are arranged in order according to a 18-column periodic table with two additional rows:

Columns 1 and 2: H, alkali elements, ammonium, alkaline earth elements

3 to 12: transition elements

13 to 17: boron, carbon, nitrogen groups; chalcogenides, halogens

18: noble gases

Row 1: Ce to Lu
Row 2: Th to the end of the known elements, in order of atomic number.

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

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

Experimental Values. Data are reported in the units used in the original publication, with the exception that modern names for units and quantities are used; e.g., mass per cent for weight per cent; mol dm⁻³ for molar; etc. Both mass and molar values are given. Usua 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 1983 atomic weights (26).

Errors in calculations and fitting equations in original papers have been noted and corrected, by computer calculations where necessary.

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

If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and and reporting errors are based on the papers by Ku and Eisenhart (27).

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

References. See the above description for Original Measurements.

Guide to the Evaluations

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

Components. See the description for the Compilations.

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

Critical Evaluation

- (a) Critical text. The evaluator produces text evaluating all the published data for each given system. Thus, in this section the evaluator reviews the merits or shortcomings of the various data. published data are considered; even published data can be considered only if the experimental data permit an assessment of reliability.
- (b) Fitting equations. If the use of a smoothing equation is justifiable the evaluator may provide an equation representing the solubility as a function of the variables reported on all the compilation sheets.
- (c) Graphical summary. In addition to (b) above, graphical summaries are often given.
- (d) Recommended values. Data are recommended if the results of at least two independent groups are available and they are in good agreement, and if the evaluator has no doubt as to the adequacy and reliability of the applied experimental and computational procedures. Data are considered as tentative if only one set of measurements is

available, or if the evaluator considers some aspect of the computational or experimental method as mildly undesirable but estimates that it should cause only minor errors. Data are considered as doubtful if the evaluator considers some aspect of the computational or experimental method as undesirable but still considers the data to have some value in those instances where the order of magnitude of the solubility is needed. Data determined by an inadequate method or under ill-defined conditions are rejected. However references to these data are included in the evaluation together with a comment by the evaluator as to the reason for their rejection.

- (e) References. All pertinent references are given here. References to those data which, by virtue of their poor precision, have been rejected and not compiled are also listed in this section.
 (f) Units. While the original data may be reported in the units
- used by the investigators, the final recommended values are reported in S.I. units (1, 28) when the data can be accurately converted.

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September, 1986

- R. Cohen-Adad, Villeurbanne, France
- J. W. Lorimer, London, Ontario, Canada
- M. Salomon, Fair Haven, New Jersey, U.S.A.

Table I-1

Quantities Used as Measures of Solubility of Solute B Conversion Table for Multicomponent Systems Containing Solvent A and Solutes s

	mole fraction %B =	mass fraction WB =	molality m _B =	concentration cg =
хв	× _B M _A	$\frac{M_{B}x_{B}}{+\sum_{S}(M_{S}-M_{A})x_{S}}$	$\frac{x_B}{M_A(1-\sum x_B)}$	$\frac{\rho x_B}{M_A + \sum_{S} (M_S - M_A) x_S}$
w _B		1/M _A)w _B w _B	$\frac{w_{B}}{M_{B}(1-\sum_{s}w_{s})}$	ρw _B /M _B
mB	MA™B 1 + MA∑m _B	$\frac{M_{\rm B}m_{\rm B}}{1+\sum\limits_{\rm S}m_{\rm S}M_{\rm S}}$	mB	$\frac{\rho_{m_{B}}}{1 + \sum_{s} M_{s} m_{s}}$
св	$\frac{M_{A}c_{B}}{\rho + \sum_{g}(M_{A} - M_{g})c_{g}}$	M _B c _B /ρ	c_B ρ - Σ ^M _S c _S	св

 ρ = density of solution M_A , M_B , M_S = molar masses of solvent, solute B, other solutes s Formulas are given in forms suitable for rapid computation; all calculations should be made using SI base units.

COMPONENTS:	EVALUATOR:
(1) Copper chlorate; Cu(ClO ₃) ₂ ; [14721-21-2] (2) Water; H ₂ O; [7732-18-5]	Hiroshi Miyamoto Niigata University Niigata, Japan
	July 1987

There is only one reported publication on $Cu(ClO_3)_2$, and this deals with the binary $Cu(ClO_3)_2$ - H_2O system (1). Meusser studied this binary system over the temperature range 248-344 K where the solid phases were ice and $Cu(ClO_3)_2$ - $4H_2O$. The temperature for the ice $\rightarrow Cu(ClO_3)_2$ - $4H_2O$ transition was not given, nor could it be determined by the evaluator since Meusser reported only two data points for the region where ice is the solid phase (see the solubility polytherm on the next page). For the region where the solid phase is $Cu(ClO_3)_2$ - $4H_2O$, the evaluator fitted the data (the data point for 274.0 K was rejected) to the following smoothing equation:

$$Y_x = \frac{-5.7735}{T/K} - 406.5856 \ln(T/K) + 2295.506 + 0.7212596(T/K)$$
[1]

where

$$Y_{x} = ln \left(\frac{\chi^{\nu} (1 - \chi)^{r} (\nu + r)^{\nu + r}}{r^{r} (1 + \chi)^{\nu + r}} \right)$$
 [2]

In eq. [2], χ is the mole fraction solubility, r is the mole ratio H₂O:salt in the solid phase, and v is the number of ions produced upon dissolution (v = 3 for Cu(ClO₃)₂). The data point for 274.0 K was rejected because $\chi_{\text{obsd}} - \chi_{\text{calcd}}$ exceeded $2\sigma_{\mathbf{x}}$ where $\sigma_{\mathbf{x}}$ is the standard error of estimate defined in the usual manner by

$$\sigma_{x} = \left\langle \frac{\sum (\chi_{obsd} - \chi_{calcd})}{N - Nc} \right\rangle^{1/2}$$
 [3]

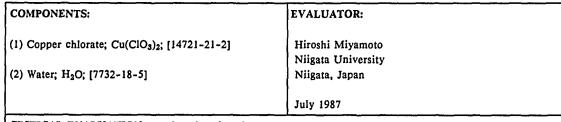
In eq. [3], N is the number of data points and Nc is the number of constants adjusted in eq. [1]. Similary, σ_Y is the standard error of estimate for the defined quantity Y_x in eq. [2]. For the present data, $\sigma_Y = 0.040$ and $\sigma_X = 0.0056$: tentative values of the solubilities in mole fraction and mol kg⁻¹ units based on eq. [1] are given below for the region where the solid phase is $Cu(ClO_3)_2 \cdot 4H_2O$. The polytherm for the entire system reported by Meusser is given on the following page.

Table 1. Tentative Solubilities of Cu(ClO₃)₂ at Rounded Temperatures From Eq. [1]

	mole fraction	molality	
T/K	X	$m_1/\text{mol kg}^{-1}$	
243,2	0.0855	5.26	
253.2	0.0958	5.89	
263.2	0.1024	6.33	
273,2	0.1070	6.65	
283.2	0.1104	6.89	
293.2	0.1140	7.14	
298.2	0.1162	7.30	
303.2	0.1188	7.48	
313.2	0.1260	8.01	
318.2	0.1311	8.38	
323.2	0.1375	8.85	
333,2	0.1568	10.32	
343.2	0.1944	13.51	

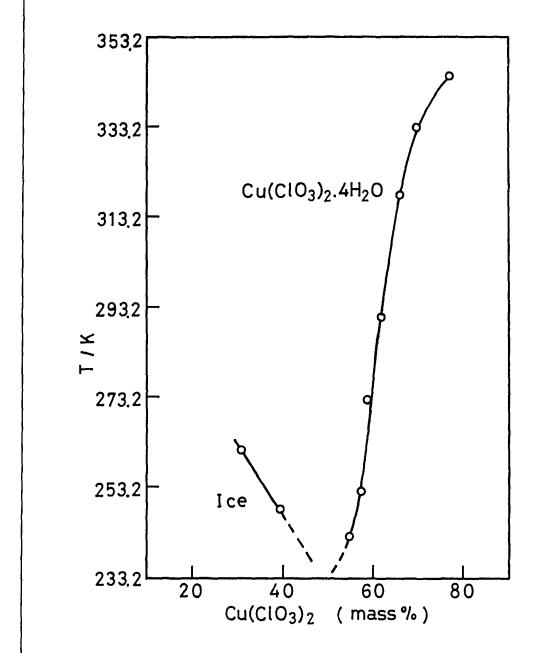
continued....

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CRITICAL EVALUATION: (continued.....)

Fig. 1. Solubility Polytherm for the binary Cu(ClO₃)₂-H₂O system



REFERENCE

1. Meusser, A. Ber. Dtsch. Chem. 1902, 36, 1414.

COMPONENTS:

(1) Copper chlorate; Cu(ClO₃)₂; [14721-21-2]

(2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Meusser, A.

Ber. Dtsch. Chem. Ges. 1902, 35, 1414-24.

VARIABLES:

PREPARED BY:

T/K = 242 - 344

H. Miyamoto and E.M. Woolley

EXPERIMENTAL VALUES:

solubility of Cu(ClO₃)₂

t/ºC	mass % (author)	mol/100 mol H ₂ O (compilers)	mol kg-1 (compilers)	nature of the solid phase
-25	39.14	5.03	2.79	ice
-12	30.53	3.44	1.91	ice
-31	54.59	9.40	5.22	Cu(ClO ₃) ₂ •4H ₂ O
-21	57.12	10.41	5.78	"
0.8	58.51	11.02	6.12	Ħ
18	62.17	12.85	7.13	•
45	66.17	15.29	8.49	#
59.6	69.42	17.75	9.85	н
71	76.90	26.02	14,45	**

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Cu(ClO₃)_{2*}4H₂O and water were placed in a test tube and shaken for one hour. Aliquots of saturated solution were withdrawn with a pipet, and the Cu content determined gravimetrically as Cu₂S. Analysis of the solid phase gave the following:

76.90 mass % $Cu(ClO_3)_2$ and 23.10 mass % H_2O .

This gives a mole ratio of H_2O to $Cu(ClO_3)_2$ of 3.84 which is slighly less than the theoretical value of 4.0.

SOURCE AND PURITY OF MATERIALS:

Pure Cu(ClO₃)₂·4H₂O was recrystallized. 1.6576 g analyzed for Cu gave 0.4316 g Cu₂S which corresponds to a hydrate about 1 % lower than the tetrahydrate.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:	EVALUATORS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	H. Miyamoto and E. M. Woolley Departments of Chemistry
(2) Water; H ₂ O; [7732-18-5]	Niigata and Brigham Young Universities Niigata Japan, and Provo, UT, USA July, 1987

THE BINARY SYSTEM

Data for the solubility of copper iodate in water have been reported in 13 publications (1-13). All publications are based on chemical analyses of saturated solutions with the exception of the work by Spencer (1) who evaluated the solubility product K_{s0} based on e.m.f. measurements on cells containing CuSO₄ or KIO₃. The paper by Vinogradov et al. (12) determined the solubility by analysis of copper (EDTA titration) whereas all other papers determined solubilities by iodometric titration of iodate. The compilers calculated the solubility based on Spencer's calculated K_{s0} . Although the solubility at 298.2 K reported by Lloyd et al. (4) may be the average of 17 independent determinations, this was not specified in the original publication and we therefore treat this value as a single measurement. Similary, the three publications by Nair et al. (7, 8, 10) all report the same solubility value at 298.2 K, and the evaluators assume that this solubility was only measured once in the first publication (7). Solubilities in multicomponent systems (13-19) will be be considered below.

The extent of hydration of Cu(IO₃)₂ is subject to some uncertainty. The synthetic material prepared by metathesis between copper salts and iodic acid or alkali metal iodates has long been considered to the the monohydrate Cu(IO₃)₂·H₂O (20). In 1940, Berman and Wolfe (21) reported that the naturally occuring mineral bellingerite found in Chuquicamata, Chile was 3Cu(IO₃)₂·2H₂O. In 1972 Nassau and Shiever (22) reported that the material usually designated as Cu(IO₃)₂·H₂O was in fact identical to the mineral bellingerite. On the basis of X-ray analysis, Gamsjäger et al. (17) reported that the synthetic material was 3Cu(IO₃)₂·2H₂O, but also based on X-ray analysis as well as infrared and thermogravimetric analyses, Vinogradov et al. (12) reported that the synthetic material was the monohydrate. The early work of Spencer (1) reported that "air dried" synthetic copper iodate analyzed as Cu(IO₃)₂·0.985H₂O. Ramette has also published two different versions of this solid material: in (15) Ramette and Broman reported the synthetic material to be the monohydrate whereas in (19), Ramette and Fan reported that heating to 300°C "suggested" an original stoichiometry of 3Cu(IO₃)₂·2H₂O. At the present time the evaluators do not believe that it possible to specify the exact nature of the solid phase of the stable synthetic copper iodate hydrate: we will however assume it to be the monohydrate.

A summary of the experimental solubility data for the binary system is given in Table 1.

Table 1. Experimental solubilities in the binary Cu(IO₃)₂-H₂O system.

T/K	$10^{3}c_{1}/\text{mol dm}^{-3}$	$10^3 m_1/{ m mol~kg^{-1}}$	reference
293.2	3.21		13
298.2		3.245	3
н	3.26		6
**	3.30		5
#	3.34		4
*	3.44		13
	3.47		9
*	3.533		7, 8, 10
	3.58		11
#	3.693a		2
*	4.2		1
303.2	3.65		13
#	3.754		7, 8, 10
308.2	3.956		7, 8
313.2	4.101		7, 8
318.2	4.633		7, 8
н	5.484		10
323.2		5.33	12
Rejected value	es, see text.		

	COMPONENTS;	EVALUATORS:	
	(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	H. Miyamoto and E. M. Woolley Departments of Chemistry	
!	(2) Water; H ₂ O; [7732-18-5]	Niigata and Brigham Young Universities Niigata Japan, and Provo, UT, USA	
		July 1987	

The solubility data given in Table 1 were fitted by a relative least squares method to the following empirical equation:

$$ln\left(\frac{10^3c_1}{\text{mol dm}^{-3}}\right) = 6409.531 - \frac{169581.8}{T/K} - 1122.868ln(T/K) + 1.871977(T/K)$$

where $\sigma = 0.098$. Based on the standard error of estimate σ , two data points were rejected on the basis that $c_{obsd} - c_{calcd} > 2\sigma$ (see Table 1). From the smoothing equation, the following recommended and tentative solubilities were calculated for rounded temperatures.

Table 2. Recommended and tentative solubilities of Cu(IO₃)₂ in water

T/K	$10^3c_1/\text{mol dm}$
293.2	3.19
298.2	3.42ª
303.2	3.66
308.2	3.91
313.2	4.21
318.2	4.58
323.2	5.05

a Recommended value.

TERNARY SYSTEMS

Vinogradov et al. (12) were the only investigators to study a three-component system with two saturating components (Cu(IO₃)₂-KBrO₃-H₂O). All other studies on ternary systems involve Cu(IO₃)₂ as the only saturating component.

Solubility of copper iodate in aqueous solutions of lithium salts.

Fedorov et al. (11) reported solubilities of copper iodate in aqueous solutions of LiClO₄ and LiNO₃ at concentrations up to 4 mol dm⁻³. Their data appear to be somewhat higher than those of other authors who studied Cu(IO₃)₂ solubilities in other salt solutions, and we conclude that there is some unknown source of error, perhaps resulting from an error in the stoichiometry of the iodometric reactions. It is difficult to determine if there are any other possible systematic errors in the experimental method.

Solubility of copper lodate in aqueous solutions of potassium chloride.

There are three independent studies of the solubility of Cu(IO₃)₂ in aqueous KCl solutions at 298.2 K (2, 3, 5), and these results are summarized graphically in Fig. 1. In this figure curve (a) is the extension of curve (b). Keefer's data are based on mol kg⁻¹ units (curve (d)) whereas all other data are based on mol dm⁻³. The results of Peterson et al. (2) are systematically higher than those of Keefer (3) and Monk (5) by about 12 % and 10 %, respectively. While the source of the error in Peterson's work is difficult to determine, perhaps they too failed to properly account for the stoichiometry of their iodometric titrations. They do state that their analytical results were independent of Cu⁺⁺ concentration which is somewhat surprising under their experimental conditions. The more reliable solubility data appear to be those of Keefer and Monk which are designated as

COMPONENTS:

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Water; H₂O; [7732-18-5]

EVALUATORS:

July, 1987

H. Miyamoto and E. M. Woolley Departments of Chemistry Niigata and Brigham Young Universities Niigata Japan, and Provo, UT, USA

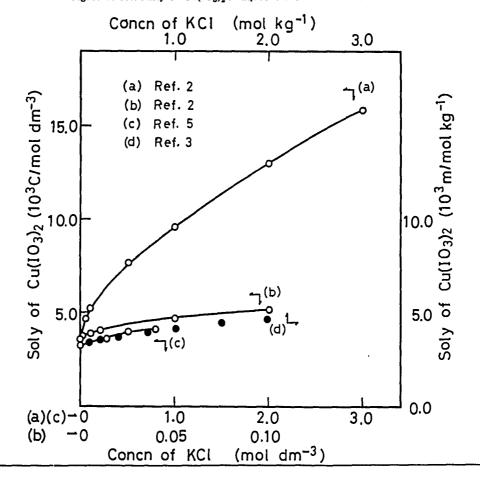
CRITICAL EVALUATION:

tentative solubilities, and the data of Peterson et al. are rejected. A summary of the solubility of $Cu(IO_3)_2$ in aqueous KCl solutions is given in Table 3 below.

Table 3. Solubility of Cu(IO₃)₂ in aqueous KCl solutions at 298.2 K.

KCl concn	$Cu(IO_3)_2$		KCl conen	$Cu(IO_3)_2$	
mol dm ⁻³	mmol dm ⁻³	ref	mol kg-1	mmol kg ⁻¹	ref
0.0005	3.724	2	0.0501	3.398	3
0.0010	3.725	2	0.01002	3.517	3
0.0050	3.825	2	0.02005	3.730	3
0.0100	3.992	2	0.03511	3.975	3
0.01309	3.65	5	0.05017	4.166	3
0.02618	3.89	5	0.07529	4.453	3
0.03927	4.10	5	0.1005	4.694	3
0.0500	4.667	2			
0.1000	5.238	2			
0.5000	7.689	2			
1.0000	9.615	2			
2.0000	13.072	2			
3.0000	15.820	2			

Figure 1. Solubility of Cu(IO₃)₂ in aqueous KCl solutions at 298.2 K



COMPONENTS:	EVALUATORS:
	H. Miyamoto and E. M. Woolley
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Departments of Chemistry
	Niigata and Brigham Young Universities
(2) Water; H ₂ O; [7732-18-5]	Niigata Japan, and Provo, UT, USA
1	July, 1987

Solubility in other salt solutions. The solubility of $Cu(IO_3)_2$ in aqueous salt solutions generally increases as the added salt concentration increases. There are two studies of the solubility of $Cu(IO_3)_2$ in aqueous sulfate solutions (1, 2), and the results of Spencer should probably be rejected as discussed above. The results of Petersen and Meyers (2) for $Cu(IO_3)_2$ solubilities in solutions of K_2SO_4 , $MgSO_4$ or $MgCl_2$ are designated as tentative. Similarly, the data of Ramette and Fan for the solubility of $Cu(IO_3)_2$ in aqueous $Cu(ClO_4)_2$ solutions are designated as tentative values since there are no other publications available for comparisons.

Solubility of Cu(IO₃)₂ in aqueous acid solutions.

Monk (5) measured the solubility of $Cu(IO_3)_2$ in aqueous HCl solutions and found that the solubility increases as the HCl concentration increases. This author also determined the ion pair dissociation constant K_d for $CuCl^+$.

Ramette (14) reported the solubility of Cu(IO₃)₂ in 1.00 mol dm⁻³ HClO₄, and although the temperature was not stated, it probably was 298.2 K by comparison with the data for the identical system studied later by Marchall and Blanchard (16). The excellent agreement between these two studies, 0.0122₅ mol dm⁻³ (14) and 0.01208 mol dm⁻³ (16) allows the evaluators to give a recommended solubility for Cu(IO₃)₂ in 1.00 mol dm⁻³ HClO₄ solution of 0.0121₅ mol dm⁻³ with a 95 % confidence interval of 0.0001₂ based on the five independent measurements reported by these authors. The solubility of Cu(IO₃)₂ in 1.000 mol dm⁻³ HClO₄ solutions at 308.2 K and 323.2 K are designated as tentative solubilities.

Ramette and Broman (15) reported the solubility of $Cu(IO_3)_2$ in aqueous solutions containing 1.0 x 10⁻⁴ mol dm⁻³ HClO₄, the stated purpose of this small acid concentration being the supression of hydrolysis. Other researchers have not reported complications due to hydrolysis of $Cu(IO_3)_2$. For these low acid concentrations, Ramette and Broman computed thermodynamic solubility products for $Cu(IO_3)_2$ from which they calculated Gibbs energies, enthalpies and entropies.

OTHER MULTICOMPONENT SYSTEMS

Solubilities in solutions containing HClO4 and an alkali metal perchlorate.

The data for the solubility of Cu(IO₃)₂ in HClO₄ solutions containing either LiClO₄ or NaClO₄ where the ionic strength is constant at 1.000 mol dm⁻³ are summarized in Table 4. Note that we assume that the data of Ramette (14) are for 298.2 K as discussed above. All three studies (14, 16 and 17) found that the solubility data could be fitted to the following equation:

$$Y = 2c_1^{3/2} = \alpha + b[HClO_4]_{total}$$
 [1]

In this equation, the constant a is associated with $(K_{s0})^{1/2}$ and the constant b is associated with $(K_{s0})^{1/2}/K_a$ where K_a is the acid dissociation constant (the concentration constant) for HIO₃. The use of the above equation implies the assumption that activity coefficients do not vary with solution composition at constant ionic strength, but this might not be strictly correct since the solubilities in NaClO₄ are consistently higher then they are in LiClO₄ solutions. Two recommended solubilities at 298.2 K determined by the evaluators from the data are given in Table 4. Finally, it is noted that Gamsjäger et al. (17) computed Gibbs enthalpies and entropies from their K_{s0} data.

Solubilities in solutions containing aliphatic monocarboxylic acids.

Lloyd et al. (4) determined the solubility of $Cu(IO_3)_2$ at 298.15 K in dilute solutions containing formic, acetic, propanoic, butanoic, 2-methylpropanoic, pentanoic, 3-methylbutanoic, 2,2-dimethylpropanoic, and hexanoic acids, each partially neutralized with NaOH. The enhanced solubilities was accounted for the the following reaction

$$Cu^{**} + RCOO^{-} \leftrightarrow Cu(RCOO)^{*}$$

	COMPONENTS:	EVALUATORS:	
	(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	H. Miyamoto and E. M. Woolley	
į		Departments of Chemistry	
	(2) Water; H ₂ O; [7732-18-5]	Niigata and Brigham Young Universities	
İ		Niigata Japan, and Provo, UT, USA	
		July, 1987	

Table 4. Solubility of Cu(IO₃)₂ in H₂O solutions containing HClO₄ and an alkali metal perchlorate (eq. [1]) (ionic strength constant at 1.000 mol dm⁻³)*.

salt	T/K	10 4 a	103b	$10^4\sigma_{ m Y}$	ref
LiClO ₄	274.2	6.6	1.08		17
	288.2	7.9	1.56		17
	298.2	9.1	1.84		16
	298.2	8.7	1.87	0.08	14
	298.2	8.9	1.85	0.1	recommended
	308.2	10.3	2.3		17
NaClO ₄	298.2	10.8	1.7	0.8	14
	298.2	9.8	1.7	0.4	16
	298.2	10.0	1.7	1.0	recommended
	308.2	12.0	2.3	0.4	16
	323.2	14.0	2.5	0.2	16

a Constants from eq. [1] where a is identified with $(K_{s0})^{1/2}$ and b is identified with $(K_{s0})^{1/2}/K_a$. Recommended data determined by the evaluators.

Solubility in Phenylethanoic acid.

Lloyd et al. (4) have also measured the solubility of Cu(IO₃)₂ at 298.15 K in dilute aqueous phenylacetic acid, partially neutralized with NaOH. The enhanced solubility was accounted for via eq. [1] above.

Solubilities in solutions containing halogen-substituted aliphatic carboxylic acids.

Lloyd et al. (4) reported the solubility of Cu(IO₃)₂ at 298.15 K in dilute aqueous solutions of containing chloroacetic acid, trichloroacetic acid, bromoacetic acid, 2-bromobutanoic acid, and 3-iodopropanoic acid, each partially neutralized with NaOH. The enhanced solubilities was accounted for with eq. [1]. All values reported in (4) are designated as tentative solubilities as they are no other publications available for comparisons.

Solubilities in sodium hydroxycarboxylates.

Evans and Monk (6) reported the solubility of $Cu(IO_3)_2$ in aqueous sodium hydroxyethanoate and in sodium 2-hydroxypropanoate solutions at 298.15 K. Standard state dissociation constants were reported for the two equilibria

$$Cu(X)^* \Leftrightarrow Cu^{**} + X^- \qquad K_{d1}^0$$
 [3]

$$Cu(X)_2(aq) \Leftrightarrow Cu^{**} + 2X^{-} \qquad K_{d2}^0 \qquad [4]$$

where X- represents the hydroxycarboxylate ion. Values for the above equilibrium constants are given in the compilations, and all solubility data are designated as tentative values.

Solubilities in hydroxy-substituted carboxylic acids.

Data are available for the solubility of Cu(IO₃)₂ in dilute aqueous buffered solutions of NaOH and: DL-2-hydroxypropanoic acid at 298.15 K (4), and at 298.2, 303.2, 313.2 and 318.2 K (7); 2-hydroxyacetic acid at 298.15 K (4) and at 298.2, 303.2, 313.2 and 318.2 K (18); and DL-hydroxysuccinic acid at 298.2, 303.2 and 318.2 K (10). Lloyd et al. (4) treated their solubility data in terms of equilibrium [1] as given above.

COMPONENTS:	EVALUATORS:
	H. Miyamoto and E. M. Woolley
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Departments of Chemistry
	Niigata and Brigham Young Universities
(2) Water; H ₂ O; [7732-18-5]	Niigata Japan, and Provo, UT, USA
	July, 1987

Das et al. (10) treated their data for 2-hydroxyacetic acid solutions in a similar manner, but they also calculated enthaply and entropy values for the reverse of reaction [2]. For *DL*-2-hydroxysuccinic acid solutions, Das et al. (10) also found evidence for the reaction

$$Cu^{**} + {}^{-}ORCOO^{-} \Leftrightarrow Cu(ORCOO)$$
 [5]

In computing Gibbs functions for this equilibrium, Das et al. accounted for activity coefficients and for the formation of the ion pairs CuIO₃- and NaIO₃. Ghosh and Nair (7) analyzed their data for *DL*-2-hydrox-ypropanoic acid solutions in terms of reactions [2] and [6].

$$Cu(RCOO)^+ + RCOO^- \Leftrightarrow Cu(RCOO)_2$$
 [6]

The average values of $\log K_{d^0}$ for the reverse of reaction [2] at 298.2 K for hydroxyacetic acid solutions are -3.05 (σ = 0.05) from Das et al. (10), and -2.91 (σ = 0.04) from Lloyd et al. (4). The value from Das et al. is based on seven measurements while the value from Lloyd et al. is based on three measurements. Because the exact [NaOH]/[C₂H₄O₃] ratio is different in these two papers, slightly different expressions were used for the activity coefficient, and becuase slightly different values for ion pairing constants for CuIO₃- and NaIO₃ were (probably) used, it is not possible to make direct comparisons and suggest recommended or tentative values for these solubility data. Similarly for DL-2-hydroxypropanoic acid solutions, it is not possible to compare the two sets of solubility data from (4) and (7). For the reverse of reaction [2] at 298.2 K, Lloyd et al. reported $\log K_{d^0} = -2.94$ (σ = 0.06) based on three measurements, and Ghosh and Nair (7) reported $\log K_{d^0} = -2.36$ (σ = 0.07) based on six measurements. However Ghosh and Nair's value of K_{d^0} includes the effect of the equilibrium given by reaction [6] above. In view of these difficulties in comparing the solubility data, all results for the solubility of Cu(IO₃)₂ in hydroxy-substituted carboxylic acid solutions are designated as tentative values.

Solubilities in dicarboxylic acids.

Ghosh and Nair (8) reported solubility data for Cu(IO₃)₂ in aqueous mixtures of NaOH with potassium hydrogen phthalate and with malonic acid from 298.2 K to 318.2 K. The increase in the solubility of Cu(IO₃)₂ was attributed to reactions [2] and [6], and thermodynamic equilibrium constants and Gibbs energies were computed. These solubility data are designated as tentative values.

Solubilities in amino acid solutions.

Keefer (3) measured the solubility of $Cu(IO_3)_2$ in aqueous glycine and in aqueous *DL*-alanine solutions, and Monk (5) studied the same systems with additions of either HCl or NaOH. Keefer analyzed his solubility data in terms of the following equilibria

$$HAA + Cu^{**} \Leftrightarrow Cu(AA)^{*} + H^{*} \qquad K_{1}$$
 [7]

$$2HAA + Cu^{**} \Leftrightarrow Cu(AA)_2 + 2H^* \qquad K_2$$
 [8]

$$HAA + Cu^{**} \Leftrightarrow Cu(HAA)^{**} \qquad K_3 \qquad [9]$$

where HAA is the neutral amino acid. Values of these equilibrium constants are given in the compilations, and all solubility data are designated as tentative values. Since Keefer studied three component systems and Monk studied four component systems, direct comparisions of the solubility data are not possible. Monk (5) studied the solubility of $Cu(IO_3)_2$ at 298.2 K in aqueous glycine, glycylglycine, and DL-alanine with either HCl or NaOH, and attributed the observed increase in solubility to the equilibria given in reactions [2] and [6]. The dissociation constants for these equilibria are given in the compilations, and all of Monk's solubility data are designated as tentative values.

COMPONENTS:

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Water; H₂O; [7732-18-5]

EVALUATORS:

H. Miyamoto and E. M. Woolley

Departments of Chemistry

Niigata and Brigham Young Universities

Niigata Japan, and Provo, UT, USA

July, 1987

CRITICAL EVALUATION:

Solubilities in mixtures of water and an organic solvent.

Miyamoto (9) and Miyamoto, Yamamoto and Maruyama (13) reported the solubility of $Cu(IO_3)_2$ in tetrahydrofuran-water and N,N-dimethylformamide-water mixtures. In both systems, the logarithm of the the $Cu(IO_3)_2$ solubility decreases almost linearly with the reciprocal of the dielectric constant of the solvent. These solubilities are designated as tentative.

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COMPONENTS:	EVALUATORS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Deuterium oxide (water-d ₂); D ₂ O; [7789-20-0]	H. Miyamoto Niigata University Niigata, Japan August, 1987

Solubility data for Cu(IO₃)₂ in deuterium oxide have been reported in two publications (1, 2). Ramette and Broman (1) reported the solubility of Cu(IO₃)₂ in 99.5 % D₂O containing 1 x 10⁻⁴ mol dm⁻³ HClO₄ and LiClO₄ from 0 to .100 mol dm⁻³. Using the Debye-Hückel extended equation, these authors computed thermodynamic solubility products for the three experimental temperatures of 287.9 K, 298.2 K, and 308.2 K. These solubility products were used in the calculations of Gibbs energies.

Gamsjäger et al. (2) measured the solubility of $Cu(IO_3)_2$ in 99.8+ % D_2O containing $DCIO_4$ and $LiCIO_4$ over the temperature range of 274.2 K to 308.2 K. $DCIO_4$ and $LiCIO_4$ were used to maintain a constant ionic strength of 1 mol kg⁻¹. The solubility data were reported graphically, and only concentration solubility products were given. The compilers used these K_{80} values and equation [1] above to compute the solubilities.

All solubility data in (1) and (2) are designated as tentative values.

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- 2. Gamsjäger, H.; Gerber, F.; Antonsen, O. Chimica 1973, 27, 94.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Monk, C.B.
(2) Water; H ₂ O; [7732-18-5]	Trans. Faraday Soc. <u>1951</u> , 47, 285-91.
VARIABLES:	PREPARED BY:
T/K = 298	E.M. Woolley and H. Miyamoto
L	

EXPERIMENTAL DATA:

The solubility of Cu(IO₃)₂ in pure water at 25°C was given as:

batch	solubility mol dm ⁻³	log K _{s0} a	K _{s0} b mol³ dm-9
1	0.00330	-7.1325	7.37 x 10 ⁻⁷
2	0.00333	-7.1311b	7.39 x 10-7
3	0.00337¢		

*K_{s0} was calculated by the authors from

$$log K_{s0} = [Cu^{2+}][IO_{3-}]^2 - 3[I^{1/2}/(1 + I^{1/2}) - 0.2I]$$

where I is the ionic strength and where formation of the species $CuIO_3^+$ and HIO_3 is taken into account by using the following values for the ion pair dissociation constants: $K_d(CuIO_3^+) = 0.15$ and $K_d(HIO_3) = 0.165$. Activity coefficients were estimated from the equation

$$log y_z = -(z^2/2)[I^{1/2}/(1 + I^{1/2}) - 0.2I]$$

where z is the ionic charge of the species.

bCalculated by the compilers.

cThis third solubility value is asserted to be suspect by the authors.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method was used, and details are given in ref. (1). The solvent was allowed to flow through the saturator sufficiently slowly for equilibrium to be established. The saturated solutions were made acidic with dilute acetic acid, and a large excess of solid KI was added. The resulting mixture was titrated to determine iodate content with Na₂S₂O₃ solution that had been standardized with Analytical Reagent KIO₃.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ crystals were prepared by allowing dilute solutions of analytical grade CuSO₄ and KIO₃ to drop slowly into a large volume of hot water. The very fine crystals were washed out insofar as possible.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

(1) Wise, W.C.A.; Davies, C.W. J. Chem. Soc. <u>1938</u>, 273.

COMPONENTS:

(1) Copper iodate; Cu(IO₃)₂; [13454-89-2]

(2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lloyd, M.; Wycherley, V.; Monk, C.B.

J. Chem. Soc. 1951, 1786-9.

VARIABLES:

PREPARED BY:

 $T/K \approx 298$

E.M. Woolley and H. Miyamoto

EXPERIMENTAL DATA:

The solubility of Cu(IO₃)₂ in pure water at 25°C was given as:

solubility mol dm ⁻³	solubility mol dm ⁻³	solubility mol dm- ³
0.00333	0.00333	0.00333
0.00336	0.00333	0.00333
0.00333	0.00333	0.00333
0.00336	0.00336	0.00333
0.00333	0.00334	0.00333
0.00334	0.00333	

Accounting for the dissociation of the ion pair $Cu(IO_3)^+$ using $K_d = 0.15$ mol dm⁻³ (assumed value as for the Ca complex reported in Davies, C.W. J. Chem. Soc. 1930, 2410 and 1938, 271), the authors calculated the thermodynamic solubility product from^a

$$log K_{s0} = [Cu^{2+}][IO_3^-]^2 - 3log (AI^{1/2}/(1 + I^{1/2}) - 0.2AI)$$

where I is the ionic strength. At zero ionic strength the authors reported $log~K_{s0} = -7.1210$ (i.e. $K_{s0} = 7.57 \times 10^{-8}$ mol³ dm⁻⁹).

aIn the original paper, the Debye-Huckel constant A was omitted from this equation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1) and modified in (2). A bulb containing the solvent solution was attached to a column containing Cu(IO₃)₂, and the solution allowed to flow through the column at a rate sufficient to insure saturation (1). The modification (2) was to connect the column to a second parallel arm in which the saturated solution was collected. The entire apparatus was thermostated. A portion of the saturated solution was run through the saturating column a second time. The iodate concentrations of the saturated solutions were determined volumetrically by using Na₂S₂O₃ solution previously standardized with KIO₃.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ crystals were prepared by allowing concentrated solutions of CuSO₄ and KIO₃ to drip slowly into nearly boiling water. The product was ground and the "fines" washed out.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.03 K.

REFERENCES:

- (1) Bronsted, N.J.; La Mer, V.K. J. Am. Chem. Soc. 1924, 46, 555.
- (2) Money, R.W.; Davies, C.W. J. Chem. Soc. <u>1934</u>, 400.

COMPONENTS:

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium nitrate; LiNO₃; [7790-69-4]

or

- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fedorov, V.A.; Robov, A.M.; Shmyd'ko, I.I.; Koneva, T.N. Simaeva, L.S.; Kukhtina, V.A.

Zh. Fiz. Khim. 1976, 50, 2213-5: Russ. J. Phys. Chem. (Engl. Transl.) 1976, 50, 1300-2.

VARIABLES:

Concentration of LiNO₃ or LiClO₄ T/K = 298

PREPARED BY:

H. Miyamoto

EXPERIMENTAL VALUES:

LiNO ₃ conen mol dm ⁻³	Cu(IO ₃) ₂ solubility mol dm ⁻³	LiClO ₄ conen mol dm ⁻³	Cu(IO ₃) ₂ solubility mol dm ⁻³
0	0.00358	0	0.00358
0.01	0.00400	0.01	0.00400
0.05	0.00458	0.05	0.00454
0.10	0.00492	0.10	0.00485
0.25	0.00495	0.25	0.00547
0.40	0.00645	0.40	0.00575
0.50	0.00666	0.50	0.00585
1.00	0.00745	1.00	0.00580
2.00	0.00830	2.00	0.00530
3.00	0.00854	3.00	0.00440
4.00	0.00850	4.00	0.00342

The solubility data were fitted to the equation $log K_{s0} = AI^{1/2}/(1 + BaI^{1/2}) = log K_{s0}^0$ - bI where the constants a and b were determined empirically. The results of these calculations are: for LiNO₃ solutions, a = 0.36 nm, b = 0.1 dm³ mol⁻¹ and $log K_{s0}^0 = -7.05$; for LiClO₄ solutions, a = 0.36 nm, b = 0.39 dm³ mol⁻¹ and $log K_{s0}^0 = -7.06$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experimental method used was similar to that described in (1). Equilibrium required 4-6 hours, and the solubilities were determined by iodometric titration with amperometric end point detection.

Each solubility value given in the data table above is the mean of 3-4 determinations.

SOURCE AND PURITY OF MATERIALS:

The source and purities of materials were not given. The authors state that the solid phase is Cu(IO₃)₂·H₂O.

ESTIMATED ERROR:

Soly: reproducibility within 2-3 %. Temp: nothing specified.

REFERENCES:

(1) Fedorov, V.A.; Shmyl'ko, I.I.; Robov, A.M.; Shimaeva, L.S.; Kukhtina, V.A.; Mironov, V.E. Zh. Neorg. Khim. 1973, 18, 1274.

COMPONENTS: (1) Copper iodate; Cu(IO₃)₂; [13454-89-2] (2) Potassium chloride; KCl; [7447-40-7] (3) Water; H₂O; [7732-18-5] VARIABLES: Concentration of KCl ORIGINAL MEASUREMENTS: Peterson, B.H.; Meyers, E.L. J. Am. Chem. Soc. 1930, 52, 4853-7. Proc. Iowa Acad. Sci. 1930, 37, 223-4.

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

 $T/K \approx 298$

The solubility of Cu(IO₃)₂ in aqueous KCl solutions at 25°C was given as:

ionic strength	KCl concna	solubility
mol dm-3	mol dm-3	mol dm-3
0.01108	0.0	0.003693b
0.01167	0.0005	0.003724
0.01217	0.0010	0.003725
0.01647	0.0050	0.003825
0.02198	0.0100	0.003992
0.06400	0.0500	0.004667
0.11571	0.1000	0.005238
0.52306	0.5000	0.007689
1.02884	1.0000	0.009615
2.03922	2.0000	0.013072
3.04746	3.0000	0.015820

aCalculated by the compilers from [KCl] = (ionic strength) - 3(solubility).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

5 g Cu(IO₃)₂·H₂O were added to 250 cm³ of KCl solution in Pyrex Erlenmeyer flasks fitted with stoppers through which a stirring rod extended. The flasks were thermostatted and gently agitated for 5 d, and then allowed to stand for 12 h. Solutions were analyzed for IO₃- by addition of KI and H₂SO₄ followed by titration with 0.05 mol dm⁻³ Na₂S₂O₃ which was previously standardized with standard KIO₃ solution. Reproducibility in the presence of varying amounts of Cu²+ was within 0.1 %.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂•H₂O prepared from purified CuSO₄ and KIO₃ solutions by dropwise addition into a large volume of doubly distilled water kept at 60°C and constantly stirred. The ppt was washed several times by decantation, and was sedimented in a tall cylinder: all particles that did not settle were siphoned off. The ppt was then filtered and dried over CaCl₂, and analyzed.

KCl was recrystallized and dried.

ESTIMATED ERROR:

Soly: precision ± 0.1 %. Temp: precision ± 0.02 K.

REFERENCES:

^bCompilers calculate $K_{s0} \approx 2.0 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$ from this data point.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Keefer, R.M.
(2) Potassium chloride; KCl; [7447-40-7]	J. Am. Chem. Soc. 1948, 70, 476-9.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of KCl T/K = 298	H. Miyamoto

EXPERIMENTAL DATA:

The solubility (S) of Cu(IO₃)₂ in aqueous KCl solutions at 25°C was given as:

KCl concn	solubility	solubility
	(experimental)	(calculated)
mol kg-1	mol kg-1	mol kg-1
0.0	0.003245	0.003243
0.00501	0.003398	0.003396
0.01002	0.003517	0.003521
0.02005	0.003730	0.003730
0.03511	0.003975	0.003969
0.05017	0.004166	0.004166
0.07529	0.004453	0.004454
0.1005	0.004694	0.004697

The author fitted the solubilities (S) to the following equation:

$$log (4S^3) = -7.1353 + 3.036 I^{1/2}/(1 + 1.08 I^{1/2})$$

where I is the ionic strength, [KCl] + 3(S). From the experimental solubility in pure water the compiler calculates $K_{s0} = 1.36 \times 10^{-7} \text{ mol}^3 \text{ kg}^{-3}$, and from the above equation the compiler calculates $K_{s0} = 7.32 \times 10^{-8} \text{ mol}^3 \text{ kg}^{-3}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method as in (1). KCl solutions prepared from distilled water using calibrated volumetric apparatus. Excess air-dried copper iodate placed in glass-stopperd Pyrex flasks and the KCl solutions added. The flasks were placed in a thermostat at 25°C and rotated for at least 12 h. By applying pressure, samples of saturated solution were removed with a pipet fitted with an asbestos filter. Solubilities were determined by iodometric titration modified for the presence of Cu²⁺ using the method of Foote and Vance (2).

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepared by adding equal volumes of 0.2 mol kg⁻¹ KIO₃ and 0.1 mol kg⁻¹ CuSO₄ solutions to a large volume of water at 60°C. The ppt was filtered and stored under water overnight. The product was sedimented several times and the smaller particles were discarded. After drying for 2 h at 250-270°C, the dried copper iodate was analyzed iodometrically and the purity was reported as 100.1 %.

ESTIMATED ERROR:

Soly: duplicates agreed to ± 0.2 %. Temp: precision ± 0.02 K.

REFERENCES:

- (1) Keefer, R.M.; Reiber, H.G.; Bisson, C.S. J. Am. Chem. Soc. <u>1940</u>, 62, 2951.
- (2) Foote, H.W.; Vance, J.E. Ind. Eng. Chem. Anal. Ed. 1936, 8, 119.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Monk, C.B.
(2) Potassium chloride; KCl; [7447-40-7]	
or	Trans. Faraday Soc. 1951, 47, 285-91.
(2) Hydrogen chloride; HCl; [7647-01-0]	
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of KCl or HCl T/K = 298	E.M. Woolley and H. Miyamoto

EXPERIMENTAL DATA:

The solubility of Cu(IO₃)₂ in aqueous KCl or HCl solution at 25°C was given as:

KCl or HCl concn	solubility	K _d (CuCl+)a
mol dm-3	mol dm-3	mol dm-3
(KCI) 0.0	0.00330	
" 0.01309	0.00365	0.31
" 0.02618	0.00389	0.43
" 0.03927	0.00410	0.35
(HCl) 0.03906	0.00445	0.53
" 0.08139	0.00535	0.37

^aThe dissociation constant for CuCl+ was calculated using the following literature values for dissociation constants of other ion pair species: $K_d(HIO_3) = 0.165$, $K_d(KIO_3) = 2.0$. For CuIO₃+, the dissociation constant was estimated as 0.15.

Activity coefficients were estimated from the equation

$$\log y_z = -(z^2/2)[I^{1/2}/(1 + I^{1/2}) - 0.2I]$$

where I is the ionic strength and z is the ionic charge of the species. Note that the Debye-Huckel A constant is missing from this equation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method was used, and details are given in ref. (1). The solvent was allowed to flow through the saturator sufficiently slowly for equilibrium to be established. The saturated solutions were made acidic with dilute acetic acid, and a large excess of solid KI was added. The resulting mixture was titrated to determine iodate content with Na₂S₂O₃ solution that had been standardized with Analytical Reagent KIO₃.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ crystals were prepared by allowing dilute solutions of analytical grade CuSO₄ and KIO₃ to drop slowly into a large volume of hot water. The very fine crystals were washed out insofar as possible.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

(1) Wise, W.C.A.; Davies, C.W. J. Chem. Soc. <u>1938</u>, 273.

COMPONENTS: (1) Copper iodate; Cu(IO₃)₂; [13454-89-2] (2) Potassium iodate; KIO₃; [7758-05-6] (3) Water; H₂O; [7732-18-5] VARIABLES: Composition T/K = 323 CORIGINAL MEASUREMENTS: Vinogradov, E.E.; Karataeva, I.M.; Lepeshkov, I.N. Phonogradov, E.E.; Karataeva, I.M.; Lepeshkov, I.N. Vinogradov, E.E.; Karataeva, I.M.; Lepeshkov, I.N. Phonogradov, E.E.; Karataeva, I.M.; Lepeshkov, I.N. Ph

EXPERIMENTAL DATA:

KIO	O ₃ composition	la.	Cu(l	(O ₃) ₂ composition	nª	nature of the solid phaseb
mass %	mol kg-1	mol %	mass %	104mol kg-1	mole %	
11.76	0.623	1.109	*			Α
9.81	0.508	0.907	0.007	1.9	0.00034	A + C
9.66	0.500	0.892	0.015	4.0	0.00072	A + C
9.24	0.476	0.850	0.025	6.7	0.00119	С
7.59	0.384	0.687	0.030	7.9	0.00141	C
5.50	0.272	0.488	0.055	14.1	0.00253	С
4.26	0.208	0.373	0.013	3.3	0.00059	С
3.10	0.149	0.269	0.015	3.7	0.00067	С
2.74	0.132	0.237	0.019	4.7	0.00085	B + C
2.36	0.113	0.203	0.012	3.0	0.00053	B + C
1.12	0.053	0.095	0.020	4.9	0.00088	В
			0.220	53.3	0.00961	В

•Molalities and mol % solubilities calculated by the compilers.

b A = KIO₃; B = Cu(IO₃)₂·H₂O; C = 2KIO₃·Cu(IO₃)₂·2H₂O.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Equilibrium reached in about one month. The copper content of the saturated solutions was determined by EDTA titration in strong alkaline medium using methyl thymol blue indicator. Potassium was determined gravimetrically by pptn with sodium tetraphenylborate. The solid phases were investigated by thermogravimetry, X-ray diffraction, and infrared methods.

SOURCE AND PURITY OF MATERIALS:

Copper iodate prepared from copper sulfate and iodic acid. The purity was checked by chemical and X-ray diffraction analysis. The extent of hydration was not given. C.p. grade KIO₃ was used.

COMMENTS AND/OR ADDITIONAL DATA:

Using the activity coefficient relationship

$$log y_{\pm} = -(z^2/2)I^{1/2}/(1 + I^{1/2})$$

the compilers calculated thermodynamic solubility products. For the last data point in the above table, $K_{s0} = 4.4 \times 10^{-7} \text{ mol}^3 \text{ kg}^{-3}$, and for the next to last data point, $K_{s0} = 3.9 \times 10^{-7} \text{ mol}^3 \text{ kg}^{-3}$.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Peterson, B.H.; Meyers, E.L.
(2) Potassium sulfate; K ₂ SO ₄ ; [7778-80-5]	J. Am. Chem. Soc. <u>1930</u> , 52, 4853-7. Proc. Iowa Acad. Sci. <u>1930</u> , 37, 223-4.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of K ₂ SO ₄ T/K = 298	H. Miyamoto and E.M. Woolley

The solubility of $Cu(IO_3)_2$ in aqueous K_2SO_4 solutions at 25°C was given as:

K ₂ SO ₄ concn ^a	solubility
mol dm ⁻³	mol dm ⁻³
0.0	0.003693 ^b
0.00050	0.003785
0.00100	0.003882
0.00500	0.004359
0.01000	0.004856
0.05000	0.006840
0.09255	0.008279
0.50000	0.015010
	mol dm-3 0.0 0.00050 0.00100 0.00500 0.01000 0.05000 0.09255

^aCalculated by the compilers from $[K_2SO_4] = \{(ionic strength) - 3(solubility)\}/3$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

5 g Cu(IO₃)₂·H₂O were added to 250 cm³ of K₂SO₄ solution in Pyrex Erlenmeyer flasks fitted with stoppers through which a stirring rod extended. The flasks were thermostatted and gently agitated for 5 d, and then allowed to stand for 12 h. Solutions were analyzed for IO₃- by addition of KI and H₂SO₄ followed by titration with 0.05 mol dm⁻³ Na₂S₂O₃ which was previously standardized with standard KIO₃ solution. Reproducibility in the presence of varying amounts of Cu²⁺ was within 0.1 %.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂·H₂O prepared from purified CuSO₄ and KIO₃ solutions by dropwise addition into a large volume of doubly distilled water kept at 60°C and constantly stirred. The ppt was washed several times by decantation, and was sedimented in a tall cylinder: all particles that did not settle were siphoned off. The ppt was then filtered and dried over CaCl₂, and analyzed.

K₂SO₄ was recrystallized and dried.

ESTIMATED ERROR:

Soly: precision ± 0.1 %. Temp: precision ± 0.02 K.

^bCompilers calculate $K_{a0} = 2.0 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$ from this data point.

^cAccording to the authors, this value seems to be too low.

COMPONENTS: (1) Copper iodate; Cu(IO ₈) ₂ ; [13454-89-2]	ORIGINAL MEASUREMENTS: Peterson, B.H.; Meyers, E.L.
(2) Magnesium chloride; MgCl ₂ ; [7786-30-3] (3) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. <u>1930</u> , 52, 4853-7. Proc. Iowa Acad. Sci. <u>1930</u> , 37, 223-4.
VARIABLES: Concentration of MgCl ₂ T/K = 298	PREPARED BY: H. Miyamoto and E.M. Woolley

The solubility of Cu(IO₃)₂ in aqueous MgCl₂ solutions at 25°C was given as:

MgCl ₂ concn ^a	solubility
mol dm-3	mol dm-3
0.0	0.0036935
0.0005	0.003775
0.0010	0.003821
0.0051	0.004151
0.0101	0.004415
0.0507	0.005742
0.1014	0.006446
0.4787	0.009892
1.0251	0.011658¢
1.4477	0.013946
	mol dm-3 0.0 0.0005 0.0010 0.0051 0.0101 0.0507 0.1014 0.4787 1.0251

aCalculated by the compilers from $[MgCl_2] = \{(ionic strength) - 3(solubility)\}/3$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

5 g Cu(IO₃)₂·H₂O were added to 250 cm³ of MgCl₂ solution in Pyrex Erlenmeyer flasks fitted with stoppers through which a stirring rod extended. The flasks were thermostatted and gently agitated for 5 d, and then allowed to stand for 12 h. Solutions were analyzed for IO₃- by addition of KI and H₂SO₄ followed by titration with 0.05 mol dm-³ Na₂S₂O₃ which was previously standardized with standard KIO₃ solution. Reproducibility in the presence of varying amounts of Cu²+ was within 0.1 %.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂•H₂O prepared from purified CuSO₄ and KIO₃ solutions by dropwise addition into a large volume of doubly distilled water kept at 60°C and constantly stirred. The ppt was washed several times by decantation, and was sedimented in a tall cylinder: all particles that did not settle were siphoned off. The ppt was then filtered and dried over CaCl₂, and analyzed.

MgCl₂ was recrystallized and dried.

ESTIMATED ERROR:

Soly: precision ± 0.1 %. Temp: precision ± 0.02 K.

bCompilers calculate $K_{s0} = 2.0 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9} \text{ from this data point.}$

cThis value seems to be unusally low (compilers).

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	ORIGINAL MEASUREMENTS: Peterson, B.H.; Meyers, E.L.
(2) Magnesium sulfate; MgSO ₄ ; [7487-88-9] (3) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. <u>1930</u> , 52, 4853-7. Proc. Iowa Acad. Sci. <u>1930</u> , 37, 223-4.
VARIABLES: Concentration of MgSO ₄ T/K = 298	PREPARED BY: H. Miyamoto and E.M. Woolley

The solubility of Cu(IO₃)₂ in aqueous MgSO₄ solutions at 25°C was given as:

ionic strength	MgSO ₄ concn ^a	solubility
mol dm-3	mol dm-3	mol dm-3
0.01108	0.0	0.0036935
0.01338	0.00050	0.003794
0.01554	0.00100	0.003845
0.03288	0.00507	0.004194
0.05358	0.01000	0.004526
0.21776	0.05000	0.005921
0.41867	0.10000	0.006225
2.03388	0.50000	0.011294

aCalculated by the compilers from [MgSO₄] = {(ionic strength) - 3(solubility)}/4.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

5 g Cu(IO₃)₂·H₂O were added to 250 cm³ of MgSO₄ solution in Pyrex Erlenmeyer flasks fitted with stoppers through which a stirring rod extended. The flasks were thermostatted and gently agitated for 5 d, and then allowed to stand for 12 h. Solutions were analyzed for IO₃- by addition of KI and H₂SO₄ followed by titration with 0.05 mol dm⁻³ Na₂S₂O₃ which was previously standardized with standard KIO₃ solution. Reproducibility in the presence of varying amounts of Cu²⁺ was within 0.1 %.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂•H₂O prepared from purified CuSO₄ and KIO₃ solutions by dropwise addition into a large volume of doubly distilled water kept at 60°C and constantly stirred. The ppt was washed several times by decantation, and was sedimented in a tall cylinder: all particles that did not settle were siphoned off. The ppt was then filtered and dried over CaCl₂, and analyzed.

MgSO₄ was recrystallized and dried.

ESTIMATED ERROR:

Soly: precision ± 0.1 %. Temp: precision ± 0.02 K.

^bCompilers calculate $K_{s0} = 2.0 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$ from this data point.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ramette, R.W.

J. Chem. Educat. 1959, 36, 191-3.

VARIABLES:

Concentrations of HClO4 and LiClO4 Temperature probably 298 K

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

HClO ₄ conen mol dm-3	LiClO ₄ concn mol dm-3	Cu(IO ₃) ₂ soly mol dm-3	
0.010	0.990	0.00580	
0.300	0.700	0.00799	
0.700	0.300	0.0106	
1.00	0.000	0.0123	

Assuming the only important equilibria to be

$$Cu(IO_3)_2(s) = Cu^{2+} + 2IO_3^{-}$$
 $K_{40} = [Cu^{2+}][IO_3^{-}]^2$

$$K_{\bullet 0} = [Cu^2 +][IO_3 -]^2$$

$$HIO_3 = H^+ + IO_3^-$$

$$K_a = [H+][IO_3-]/[HIO_3]$$

the author derived the equation for the solubility, S (neglecting activity coefficients)

$$2S^{3/2} = (K_{s0})^{1/2}\{1 + [HClO_4]/K_a]\}$$

The data give $K_a = 0.47$ mol dm⁻³ and $K_{s0} = 7.6 \times 10^{-7}$ mol³ dm⁻⁹ at an ionic strength of 1 mol dm⁻³ (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess solid copper iodate and water containing HClO₄ |Solid copper iodate was prepared as described by and NaClO₄ were placed into a bottle. A motor driven stirrer was inserted into the bottle, and the system stirred for 2 or 3 days. Excess copper iodate removed by filtration, and 5 cm³ aliquots of saturated solution removed with a pipet. Adding water and HCl, the idoate concentration was determined by titration with 0.02 mol dm-3 Na₂S₂O₃ solution using starch as the indicator.

The experimental temperature was not specified, but the compiler assumes it was around 25°C.

SOURCE AND PURITY OF MATERIALS:

Peterson (1,2), although HIO3 may have been used in place of KIO₃. The purities and sources of other materials are not given.

ESTIMATED ERROR:

Nothing specified.

- (1) Peterson, B.H.; Meyers, E.L. J. Am. Chem. Soc. 1930, 52, 4853.
- (2) Peterson, B.H. J. Chem. Educat. 1957, 34, 612.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ramette, R.W.; Broman, R.F.

J. Phys. Chem. 1963, 67, 942-4.

VARIABLES:

Conen of LiClO₄ at $[HClO_4] = 0.0001$ mol dm⁻³ T/K = 288, 298 and 308

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

Note that for all solutions below, the concentration of HClO₄ is constant at 0.0001 mol dm-3.

t/ºC	LiClO ₄ concn mol dm-3	Cu(IO ₃) ₂ soly mol dm-3	t/ºC	LiClO ₄ concn mol dm ⁻³	Cu(IO ₃) ₂ soly mol dm ⁻³
14.7	0.000	0.00276	25.0	0.000	0.00324
H	0.025	0.00330	11	0.0025	0.00329
#	0.050	0.00352	19	0.0060	0.00338
#	0.075	0.00378	**	0.025	0.00378
Ħ	0.100	0.00389		0.050	0.00400
			**	0.075	0.00418
			19	0.100	0.00437
35.0	0.000	0.00369			
**	0.025	0.00416			
#	0.050	0.00444			
tt .	0.075	0.00469			
u	0.100	0.00486			

continued....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method same as in (1). Excess Cu(IO₃)₂·H₂O added to LiClO₄ solutions containing HClO₄ to supress hydrolysis. Solutions were rotated in borosilicate glass bottles for 2 d in a thermostat at 38°C, and then transferred to a water bath thermostated at 35.0°C where they stood for 3 d with occasional shaking. Saturated solutions were filtered through fine porous glass by pressure, and 5 cm³ aliquots were pipetted into titration flasks. Aliquots were treated with 2 ml of 0.1 mol dm⁻³ acetic acid + 0.1 mol dm⁻³ sodium acetate buffer, and 1 drop of Snazoxs indicator: the solution was then titrated with EDTA. The EDTA solutions were standardized with weighed quantities of pure electrolytic copper, and duplicate titrations agreed to within 0.2 %.

The bottles and remaining solutions were then equilibrated in a similar manner at 25.0°C, and finally at 14.7°C, and aliquots for analyses were taken at each temperature.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂·H₂O prepared by adding 3 mol dm⁻³ HIO₃ and 1 mol dm⁻³ CuSO₄ solutions to hot water with constant stirring. The product was washed with hot water using a repetitive process of partial sedimentation followed by decantation to remove the smaller particles. After drying, analysis by iodometric titration with thiosulfate gave a purity of 99.9 %.

LiClO₄ and HClO₄ were reagent grade.

ESTIMATED ERROR:

Soly: reproducibility within 0.2 %. Temp: nothing specified.

REFERENCES:

(1) Ramette, R.W.; Dratz, E.A. J. Phys. Chem. <u>1963</u>, 67, 940.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ramette, R.W.; Broman, R.F.

J. Phys. Chem. 1963, 67, 942-4.

EXPERIMENTAL DATA: (continued.....)

 K_{s0} was calculated by the authors as $K_{s0} = 4S^3Y$ where S is the experimental solubility and Y is the Debye-Huckel activity relation

$$\log Y = -6AI^{1/2}/(1 + BI^{1/2})$$

[1]

$$I = 3S + [LiClO_4] + [HClO_4]$$

[2]

The calculations were carried out by plotting $-\log(4S^3)$ versus $I^{1/2}$ while varying B so that the value of A was precisely the theoretical value at each temperature. The results are summarized below, and include the evaluation of the Gibbs free energy, enthalpy and entropy obtained in the usual way from a $-\log K_{*0}$ vs 1/(T/K) plot. All are based on mol dm⁻³ units, and the uncertainties expressed refer to the 90 % confidence intervals.

Aª	В	
mol ^{-1/2} dm ^{3/2}	mol ^{-1/2} dm ^{3/2}	-log K_{s0}
0.501	1.33	7.31 ± 0.04
0.509	1.72	7.13 ± 0.03
0.519	1.97	6.97 ± 0.02
	mol ^{-1/2} dm ^{3/2} 0.501 0.509	mol ^{-1/2} dm ^{3/2} mol ^{-1/2} dm ^{3/2} 0.501 1.33 0.509 1.72

*Note: The authors point out that in carrying out the least squares treatment of the solubility data, the "best fit" does not correspond to the case where A is the theoretical value in eq. [1]. In fact, at 25° C, the sum of squares of deviations for the fit with A constrained to equal the theoretical values is 0.00059, whereas the "best fit" gives 0.00039 for the sum of the squares of deviations: in this case B = 3.2 mol^{-1/2} dm^{-3/2} and A = 0.752 mol^{-1/2} dm^{3/2} which gives $-\log K_{*0} = -7.21$.

∆G _{s0} kcal mol ⁻¹	ΔH _{s0} kcal mol ⁻¹	ΔS _{s0} cal K ⁻¹ mol ⁻¹
9.73 ± 0.03	6.77± 0.042	-9.91 ± 1.5

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄; [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gamsjager, H.; Gerber, F.; Antonsen, O.

Chimica 1973, 27, 94-7

VARIABLES:

Concentration of LiClO₄ and HClO₄. T/K = 274, 288, 298 and 308.

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

Using LiClO₄ and HClO₄ to maintain a constant ionic strength of 1.0 mol kg⁻¹, the soly of Cu(IO₃)₂ was reported graphically. The data were analyzed in terms of the following eqns defining F as 2(soly)^{1.5} where concentrations are based on mol kg⁻¹ units (note that activity coefficients are assumed to equal unity):

$$F = 2\{Cu^{2*}\}^{1.5} = K_{*0}^{1/2} \left(1 + \frac{\{H^*\}}{K_a}\right)$$

where

$$K_{s0} = \{Cu^{2*}\}\{IO_3^-\}^2$$
 and $K_a = \{H^*\}\frac{\{IO_3^-\}}{\{HIO_3^-\}}$

From material balance requirements and least squares fitting, the following were reported:

t/°C	$-\log K_{s0}$	$-\log K_{\mathbf{a}}$	Cu(IO ₃) ₂ /mol kg ^{-1a}
1	$6.366 \ (\sigma = 0.025)$	$0.215 \ (\sigma = 0.018)$	0.0047 ₅
15	$6.207 \ (\sigma = 0.015)$	$0.297 \ (\sigma = 0.010)$	0.00537
25	$6.083 \ (\sigma = 0.030)$	$0.306 \ (\sigma = 0.020)$	0.00592
35	$5.978 \ (\sigma = 0.035)$	$0.351 \ (\sigma = 0.025)$	0.0064

*Solubilities calcd by compilers from $(K_{s0}/4)^{1/3}$ (note ionic strength = 1.0 mol kg⁻¹).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess cupric iodate hydrate was placed in glass ampoules and LiClO₄ and HClO₄ solutions added to maintain the ionic strength at 1.0 mol kg⁻¹. The ampoules were sealed and shaken in a water thermostat with a precision in temperature of \pm 0.1°C. After equilibrium was reached, samples of saturated solution were removed by millipore filtration and analyzed for cupric iodate by iodometric titration. X-ray powder diffraction patterns of the solid phase before and after equilibration indicated the solid phase to be Cu₃(IO₃)₆·2H₂O.

SOURCE AND PURITY OF MATERIALS:

Cu₃(IO₃)₆·2H₂O prepared as in (1) and structure confirmed by X-ray analysis. LiClO₄ prepd from Li₂CO₃ and HClO₄ followed by several recrystallizations. HClO₄ was reagent grade, water was distilled twice from a quartz still.

ESTIMATED ERROR:

Standard deviations for K_{s0} given above. Temp: precision \pm 0.1 K.

REFERENCES:

 Ramette, R.W.; Broman, R.F. J. Phys. Chem., 1963, 67, 942.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium chloride; NaCl; [7647-14-5] (3) Sodium perchlorate; NaClO ₄ ; [7775-09-9]	Ramette, R.W.; Fan, G.
(4) Water; H ₂ O; [7732-18-5]	Inorg. Chem. <u>1983</u> , 22, 3323-6.
VARIABLES:	PREPARED BY:
Concentration of NaCl and NaClO ₄ . T/K = 298 and 308.	H. Miyamoto and M. Salomon

Using NaClO₄ to maintain a constant ionic strength of 5.0 mol dm⁻³, the soly of Cu(IO₃)₂ in solutions of varying NaCl concentration was given as (all concentrations in units of mol dm⁻³):

$t/^{0}C = 2$	25	t/ºC =	= 35	
NaCl conen	Cu(IO ₃) ₂ soly	NaCl conen	Cu(IO ₃) ₂ soly	
0.09900	0.003994	0.09870	0.004060	j 1
0.19960	0.004219	0.19899	0.004384	
0.29807	0.004477	0.29717	0.004377	
0.40141	0.004739	0.40020	0.005001	SOLVENT
0.50233	0.005003	0.50080	0.005305	
0.69875	0.005555	0.69662	0.005936	
0.79683	0.005864	0.79619	0.006290	= -
1.2964	0.007302	1.2924	0.007952	
1.6967	0.008513	1.6915	0.009337	
2.4967	0.01106	2.4889	0.01221	SOLUTE
3.5032	0.01440	3.4921	0.01613	SOLUTE
4.9904	0.01986	4.9742	0.02235	
				FRIT —
				SATURATED SOLUTION

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method previously described in (1) which is basically very similar to the saturation column method originated by Monk et al. (see the compilations of the papers by Monk et al. throughout this volume). The solubility vessel (see figure above) consisted of a fine porosity sealing tube, the upper half of which was packed with about 7 g of Cu(IO₃)₂. A few ml of solvent (NaCiO₄ + NaCl solution) were added to the top of the tube, and the fritted tube placed in a screw-capped test tube. The sealed assembly was placed in a water bath controlled at 25.06 ± 0.005°C. The initial output of solution was discarded, and the inner fritted tubes refilled with fresh solvent. Aliquots (0.005 ml accurate to ± 0.0001 g) were withdrawn for analysis with a calibrated transfer pipet. Saturated solutions were analyzed coulometrically with 0.02 mol dm⁻³ EDTA added to mask copper(II) against reduction. Saturated solutions were prepared and analyzed on a mass basis, and final conversion to volume units were made with density measurements (densities were not reported). Saturated solutions coulometrically analyzed for iodate by reduction at a mercury pool or Pt gauze electrode. Calibration of the method using recrystallized KIO₃ gave an accuracy of analysis of about 0.03 %. The solid phases of copper iodate were stated to be slow to equilibrate, and fresh portions of solvent were added repeatedly until the observed solubilities were reproducible to within 1 ppt.

The authors fitted the solubility data to a smoothing equation assuming the species in solution were Cu^{2+} , $CuIO_3^+$, $Cu(IO_3)_2$, and $CuCI_n^{2-n}$ for n=1 to 4. Neglecting activity coefficients in these solutions of 5.0 mol dm⁻³ total ionic strength, excellent fits were obtained based on the agreement between observed and calculated solutilities. The authors also computed Gibbs energies, enthalpies and entropies of solution based on this least squares smoothing equation applied to two temperatures: the reader is referred to the original literature in the event that these calculations are of interest.

continued.....

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium chloride; NaCl; [7647-14-5]
- (3) Sodium perchlorate; NaClO₄; [7775-09-9]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ramette, R.W.; Fan, G.

Inorg. Chem. 1983, 22, 3323-6.

AUXILIARY INFORMATION (continued.....)

SOURCE AND PURITY OF MATERIALS:

 $Cu(IO_3)_2$ was prepared by slow addition of NaIO₃ and CuSO₄ solutions to hot 0.1 mol dm-3 HNO₃. The precipitate was thoroughly washed and placed in a Soxhlet with 0.02 mol dm-3 HNO₃ in the boiling flask, and a recrystallized product was obtained after 1 week. The mass loss upon heating to 300°C suggested an original solid stoichiometry of $3Cu(IO_3)_2 \cdot 2H_2O$.

Cu(ClO₄)₂ stock solutions were analyzed by EDTA titration with Murexide indicator by potentiometric titration using a Hg indicator electrode, and by controlled potential coulometric deposition using both Hg-pool and Pt gauze electrodes. Accuracy and precision of iodate determination checked with recrystallized KIO₃, and the authors report standard deviations of around 0.03 %.

All solutions were prepared with AR grade NaCl using NaClO₄ to adjust the ionic strength to 5.00 mol dm⁻⁸.

ESTIMATED ERROR:

Standard deviation in the coulometric determination of iodate reported to be about 0.03 %, and the reproducibility in the observed solubilities was stated to be less than 1 ppt.

The temperature control (precision) was stated to be \pm 0.005 K.

REFERENCES:

(1) Ramette, R.W. Anal. Chem. 1981, 53, 2244.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium perchlorate; NaClO₄; [7775-09-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ramette, R.W.

J. Chem. Educat. 1959, 36, 191-3.

VARIABLES:

Concentrations of HCIO₄ and NaClO₄ Temperature probably 298 K

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

HClO ₄ concn mol dm ⁻³	NaClO ₄ concn mol dm ⁻³	Cu(IO ₃) ₂ soly mol dm ⁻³
0.010	0.990	0.00649
0.300	0.700	0.00872
0.700	0.300	0.0110
1.00	0.000	0.0122

Assuming the only important equilibria to be

$$Cu(IO_3)_2(s) = Cu^{2+} + 2IO_3^{-}$$

$$K_{a0} = [Cu^{2+}][IO_3^{-}]^2$$

$$HIO_3 = H^+ + IO_3^-$$

$$K_3 = [H^+][IO_3^-]/[HIO_3]$$

the author derived the equation for the solubility, S (neglecting activity coefficients)

$$2S^{3/2} = (K_{a0})^{1/2} \{1 + [HClO_4]/K_a\}$$

The data give $K_a = 0.5_2$ mol dm⁻³ and $K_{a0} = 1.0_6 \times 10^{-6}$ mol³ dm⁻⁹ (compilers result using the slope at low HClO₄ concentrations for an ionic strength of 1 mol dm⁻³).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess solid copper iodate and water containing HClO₄ and NaClO₄ were placed into a bottle. A motor driven stirrer was inserted into the bottle, and the system stirred for 2 or 3 days. Excess copper iodate removed by filtration, and 5 cm³ aliquots of saturated solution removed with a pipet. Adding water and HCl, the idoate concentration was determined by titration with 0.02 mol dm⁻³ Na₂S₂O₃ solution using starch as the indicator.

The experimental temperature was not specified, but the compiler assumes it was around 25°C.

SOURCE AND PURITY OF MATERIALS:

Solid copper iodate was prepared as described by Peterson (1,2), although HIO₃ may have been used in place of KIO₃. The purities and sources of other materials are not given.

ESTIMATED ERROR:

Nothing specified.

- (1) Peterson, B.H.; Meyers, E.L. J. Am. Chem. Soc. 1930, 52, 4853.
- (2) Peterson, B.H. J. Chem. Educat. 1957, 34, 612.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium perchlorate; NaClO₄; [7775-09-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Marchall, J.C.; Blanchard, D.P.

At. Absorption Newsletter 1967, 6, 109-11.

VARIABLES:

Concentrations of NaClO₄ and HClO₄ T/K = 298, 308 and 323

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA: Final solubility, S, is the average of three results from the same saturated solution.

t/ºC	HClO ₄ concn mol dm ⁻³	NaClO ₄ concn mol dm ⁻³	values of 10 ³ S mol dm ⁻³	ave 10 ³ S mol dm ⁻³
25	0.010	0.990	6.17, 6.17, 6.15	6.16
	0.300	0.700	8.40, 8.35, 8.35	8.37ª
	0.700	0.300	10.52, 10.59	10.56
	1.000	0.000	12.09, 12.11, 12.05	12.08
35	0.010	0.990	not reported	7.12
	0.300	0.700		9.75
	0.700	0.300		12.69
	1.000	0.000		14.52
50	0.010	0.990		7.95
	0.300	0.700		10.58
	0.700	0.300		13.58
	1.000	0.000		17.10

^aCalculated by compilers: the authors gave an incorrect value for this average.

The authors suggest that the data can be interpreted in terms of solubility equilibria and the acid association constant K_a for HIO₃ according to: $2S^{3/2} = (K_{a0})^{1/2}\{1 + [HCIO_4]/K_a\}$. For 25, 35 and 50°C, respectively, the compilers estimate K_{a0}/mol^3 dm⁻⁹ = 9.0 x 10⁻⁷, 1.38 x 10⁻⁶, and 1.94 x 10⁻⁶ and with respective values for K_a/mol dm⁻³ = 0.49, 0.47 and 0.53.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were equilibrated with stirring in a bath at the desired temperature for a minimum of 24 h. Samples were withdrawn for analyses through a medium porosity frit. The Cu determinations were made with a Perkin Elmer 303 atomic absorption spectrometer with the input stabilized. A multielement lamp (Cu, Mn, Co, Ni and Cr) was used at 324.7 nm. Because of the relative high solubility of Cu(IO₃)₂, further dilutions of the saturated solutions by factors of 3, 4, or 5 to 100 was necessary to bring the absorption into the 60-80 % range, which is the range giving maxium precision. Standards were prepared to closely bracket (within 10 %) the absorption of the sample. Each sample was prepared in triplicate and run in alternate sequence with appropriate standards. Water was run between each solution analysis, and zero checks were made after each reading.

SOURCE AND PURITY OF MATERIALS:

Copper iodate was prepared according to ref. (1) by adding dilute solutions of CuSO₄ and KIO₃ to a large volume of water. Fine particles resulting from this preparation were separated by repeated decantation, and the product was air-dried.

All other reagents were of the best commercial grades available, and were used as received.

ESTIMATED ERROR:

Soly: reproducibility indicated in above table. Temp: nothing specified.

REFERENCES:

(1) Peterson, B.H. J. Chem. Educat. 1957, 34, 612.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Potassium iodate; KIO ₃ ; [7758-05-6] (3) Copper sulfate; CuSO ₄ ; [10124-44-4] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Spencer, J.F. Z. Phys. Chem. 1913, 83, 290-6.
VARIABLES: Concentration of CuSO ₄ or KIO ₃ T/K = 298	PREPARED BY: E.M. Woolley

EXPERIMENTAL DATA: Equilibrium activities of Cu²⁺ and IO₃- were determined by emf measurements on satd Cu(IO₃)₂ solutions containing CuSO₄ or KIO₃, with the following results:

CuSO ₄ concn mol dm-3	KIO ₃ concn mol dm- ³	E ₁ volts	10 ³ a(Cu ²⁺) (eq. [2])	10 ³ a(IO ₃ -) (eq. [3])	10 ⁷ K _{s0} (eq. [4])
1.000	0.0000	0.2480	196.3	0.865	1.47
0.500	0.0000	0.2381	91.1a	1.27	1.47a
0.250	0.0000	0.2361	78.0	1.37	1.46
0.100	0.0000	0.2236	29.6	2.22	1.46
0.050	0.0000	0.2193	21.2	2.63	1.46
0.010	0.0000	0.1976	3.94a	6.09	1.46a
0.000	0.0625	0.1440	0.0619	48.4	1.44
0.000	0.0312	0.1608	0.0228	25.2ª	1.45ª
0.000	0.0156	0.1759	0.735	14.0	1.45
0.000	0.0078	0.1805	0.105	11.8	1.45
0.000	0.0039	0.1936	2.89a	7.10	1.46a
0.000	0.00195	0.1981	4.11	5.95	1.45
0.000	0.0000	0.2065	7.88	4.31	1.46

^{*}Calculated by compiler from eqs. [2]-[4]: the author made an error in computation in eqs. [2] and [3] with these data points.

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Emf measurements were made on the cell

$$Hg,Hg(IO_3)_2 | sln | | KCl(c_1) | Hg_2Cl_2,Hg$$
 [1]

where c₁ = 0.1 mol dm⁻³ and "sln" is the experimental solution. Hg,Hg(IO₃)₂ and "sln" were equilibrated for 3 d with shaking and over which period the potentials were constant to 1.0 mV per day. Activities based on mol dm⁻³ units were calcd from eqs. [2] and [3].

$$E = 0.6060 + 0.0297 log a(Cu2+)$$
 [2]

$$E = 0.4027 - 0.0595 log a(IO3-)$$
 [3]

These were obtained from [1] above where the "sln" was 0.010 to 1.0000 mol dm⁻³ CuSO₄ or KIO₃ (see ref. (1)). Solutions were corrected for ion pairing evaluated from conductivity data.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂·H₂O prepared by adding excess KIO₃ solution to concentrated Cu(NO₃)₂ solution. The crystals were washed and dried in air. Water content was found to be 4.12 % by heating in an air bath to 250°C. Iodate detd by treating an aqueous solution with KI and HCl followed by titrn with Na₂S₂O₃ yielding 81.28 %. Similar analysis of the anhydrous solid yielded 84.74 % iodate. Heating a sample to CuO gave 18.77 % CuO.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

(1) Spencer, J.F. Z. Phys. Chem. 1913, 80, 701.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Potassium iodate; KIO₃; [7758-05-6]
- (3) Copper sulfate; CuSO₄; [10124-44-4]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Spencer, J.F.

Z. Phys. Chem. 1913, 83, 290-6.

EXPERIMENTAL DATA: (continued.....)

The values of the thermodynamic solubility product, K_{s0}, were calculated from

$$log K_{s0} = {a(Cu^{2+})}{a(IO_{3^{-}})}^{2}$$

[4]

and are therefore in units of mol³ dm-⁹. From eqs. [2] and [3] the compiler calculates

$$-log K_{s0} = 2(0.6060 - 0.4027)/0.0595 = 6.834$$

[5]

which gives $K_{s0} = 1.47 \times 10^{-7} \text{ mol}^3 \text{ dm}^{-9}$. The average value of K_{s0} for the data table on the previous page is $1.45_7 \times 10^{-7}$. Using $K_{s0} = 1.46_7 \times 10^{-7}$ and eqs. [6] to [8] below, the compiler calculated the solubility, S, of $Cu(IO_3)_2$ in pure water.

$$K_{s0} = (4S^3)(Y) = 1.467 \times 10^{-7}$$

$$log Y = -6(0.509)I^{1/2}/(1 + I^{1/2})$$

$$I = 3S$$

$$S = 4.2_0 \times 10^{-3} \text{ mol dm}^{-3}$$

[9]

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Potassium hydrogen phthalate; C₈H₅O₄K; [877-24-7] J. Inorg. Nucl. Chem. <u>1970</u>, 32, 3033-9.
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ghosh, R.; Nair, V.S.K.

VARIABLES:

Concentrations of NaOH and C8H5O4K T/K = 298, 303, 308and 318

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL VALUES:

C٤	H ₅ O ₄ K total conen	Cu(IO ₃) ₂ soly	- log K _{d1}	- log K _{d2}	- log K _{s0}
t/ºC	mol dm ⁻³	mol dm ⁻³			
25	0	0.003533			7.048
	0.002462	0.004137	3.11		
	0.004925	0.004187	3.14	0.99	
	0.012362	0.004901	3.16	1.02	
	0.024003	0.005640	3.15	0.99	
	0.024623	0.005645	3.14	0.98	
		a	verages: 3.14 ± 0.03	0.99 ± 0.03	
30	0	0.003764			6.980
	0.001234	0.004151	3.36		
	0.002463	0.004427	3.27	1.13	
	0.004928	0.004603	3.26	1.04	
	0.009948	0.004739	3.26	1.03	
	0.012311	0.005314	3.28	1,11	
		a [,]	verages: 3.28 ± 0.08	1.08 ± 0.05	

Note that in each solution, [NaOH]_{tot} = $\frac{1}{2}$ [C₈H₅O₄K]_{tot}

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1). All slns prepd by dilution of a stock sln, and the pH measured before and after equilibration through the column at least 4 times (twice was sufficient for saturation). The pH of all slns were in the range of 3.7 to 3.8. Slns analyzed for iodate by iodometric titrn in a nitrogen atmos. The thermodynamic solublity product constant was calcd from

$$K_{s0} = [Cu^{2+}][IO_3^-]^2y_1y_2$$

where activity coefficients y₁ and y₂ were calcd from the modified Davies eqn (2). K_d for the CuIO₃- ion pair included in the calculations. Kd(NaIO3) assumed to be 3.0 mol dm-3 at 298 K, and values at higher temperatures were estimated.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepared by dropwise addition of KIO₃ and CuCl₂ solutions into a large volume of dist water at 65°C with stirring for 2 h. The ppt was washed 6 times and digested in double dist water for 4 h at 80°C. AnalaR chemicals were used wherever possible. Sodium potassium phthalate solutions prepd with CO₂free NaOH solution so as to obtain a 1:1 buffer ratio. Conductivity water was prepared by mixed bed deionization.

ESTIMATED ERROR:

Soly: nothing specified. Average errors in K_d values given in data tables.

Temp: precision ± 0.1 K.

- (1) Davies, C.W. J. Chem. Soc. 1930, 2471.
- (2) Davies, C.W. Ion Association. Butterworths, London, 1960.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Potassium hydrogen phthalate; C₈H₅O₄K; [877-24-7] J. Inorg. Nucl. Chem. <u>1970</u>, 32, 3025-32.
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ghosh, R.; Nair, V.S.K.

EXPERIMENTAL	WATTIEC.	(continued)

C ₈	H ₅ O ₄ K total concu	Cu(IO ₃) ₂ soly	- log K _{d1}	- log K _{d2}	- log K _{s0}
t/ºC	mol dm-3	mol dm-3			
35	0	0.003956			6.929
	0.001806	0.004176	3.55		•
	0.004925	0.004642	3.50	1.12	
	0.009948	0.005067	3.51	1.12	
	0.019698	0.005800	3.49	1.12	
	0.020742	0.005807	3.49	1.12	
		avers	ages: 3.50 ± 0.01	1.12	
40	0	0.004101			6.888
	0.002462	0.004491	3.81	*	
	0.004925	0.004744	3.86	1.36	
	0.009947	0.005283	3.70	1.31	
	0.012301	0.005452	3.84	1.37	
	0.042352	0.006686	3.80	1.33	
	0.049246	0.008825	3.75	1.34	
		avera	ages: 3.79 ± 0.07	1.34 ± 0.03	
45	0	0.005484			6.536
	0.002802	0.005787	4.12		
	0.005604	0.006002	4.10	1.48	
	0.016812	0.006912	4.12	1.50	
	0.024623	0.007690	4.12	1.49	
	0.028020	0.008034	4.12	1.48	
	0.049246	0.009751	4.12	1,49	
		aver	ages: 4.12 ± 0.02	1.49 ± 0.01	

K_{d1} and K_{d2} calculated from eqs. [1] and [2] using using activity coefficients calculated from a modified Davies equation (2). The thermodynamic equilibrium constants are defined as follows:

$$K_{d1} = [Cu^{2+}]y_1[C_8H_4O_4^{2-}]y_2/[Cu(C_8H_4O_4))^+]$$
 [1]

$$K_{d2} = [Cu^{2+}]y_1[C_8H_5O_4^-]y_2/[Cu(C_8H_5O_4)^+]y_2$$
 [2]

The authors fitted the K_d values to the smoothing equation $\log K_d = a + b(T/K) + c(T/K)^2$ and derived the following thermodynamic parameters for 298 K (based on mol dm-3 units).

reaction	∆G/kcal mol-1	∆H/kcal mol-1	ΔS/cal K-1 mol-1
[1]	4.28 ± 0.04	-9.49 ± 0.09	-46.2 ± 1.0
[2]	1.36 ± 0.054	-5.53 ± 0.06	-23.1 ± 0.8

From a plot of $log K_{s0}$ vs 1/(T/K), the compilers obtain (for 298 K) $\Delta H = 4.5$ kcal mol-1 and $\Delta S = -17$ cal K-1 mol-1.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Methanoic acid (formic acid); CH₂O₂; [64-18-6]
- (4) Water; H₂O; [7732-18-5]

0.04343

ORIGINAL MEASUREMENTS:

Lloyd, M.; Wycherley, V.; Monk, C.B.

J. Chem. Soc. 1951, 1786-9.

VARIABLES:

Concentrations of NaOH and formic acid

T/K = 298

PREPARED BY:

H. Miyamoto

0.00521

EXPERIMENTAL DATA: formic acid concn mol dm-3	NaOH conen mol dm-3	solubility mol dm-3	pН	102K _d a
0.0	0.0	0.00333		
0.03040	0.01237	0.00416	3.7	1.04
0.03462	0.02442	0.00484	4.0	1.06

*Kd for the copper-acid complex reaction

$$Cu(CHO_2)^+ = Cu^{2+} + CHO_2^-$$
:

$$K_d = [Cu^{2+}][CHO_2^-]/[Cu(CHO_2)^+]$$

calculated using estimated activity coefficients from the following equationb:

0.03165

$$log y_z = -(z^2/2)[AI^{1/2}/(1 + I^{1/2}) - 0.2AI]$$

In these calculations, the authors assumed that the ion pairing dissociation constants for both CuIO₃- and NaIO₃ were equal to 0.15.

aIn the original paper, the Debye-Huckel constant A was omitted from this equation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1) and modified in (2). A bulb containing the solvent solution was attached to a column containing Cu(IO₃)₂, and the solution allowed to flow through the column at a rate sufficient to insure saturation (1). The modification (2) was to connect the column to a second parallel arm in which the saturated solution was collected. The entire apparatus was thermostated. A portion of the saturated solution was run through the saturating column a second time. The iodate concentrations of the saturated solutions were determined volumetrically by using Na₂S₂O₃ solution previously standardized with KiO₃. Th pH was measured with a glass electrode.

SOURCE AND PURITY OF MATERIALS:

4.1

1.06

Cu(IO₃)₂ crystals were prepared by allowing concentrated solutions of CuSO₄ and KIO₃ to drip slowly into nearly boiling water. The product was ground and the "fines" washed out.

The formic acid used was of AnalaR or Kahlbaum quality.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.03 K.

- (1) Bronsted, N.J.; La Mer, V.K. J. Am. Chem. Soc. 1924, 46, 555.
- (2) Money, R.W.; Davies, C.W. J. Chem. Soc. <u>1934</u>, 400.

COMPONENTS:		ORIGINAL MEAS	SUREMENTS:		
(1) Copper iodate; Cu(IO ₃) ₂ ; (2) Sodium hydroxide; NaOH	I; [1310-73-2]	Lloyd, M.; Wyche	erley, V.; Mon	k, C.B.	
(3) Ethanoic acid (acetic acid(4) Water; H₂O; [7732-18-5]	i); C ₂ H ₄ O ₂ ; [64-19-7]	J. Chem. Soc. 19	<u>51</u> , 1786-9.		
VARIABLES: Concentrations of NaOH and	1 acetic acid	PREPARED BY:			
T/K = 298	a acotto acia	H. Miyamoto			
		ŀ			
EXPERIMENTAL DATA:			- MANA		
EXPERIMENTAL DATA: acetic acid concn	NaOH concn	solubility	1999		
	NaOH concn mol dm-3	solubility mol dm ⁻³	pН	103K _d s	··········
acetic acid concn		•	pH 	10 ³ K _d *	
acetic acid concn mol dm-3	mol dm-3	mol dm ⁻³	pH 4.5	10 ⁸ K _d ^a	
acetic acid concn mol dm-3	mol dm ⁻³	mol dm ⁻³			

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors on the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; (2) Sodium hydroxide; NaOH (3) Propanoic acid (propionic (4) Water; H ₂ O; [7732-18-5]	[1310-73-2]	ORIGINAL MEAS Lloyd, M.; Wyche J. Chem. Soc. 19	erley, V.; Mon	k, C.B.	
VARIABLES: Concentrations of NaOH and T/K = 298	propanoic acid	PREPARED BY: H. Miyamoto			
propanoic acid conen mol dm ⁻³	NaOH concn mol dm ⁻³	solubility mol dm-3	pН	10 ³ K _d a	
0.0	0.0	0.00333			
0.02700	0.01363	0.00461	4.8	5.9	
0.08385	0.02727	0.00552	4.5	6.1	
0.1288	0.02998	0.00571	4.2	5.9	

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors on the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Hydroxyethanoic acid (hydroxyacetic acid; glycolic J. Inorg. Nucl. Chem. 1975, 37, 991-3. acid); C₂H₄O₃; [79-14-1]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Das, A.R.; Nair, V.S.K.

VARIABLES:

Concentrations of NaOH and C2H4O3 T/K = 298, 303, 308, 313and 318

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL VALUES:

AI EKIMI	MIAL VALUES.		
	C ₂ H ₄ O ₃ total concn	Cu(IO ₃) ₂ solubility	- log K _d
t/ºC	mol dm-3	mol dm-3	
25	0.008871	0.005931	3.08
	0.010390	0.006368	3.11
	0.011825	0.006573	3.08
	0.014785	0.007322	3.11
	0.017741	0.008018	3.13
	0.021025	0.008587	3.11
	0.027175	0.009457	3.11
			average: 3.10 ± 0.05
30	0.004115	0.004988	3.16
	0.007983	0.006181	3.17
	0.019950	0.008827	3.14
	0.023948	0.009673	3.16
	0.027940	0.010407	3.17
	0.031930	0.011052	3.18
			average: 3.16 ± 0.03

Note that in each solution, $[NaOH]_{tot} = 1/2[C_2H_4O_3]_{tot}$

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1). All slns prepd by dilution of a stock sln, and the pH measured before and after equilibration through the column at least 4 times (twice was sufficient for saturation). The pH of all slns were in the range of 3.6 to 3.8, and the pK_a of $C_2H_4O_3$ at 298 K = 3.80.

Sins analyzed for iodate by iodometric titrn in a nitrogen atmos. The thermodynamic solublity product constant was calcd from

$K_{*0} = [Cu^{2+}][IO_3^-]^2y_1y_2$

where activity coefficients y₁ and y₂ were calcd from the modified Davies eqn (2). Kd for the CuIOs- ion pair included in the calculations, and $K_d(NaIO_3)$ assumed to be constant at 3.0 mol dm-3 at 298 K.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepd as in (3). AnalaR chemicals used whenever possible. Sodium glycollate slns prepd from vacuum dried, recrystd, sublimed acid and CO₂-free water so as to obtain a 1:1 buffer ratio (details in (3)).

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision \pm 0.1 K (see ref. (3)).

- (1) Davies, C.W. J. Chem. Soc. 1930, 2471.
- (2) Davies, C.W. Ion Association. Butterworths, London, 1960.
- (3) Ghosh, R.; Nair, V.S.K. J. Inorg. Nucl. Chem. 1970, 32, 3025.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Hydroxyethanoic acid (hydroxyacetic acid; glycolic acid); C₂H₄O₃; [79-14-1]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Das, A.R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1975, 37, 991-3

	C ₂ H ₄ O ₃ total conen	Cu(IO ₃) ₂ solubility	- log K _d
t/ºC	mol dm-3	mol dm-3	
35	0.007983	0.006552	3.24
	0.011800	0.007558	3.20
	0.011974	0.007674	3.22
	0.014801	0.008421	3.22
	0.024900	0.010456	3.20
	0.029050	0.011237	3.21
	0.033200	0.012120	3.24
			average: 3.22 ± 0.02
40	0.004306	0.005578	3.35
	0.020810	0.010488	3.31
	0.024952	0.011368	3.31
	0.029095	0.012287	3.31
	0.033245	0.013296	3.33
			average: 3.32 ± 0.03
45	0.004300	0.006137	3.37
	0.010500	0.008540	3.37
	0.020550	0.011850	3.39
	0.024810	0.012750	3.36
	0.029050	0.013730	3.36
	0.033070	0.014650	3.36
			average: $3.37 + 0.02$

average: 3.37 ± 0.02

Values of K_d were calculated from eq. [1] below, and activity coefficients were calculated from the modified Davies equation (2).

$$K_d = [Cu^{2+}]y_2[C_2H_3O_3^-]y_1/[Cu(C_2H_3O_3)^+]y_1$$
 [1]

The authors state that plots of $log K_d$ vs 1/T(K) are linear, and from these plots they calculate the following thermodynamic quantities for ion association at 298 K:

ΔG/kcal mol⁻¹ ΔH/kcal mol⁻¹ ΔS/cal K⁻¹ mol⁻¹ 17.69 ± 0.03 -24.52 ± 0.04 -141.59 ± 0.08

For the thermodynamic solubility product, the authors give the following values:

t/ºC	25	30	35	40	45
- log K-0	7.05	6.98	6.93	6.89	6.75

From the above K_{s0} data, the compilers estimate (for 298 K) that $\Delta H = 6.0$ kcal mol⁻¹ and $\Delta S = -12$ cal K⁻¹ mol⁻¹. However, using the K_{s0} data for the first four temperatures which are <u>identical</u> to those given in ref. (3), the compilers estimate that $\Delta = 4.5$ kcal mol⁻¹ and $\Delta S = -17$ cal K⁻¹ mol⁻¹ at 298 K (see the compilation for ref. (3)).

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) DL-Hydroxysuccinic acid (DL-malic acid); C₄H₆O₅;[6915-15-7]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Das, A.R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1975, 37, 2121-3.

VARIABLES:

Concentrations of NaOH and C₄H₆O₅

T/K = 298, 303, and 318

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL VALUES:

С	4H6O5 total concn	Cu(IO ₃) ₂ soly	- log K _{d1}	- log Kd2	- log Ks0
t/ºC	mol dm-3	mol dm-3			
25	0	0.003533			7.048
	0.03107	0.010699	4.49		
	0.03604	0.011590	4.52		
	0.04101	0.012420	4.43	2.41	
	0.04605	0.013264	4.54	2.45	
	0.05095	0.013855	4.55	2.45	
	0.05593	0.014663	4.56	2.46	
		av	erages: 4.53 ± 0.03	2.44 ± 0.02	
30	0	0.003764			6.929a
	0.03356	0.012376	4.61		
	0.04113	0.013683	4.64		
	0.04871	0.015078	4.65	2.50	
	0.05908	0.016167	4.65	2.49	
	0.06714	0.017129	4.65	2.51	
		av	erages: 4.64 ± 0.02	2.50 ± 0.03	

Note that in each solution, $[NaOH]_{tot} = 1/2[C_4H_6O_5]_{tot}$

continued......

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1). All slns prepd by dilution of a stock sln, and the pH measured before and after equilibration through the column at least 4 times (twice was sufficient for saturation).

Sins analyzed for iodate by iodometric titrn in a nitrogen atmos. The thermodynamic solublity product constant was calcd from

$$K_{s0} = [Cu^{2+}][IO_3^-]^2y_1y_2$$

where activity coefficients y_1 and y_2 were calcd from the modified Davies eqn (2). K_d for the CuIO₃- ion pair included in the calculations, and $K_d(NaIO_3)$ assumed to be constant at 3.0 mol dm⁻³ at 298 K.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepd as in (3). AnalaR chemicals used whenever possible. Sodium malate slns prepd from vacuum dried and recrystd acid, and CO₂-free water so as to obtain a 1:1 buffer ratio (details in (3)).

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision \pm 0.1 K (see ref. (3)).

- (1) Davies, C.W. J. Chem. Soc. 1930, 2471.
- (2) Davies, C.W. Ion Association. Butterworths, London, 1960.
- (3) Ghosh, R.; Nair, V.S.K. J. Inorg. Nucl. Chem. 1970, 32, 3025.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) DL-Hydroxysuccinic acid (DL-malic acid); C₄H₆O₅; [6915-15-7]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Das, A.R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1975, 37, 2121-3.

EXPERIMENTAL VALUES:

С	4H6O5 total concn	Cu(IO ₃) ₂ soly	- log K _{d1}	- log Kd2	- log K _{s0}
t/ºC	mol dm-3	mol dm-3			
45	0	0.004633			6.754a
	0.02599	0.015470	5.01b		•
	0.03355	0.017732	5.02	~ ~ ~ ~	
	0.04113	0.020114	5.04	2.85	
	0.04871	0.021869	5.05	2.83	
	0.05629	0.023543	5.05	2.83	
		ave	rages: 4.53 ± 0.03	2.44 ± 0.02	

^{*}These values differ from the more accurate values reported earlier (e.g. see the compilation of ref. (3) in this volume).

 K_{d1} and K_{d2} calculated from eqs. [1] and [2] using using activity coefficients calculated from a modified Davies equation (2). The thermodynamic equilibrium constants are defined as follows:

$$K_{d1} = [Cu^{2+}]y_2[C_4H_5O_5^-]y_1/[Cu(C_4H_5O_5^+)]y_1$$
 [1]

$$K_{d2} = [Cu^{2+}]y_2[C_4H_4O_5^{2-}]y_1/[Cu(C_4H_4O_5)]$$
 [2]

The authors state that plots of $log K_d$ are not linear, and the thermodynamic quantities were therefore calculated from the smoothing equation

$$ln K_d = a + b(T/K) + c(T/K)^2$$
 [3]

From the smoothing equations, the following results were obtained.

reaction	∆G/k¢al mol-1	∆H/kcal mol-1	ΔS/cal K-1 mol-1
[1]	13.93 ± 0.08	-36.98 ± 0.02	-170.71 ± 0.3
[2]	25.89 ± 0.06	-45.93 ± 0.01	-240.89 ± 0.5

From a plot of $log K_{s0}$ vs 1/T, the compilers obtain (for 298 K) $\Delta H = 6$ kcal mol-1 and $\Delta S = -12$ cal K-1 mol-1. These results differ from those previously calculated by the compilers from the data reported in earlier studies (e.g. see the compilations of ref. (3) in this volume).

bIn the original article, a value of 6.01 was given which is apparently a typographical error.

0.1230

40	Coppe	er (II) logate		
COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ (2) Sodium hydroxide; NaOH (3) Trimethylacetic acid (piv [75-98-9] (4) Water; H ₂ O; [7732-18-5]	I; [1310-73-2]	ORIGINAL MEAS Lloyd, M.; Wych J. Chem. Soc. 19	erley, V.; Mor	
VARIABLES: Concentrations of NaOH and T/K = 298	1 pivalic acid	PREPARED BY: H. Miyamoto	- energy	
EXPERIMENTAL DATA:				
pivalic acid concn mol dm ⁻³	NaOH concn mol dm-3	solubility mol dm-3	pН	10 ³ K _d a
0.0	0.0	0.00333		
0.04802	0.01006	0.00425	4.3	6.7
0.09603	0.02012	0.00498	4.3	6.6

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

0.00536

0.02580

4.3

6.3

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; (2) Sodium hydroxide; NaOH (3) Phenylethanoic acid (phenylethanoic acid (phenylethanoic)	; [1310-73-2]	ORIGINAL MEAS Lloyd, M.; Wych J. Chem. Soc. 19	erley, V.; Mor		
(4) Water; H ₂ O; [7732-18-5]					
VARIABLES: Concentrations of NaOH and T/K = 298	phenylacetic acid	PREPARED BY: H. Miyamoto	<u> </u>		
EXPERIMENTAL DATA:			-		
phenylacetic acid concn mol dm ⁻³	NaOH concn mol dm ⁻³	solubility mol dm-3	pН	$10^2 \mathrm{K_{d^8}}$	
0.0	0.0	0.00333			
0.02350	0.01039	0.00407	4.2	1.08	
0.02937	0.01290	0.00423	4.1	1.05	
0.04406	0.01948	0.00460	4.2	1.05	

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

; [13454-89-2] I; [1310-73-2] (iso-butyric acid); C ₄ H ₈ O ₂ ;		erley, V.; Mor	
l iso-butyric acid	PREPARED BY: H. Miyamoto		
	1 	··········	
NaOH concn mol dm-3	solubility mol dm ⁻³	pН	10 ³ K _d a
0.0	0.00333		
0.01113	0.00436	4.4	6.4
0.01899	0.00486	4.3	6.9
0.02890	0.00548	4.3	6.7
(I; [1310-73-2] (iso-butyric acid); C ₄ H ₈ O ₂ ; I iso-butyric acid NaOH concn mol dm ⁻³ 0.0 0.01113 0.01899	Lloyd, M.; Wyche Lloyd, M.; Wyche I; [1310-73-2] J. Chem. Soc. 19 J. Chem. So	Lloyd, M.; Wycherley, V.; More I; [1310-73-2] Lloyd, M.; Wycherley, V.; More I; [1310-73-2] J. Chem. Soc. 1951, 1786-9. Iso-butyric acid PREPARED BY: H. Miyamoto

COMPONENTS:		ORIGINAL MEAS	SUREMENTS:	
(1) Copper iodate; Cu(IO ₃);	; [13454-89-2]	Lloyd, M.; Wych	erley, V.; Mon	ık, C.B.
(2) Sodium hydroxide; NaC	H; [1310-73-2]			
(3) Pentanoic acid (n-valer	c acid); C ₅ H ₁₀ O ₂ ;	J. Chem. Soc. <u>19</u>	<u>51</u> , 1786-9.	
[109-52-4]				
(4) Water; H ₂ O; [7732-18-5]			
VARIABLES:		PREPARED BY:		
Concentrations of NaOH as	nd n-valeric acid	77 36		
T/K = 298		H. Miyamoto		
EXPERIMENTAL DATA:				
EXPERIMENTAL DATA:	NaOH concn	solubility		
	NaOH concn mol dm ⁻³	solubility mol dm-3	рН	103K ^d s
n-valeric acid concn		•	pH 	10 ³ K _d a
n-valeric acid concn mol dm ⁻³	mol dm ⁻³	mol dm ⁻³	pH 4.0	10 ⁸ K _d ^a 7.6
n-valeric acid concn mol dm ⁻³	mol dm ⁻³	mol dm ⁻³		

a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the $Cu(IO_3)_2$ -NaOH-CH $_2O_2$ -H $_2O$ system. ^bThis data point appears to be in error (compiler).

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Hexanoic acid (caproic acid); C ₆ H ₁₂ O ₂ ; [142-62-1] (4) Water; H ₂ O; [7732-18-5] VARIABLES: Concentrations of NaOH and caproic acid T/K = 298		ORIGINAL MEAS Lloyd, M.; Wycho J. Chem. Soc. 19	erley, V.; Mon	k, C.B.	
		PREPARED BY: H. Miyamoto			
EXPERIMENTAL DATA:					
EXPERIMENTAL DATA: caproic acid concn mol dm-3	NaOH concn mol dm ⁻³	solubility mol dm-3	pН	103K _d a	
caproic acid concn		•	pH	103K _d a	
caproic acid concn mol dm ⁻³	mol dm-3	mol dm-3	pH 4.5	10 ³ K _d a 8.7	

a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

 (1) Copper iodate; Cu(IO₃)₂; [13454-89-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Hydroxyethanoic acid (glycolic acid); C₂H₄O₃; [79-14-1] (4) Water; H₂O; [7732-18-5] 		J. Chem. Soc. 19	• • •	ık, C.B.	
VARIABLES: Concentrations of NaOH an T/K = 298	d glycolic acid	PREPARED BY: H. Miyamoto			
EXPERIMENTAL DATA:					
glycolic acid concn mol dm ⁻³	NaOH conen mol dm-3	solubility mol dm- ³	pН	10 ³ K _d a	
0.0	0.0	0.00333			
0.01367	0.01311	0.00596	4.4	1.3	
0.01823	0.01719	0.00665	4.6	1.3	
0.02278	0.02216	0.00755	4.6	1.1	

a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION,

see the compilation of the paper by these authors for the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

ORIGINAL MEASUREMENTS:

COMPONENTS:		ORIGINAL MEAS	ORIGINAL MEASUREMENTS:		
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]		Lloyd, M.; Wyche	Lloyd, M.; Wycherley, V.; Monk, C.B.		
(2) Sodium hydroxide; NaOH; [1310-73-2]					
(3) <i>DL</i> -2-Hydroxypropanoic a	icid (DL-lactic acid);	J. Chem. Soc. 19	<u>51</u> , 1786-9.		
C ₃ H ₆ O ₃ ; [598-82-3]					
(4) Water; H ₂ O; [7732-18-5]					
VARIABLES:	nr 1	PREPARED BY:			
Concentrations of NaOH and T/K = 298	DL-lactic acid	H. Miyamoto			
-, 2,0		,			
EXPERIMENTAL DATA:					
DL-lactic acid concn	NaOH concn	solubility		•	
mol dm-\$	mol dm-3	mol dm-3	pН	$10^3 \mathrm{K_{d}^a}$	
0.0	0.0	0.00333			
0.00717	0.00624	0.00475	4.4	1.3	
0.01090	0.00949	0.00542	4.3	1.2	
0.01433	0.01356	0.00636	5.0	1.0	
a For complete descriptions of	computation of equilil	orium constants and fo	r all AUXILIA	ARY INFORMATION,	

see the compilation of the paper by these authors for the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Chloroethanoic acid (chloroacetic acid); C ₂ H ₃ ClO ₂ ; [79-11-8] (4) Water; H ₂ O; [7732-18-5] VARIABLES: Concentrations of NaOH and chloroacetic acid T/K = 298		ORIGINAL MEASUREMENTS: Lloyd, M.; Wycherley, V.; Monk, C.B. J. Chem. Soc. 1951, 1786-9. PREPARED BY: H. Miyamoto			
					
EXPERIMENTAL DATA:					
chloroacetic acid concn mol dm ⁻³	NaOH concn mol dm ⁻³	solubility mol dm ⁻³	рН	$10^2 \mathrm{K_{d^a}}$	
0.0	0.0	0.00333			
0.03977	0.03767	0.00475	4.0	2.64	
0.07008	0.06711	0.00551	4.0	2.40	
0.08872	0.08728	0.00604	4.0	2.25	

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the $Cu(IO_3)_2$ -NaOH- CH_2O_2 - H_2O system.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Lloyd, M.; Wycherley, V.; Monk, C.B.
(2) Sodium hydroxide; NaOH; [1310-73-2]	
(3) Trichloroethanoic acid (trichloracetic acid);	J. Chem. Soc. 1951, 1786-9.
C ₂ HCl ₃ O ₂ ; [76-03-9]	
(4) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concns of NaOH and trichloroacetic acid T/K = 298	H. Miyamoto
EXPEDIMENTAL DATA	ri. Wilyamoto

NaOH concn mol dm ⁻³	solubility mol dm ⁻³	pН	$10^2 \mathrm{K_{d^a}}$
0.0	0.00333		
0.01266	0.00394	3.7	2.41
0.02577	0.00442	3.9	2.34
0.02954	0.00445	4.2	2.81
	mol dm- ³ 0.0 0.01266 0.02577	mol dm-3 mol dm-3 0.0 0.00333 0.01266 0.00394 0.02577 0.00442	mol dm-3 mol dm-3 pH 0.0 0.00333 0.01266 0.00394 3.7 0.02577 0.00442 3.9

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the Cu(IO₃)₂-NaOH-CH₂O₂-H₂O system.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Bromoethanoic acid (bromoacetic acid); C ₂ H ₃ BrO ₂ ; [79-08-3] (4) Water; H ₂ O; [7732-18-5]		ORIGINAL MEAS Lloyd, M.; Wych J. Chem. Soc. 19	erley, V.; Mor		
VARIABLES: Concentrations of NaOH and T/K = 298	bromoacetic acid	PREPARED BY: H. Miyamoto			
EXPERIMENTAL DATA:					
bromoacetic acid concn mol dm-3	NaOH concn mol dm-3	solubility mol dm ⁻³	pН	102K _d a	
0.0	0.0	0.00333			
0.05475	0.05201	0.00507	4.5	2.85	
0.06958	0.06692	0.00553	4.1	2.45	
0.08974	0.08728	0.00599	4.6	2.35	

a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION,

see the compilation of the paper by these authors for the $Cu(IO_3)_2$ -NaOH-CH₂O₂-H₂O system.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) 2-Bromobutanoic acid (α-bromobutyric acid); C ₄ H ₇ BrO ₂ ; [80-58-0] (4) Water; H ₂ O; [7732-18-5]		ORIGINAL MEAS Lloyd, M.; Wyche		k, C.B.
		J. Chem. Soc. 1951, 1786-9.		
VARIABLES:		PREPARED BY:		
Concus of NaOH and α-bron T/K = 298	nobutyric acid	H. Miyamoto		
EXPERIMENTAL DATA:	***************************************			
C ₄ H ₇ BrO ₂ concn	NaOH concn	solubility		
mol dm-3	mol dm-3	mol dm-8	pН	102Kd2
	0.0	0.00333		
0.0	0.01266	0.00394	3.7	2.41
0.0 0.01358	0.01200			
	0.02577	0.00442	3.9	2.34

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ (2) Sodium hydroxide; NaO (3) 3-Iodopropanoic acid (β C ₃ H ₅ IO ₂ ; [141-76-4] (4) Water; H ₂ O; [7732-18-5	H; [1310-73-2] -iodopropionic acid);	ORIGINAL MEASUREMENTS: Lloyd, M.; Wycherley, V.; Monk, C.B. J. Chem. Soc. 1951, 1786-9.		
VARIABLES: Concentrations of NaOH an T/K = 298	d C ₃ H ₅ IO ₂	PREPARED BY: H. Miyamoto		
EXPERIMENTAL DATA:				
C ₃ H ₅ IO ₂ concn mol dm ⁻³	NaOH concn mol dm ⁻³	solubility mol dm-3	pН	102Kd2
0.0	0.0	0.00333		
0.05320	0.02988	0.00495	4.2	1.23
0.06385	0.03737	0.00527	4.1	1.22
0.08512	0.04782	0.00566	4.2	1.20

^a For complete descriptions of computation of equilibrium constants and for all AUXILIARY INFORMATION, see the compilation of the paper by these authors for the $Cu(IO_3)_2$ -NaOH- CH_2O_2 - H_2O system.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	ORIGINAL MEASUREMENTS: Keefer, R.M.
(2) Glycine; C ₂ H ₈ NO ₂ ; [56-40-6] (3) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. <u>1948</u> , 70, 476-9.
VARIABLES: Concentration of H ₂ NCH ₂ CO ₂ H T/K = 298	PREPARED BY: H. Miyamoto

The solubility of Cu(IO₃)₂ in aqueous glycine solutions at 25°C was given as:

$[C_2H_5NO_2]$	solubility	
mol kg-1	mol kg-1	pHa
0.0	0.003245	
0.01253	0.004096	3.32
0.02509	0.004805	3.31
0.05023	0.00617	3.32 (3.35)
0.07542	0.00746	3.37
0.1008	0.00872	3.38
0.1515	0.01116	3.39
0.2025	0.01352	3.41

aValues in parenthesis stated to be "Cor. pH" which was not defined. Using the extended Debye-Huckel activity coefficient equation as in (1), the solubility-pH data were interpreted in terms of the following complex equilibria.

$$C_2H_5NO_2 + Cu^{2+} = Cu(C_2H_4NO_2)^+ + H^+$$
 $K_1 = 0.032$ $2C_2H_5NO_2 + Cu^{2+} = Cu(C_2H_4NO_2)_2 + 2H^+$ $K_2 = 2.8 \times 10^{-4}$

 $C_2H_5NO_2 + Cu^{2+} = Cu(C_2H_5NO_2)^{2+}$

$K_3 = 39 \text{ kg mol}^{-1}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method as in (1). Glycine solutions prepared from distilled water using calibrated volumetric apparatus. Excess air-dried copper iodate placed in glass-stopperd Pyrex flasks and the glycine solutions added. The flasks were placed in a thermostat at 25°C and rotated for at least 12 h. By applying pressure, samples of saturated solution were removed with a pipet fitted with an asbestos filter. Solubilities were determined by iodometric titration modified for the presence of Cu²⁺ using the method of Foote and Vance (2).

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepared by adding equal volumes of 0.2 mol kg⁻¹ KIO₃ and 0.1 mol kg⁻¹ CuSO₄ solutions to a large volume of water at 60°C. The ppt was filtered and stored under water overnight. The product was sedimented several times and the smaller particles were discarded. After drying for 2 h at 250-270°C, the dried copper iodate was analyzed iodometrically and the purity was found to equal 100.1 %.

ESTIMATED ERROR:

Soly: duplicates agreed to ± 0.2 %. Temp: precision ± 0.02 K.

- (1) Keefer, R.M.; Reiber, H.G.; Bisson, C.S. J. Am. Chem. Soc. <u>1940</u>, 62, 2951.
- (2) Foote, H.W.; Vance, J.E. Ind. Eng. Chem. Anal. Ed. 1936, 8, 119.

(1) Copper iodate; Cu(IO₃)₂; [13454-89-2]

(2) DL-Alanine; C₃H₇NO₂; [302-72-7]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R.M.

J. Am. Chem. Soc. 1948, 70, 476-9.

VARIABLES:

Concentration of CH₃CH(NH₂)CO₂H

T/K = 298

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

The solubility of Cu(IO₃)₂ in aqueous alanine solutions at 25°C was given as:

$[C_3H_7NO_2]$	solubility	
mol kg-1	mol kg-1	pHa
0.0	0.003245	
0.01252	0.00398	3.40
0.02508	0.00460	3.37
0.05019	0.00584	3.40 (3.405)
0.07541	0.00698	3.42 (3.43)
0.1008	0.00806	3.44
0.1516	0.01022	3.48 (3.47)
0.2027	0.01230	3.49

*Values in parentheses are "Cor. pH" values, but the term Cor. pH was not defined. Using the extended Debye-Huckel equation to compute activity coefficients, the author interpreted the solubility data in terms of the following complex equilibria.

$$C_3H_7NO_2 + Cu^{2+} = Cu(C_3H_6NO_2)^+ + H^+$$

 $K_1 \approx 0.034$

 $2C_3H_7NO_2 + Cu^{2+} = Cu(C_3H_6NO_2)_2 + 2H^+$

 $K_2 = 1.0_7 \times 10^{-4}$

 $C_3H_7NO_2 + Cu^{2+} = Cu(C_3H_7NO_2)^{2+}$

 $K_3 = 29 \text{ kg mol}^{-1}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method as in (1). Alanine solutions prepared from distilled water using calibrated volumetric apparatus. Excess air-dried copper iodate placed in glass-stopperd Pyrex flasks and the alanine solutions added. The flasks were placed in a thermostat at 25°C and rotated for at least 12 h. By applying pressure, samples of saturated solution were removed with a pipet fitted with an asbestos filter. Solubilities were determined by iodometric titration modified for the presence of Cu²⁺ using the method of Foote and Vance (2).

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepared by adding equal volumes of 0.2 mol kg⁻¹ KIO₃ and 0.1 mol kg⁻¹ CuSO₄ solutions to a large volume of water at 60°C. The ppt was filtered and stored under water overnight. The product was sedimented several times and the smaller particles were discarded. After drying for 2 h at 250-270°C, the dried copper iodate was analyzed iodometrically and the purity was found to equal 100.1 %.

ESTIMATED ERROR:

Soly: duplicates agreed to ± 0.2 %. Temp: precision ± 0.02 K.

- (1) Keefer, R.M.; Reiber, H.G.; Bisson, C.S. J. Am. Chem. Soc. <u>1940</u>, 62, 2951.
- (2) Foote, H.W.; Vance, J.E. Ind. Eng. Chem. Anal. Ed. 1936, 8, 119.

COMPONENTS: (1) Copper iodate; Cu(IO₃)₂; [13454-89-2] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Glycine; C₂H₅NO₂; [56-40-6] (4) Water; H₂O; [7732-18-5] VARIABLES: Concns of HCl and glycine T/K = 298 ORIGINAL MEASUREMENTS: Monk, C.B. Trans. Faraday Soc. 1951, 47, 285-91.

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous HCl-glycine solutions at 25°C.

HCl concn mol dm ⁻³	glycine concn mol dm ⁻³	solubility mol dm ⁻³	pН	109K _d a mol dm-3
0.0	0.0	0.00333		
0.00122	0.01971	0.00434	3.125	2.20
0.00081	0.01971	0.00439	3.20	2.20
0.0	0.01971	0.00450	3.29	2.44

^aThe dissociation constant for CuC₂H₄NO₂+ calculated using literature values for the dissociation constants of HIO₃, CuCl+, CuIO₃+, and for acid/base dissociation constants for C₂H₅NO₂. Details on these calculations as well as for all AUXILIARY INFORMATION are given in the compilation for the Cu(IO₃)₂-KCl-H₂O system by this author as well as in other compilations based on this author's publications.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium Hydroxide; NaOH; [1310-73-2] (3) Glycine; C ₂ H ₅ NO ₂ ; [56-40-6] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Monk, C.B. Trans. Faraday Soc. 1951, 47, 285-91.
VARIABLES: Concns of NaOH and glycine T/K = 298	PREPARED BY: H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous NaOH-glycine solutions at 25°C.

NaOH concn mol dm-3	glycine concn mol dm ⁻³	solubility mol dm-3	pН	109K _{d1} a mol dm-3	10 ⁷ K _{d2} a mol ² dm ⁻⁶
0.0	0.01971	0.00450	3.29	2.44	
0.00659	0.01288	0.00676	4.33	2.53	1.16
0.00701	0.01209	0.00694	4.45	2.51	1.04
0.00783	0.01226	0.00739	4.585	2.56	1.06
0.00879	0.01288	0.00792	4.685	2.52	1.02

 $^{a}K_{d1}$ for the dissociation of $CuC_{2}H_{4}NO_{2}^{-}$, to $Cu^{2}+$ and $C_{2}H_{4}NO_{2}^{-}$, and K_{d2} for the dissociation of $Cu(C_{2}H_{4}NO_{2})_{2}$ to $Cu^{2}+$ and $2C_{2}H_{4}NO_{2}^{-}$. All other equilibrium constants taken from the literature. For details on these calculations and for other AUXILIARY INFORMATION, see previous compilations of this author's publications.

COMPONENTS: (1) Copper iodate; Cu(IO₃)₂; [13454-89-2] (2) Hydrogen chloride; HCl; [7647-01-0] (3) DL-Alanine; C₃H₇NO₂; [302-72-7] (4) Water; H₂O; [7732-18-5] VARIABLES: Concns of HCl and DL-alanine T/K = 298 ORIGINAL MEASUREMENTS: Monk, C.B. Trans. Faraday Soc. 1951, 47, 285-91.

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous HCl-alanine solutions at 25°C.

HCl conen mol dm ⁻³	alanine concn mol dm ⁻³	solubility mol dm- ³	pН	109K _d a , mol dm-3
0.0	0.0	0.00333		
0.00344	0.01427	0.00374	2.96	3.19
0.00203	0.01434	0.00382	3.09	3.11
0.00122	0.01427	0.00390	3.19	3.00
0.00041	0.01427	0.00397	3.28	3.18

^aThe dissociation constant for $CuC_3H_6NO_2$ + calculated using literature values for the dissociation constants of HIO_3 , CuCl+, $CuIO_3$ +, and for acid/base dissociation constants for $C_3H_7NO_2$. Details on these calculations as well as for all AUXILIARY INFORMATION are given in the compilation for the $Cu(IO_3)_2$ -KCl- H_2O system by this author as well as in other compilations based on this author's publications.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium Hydroxide; NaOH; [1310-73-2]	ORIGINAL MEASUREMENTS: Monk, C.B.
(3) DL-Alanine; C ₃ H ₇ NO ₂ ; [302-72-7] (4) Water; H ₂ O; [7732-18-5]	Trans. Faraday Soc. <u>1951</u> , 47, 285-91.
VARIABLES: Concus of NaOH and DL-alanine T/K = 298	PREPARED BY: H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous NaOH-alanine solutions at 25°C.

NaOH concn mol dm ⁻³	alanine concn mol dm-3	solubility mol dm-3	рH	109K _{d1} a mol dm-3	10 ⁷ K _{d2} ^a mol ² dm ⁻⁶
0.00616	0.01563	0.00653	4.29	3.27	1.31
0.00750	0.01570	0.00726	4.47	3.06	1.34
0.00750	0.01262	0.00727	4.68	3.06	1.47

 $^{a}K_{d1}$ for the dissociation of CuC₃H₆NO₂+ to Cu²⁺ and C₃H₆NO₂-, and K_{d2} for the dissociation of Cu(C₃H₆NO₂)₂ to Cu²⁺ and 2C₃H₆NO₂-. All other equilibrium constants taken from the literature. For details on these calculations and for other AUXILIARY INFORMATION, see previous compilations of this author's publications.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Malonic acid; C₃H₄O₄; [141-82-2]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ghosh, R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1970, 32, 3033-9.

VARIABLES:

Concentrations of NaOH and $C_3H_4O_4$ T/K = 298, 303, and 308 and 318

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL VALUES:

	[C ₃ H ₄ O ₄]	[NaOH]	Cu(IO ₃) ₂ soly			
t/ºC	mol dm-3	mol dm-3	mol dm-3	-log K _{d1}	-log K _{d2}	-log K _{s0}
25	0.0	0.0	0.003533			7.048
1	0.013887	0.006967	0.004132	<i>5</i> .07		
ļ	0.027773	0.013934	0.004951	<i>5</i> .10		
1	0.034716	0.017403	0.005406	5.09	0.91	
ļ	0.041659	0.020870	0.005822	5.10	0.90	
ſ	0.055545	0.027808	0.006664	5.10	0.90	
			averages:	5.09 ± 0.02	0.90 ± 0.01	
30	0.0	0.0	0.003764			6.980
1	0.013887	0.006967	0.004829	5.15		
	0.027773	0.013934	0.005515	5.15		
	0.034716	0.017403	0.006004	5.14	0.98	
}	0.041659	0.020870	0.006060	5.14	0.98	
1	0.055545	0.027808	0.006941	5.14	0.99	
	0.041659	0.031527	0.008093	5.14	0.98	
ļ			averages:	5.14 ± 0.01	10.0 ± 82.0	

Note that in each solution, $[NaOH]_{tot} = 1/2[C_3H_4O_4]_{tot}$

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1). All slns prepd by dilution of a stock sln, and the pH measured before and after equilibration through the column at least 4 times (twice was sufficient for saturation). The pH of all slns were in the range of 3.7 to 3.8. Slns analyzed for iodate by iodometric titrn in a nitrogen atmos. The thermodynamic solublity product constant was calcd from

$$K_{s0} = [Cu^{2+}][IO_3^{-}]^2y_1y_2$$

where activity coefficients y_1 and y_2 were calcd from the modified Davies eqn (2). K_d for the CuIO₃- ion pair included in the calculations. $K_d(NaIO_3)$ assumed to be 3.0 mol dm-3 at 298 K, and values at higher temperatures were estimated.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepared by dropwise addition of KIO₃ and CuCl₂ solutions into a large volume of dist water at 65°C with stirring for 2 h. The ppt was washed 6 times and digested in double dist water for 4 h at 80°C. AnalaR chemicals were used wherever possible. Sodium malonate solutions prepd from the acid and CO₂-free NaOH solution so as to obtain a 1:1 buffer ratio. Conductivity water was prepared by mixed bed deionization.

ESTIMATED ERROR:

Soly: nothing specified. Average errors in K_d values given in data tables.

Temp: precision \pm 0.1 K.

- (1) Davies, C.W. J. Chem. Soc. 1930, 2471.
- (2) Davies, C.W. Ion Association. Butterworths, London, 1960.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Malonic acid; C₃H₄O₄; [141-82-2]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ghosh, R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1970, 32, 3033-9.

EXPERIMENTAL VALUES:	(continued)
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t/ºC	[C ₃ H ₄ O ₄] mol dm ⁻³	[NaOH] mol dm-3	Cu(IO ₃) ₂ soly mol dm-3	-log K _{d1}	-log K _{d2}	-log K _{s0}
35	0.0	0.0	0.003956			6.929
	0.013887	0.006967	0.005063	5.19		•
	0.027773	0.013934	0.005964	5.19		
	0.034716	0.017403	0.006491	5.18	1.05	
	0.041659	0.020870	0.006881	5.18	1.05	
	0.055545	0.027808	0.007663	5.19	1.05	
			averages:	5.19 ± 0.01	1.05	
40	0.0	0.0	0.004101			6.888
	0.013887	0.006967	0.005322	5.28		
	0.027773	0.013934	0.006366	5.28	1.13	
	0.034716	0.017403	0.006953	5.28	1.14	
	0.041659	0.020870	0.007362	5.28	1.14	
	0.055545	0.027808	0.008486	5.28	1.13	
	0.041659	0.031527	0.009663	5.28	1.13	
			averages:	5.28	1.13 ± 0.01	

Values of K_{d1} and K_{d2} were calculated for reactions [1] and [2] using activity coefficients, y_1 and y_2 calculated from a modified Davies equation (2).

$$K_{d1} = [Cu^{2+}]y_2[C_3H_2O_4^{2-}]y_1/[Cu(C_3H_2O_4)]$$
 [1]

$$K_{d2} = [Cu^{2+}]y_2[C_3H_3O_4]y_1/[Cu(C_3H_3O_4)+]y_1$$
 [2]

All K_d and K_{s0} values are based on mol dm-3 concentration units. The authors fitted the K_d data to the smoothing equation

$$log K_d = a + b(T/K) + c(T/K)^2$$
 [3]

and the following thermodynamic parameters were obtained (for 298 K).

reaction	∆G/kcal mol-1	-∆H/kcal mol-1	-ΔS/cal K-1 mol-1
[1]	6.95 ± 0.03	3.50 ± 0.03	$35.0_5 \pm 0.5$
[2]	1.23 ± 0.01	6.58 ± 0.03	26.2 ± 0.2

From a plot of $log K_{s0}$ vs 1/(T/K), the compilers estimate that $\Delta H = 4.5$ kcal mol-1 and $\Delta S = -17$ cal mol-1 K-1 (for 298 K).

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) DL-2-Hydroxypropanoic acid (DL-lactic acid); C₃H₆O₃; [598-82-3]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ghosh, R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1970, 32, 3025-32

VARIABLES:

Concentrations of NaOH and $C_3H_6O_3$ T/K = 298, 303, 308 and 318

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL VALUES:

	C ₃ H ₆ O ₃ total concn	Cu(IO ₃) ₂ soly	- log K _{d1}	- log K _{d2}	- log K _{s0}
t/ºC	mol dm-3	mol dm-3			
25	0	0.003533			7.048
	0.002493	0.003854	2.33		
	0.004985	0.004122	2.29		
	0.009970	0.004728	2.31	1.56	
	0.02492	0.006523	2.40	1.54	
	0.03739	0.007727	2.39	1.53	
	0.04985	0.008933	2,41	1.51	
		a	verages: 4.36 ± 0.07	1.54 ± 0.03	
30	0	0.003764			6.980
	0.004980	0.004553	2.49		
	0.009960	0.005079	2.41	*	
	0.01494	0.005731	2.44	1.05	
	0.02490	0.006823	2.46	1.06	
	0.03735	0.008013	2.47	1.06	
	0.04980	0.009189	2.50	1.07	
		a	verages: 2.46 ± 0.05	1.06 ± 0.01	

Note that in each solution, $[NaOH]_{tot} = 1/2[C_3H_6O_3]_{tot}$

continued......

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used as in (1). All slns prepd by dilution of a stock sln, and the pH measured before and after equilibration through the column at least 4 times (twice was sufficient for saturation). The pH of all slns were in the range of 3.7 to 3.8. Slns analyzed for iodate by iodometric titrn in a nitrogen atmos. The thermodynamic solublity product constant was calcd from

$$K_{*0} = [Cu^{2+}][IO_3^-]^2y_1y_2$$

where activity coefficients y_1 and y_2 were calcd from the modified Davies eqn (2). K_d for the CuIO₃- ion pair included in the calculations. $K_d(NaIO_3)$ assumed to be 3.0 mol dm-8 at 298 K, and values at higher temperatures were estimated.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂ prepared by dropwise addition of KIO₃ and CuCl₂ solutions into a large volume of dist water at 65°C with stirring for 2 h. The ppt was washed 6 times and digested in double dist water for 4 h at 80°C. AnalaR chemicals were used wherever possible. Sodium lactate solutions prepd from the acid and CO₂-free NaOH solution so as to obtain a 1:1 buffer ratio. Conductivity water was prepared by mixed bed deionization.

ESTIMATED ERROR:

Soly: nothing specified. Average errors in K_d values given in data tables.

Temp: precision ± 0.1 K.

- (1) Davies, C.W. J. Chem. Soc. 1930, 2471.
- (2) Davies, C.W. Ion Association. Butterworths, London, 1960.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) DL-2-Hydroxypropanoic acid (DL-lactic acid); C₃H₆O₃; [598-82-3]

(4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ghosh, R.; Nair, V.S.K.

J. Inorg. Nucl. Chem. 1970, 32, 3025-32.

EXPERIMENTAL VALUES: (continued.....)

C	3H6O3 total concn	Cu(IO ₃) ₂ soly	- log K _{d1}	- log K _{d2}	- log K _s (
:/ºC	mol dm-3	mol dm-3			
35	0	0.003956			6.929
	0.005169	0.004830	2.55		
	0.009940	0.005438	2.49		
	0.01491	0.006192	2.53	0.91	
	0.02485	0.007354	2.54	0.89	
	0.03727	0.008366	2.53	0.89	
	0.04970	0.009714	2.55	0.92	
		ave	rages: 2.54 ± 0.05	0.90 ± 0.02	
40	0	0.004101			6.888
	0.004464	0.004956	2.64		
	0.008928	0.005751	2.64		
	0.01488	0.006687	2.65	0.61	
	0.02976	0.008691	2.69	0.62	
	0.04464	0.010083	2.67	0.61	
	0.08928	0.013531	2.67	0.60	
		ave	rages: 2.66 ± 0.03	0.61 ± 0.01	
45	0	0.005484			6.536
	0.005098	0.006750	2.74		
	0.01485	0.008796	2.74		
	0.02475	0.011002	2.81	0.30	
	0.02970	0.011620	2.79	0.34	
	0.04455	0.014119	2.78	0.31	
	0.04950	0.014828	2.77	0.30	
		ave	rages: 2.77 ± 0.04	0.31 ± 0.03	

 K_{d1} and K_{d2} calculated from eqs. [1] and [2] using using activity coefficients calculated from a modified Davies equation (2). The thermodynamic equilibrium constants are defined as follows:

$$K_{d1} = [Cu^{2+}]y_2[C_3H_5O_3^-]y_1/[Cu(C_3H_5O_3^+)]y_1$$
 [1]

$$K_{d2} = [Cu(C_3H_5O_3)^+][C_3H_5O_3^-]y_1^2/[Cu(C_3H_5O_3)_2]$$
 [2]

Authors give p K_a for HC₃H₅O₃ as 3.83 at 25°C (volume unit basis). Authors state that plots of $log K_d$ vs 1/(T/K) are linear. From these plots, the following results were reported (presumably at 25°C):

reaction	∆G/kcal mol-1	ΔH/kcal mol ⁻¹	ΔS/cal K-1 mol-1
[1]	3.22 ± 0.06	-8.90 ± 0.24	-40.6 ± 0.2
[2]	2.10 ± 0.05	2.77 ± 0.14	2.2 ± 0.3

From a plot of $log K_{s0}$ vs 1/(T/K) using the data for 25, 30, 35, and 40°C, the compilers obtain (for 298 K) \triangle H = 4.5 kcal mol⁻¹ and \triangle S = -17 cal K⁻¹ mol⁻¹.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Glycylglycine; C ₄ H ₈ N ₂ O ₃ ; [556-50-3] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Monk, C.B. Trans. Faraday Soc. 1951, 47, 285-91.
VARIABLES: Concns of HCl and glycylglycine T/K = 298	PREPARED BY: H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous HCl-glycylglycine solutions at 25°C.

HCl concn mol dm ⁻³	$C_4H_8N_2O_3$ concumol dm-3	solubility mol dm ⁻³	pН	10 ⁷ K _d a mol dm-3
0.00033	0.01006	0.00366	3.97	9.27
0.00246	0.01382	0.00367	2.75	9.47
0.00020	0.01356	0.00383	3.99	9.31
0.00132	0.02046	0.00406	3.95	9.12

^aThe dissociation constant for $CuC_4H_7N_2O_3^+$ calculated using literature values for the dissociation constants of HIO_3 , $CuCl^+$, $CuIO_3^+$, and for acid/base dissociation constants for $C_4H_8N_2O_3$. Details on these calculations as well as for all AUXILIARY INFORMATION are given in the compilation for the $Cu(IO_3)_2$ -KCl-H₂O system by this author as well as in other compilations based on this author's publications.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium Hydroxide; NaOH; [1310-73-2]	ORIGINAL MEASUREMENTS: Monk, C.B.
(3) Glycylglycine; C ₄ H ₈ N ₂ O ₃ ; [556-50-3] (4) Water; H ₂ O; [7732-18-5]	Trans. Faraday Soc. <u>1951</u> , 47, 285-91.
VARIABLES: Concns of NaOH and glycylglycine T/K = 298	PREPARED BY: H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous NaOH-glycylglycine solutions at 25°C.

NaOH concn mol dm-3	C ₄ H ₈ N ₂ O ₃ concn mol dm ⁻³	solubility mol dm-3	pН	10 ⁷ K _{d1} a mol dm- ³	106K _{d2} a mol ² dm-6
0.00400	0.01587	0.00483	4.40	9.06	2.34
0.00457	0.01580	0.00507	4.44	7.7b	2.60
0.00601	0.01932	0.00557	4.50	8.8	2.31
0.00627	0.01892	0.00568	4.52	8.2	2.20

^aK_{d1} for the dissociation of CuC₄H₇N₂O₃+ to Cu²+ and C₄H₇N₂O₃-, and K_{d2} for the dissociation of Cu(C₄H₇N₂O₃)₂ to Cu²+ and 2C₄H₇N₂O₃-. All other equilibrium constants taken from the literature. For details on these calculations and for other AUXILIARY INFORMATION, see previous compilations of this author's publications.

bThe author indicated that this value may be in error.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium glycollate (sodium hydroxyacetate);	ORIGINAL MEASUREMENTS: Evans, W.P.; Monk, C.B.
C ₂ H ₃ O ₃ Na; [2836-32-0] (3) Water; H ₂ O; [7732-18-5]	J. Chem. Soc. <u>1951</u> , 550-7.
VARIABLES: Concentration of sodium glycollate T/K = 298	PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous sodium glycollate solutions at 25°C.

C ₂ H ₃ O ₃ Na concn mol dm ⁻³	Cu(IO ₃) ₂ soly mol dm-3	K _{d2} ª mol² dm-6
0.0	0.00326	
0.01512	0.00645	0.0180
0.02016	0.00736	0.0169
0.03017	0.00899	0.0173

 $^{a}K_{d2}$ for $Cu(C_{2}H_{3}O_{3})_{z} = Cu^{2} + 2C_{2}H_{3}O_{3}^{-}$ calculated from material balance equations using an adjusted value for $K_{d1} = 0.00128$ mol dm⁻³. K_{d1} is the equilibrium constant for the reaction $CuC_{2}H_{3}O_{3}^{+} = Cu^{2}^{+} + CuC_{2}H_{3}O_{3}^{-}$. Activity coefficients estimated, and all AUXILIARY INFORMATION essentially identical to previous works: e.g. see the compilations on the publication by Lloyd, M.; Wycherley, V.; Monk, C.B. J. Chem. Soc. 1951, 1786.

COMPONENTS: (1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2] (2) Sodium <i>DL</i> -lactate (sodium 2-hydroxypropionate);	ORIGINAL MEASUREMENTS: Evans, W.P.; Monk, C.B.
C ₃ H ₅ O ₃ Na; [72-17-3] (3) Water; H ₂ O; [7732-18-5]	J. Chem. Soc. 1951, 550-7.
VARIABLES: Concentration of sodium <i>DL</i> -lactate T/K = 298	PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA: The solubility of Cu(IO₃)₂ in aqueous sodium DL-lactate solutions at 25°C.

C ₃ H ₅ O ₃ Na concn mol dm ⁻³	Cu(IO ₃) ₂ soly mol dm-3	K _{d2} a mol² dm-
0.0	0.00326	
0.01269	0.00634	0.0160
0.01904	0.00770	0.0124
0.02538	0.00883	0.0154

 $^{8}K_{d2}$ for $Cu(C_{3}H_{5}O_{3})_{2} = Cu^{2} + 2C_{3}H_{5}O_{3}^{-}$ calculated from material balance equations using an adjusted value for $K_{d1} = 0.00095$ mol dm⁻³. K_{d1} is the equilibrium constant for the reaction $CuC_{3}H_{5}O_{3}^{+} = Cu^{2} + CuC_{3}H_{5}O_{3}^{-}$. Activity coefficients estimated, and all AUXILIARY INFORMATION essentially identical to previous works: e.g. see the compilations on the publication by Lloyd, M.; Wycherley, V.; Monk, C.B. J. Chem. Soc. 1951, 1786.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Deuterium oxide (water-d₂); D₂O; [7789-20-0]

ORIGINAL MEASUREMENTS:

Ramette, R.W.; Broman, R.F.

J. Phys. Chem. 1963, 67, 942-4.

VARIABLES:

Concn of LiClO₄ at [HClO₄] = 0.0001 mol dm⁻³ T/K = 288, 298 and 308

PREPARED BY:

G. Jancso, H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

Note that for all solutions below, the concentration of HClO4 is constant at 0.0001 mol dm-3.

t/ºC	LiClO ₄ concn	Cu(IO ₃) ₂ soly	t/ºC	LiClO ₄ concn mol dm-3	Cu(IO ₃) ₂ soly mol dm ⁻³
1,50	mor am -	mor am s	1,50	mor am •	mor am •
14.7	0.000	0.00203	25.0	0.000	0.00235
17	0.025	0.00236	H	0.025	0.00274
**	0.050	0.00255	11	0.050	0.00294
*	0.075	0.00271	H	0.075	0.00309
#	0.100	0.00279	Ħ	0.100	0.00321
			ŧ		
			ti .		
35.0	0.000	0.00273			
11	0.025	0.00309			
n	0.050	0.00336			
**	0.075	0.00352			
н	0.100	0.00366			

continued....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method same as in (1). Excess Cu(IO₃)₂•D₂O added to LiClO₄ solutions containing HClO₄ to supress hydrolysis. Solutions were rotated in borosilicate glass bottles for 2 d in a thermostat at 38°C, and then transferred to a water bath thermostated at 35.0°C where they stood for 3 d with occasional shaking. Saturated solutions were filtered through fine porous glass by pressure, and 5 cm³ aliquots were pipetted into titration flasks. Aliquots were treated with 2 ml of 0.1 mol dm⁻³ acetic LiClO₄ and HClO₄ were reagent grade. acid + 0.1 mol dm-3 sodium acetate buffer, and 1 drop of Snazoxs indicator: the solution was then titrated with EDTA. The EDTA solutions were standardized with weighed quantities of pure electrolytic copper, and duplicate titrations agreed to within 0.2 %.

The bottles and remaining solutions were then equilibrated in a similar manner at 25.0°C, and finally at 14.70C, and aliquots for analyses were taken at each temperature.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂•D₂O prepared by adding 0.3 mol dm-3 KIO₃ and 0.15 mol dm-3 CuSO₄ solutions (both in D₂O) to 60°C D₂O with constant stirring. The solid was digested at this temperature for one hour, collected on a glass filter, and dried at 100°C. Assay with EDTA gave 99.9 % purity. D₂O (General Dynamics Corp.) was specified as 99.5 % pure.

ESTIMATED ERROR:

Soly: reproducibility within 0.2 %.

Temp: nothing specified.

REFERENCES:

(1) Ramette, R.W.; Dratz, E.A. J. Phys. Chem. 1963, 67, 940.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄ [7601-90-3]
- (4) Deuterium oxide (water-d₂); D₂O; [7789-20-0]

ORIGINAL MEASUREMENTS:

Ramette, R.W.; Broman, R.F.

J. Phys. Chem. 1963, 67, 942-4.

EXPERIMENTAL DATA: (continued.....)

 K_{s0} was calculated by the authors as $K_{s0} = 4S^3Y$ where S is the experimental solubility and Y is the Debye-Huckel activity relation

$$log Y = -6AI^{1/2}/(1 + BI^{1/2})$$
 [1]

$$I = 3S + [LiClO_4] + [HClO_4]$$
 [2]

The calculations were carried out by plotting $-log(4S^3)$ versus I^{1/2} while varying B so that the value of A was precisely the theoretical value at each temperature. The results are summarized below, and include the evaluation of the Gibbs free energy, enthalpy and entropy obtained in the usual way from a $-log K_{s0}$ vs 1/(T/K) plot. All are based on mol dm⁻³ units, and the uncertainties expressed refer to the 90 % confidence intervals.

l_{s0} /2 dm ^{3/2} -log K _{s0}
9 7.69 ± 0.02
7.51 ± 0.01
7.34 ± 0.03

aNote: The authors point out that in carrying out the least squares treatment of the solubility data, the "best fit" does not correspond to the case where A is the theoretical value in eq. [1]. In fact, at 25°C in protium oxide (H₂O), the sum of squares of deviations for the fit with A constrained to equal the theoretical values is 0.00059, whereas the "best fit" gives 0.00039 for the sum of the squares of deviations: in this case $B = 3.2 \text{ mol}^{-1/2} \text{ dm}^{-3/2}$ and $A = 0.752 \text{ mol}^{-1/2} \text{ dm}^{3/2}$ which gives $-\log K_{s0} = -7.21$ rather than $-\log K_{s0} = 7.13$ (see the compilation of the paper by these authors for the corresponding H₂O system). Nothing analogous is mentioned about the treatment of D₂O solubility data.

ΔG_{s0} kcal mol-1	ΔH _{s0} kcal mol ⁻¹	ΔS _{s0} cal K-1 mol-1
10.25 ± 0.01	7.00 ± 0.30	-10.9 ± 0.9

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Deuteroperchloric acid; DClO₄; [19029-50-6]
- (4) Deuterium oxide; D₂O; [7789-20-0]

ORIGINAL MEASUREMENTS:

Gamjager, H.; Gerber, F.; Antonsen, O.

Chimica 1973, 27, 94-7

VARIABLES:

Concentration of LiClO₄ and DClO₄. T/K = 274, 288, 298 and 308.

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

Using LiClO₄ and DClO₄ to maintain a constant ionic strength of 1.0 mol kg⁻¹, the soly of Cu(IO₅)₂ was reported graphically. The data were analyzed in terms of the following eqns defining F as 2(soly)^{1.5} where concentrations are based on mol kg⁻¹ units (note that activity coefficients are assumed to equal unity):

$$F = 2\{Cu^{2+}\}^{1.5} = K_{s0}^{1/2} \left(1 + \frac{\{D^{+}\}}{K_a}\right)$$

where

$$K_{s0} = (Cu^{2+})(IO_3^-)^2$$
 and $K_a = \{D^+\}\frac{\{IO_3^-\}}{\{DIO_3^-\}}$

From material balance requirements and least squares fitting, the following were reported:

t/ºC	-log K _{s0}	-log Ka	Cu(IO ₃) ₂ soly/mol kg ⁻¹ a
1	$6.821 \ (\sigma = 0.036)$	$0.574 \ (\sigma = 0.020)$	0.0033₅
15	$6.558 \ (\sigma = 0.019)$	$0.602 (\sigma = 0.011)$	0.00402
25	$6.411 \ (\sigma = 0.080)$	$0.629 (\sigma = 0.023)$	0.0046 ₀
35	$6.293 \ (\sigma = 0.021)$	$0.731 \ (\sigma = 0.011)$	0.00503

*Solubilities calcd by compilers from $(K_{s0}/4)^{1/3}$ (note ionic strength = 1.0 mol kg⁻¹).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess cupric iodate deuterate was placed in glass ampoules and LiClO₄ and DClO₄ solutions added to maintain the ionic strength at 1.0 mol kg-1. The ampoules were sealed and shaken in a water thermostat with a precision in temperature of \pm 0.1°C. After equilibrium was reached, samples of saturated solution were removed by millipore filtration and analyzed for cupric iodate by iodometric titration. X-ray powder diffraction patterns of the solid phase before and after equilibration indicated the solid phase to be Cu₃(IO₃)₆.2D₂O.

SOURCE AND PURITY OF MATERIALS:

Cu₃(IO₃)₆.2D₂O prepared as in (1). DClO₄ prepd by ion exchange of an NaClO₄ solution. DClO₄ contained < 0.01 % Na and < 0.2 % H. LiClO₄ prepd from Li₂CO₃ and HClO₄ followed by several recrystallizations. D₂O was > 99.8 % D as obtained from Wurlington E.I.R.

ESTIMATED ERROR:

Standard deviations for K_{s0} given above. Temp: precision \pm 0.1 K.

REFERENCES:

(1) Ramette, R.W.; Broman, R.F. J. Phys. Chem., 1963, 67, 942.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper iodate; Cu(IO ₃) ₂ ; [13454-89-2]	Miyamoto, H.
(2) Tetrahydrofuran; C ₄ H ₈ O; [109-99-9]	Nippon Kagaku Kaishi <u>1972</u> , 659-61.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Solvent composition. T/K = 298.	H. Miyamoto

The solubility of Cu(IO₃)₂ in water-tetrahydrofuran mixtures at 25°C is given below.

C ₄ H ₈ O composition		solubility
mass %	moi %	mole dm-3
0	0.0	0.00347
5	1.3	0.00235
10	2.7	0.00172
15	4.2	0.00125
20	5.9	0.00092
25	7.7	0.00064
30	9.7	0.00050
40	14.3	0.00026

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess copper iodate and solvent were placed in glass stoppered bottles, and the bottles were placed in a thermostat at 25°C and rotated for 48 hours. The solutions were allowed to settle, and aliquots withdrawn through a siphon tube equipped with a sintered glass filter. The iodate content in the saturated solutions was determined by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

Cu(IO₃)₂•H₂O was prepared by dropwise addition of equivalent solutions of Cu(NO₃)₂ (Wako Co., reagent grade) and KIO₃ (Wako, reagent grade) into a large volume of KNO₃ solution. The ppt was washed and dried under reduced pressure. Tetrahydrofuran was distilled from NaOH and then redistilled from metallic sodium.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

- (1) Copper iodate; Cu(IO₃)₂; [13454-89-2]
- (2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.; Yamamoto, M.; Maruyama, Y.

Nippon Kagaku Kaishi 1979, 546-8.

VARIABLES:

Solvent composition. T/K = 293, 298 and 303.

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

	SH7NO com	position	solubility		C ₃ H ₇ NO com	position	solubility
t/ºC	mass %	mol %	mol dm-3	t/ºC	mass %	mol %	mol dm-3
20.0	0.0	0.0	0.00321	30.0	0.0	0.0	0.00365
	5.04	1.29	0.00255		5.31	1.36	0.00290
	9.99	2.66	0.00200		9.76	2.60	0.00236
	14.59	4.04	0.00157		15.44	4.31	0.00179
	20.35	5.92	0.00118		19.84	5.75	0.00145
	24.89	7.55	0.00093		24.85	7.54	0.00113
	30.53	9.77	0.00070		30.14	9.61	0.00083
	40.49	14.36	0.00038		40.58	14.41	0.00046
25.0	0.0	0.0	0.00344				
	4.93	1.26	0.00277				
	9.89	2.63	0.00218				
	14.99	4.16	0.00171				
	20.11	5.84	0.00131				
	24.76	7.50	0.00104				
	29.73	9.44	0.00078				
	40.44	14.34	0.00041				

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess copper iodate and solvent were placed in glass stoppered bottles, and the bottles were placed in a thermostat at a specified temperature and rotated for 72 hours. Samples of saturated solution were filtered through glass filters, and aliquots were diluted with water. The iodate concentration was then determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

Cu(lO₃)₂.H₂O was prepared by addition of dilute solutions of Cu(NO₃)₂ and KIO₃ to boiling water. The ppt was washed and dried at room temp. The monohydrate was obtained. C₃H₇NO (Mitsubishi Gas Chem. Co.) was distilled under reduced pressure, dried with Na₂CO₃ and redistilled three more times.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

COMPONENTS:	EVALUATORS:
(1) Silver chlorate; AgClO ₃ ; [7783-92-8]	H. Miyamoto Niigata University
(2) Water; H ₂ O; [7732-18-5]	Niigata, Japan July, 1987

THE BINARY SYSTEM

Data for the solubility of AgClO₃ in water have been reported in three publications (1-3). Noonan (1) and Ricci and Offenbach (2) reported solubilities in mass units (converted to molalities by the compilers), and Mel'nichenko and Gyunner (3) reported the solubility of AgClO₃ at 293.2 K in mol dm⁻³ units. In the absence of density data, direct comparisons of the results of (3) to those in (1, 2) cannot be made. However, the singular value for the solubility of AgClO₃ in pure water at 293.2 K reported in (3) appears to be low. No hydrates of AgClO₃ have been reported, and Ricci and Offenbach (2) have confirmed that the solid phase at 298.2 K is the anhydrous salt.

The experimental solubilities reported in (1) for 278.2 K to 308.2 K and the singular value from (2) for 298.2 K were fitted to the following smoothing equation:

$$Y_{x} = \frac{-220207.71}{T/K} - 1480.209 \ln(T/K) + 8404.654 - 2.55109(T/K)$$
[1]

where $\sigma_Y = 0.009$ and $\sigma_X = 7.4 \times 10^{-5}$ (Y_X and the standard errors, σ are defined in the PREFACE). Based on this smoothing equation, the evaluator calculated tentative solubilities at selected temperatures which are given in Table 1 below.

Table 1. Tentative solubilities of AgClO₃ in water calculated from eq. [1]

T/K	AgClO ₃ mol kg ⁻¹	AgClO mol %
278.2	0.445	0.795
283.2	0.535	0.955
288.2	0.637	1.035
293.2	0.753	1.338
298.2	0.887	1.573
303.2	1.047	1.851
308.2	1,241	2.187

- 1. Noonan, E. C. J. Am. Chem. Soc. 1948, 70, 2915.
- 2. Ricci, J. E.; Offenbach, J. A. J. Am. Chem. Soc. 1951, 73, 1597.
- Mel'nichenko, L. M.; Gyunner, E. A. Zh. Neorg. Khim. 1967, 12, 1524; Russ. J. Inorganic Chem. (Engl. Transl.) 1967, 12, 801.

- (1) Silver chlorate; AgClO₃; [7783-92-8]
- (2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Noonan, E.C.

J. Am. Chem. Soc. 1948, 70, 2915-8.

VARIABLES:

PREPARED BY:

T/K = 278.15, 288.15, 298.15 and 308.15

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

t/ºC	AgClO ₃ solubility mol/100 mol water	AgClO ₃ solubility ^a mol kg-1
5.0	0.8017	0.445 ₀
15.0	1.1481	0.637 ₃
25.0	1.604 ₀	0.8904
35.0	2.235 ₃	1.2408

^{*}Molalities calculated by the compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgClO₃ was placed into 6-8 ml Pyrex capsules, water was added, and the ampoules sealed. Equilibrium was approached from the high temperature side only. Samples were rotated 12 to 48 hours in a water bath controlled to ± 0.05 K or better. They were then allowed to settle for one hour, and 2-5 cm³ aliquots were withdrawn through glass wool. The samples were transferred to 30 cm³ Pt crucibles, weighed to 1 mg and carefully evaporated and dried to constant mass (to 0.05 mg) in an oven or desiccator. Buoyancy corrections were applied. All determinations were performed in duplicate and repeated if discrepancies were greater than 0.5 %.

SOURCE AND PURITY OF MATERIALS:

AgClO₃ was prepared from NaClO₃ and AgNO₃, and the product then recrystallized two to five times. Water was probably distilled from alkaline permanganate solution, and the electrolytic conductivity was checked.

ESTIMATED ERROR:

Soly: precision at least ± 0.5 %. Temp: precision ± 0.05 K or better.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver chlorate; AgClO ₃ ; [7783-92-8]	Ricci, J.E.; Offenbach, J.A.
(2) Sodium chlorate; NaClO ₃ ; [7775-09-9]	J. Am. Chem. Soc. 1951, 73, 1597-9.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Composition T/K = 298	H. Miyamoto

In the ternary AgClO₃-NaClO₃-H₂O system, 'type five' Roozeboom solid solutions were reported.

NaClO ₃ mass %	NaClO ₃ mol %a	AgClO ₃ mass %	AgClO ₃ mol %ª	nature of the solid phaseb
0	0	14.46	1.567	AgClO ₃
8.11	1.630	10.02	1.121	SSI
17.49	3.762	7.48	0.895	SSI
27.53	6.463	5.56	0.726	SSI
34.39	8.610	4.23	0.589	SSI
41.78	11.276	2.85	0.428	SSI
46.57	13.275	2.14	0.339	SSI + SSII
46.54	13.263	2.15	0.341	SSI + SSII
46.55	13.268	2.15	0.341	SSI + SSII
47.52	13.628	1.66	0.265	SSII
49.23	14.220	0.56	0.090	SSII
50.04	14.495	0	0	NaClO ₃

*Mass % solubilities calculated by the compiler. In pure water, the compiler calculates a solubility of 0.755₈ mol kg⁻¹ for AgClO₃ at 25°C.

bThe limiting compositions of solid solutions I and II were estimated as ~ 37 mass % NaClO₃ in solid solution SSI, and ~ 26 mass % AgClO₃ in solid solution SSII. The composition of the isothermally invariant liquid with these two limiting solid solutions is 2.15 mass % AgClO₃ and 46.55 mass % NaClO₃.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Ternary mixtures of known composition were allowed to equilibrate at 25°C for two weeks with stirring. The equilibrium compositions were unchanged after an additional 1-3 weeks of stirring. Aliquots of saturated solution were filtered and analyzed for silver and for total solids. Silver was analyzed by titration with standard KSCN solution, and total solids determined by evaporation to dryness at 110-125°C. NaClO₃ was determined by difference.

SOURCE AND PURITY OF MATERIALS:

AgClO₃ was prepared from 'c.p. grade' AgNO₃ and NaClO₃. The product was recrystallized three times and analyzed gravimetrically as AgCl after reduction with NaNO₃ in the presence of NaCl. Purity was reported as 99.72 %.

ESTIMATED ERROR:

Soly: precision ~ ± 0.03 mass % (compiler).

Temp: precision probably better than ± 0.1 K (compiler).

COMPONENTS: (1) Silver chlorate; AgClO₃; [7783-92-8] (2) 1,3,5,7-Tetraazatricylo[3.3.1.1^{3,7}]-decane (hexamethylenetetramine); C₆H₁₂N₄; [100-97-0] (3) Water; H₂O; [7732-18-5] VARIABLES: Composition T/K = 293.2 ORIGINAL MEASUREMENTS: Mel'nichenko, L.M.; Gyunner, E.A. Zh. Neorg. Khim. 1967, 12, 1524-8: Russ. J. Inorg. Chem. (Engl. Transl.) 1967, 12, 801-4.

EXPERIMENTAL DATA:

The solid phase was probably not simply $AgClO_3$, but was instead either (A) hexamethylenetetramine disilver(I) dichlorate, $[Ag_2C_6H_{12}N_4](ClO_3)_2$, or (B) hexamethylenetetramine silver(I) chlorate, $[AgC_6H_{12}N_4]ClO_3$.

mol ratio of	solubility	[C ₆ H ₁₂ N ₄]totb	probable
$C_6H_{12}N_4^a$	mol dm-3	mol dm-3	solid phase
0	0.285	0	Α
0.10	0.187	0.029	Α
0.20	0.102	0.057	Α
0.30	0.048	0.086	A and B
0.333	0.028	0.095	В
0.40	0.022	0.114	В
0.45	0.018	0.128	В
0.50	0.010	0.143	В
0.55	0.010	0.157	В
0.60	0.011	0.171	В
0.70	0.012	0.200	В
0.80	0.013	0.228	В
0.90	0.014	0.257	В
0.95	0.014	0.271	В
1.00	0	0.285	none

^{*}Defined as initial $[C_6H_{12}N_4]/(initial [C_6H_{12}N_4] + initial [AgClO_3])$.

continued......

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Aqueous solutions of AgClO₃ and C₆H₁₂N₄ (each 0.285 mol dm⁻³) were mixed to give 20 cm³ total volume. The mixtures were stirred vigorously for 24 hours at 20°C. White crystalline precipitates formed in mixtures containing less than 19 moles of the amine for each mole of AgClO₃. The total silver in the liquid phase was determined gravimetrically by precipitation as the chloride after decomposing the hexamethylenetetramine with nitric acid. Solid [AgC₆H₁₂N₄]ClO₃ was equilibrated for 48 hours while shaking.

SOURCE AND PURITY OF MATERIALS:

"Analytical reagent" grade silver chlorate and hexamethylenetetramine, and twice distilled water were used. [AgC₆H₁₂N₄]ClO₃ was prepared from equimolar solutions of the chlorate and the amine. After 24 hours, the product was filtered and dried at room temperature, and then at 108°C to constant mass. Analysis showed the hydrate to be stable at room temperature, and the anhydrous form at 108°C.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.1 K.

bCalculated by the compilers.

- (1) Silver chlorate; AgClO₃; [7783-92-8]
- (2) 1,3,5,7-Tetraazatricylo[3.3.1.13.7]-decane (hexamethylenetetramine); C₆H₁₂N₄; [100-97-0]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Mel'nichenko, L.M.; Gyunner, E.A.

Zh. Neorg. Khim. 1967, 12, 1524-8: Russ. J. Inorg. Chem. (Engl. Transl.) 1967, 12, 801-4.

COMMENTS AND/OR ADDITIONAL DATA:

(continued.....)

The author also measured the refractive indices of the solutions. The formation of two sparingly soluble compounds $[Ag_2C_6H_{12}N_4](ClO_3)_2$ and $[AgC_6H_{12}N_4]ClO_3$ was postulated. A compound $[AgC_6H_{12}N_4]ClO_3 \cdot H_2O$ was prepared and confirmed from solutions containing equal moles of $AgClO_3$ and $C_6H_{12}N_4$. This compound was dried and equilibrated with several aqueous $C_6H_{12}N_4$ solutions which were then analyzed for silver, and the results of these experiments are given in the table below.

lity
im-3
032
224
534
781
975
118
400

The solubility data were analyzed in terms of three equilibria, and using the method of least squares the authors reported the following:

$$(A_8C_6H_{12}N_4)CIO_3(s) = A_8C_6H_{12}N_4^+ + CIO_3^-$$

 $log K_{s0} = [AgC_6H_{12}N_4^+][ClO_3^-] = 1.065 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$

$$(AgC_6H_{12}N_4)CIO_3(s) + C_6H_{12}N_4 = Ag(C_6H_{12}N_4)_2 + CIO_3$$

 $log K_{s1} = [Ag(C_6H_{12}N_4)_2^+][ClO_3^-]/[C_6H_{12}N_4] = 2.25 \times 10^{-4} \text{ mol dm}^{-3}$

$$(AgC_6H_{12}N_4)CIO_3(s) + 2C_6H_{12}N_4 = Ag(C_6H_{12}N_4)_3 + CIO_3$$

$$log K_{s2} = [Ag(C_6H_{12}N_4)_3^+][ClO_3^-]/[C_6H_{12}N_4]^2 = 7.90 \times 10^{-4}$$

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver chlorate; AgClO ₃ ; [7783-92-8]	Noonan, E.C.
(2) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. 1948, 70, 2915-8.
(3) Deuterium oxide (water-d ₂); D ₂ O; [7789-20-0]	
VARIABLES:	PREPARED BY:
T/K = 278.15, 288.15, 298.15 and 308.15	W.A. Van Hook and E.M. Woolley

t/ºC	D ₂ O content mol %	AgCIO ₃ solubility mol/100 mol water	AgClO ₃ solubility ^a mol kg ⁻¹
5.0	98.3 ₈	0.6532	0.3267
15.0	98.3 ₈	0.9567	0.4785
25.0	98.3 ₈	1.3578	0.6791
35.0	98.1 ₈	1.9076	0.9542

The authors computed the expected solubility in pure (100 %) D_2O assuming a linear change in solubility with mol % D_2O . The results of these calculations are given below.

t/ ₀ C	AgClO ₃ solubility mol/100 mol D ₂ O	AgClO ₃ solubility ^a mol kg ⁻¹
5.0	0.6508	0.3250
15.0	0.953 ₅	0.4761
25.0	0.1353 ₇	0.675 ₉
35.0	0.1901 ₅	0.9494

aMolalities calculated by the compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgClO₃ was placed into 6-8 ml Pyrex capsules, water was added, and the ampoules sealed. Equilibrium was approached from the high temperature side only. Samples were rotated 12 to 48 hours in a water bath controlled to ± 0.05 K or better. They were then allowed to settle for one hour, and 2-5 cm³ aliquots were withdrawn through glass wool. The samples were transferred to 30 cm³ Pt crucibles, weighed to 1 mg and carefully evaporated and dried to constant mass (to 0.05 mg) in an oven or desiccator. Buoyancy corrections were applied. All determinations were performed in duplicate and repeated if discrepancies were greater than 0.5 %.

SOURCE AND PURITY OF MATERIALS:

AgClO₃ was prepared from NaClO₃ and AgNO₃, and the product then recrystallized two to five times. D_2O was distilled consecutively from alkaline permanganate solution and then from $K_2Cr_2O_7$ or CrO_3 solution, and the electrolytic conductivity of the final product was 2 x 10⁻⁶ S cm⁻¹ or less. The D_2O content was computed from the measured density at 25°C relative to 1.10763 g cm⁻³ for pure D_2O .

ESTIMATED ERROR:

Soly: precision at least ± 0.5 %. Temp: precision ± 0.05 K or better.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver chlorate; AgClO ₃ ; [7783-92-8]	Mel'nichenko, L.M.; Gyunner, E.A.
(2) 1,3,5,7-Tetraazatricylo[3.3.1.13.7]-decane (hexamethylenetetramine); C ₆ H ₁₂ N ₄ ; [100-97-0]	Zh. Neorg. Khim. <u>1967</u> , 12, 1524-8: Russ. J. Inorg.
(3) Methanol; CH ₄ O; [67-56-1]	Chem. (Engl. Transl.) 1967, 12, 801-4.
VARIABLES: Composition	PREPARED BY:
T/K = 293.2	H. Miyamoto and E.M. Woolley

The solid phase was probably not simply $AgCIO_3$, but was instead either (A) hexamethylenetetramine disilver(I) dichlorate, $[Ag_2C_6H_{12}N_4](CIO_3)_2$, or (B) hexamethylenetetramine silver(I) chlorate, $[AgC_6H_{12}N_4]CIO_3$.

$C_6H_{12}N_4$ a	solubility	probable
mol %	mol dm-3	solid phase
0	0.0184	none
10	0.0101	$(Ag_2C_6H_{12}N_4)(ClO_3)_2$
20	0.0063	н
30	0.0023	n
33	0	$(Ag_2C_6H_{12}N_4)(ClO_3)_2 + (AgC_6H_{12}N_4)ClO_3$
35 to 100	0	$(AgC_6H_{12}N_4)CIO_3$

*Defined as (100 %) x initial $[C_6H_{12}N_4]/\{\text{initial }[C_6H_{12}N_4] + \text{initial }[AgClO_3]\}$. The authors also measured the refractive indices of the solutions. The formation of complexes with more than one mole of hexamethylene-tetramine per mole of silver chlorate does not take place.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Methanolic solutions of $AgClO_3$ and $C_6H_{12}N_4$ (each 0.0184 mol dm-3) were mixed to give 20 cm³ total volume. The mixtures were stirred vigorously for 24 hours at 20°C. White crystalline precipitates formed in all mixtures. The total silver in the liquid phase was determined gravimetrically by precipitation as the chloride after decomposing the hexamethylenetetramine with nitric acid.

SOURCE AND PURITY OF MATERIALS:

"Analytical reagent" grade silver chlorate and hexamethylenetetramine were used. Methanol was distilled twice.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.1 K.

EVALUATORS:	
H. Miyamoto Niigata University Niigata, Japan July, 1987	M. Salomon U.S. Army, ET & DL Ft. Monmouth, NJ, USA
	H. Miyamoto Niigata University Niigata, Japan

THE BINARY SYSTEM

Data for the solubility of AgBrO₃ in water have been reported in 36 publications (1-36). Eight publications reported the solubilities in mass units (6, 7, 10, 11, 13, 33-35), and the remaining 28 publications (1-5, 8, 9, 12, 14-32, 36) reported solubilities in mol dm⁻³ units. Table 1 summarizes the experimental solubilities based on mass units, and Table 2 summarizes the solubilities based on mol dm⁻³ units. The solid phase down to at least 278 K is the anhydrous AgBrO₃ (11).

Table 1. Summary of experimental solubilities based on mass units.

T/K	mmol kg ⁻¹	$10^4\chi$	ref
278.2	3.84	0.692	11
298.2	8.062	1.463	7
	8.19	1.475	13
*	8.27	1.490	10
*	8.31	1.497	6
•	8.67	1.562	11
303.2	9.63	1.735	6
H	9.8	1.765	33
H	10.2	1.837	34
**	10.2	1.837	35
308.2	11.41	2.055	6
313.2	13.40	2.413	6
318.2	15.74	2.835	6
323.2	18.3	3.296	6
*	18.36	3.307	11
328.2	21.08	3.796	6
333.2	24.18	4.354	6
338.2	27.48	4.948	6
343.2	31.17	5.612	6
348.2	35.29	6.354	6
353.2	39.70	7.147	6
358.2	44.75°	8.055	6
363.2	56.20a	10.11	6

^{*}Rejected values

The experimental mole fraction (χ) solubilities in Table 1 were fitted to the following smoothing equation

$$Y_{x} = \frac{-25941.73}{T/K} - 117.4041 \ln(T/K) + 688.443 + 0.171916(T/K)$$
 [1]

where

$$Y_{x} = ln \left\langle \frac{\chi^{\nu} (1-\chi)^{r} (\nu+r)^{\nu+r}}{r^{r} (1+\chi)^{\nu+r}} \right\rangle$$
 [2]

All terms in eq. [2] are defined in the PREFACE. The standard error in the function Y_x of eq. [2] is $\sigma_Y = 0.038$, and for the mole fraction solubilities, $\sigma_x = 3.3 \times 10^{-6}$; two data points were rejected on the basis that

COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto Niigata University	M. Salomon US Army, ET & DL
(2) Water; H ₂ O; [7732-18-5]	Niigata, Japan July, 1987	Ft. Monmouth, NJ, USA

Table 2. Summary of experimental solubilities based on mol dm⁻³ units.

T/K	mmol dm-3	references
288.2	6.07	26, 27
293.1	6.31ª	3
293.2	7.28*	16, 18-23, 25-29
297.7	8.10	2
298.2	7.10a	1
Ħ	8.03	30
**	8.09	14
n	8.11	15
	8.12	8
w	8.131	9
#	8.25	17, 24
W	8.26	12
#	8.2668	5
н	8.59a	16, 18-23, 25-29, 31, 32
300.2	7.25ª	4
303.2	10.02ª	16, 18-23, 25-29
308.2	11.62ª	31, 32

^{*}Rejected values

 $(\chi_{\rm obsd} - \chi_{\rm calcd}) > 2\sigma_{\rm x}$. Thus the smoothing equation [1] is based on the remaining 21 data points. Solubilities calculated from eq. [1] are designated as recommended, and values at selected temperatures are given in Table 4.

For the solubilities reported in mol dm⁻³ units, and using the criteria that $c_{obsd} - c_{calcd} \le 2\sigma$, 10 data points were fitted by a relative least squares method to the following empirical smoothing equation:

$$\ln(c_1/\text{mol dm}^{-3}) = -250101.7 + 340886.6/(T/100K) + 231859\ln(T/100K) - 39418.4(T/100K)$$
[3]

where $\sigma_c = 7 \times 10^{-5}$. Solubilities calculated from eq. [3] are designated as tentative, and are also included in Table 4. It should be noted that using the recommended solubility of 0.00831 mol kg⁻¹ at 298.2 K and Owen's density of 0.9987 g cc⁻¹ (8) yields a solubility of 0.00828 mol dm⁻³ which differs from the tentative value in Table 4. For this reason, the mol dm⁻³ solubilities calculated from eq. [3] are designated tentative.

The thermodynamic solubility product has been reported in 9 publications (12, 14, 17, 24, 30, 36, 39-41). All but one are based on mol dm⁻³ units, the exception being (36) where $K_{\rm s0}^{0}$ is based on mol kg⁻¹ units. A summary of the results and methods used to compute the solubility products is given in Table 3. It appears that some authors reported the same value for the solubility product in several publications as indicated in Table 3, and in fitting these data to the empirical smoothing equation below, these data points were treated as singular determinations. Only one data point was rejected from (40, 41) since it is obviously too low. The studies in (40, 41) do not report solubility data, but report solubility products based on e.m.f. measurements in pure water and in aqueous mixtures with 1,4-dioxane, glycerol or urea: these papers have been rejected and therefore not compiled. The remaining 6 data points based on mol dm⁻³ units were fitted to the following smoothing equation:

$$\ln\left(\frac{K_{s0}^{0}}{\text{mol}^{2}\text{dm}^{-6}}\right) = 37.0874 - 97.4716(T/100\text{K}) - 13.0224\ln(T/100\text{K})$$
 [4]

COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto	M. Salomon
(2) Water; H ₂ O; [7732-18-5]	Niigata University Niigata, Japan	US Army, ET & DL Ft. Monmouth, NJ, USA
	July, 1987	- w www, www, w w

From eq. [4], the standard error in K_{s0}^0 , σ_{K} , = 9.0 x 10⁻⁷. The thermodynamic solubility products calculated from eq. [4] are designated as recommended, and values at selected temperatures are given in Table 4.

Table 3. Summary of thermodynamic solubility products in water based on mol dm-3 units

T/K	$10^5 K_{s0}^0$	method ^b	reference
287.9	2.648	Α	39
298.2	2.40ª	D	40, 41
•	5.291	В	14
*	5.358	В	30
W	5.433	Α	39
**	5.5	С	12, 17, 24
308.2	10.14	Α	39

^{*}Rejected value (papers not compiled).

Table 4. Recommended solubilities based on mass units calculated from eq. [1] (columns 2-3)

Tentative mol dm⁻³ solubilities calculated from eq. [3] (column 4)

Recommended solubility products calculated from eq. [4] (column 5)

T/K	$10^4\chi$	mmol kg-1	mmol dm-3	$10^5 K_{s0}^{0}$
278.2	0.693	3.85		
283.2	0.852	4.73		
288.2	1.038	5.76	6.06	2.71
293.2	1.252	6.95	6.37	3.85
298.2	1.497	8.31	8.16	5.39
303.2	1.777	9.86		7.44
308.2	2.093	11.62		10.14
313.2	2.449	13.58		
318.2	2.847	15.81		
323.2	3.292	18.28		
328.2	3.787	21.03		
333.2	4.336	24.08		
338.2	4.943	27.45		
343.2	5.613	31.17		
348.2	6.351	35.28		
353.2	7,163	39.79		

^bMethods A-C all based on calculations of $K_{s0}^0 = [AgBrO_3]^2y_{\pm}^2$.

A: from solubility measurements in LiClO₄ + HClO₄, y_{\pm} calculated from the Debye-Hückel equation In $y_{\pm} = -A I^{1/2}/(1 + B I^{1/2})$.

B: from solubility measurements in the presence of added electrolytes, y_± calculated from the Davies equation.

C: from solubility measurements in the presence of added electrolytes, y_{\pm} calculated as in A above.

D: solubility product calculated from standard e.m.f. values.

COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto	M. Salomon
	Niigata University	US Army, ET & DL
(2) Water; H ₂ O; [7732-18-5]	Niigata, Japan	Ft. Monmouth, NJ, USA
	July, 1987	

MULTICOMPONENT SYSTEMS

Solubility in inorganic systems.

The existing data constitute mainly ternary systems where AgBrO₃ is the only saturating component. The only studies reporting the solubility of AgBrO₃ in the presence of a second saturating component are those of Ricci et al. where the second saturating component is either NaBrO₃ (11) or KBrO₃ (13). For the multicomponent systems in which AgBrO₃ is the only saturating component, insufficient information prevents direct comparisons due to (1) existence of only one study, (2) use of different concentration units, (3) too wide a difference in the concentration of the non-saturating component, and (4) significant differences in results when two independent studies can be compared. For example, the solubility of AgBrO₃ in the presence of KNO₃ has been reported by Dalton et al. (7), Vosburgh and Cogswell (10), and by Keefer et al. (43). The only results which can be compared are those from (7) and (10) which are based on mass units, but as seen in Figure 1 below, the differences between these two studies are large thereby preventing comparisons. We can only point out that for pure water, the solubility of AgBrO₃ (0.008062 mol kg-1) reported in (7) is significantly lower than the recommended value given in Table 4, whereas Vosburgh and Cogswell's value (0.00827 mol kg-1) is almost identical to this recommended value.

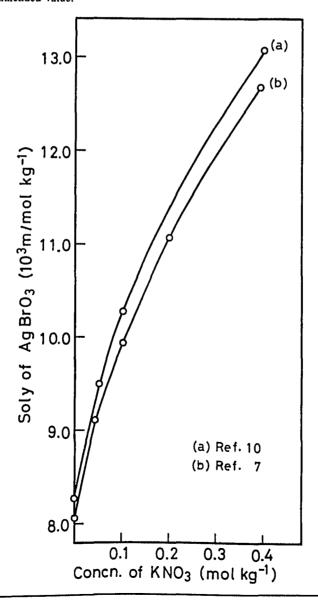


Figure 1.

COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto	M. Salomon
(2) Organic solvents	Niigata University	US Army, ET & DL
(3) Water; H ₂ O; [7732-18-5]	Niigata, Japan	Ft. Monmouth, NJ, USA
_	July, 1987	

Solubility in aqueous-organic mixed solvents.

For T = 298.2 K, there are four major groups of investigators whose results may be compared. In general, when comparisons are made, it is found that there is excellent agreement between the results of Owen (8), Neuman (9), and Davies and Monk (15). The studies by Miyamoto et al. (specific references given below) are consistently higher by up to 20 % than those from (8, 9 and 15), and in arriving at the final smoothed solubilities below, the data of Miyamoto et al. were omitted. The source of these differences can probably be attributed to the experimental method: Miyamoto et al. consistently analyzed the saturated solutions by argentometric titration whereas most other studies used gravimetric, iodometric or radio assay methods. There are two publications by Dash et al. which have been rejected on the basis that no solubility data are reported: these authors used standard half-cell potentials to compute the solubility products of AgBrO3 in water-glycerol (40) and water-urea (41) mixtures. Below, we discuss only those systems where two or more studies are available for comparisons, and the reader is referred to the compilations for solubility data in mixed water-organic solvents which have been published only in one study. In all cases below, we consider solubilities only at 298.2 K based on mol dm-3 units, and the data were fitted by a relative least squares method to a simple power series smoothing equation. For temperatures other than 298.2 K, the compilations for the publications by Miyamoto et al. should be consulted. It is difficult to decide whether the smoothed solubilities given below should be designated as tentative or recommended. The smoothing equations generally predict a solubility in pure water of around 0.0081 to 0.0082 mol dm-3 which is in agreement with the tentative value given in Table 4, but is slightly lower than that calculated from the recommended value of 0.00831 mol kg-1 which correlates to 0.00826 mol dm⁻³ using the density of 0.9987 g cc⁻¹ from (8). In light of this uncertainty, we arrive at the conservative conclusion that the smoothed solubilities given below be designated as tentative values.

(1) Water-methanol mixtures. The 298.2 K solubility data of Miyamoto (28) were rejected, and the remaining 22 data points from (8, 9, 15) were fitted to the following smoothing equation.

```
c_1/\text{mmol dm}^{-3} = 8.086 - 0.31656(100w_2) + 0.0063338(100w_2)^2 - 7.2542 \times 10^{-5}(100w_2)^3 + 3.5555 \times 10^{-7}(100w_2)^4
```

In this equation, $100w_2$ is the content of the organic component in mass %, and the standard error of estimate for the calculated solubilities is $\sigma = 0.02_5$. Note that the solubilities c_1 in this smoothing equation are based on mmol dm⁻³ units, and $100w_2(\text{max}) = 60$ mass %.

(II) Water-ethanol mixtures. The 298.2 K solubility data of Miyamoto and Koizumi (20) were rejected, and the remaining 20 data points from (8, 9, 15) were fitted to the following smoothing equation $(\sigma = 0.042)$

```
c_1/\text{mmol dm}^{-3} = 8.041 - 0.30081(100w_2) + 0.0052252(100w_2)^2 - 3.8209 \times 10^{-5}(100w_2)^3 + 3.1101 \times 10^{-9}(100w_2)^4
```

where $100w_2(max) = 50$ mass %. For solubilities at 293.2 K and 303.2 K, the compilation of (20) should be consulted.

(iii) Water-ethylene glycol mixtures. The 10 data points at 298.2 K from Owen (8) and Davies and Monk (15) were fitted to the following smoothing equation ($\sigma = 0.0086$) where $100w_2(max) = 70$ mass %.

```
c_1/\text{mmol dm}^{-3} = 8.117 - 0.091914(100w_2) + 0.00065184(100w_2)^2 - 3.70002 \times 10^{-6}(100w_2)^3
```

Solubility data at 293.2 K and 303.2 K are given in (29).

(iv) Water-1-propanol mixtures. The 15 data points from (8, 9) were fitted to the following smoothing equation $(\sigma = 0.019)$ where $100w_2(max) = 65$ mass %.

```
c_1/\text{mmol dm}^{-3} = 8.101 - 0.28549(100w_2) + 0.0068782(100w_2)^2 - 1.09640 \times 10^{-4}(100w_2)^3 + 6.9007 \times 10^{-7}(100w_2)^4
```

Solubility data at 293.2 K and 303.2 K are given in (23).

COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto	M. Salomon
(2) Organic solvents	Niigata University	US Army, ET & DL
(3) Water; H ₂ O; [7732-18-5]	Niigata, Japan	Ft. Monmouth, NJ, USA
	Tuly 1087	

(v) Water-2-propanol mixtures. There are two publications reporting the solubility of AgBrO₃ in these mixed solvents at 298.2 K (9, 25), and only the 10 data points of Neuman were used to arrive at the following smoothing equation ($\sigma = 0.010$) where $100w_2(max) = 50$ mass %.

 c_1 /mmol dm⁻³ = 8.176 - 0.35344(100 w_2) + 0.010106(100 w_2)² - 1.7698 x 10⁻⁴(100 w_2)³ + 1.25174 x 10⁻⁶(100 w_2)⁴

(vi) Water-glycerol mixtures. For glycerol contents up to $100w_2(\text{max}) = 80$ mass %, the 12 data points from (8 and 15) were fitted to the following smoothing equation ($\sigma = 0.0064$).

$$c_1/\text{mmol dm}^{-3} = 8.115 - 0.029759(100w_2) - 1.8548 \times 10^{-4}(100w_2)^2 + 5.4939 \times 10^{-6}(100w_2)^3 - 5.9074 \times 10^{-8}(100w_2)^4$$

For solubilities up to 90 mass % glycerol at 293.2 K and 303.2 K, see the compilation of Miyamoto's study (26).

(vii) Water -1,4-dioxane mixtures. The solubility of AgBrO₃ in aqueous mixtures with 1,4-dioxane were reported in (15, 16, 45 and 46). The data of Monk (45) are in mol kg⁻¹ units, and the data of Koizumi and Miyamoto (16) and Davies and Monk (15) are in mol dm⁻³ units, but these data cannot be compared since those in (16) are 10-20 % higher than those in (15). The results of Dash et al. (46) are rejected for several reasons. While Dash et al. obviously measured the solubility of AgBrO₃ in 10, 20 and 40 mass % dioxane solutions, the results are not given in the paper. These authors used the solubility data to compute thermodynamic solubility products, but there is some confusion as to whether or not the reported solubility products are indeed thermodynamic values. The compilers (H. Miyamoto and E.M. Woolley) interpret Dash's solubility product constants. In view of these problems in clarity and the absence of numerical solubility data, this paper (46) is rejected, and a compilation is not given. The paper by Dash et al. (47) was also rejected and not compiled as it reports calculated solubility products based on standard half-cell potentials.

(viii) Water-acetone mixtures. The 10 data points from (8, 15) for $100w_2(max) = 40$ mass % were fitted to the following smoothing equation ($\sigma = 0.086$).

 $c_1/\text{mmol dm}^{-3} = 8.106 - 0.19804(100w_2) - 0.0035492(100w_2)^2 + 2.3152 \times 10^{-4}(100w_2)^3 - 2.8521 \times 10^{-6}(100w_2)^4$

For $100w_2(max) = 56$ mass %, and for temperatures of 293.2 K and 303.2 K, the compilation of the paper by Miyamoto and Koizumi should be consulted.

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COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto	M. Salomon
	Niigata University	US Army, ET & DL
(2) Water; H ₂ O; [7732-18-5]	Niigata, Japan	Ft. Monmouth, NJ, USA
	July, 1987	

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COMPONENTS:	EVALUATORS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	H. Miyamoto Niigata University	M. Salomon US Army, ET & DL
(2) Deuterium oxide (water-d ₂); D ₂ O; [7789-20-0]	Niigata, Japan July, 1987	Ft. Monmouth, NJ, USA

The solubility of $AgBrO_3$ in deuterium oxide has been reported by Ramette et al. in two publications (1, 2). In both publications, the D_2O used was stated to be 99.5 % pure, and small additions of $HClO_4$ were used to surpress hydrolysis (evaluators' note: Ramette et al. are the only researchers to mention the possible hydrolysis of $AgBrO_3$ solutions).

In (1) Ramette and Dratz determined the solubility of AgBrO₃ in deuterium oxide containing 0 to 0.1 mol dm⁻³ LiClO₄ and 0.0001 mol dm⁻³ HClO₄ at 289.9, 298.2, and 308.2 K. Thermodynamic solubility products were calculated using the Debye-Hückel equation. At 298.2 K, these authors reported a solubility of 0.00676 mol dm⁻³ in D₂O containing 0.0001 mol dm⁻³ HClO₄, and a thermodynamic solubility product of $10^{-4.414}$ (i.e. $K_{80} = 3.855 \times 10^{-5}$ mol² dm⁻⁶, evaluators).

In (2) Ramette and Spencer measured the solubility of AgBrO₃ at 298.2 K in 0.0001 mol dm⁻³ HClO₄ solutions containing either LiNO₅ or LiClO₄ up to 0.3 mol dm⁻³. The solubility was reported as 0.00678 mol dm⁻³ in the solvent (i.e. containing 0.0001 mol dm⁻³ HClO₄), and using the Davies equation to calculate activity coefficients, the authors reported a value of $10^{-4.412}$ for the thermodynamic solubility product (i.e. $K_{80} = 3.872 \times 10^{-5} \text{ mol}^2$ dm⁻⁶ in 0.0001 mol dm⁻³ HClO₄ in D₂O).

For 298.2 K in 99.5 % D₂O containing 0.0001 mol dm⁻³ HClO₄, the evaluators computed the following averages which are designated as tentative values.

AgBrO₃ solubility = 0.00677 mol dm⁻³

 $K_{a0} = 3.86 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$

- 1. Ramette, R. W.; Dratz, E. A. J. Phys. Chem. 1963, 67, 940.
- 2. Ramette, R. W.; Spencer, J. B. J. Phys. Chem. 1963, 67, 944.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3]	ORIGINAL MEASUREMENTS: Böttger, W.
(2) Water; H ₂ O; [7732-18-5]	Z. Phys. Chem. 1903, 46, 521-619.
VARIABLES:	PREPARED BY:
T/K = 293.09	H. Miyamoto and E. M. Woolley

The solubility of AgBrO₃ in water at 19.94°C was determined from measurements of the electrolytic conductivities of saturated solutions, $\kappa(\sin)$, and of pure water, $\kappa(\text{water})$. For pure water, $\kappa(\text{water}) = 9.3 \times 10^{-7} \text{ S cm}^{-1}$, and for saturated solutions, the electrolytic conductivities are given in the following table.

equilibration time	κ(sln)		
hours	106S cm-1		
26	665.0		
8	663.8		
11	663.8		
8	664.2		
19	663.5		
	663.3		
average:	663.9		

The solubility S was calculated from the following two equations.

$$\kappa (AgBrO_3) = \kappa(sln) - \kappa(water)$$

$$S = \frac{1000\kappa (AgBrO_3)}{(\lambda^{\infty}(Ag^*) + \lambda^{\infty}(BrO_3^*))}$$

For Ag⁺ and BrO₅, $\lambda \infty = 57.0$ and 48.3 S cm² mol⁻¹, respectively, and the solubility is thus 0.00630₅ mol dm⁻³, and K_{*0} = S² = 3.97 x 10⁻⁵ mol² dm⁻⁶.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Conductivity method. The conductivity cells which employed Pt electrodes was designed to prevent entrapment of air bubbles. After sealing, the entire cell was immersed in a water bath and rotated in the dark. Equilibrium was taken when the conductivity remained constant within experimental error (usually within 20-30 min). The bridge and the thermometer were calibrated, and the cell constants determined with 0.010 mol dm⁻³ KCl solution.

SOURCE AND PURITY OF MATERIALS:

Analytically pure chemicals (Merck) were used.

AgBrO₃ was precipitated from AgNO₃ and KBrO₃

solutions. The ppt was stored in a dark grey bottle in
a dark place. KCl was purified by precipitation from
a saturated solution with alcohol. Laboratory distilled
was was redistilled from a tin-platted still, and stored
in a flask fitted with a drying tube containing NaOH
and CaO.

ESTIMATED ERROR:

κ: accuracy ± 1 x 10-6 S cm⁻¹ (compilers). Soly: precision ± 15 % (compilers). Temp: accuracy ± 0.01 to 0.02 K

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3]	ORIGINAL MEASUREMENTS: Longi, A.
(2) Water; H ₂ O; [7732-18-5]	Gazz. Chim. Ital. 1883, 13, 87-9.
VARIABLES:	PREPARED BY:
T/K = 298	B. Scrosati

The author reported that at 25°C, one g of AgBrO₃ dissolves in 595.1 g water. This is equivalent to 0.00712 mol kg⁻¹ (compiler).

The author also reported that at 25°C, one g AgBrO₃ dissolves in 597.73 cm³ water, and this is equivalent to 0.00710 mol dm⁻³ (compiler).

AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: Nothing specified, but the solubility was probably detd gravimetrically after evaporation to dryness. SOURCE AND PURITY OF MATERIALS: Nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Whitby, G. S.
(2) Water; H ₂ O; [7732-18-5]	Z. Anorg. Chem. 1910, 67, 107-9 and 62-4.
VARIABLES:	PREPARED BY:
T/K = 300	H. Miyamoto and E. M. Woolley

EXPERIMENTAL DATA:

The solubility of AgBrO₃ in water at 27°C was given as 1.71 g dm⁻³. This is equivalent to 0.00725 mol dm⁻³ (compilers).

AUXILIARY IN	FORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Complete details given in the compilation of this author's simultaneous study of the system AgIO ₃ -water.	Nothing specified.
The detection limit of the colorimetric determination of Ag stated to be 4 x 10 ⁻⁵ g Ag dm ⁻³ (see the AgIO-H ₂ O compilation).	

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Reedy, J. H.

J. Am. Chem. Soc. 1921, 43, 1440-5.

VARIABLES:

T/K = 298 - 363

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

	solubility of AgBrO3ª		
t/ºC	g/100 g H ₂ O	103mol kg-1	
2.5	0.406		
25	0.196	8.31	
30	0.227	9.63	
35	0.269	11.41	
40	0.316	13.40	
45	0.371	15.74	
50	0.433	18.36	
55	0.497	21.08	
60	0.570	24.18	
65	0.648	27.48	
70	0.735	31.17	
75	0.832	35.29	
80	0.936	39.70	
85	1.055	44.75	
90	1.325	56.20	

^{*}Molalities calculated by the compiler.

Based on emf measurements, the author reported a solubility of 0.00827 mol dm-3 at 25°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Primary method was standard isothermal method where aliquots of solutions saturated at various temperatures were removed, placed in glass stoppered bottles and weighed. The solubilities were detd iodometrically by adding excess KI, dil HCl, and then titrating with standard thiosulfate solution. The solubility at 25°C was also determined by emf measurements on the cell:

Ag,AgBrO₃(s) | KBrO₃(c), AgBrO₃(satd) \parallel con KNO₃ \parallel AgNO₃(c) | Ag

For c = 0.1 mol dm⁻³, the emf of this cell is 0.1193 V. Assuming KBrO₃ is 82.5 % dissociated and AgBrO₃ is 98 % dissociated, the soly was calcd to be 0.00827 mol dm⁻³.

Four data points for the soly of metastable AgBrO₃ were reported graphically. They show increased soly, as expected, and appear to be associated with a large experimental error.

SOURCE AND PURITY OF MATERIALS:

Technical grade AgBrO₃ prepd by reaction of excess bromine with AgNO₃ solution. The product was purified by extraction with hot water, recrystallized, washed and dried in vacuum. The purity was 99.6 to 100 %, detd gravimetrically. Two crystalline forms of AgBrO₃ were obtained: a metastable "hair form" stable above 98.5°C, and a stable "tetragonal" form stable below 98.5°C.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS: (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Lithium sulfate; Li₂SO₄; [10377-48-7] (3) Water; H₂O; [7732-18-5] VARIABLES: Concentration of lithium sulfate T/K = 298 CORIGINAL MEASUREMENTS: Lel'chuk, Yu. L. Zh. Neorg. Khim. 1958, 3, 2453-7: Russ. J. Inorg. Chem. (Engl. Transl.) 1958, 3, 29-35. PREPARED BY: E. M. Woolley

EXPERIMENTAL DATA:

conen of Li ₂ SO ₄ mol dm ⁻³	soly, S, of AgBrO ₃ mmol dm-3	$10^{5}K_{80} = S^{2}$ mol ² dm ⁻⁶	10⁵K⁰ ₉₀	y _± a
0	8.25	6.80	5.50	0.900
0.001	8.26	6.82	5.43	0.892
0.003	8.54	7.29	5.50	0.869
0.010	9.03	8.15	5.45	0.818
0.030	9.90	9.80	5.37	0.740
0.100	11.5	13.20	5.20	0.628
0.300	14.6	21.30	5.66	0.516
1.000	18.3	33.50	5.50	0.405

*Mean molar activity coefficients y_{\pm} calculated from an unspecified form of the Debye-Hückel equation using an ion size parameter of 2.155 x 10⁻¹⁰ m. Thermodynamic solubility product K^{0}_{s0} calculated from $y_{\pm}{}^{2}K_{s0}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method follows that of ref. (1). AgBrO₃ crystals and Li₂SO₄ solutions were placed in brown bottles. The mixtures were vigorously stirred for 6-8 hours in a thermostat at 25°C. The Ag content of saturated solutions was determined gravimetrically as AgCl, and the bromate concentration determined iodometrically. Samples were prepared in duplicate, and the solubility values in the above table are averages of the four analyses for each specified Li₂SO₄ concentration.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by dropwise addition of 5 % KBrO₃ solution to cold 10 % AgNO₃ solution (1). The precipitate was washed repeatedly, recrystallized, washed with doubly distilled water, air dried and stored in a dark glass jar. Li₂SO₄·H₂O prepared from equivalent amounts of Li₂CO₃ and H₂SO₄.

Doubly distilled water was used to prepare the solutions.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.1 K as in (1).

REFERENCES:

Tananaev, I.V.; Lel'chuk, Yu. L.; Petrovitskaya, B.K.
 Zh. Obshch. Khim. 1949, 19, 1207: J. General
 Chem. USSR (Engl. Transl.) 1949, 19, 1201.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium bromate; NaBrO₃; [7789-38-0]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ricci, J. E.; Aleshnick, J. J.

J. Am. Chem. Soc. 1944, 66, 980-3.

VARIABLES:

Composition

T/K = 278, 298 and 323

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

	NaBrO ₃	content	AgBrO ₃	content	density	nature of the
t/ºC	mass %	mol kg-1a	mass %	mol kg-1a	kg dm-3	solid phases
5	21.41	1.805	~~=		1.192	N
	21.32	1.796			1.190	SSI + AN
			0.0095b	0.000384	0.9998	Α
25	28.26	2,611			1.264	N
	28.26	2.611			1.264	SSI
	28.24	2.608			1.261	SSI
	28.21	2.604			1.262	SSI
	28.16	2.598			1.261	SSI
	28.14	2.595			1.260	SSI
	28.08	2.587			1.260	SSI
	27.97ь	2.573			1.260	SSI + AN
	27.84	2.557			1.257	AN
	27.78	2.549			1.257	AN
	27.66	2.534			1.256	AN
	27.41	2.502			1.252	AN
	27.35	2.495			1.251	AN
	27.05	2.457			1.248	AN
	26.42	2.380			1.241	AN
	25.36	2.252			1.232	AN
	24.32	2.130			1.220	AN
	22.71	1.947			1.203	AN

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ternary complexes were prepared by weight using distilled water, and c.p. grade NaBrO₃ and AgBrO₃. The complexes were stirred for periods of 2 or 8 weeks, and attainment of equilibrium was established in almost all cases by repeated analysis of the solution after further stirring. In the last one or two of the the mixtures at 25°C in the data table (see next page), AgBrO₃ was determined gravimetrically as AgBr after reduction with NaNO2

NaBrO₃ was determined gravimetrically after evaporation of the solution to dryness.

SOURCE AND PURITY OF MATERIALS:

C.p. grade AgBrO₃ and c.p. grade NaBrO₃ were used. The purity of NaBrO₃ was found to be 100 ± 0.1 %, and the purity of the AgBrO₃ was found to be ± 98.2 % silver bromate and 1.8 % sodium bromate.

ESTIMATED ERROR:

Soly: AgBrO₃ precision ± 0.004 mass %. NaBrO₃ precision ± 0.02 mass %. Temp: nothing specified.

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Sodium bromate; NaBrO₃; [7789-38-0]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ricci, J. E.; Aleshnick, J. J.

J. Am. Chem. Soc. 1944, 66, 980-3.

EXPERIMENTAL DATA: (continued......)

	NaBrO ₃	NaBrO ₃ content		AgBrO ₃ content		nature of the
t/ºC	mass %	mol kg-1a	mass %	mol kg-1a	kg dm-3	solid phasec
25	16.99	1.356			1.143	SSII
	13.04	0.994			1.108	SSII
	10.28	0.759			1.079	SSII
	8.39	0.607			1.062	SSII
	7.17	0.512	0.01	0.0004	1.051	SSII
	3.92	0.270	0.03	0.0013	1.025	SSII
			0.204d	0.00867	0.9985	Α
50	35.64	3.670			1.341	N
	35.24	3.606			1.334	SSI + AN
	35.05	3.576			1.334	AN
	34.73	3.526			1.331	AN
	34.57	3.501				AN
	28.77	2.677			1.258	SSII
	23.32	2.015			1.196	SSII
			0.430 ^d	0.0183	0.9934	Α

*Molalities calculated by the compiler.

bAverage of 15 determinations.

cSolid phase designations: $N = NaBrO_3$; $A = AgBrO_3$; SSI is a solid solution containing up to 2.5 to 3.0 mass % $AgBrO_3$, and SSII is a solid solution containing $AgBrO_3$ from 61 to 95 mass.

dThe solubilities of AgBrO₃ in pure water were determined with c.p. grade AgBrO₃ which was repeatedly washed with considerable quantities of water. The purity of about 99.7 % was finally obtained, but the authors stated that great accuracy cannot be claimed for these solubilities.

Average of three determinations.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Lel'chuk, Yu. L.; Surina, L. V.; Barkhatova, V. I.
(2) Sodium nitrate; NaNO ₃ ; [7631-99-4]	Zh. Obshch. Khim. 1955, 25, 1685-93: J. General
(3) Water; H ₂ O; [7732-18-5]	Chem. USSR (Engl. Transl.) 1955, 25, 1641-6.
VARIABLES: Concentration of sodium nitrate	PREPARED BY:
T/K = 298	E. M. Woolley and H. Miyamoto

The solubilities reported below are from the source paper in Zh. Obshch. Khim., but these data were probably originally reported in reference 1 below.

concn of NaNO ₃ mol dm ⁻³	soly, S, of AgBrO ₃ mmol dm-3	$10^{5}K_{*0} = S^{2}$ mol ² dm ⁻⁶	105K° _{s0} a
0.001	8.22	6.76	6.08
0.003	8.51	6.91	5.49
0.010	8.50	7.23	5.41
0.030	9.27	8.59	5.72
0.100	10.08	10.2	5.44
0.300	11.38	13.0	5.09
1.000	14.8	21.9	5.50

aMean molar activity coefficients y_{\pm} calculated from the extended Debye-Hückel equation, and the thermodynamic solubility product K^0_{s0} calculated from $y_{\pm}^2K_{s0}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgBrO₃ crystals and aqueous NaNO₃ solutions were placed in 400-500 cm³ paraffined brown bottles. The mixtures were vigorously stirred for 8 hours in a thermostat at 25°C. Details of the solubility analysis given in ref. (1), and probably involved gravimetric Ag analysis as AgCl, and iodometric bromate analysis.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by dropwise addition of KBrO₃ solution to AgNO₃ solution. Sodium nitrate was recrystallized twice.

Doubly distilled water was used to prepare the solutions.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.1 K.

REFERENCES:

Lel'chuk, Yu. L.; Sasonko, S. M.
 Izv. Tomsk. Politekhn. Inst. 1952, 71, 52.

COMPONENTS: (1) Silver bromat

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Sodium sulfate; Na₂SO₄; [7757-82-6]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Dalton, R. H.; Pomeroy, R.; Weymouth, L. E.

J. Am. Chem. Soc. 1924, 46, 60-4.

VARIABLES: PREPARED BY:

Concentration of sodium sulfate T/K = 298.15

H. Miyamoto

EXPERIMENTAL DATA:

number of experiments	Na ₂ SO ₄ concn mol kg-1	AgBrO ₃ soly mmol kg-1	av deviation %	density kg dm- ³
12	0	8.062a	0.14	0.9990
2	0.05	9.965	0.02	1.0025
4	0.10	10.973	0.17	1.0059
3	1.00	18.619	0.28	1.0622

aThis value in pure water obtained using three separate samples of AgBrO3:

- 1. soly = 8.013 mmol dm-3, average of 5 values with ave deviation of 0.001 mmol dm-3.
- 2. soly = 8.097 mmol dm-3, average of 5 values with ave deviation of 0.003 mmol dm-3.
- 3. soly = 8.097 mmol dm⁻³, average of 2 values with ave deviation of 0.003 mmol dm⁻³.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached by rotating solid AgBrO₃ with Na₂SO₂ solutions in a thermostat at 25.00°C for 15 hours. Equilibrium was always reached from both above and below 25°C, and no significant differences were observed. Saturated solutions were filtered, and about 25°0 cm³ portions weighed to determine densities. To these solutions were added 6 cm³ of 6 mol dm⁻³ and 7 mol dm⁻³ NH₄Br per mol Ag. These solutions were heated to near boiling while air was continuously passed through the solutions. The precipitated AgBr was filtered, washed, dried at 210-220°C, cooled, and weighed.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd by pouring a hot solution of 0.6 mol dm-3 KBrO₃ into an excess of cold 1.3 mol dm-3 solution of AgNO₃. The precipitate was collected on a hardened filter, washed, and dried at (1) 50-60°C or (2) at 105°C. A preparation as in (1) was used to prepare a third solid sample by recrystallizing from boiling water followed by drying at 105°C. Na₂SO₄ was dried, and it's halide content stated to be 0.011 %.

ESTIMATED ERROR:

Soly: see table and footnote a above. Temp: precision ± 0.05 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Lel'chuk, Yu. L.
 (2) Sodium sulfate; Na₂SO₄; [7757-82-6] (3) Water; H₂O; [7732-18-5] 	Zh. Neorg. Khim. 1958, 3, 2453-7: Russ. J. Inorg. Chem. (Engl. Transl.) 1958, 3, 29-35.
VARIABLES:	PREPARED BY:
Concentration of sodium sulfate T/K = 298	E. M. Woolley

conen of Na ₂ SO ₄ mol dm-3	soly, S, of AgBrO ₃ mmol dm ⁻³	$10^{5}K_{s0} = S^{2}$ $mol^{2} dm^{-6}$	10 ⁵ K ⁰ s0	У± ^в
0	8.25	6.80	5.50	0.900
0.001	8.47	7.17	5.66	0.889
0.003	8.78	7.71	5.77	0.865
0.010	9.37	8.78	5.78	0.811
0.030	10.5	11.00	5.81	0.727
0.100	12.3	15.10	5.45	0.601
0.300	16.0	25.50	5.63	0.470
1.000	22.0	48.40	5.50	0.337

*Mean molar activity coefficients y_{\pm} calculated from an unspecified form of the Debye-Hückel equation using an ion size parameter of 1.497 x 10⁻¹⁰ m. Thermodynamic solubility product K^{0}_{s0} calculated from $y_{\pm}^{2}K_{s0}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method follows that of ref. (1). AgBrO₃ crystals and Na₂SO₄ solutions were placed in brown bottles. The mixtures were vigorously stirred for 6-8 hours in a thermostat at 25°C. The Ag content of saturated solutions was determined gravimetrically as AgCl, and the bromate concentration determined iodometrically. Samples were prepared in duplicate, and the solubility values in the above table are averages of the four analyses for each specified Na₂SO₄ concentration.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by dropwise addition of 5 % KBrO₃ solution to cold 10 % AgNO₃ solution (1). The precipitate was washed repeatedly, recrystallized, washed with doubly distilled water, air dried and stored in a dark glass jar. Na₂SO₄ purified by recrystallization two time.

Doubly distilled water was used to prepare the solutions.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.1 K as in (1).

REFERENCES:

Tananaev, I.V.; Lel'chuk, Yu. L.; Petrovitskaya, B.K.
 Zh. Obshch. Khim. 1949, 19, 1207: J. General
 Chem. USSR (Engl. Transl.) 1949, 19, 1201.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Potassium bromate; KBrO ₃ ; [7758-01-2] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Lel'chuk, Yu. L.; Surnina, L. V.; Barkhatova, V. I. Zh. Obshch. Khim. 1955, 25, 1685-93: J. General Chem. 1955, 25, 1641-6.
VARIABLES: Concentration of potassium bromate T/K = 298.2	PREPARED BY: H. Miyamoto and E. M. Woolley

KBrO ₃ concn	AgBrOs	solubility/mmol	dm-3		105Kso*
mol dm-3	exp. 1	exp. 2	exp. 3	mean	mol ² dm ⁻⁶
0	8.244	8.252	8.249	8.25	6.80
0.001	7.25	7.33	7.37	7.32	6.09
0.003	5.29	5.31	5.28	5.29	4.38
0.010	3.98	4.01	3.97	3.99	5.58
0.030	2.48	2.47	2.52	2.49	8.09
0.100	0.975	1.10	1.10	1.06	10.7
0.300	0.700	0.712	0.696	0.703	21.1

a Solubility products calculated from S(S + [KBrO₃]) where S = solubility of AgBrO₃.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Method completely described in the compilation of Lel'chuk's study on the Li₂SO₄-AgBrO₃-H₂O and the NaNO₃-AgBrO₃-H₂O systems.

several days and frequently agitated. The Ag content

detd gravimetrically as AgBr.

SOURCE AND PURITY OF MATERIALS:

KBrO₃ prepd from KOH and Br₂. All other details found in the compilations cited on the left.

ESTIMATED ERROR:

Soly: from above table, precision is about \pm 0.2 % to 1 %.

Temp: precision ± 0.1 K.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Noyes, A. A.
(2) Potassium bromate; KBrO ₃ ; [7758-01-2]	
(3) Water; H ₂ O; [7732-18-5]	Z. Phys. Chem. 1890, 6, 241-67.
VARIABLES:	PREPARED BY:
Concentration of potassium bromate T/K = 297.7	H. Miyamoto
EXPERIMENTAL DATA:	
KBrO ₃ co	onen AgBrO ₃ soly
mmol dn	m-3 mmol dm-3
0	8.10
8.50	5.19
34.6	2.27
AU	XILIARY INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Excess AgBrO ₃ in aq KBrO ₃ thermostated at	t 24.5% for intenting specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Dalton, R. H.; Pomeroy, R.; Weymouth, L. E.
(2) Potassium nitrate; KNO ₃ ; [7757-79-1]	J. Am. Chem. Soc. 1924, 46, 60-4.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of potassium nitrate T/K = 298.15	H. Miyamoto

number of experiments	KNO ₃ concn mol kg-1	AgBrO ₃ soly mmol kg-1	av deviation %
12	0	8.062a	0.14
2	0.040	9.12	0.12
3	0.100	9.12	0.29
3	0.200	11.06	0.04
3	0.393	12.66	0.18

aThis value in pure water obtained using three separate samples of AgBrO3:

- 1. soly = 8.013 mmol dm-3, average of 5 values with ave deviation of 0.001 mmol dm-3.
- 2. soly = 8.097 mmol dm⁻³, average of 5 values with ave deviation of 0.003 mmol dm⁻³.
- 3. soly = 8.097 mmol dm⁻³, average of 2 values with ave deviation of 0.003 mmol dm⁻³.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached by rotating solid AgBrO₃ with KNO₃ solutions in a thermostat at 25.00°C for 15 hours. Equilibrium was always reached from both above and below 25°C, and no significant differences were observed. Saturated solutions were analyzed by precipitating the silver as AgCl, collecting the precipitate on an asbestos filter followed by drying in an oven and weighing.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd by pouring a hot solution of 0.6 mol dm⁻³ KBrO₃ into an excess of cold 1.3 mol dm⁻³ solution of AgNO₃. The precipitate was collected on a hardened filter, washed, and dried at (1) 50-60°C or (2) at 105°C. A preparation as in (1) was used to prepare a third solid sample by recrystallizing from boiling water followed by drying at 105°C. Source and purity of potassium nitrate not specified.

ESTIMATED ERROR:

Soly: see table and footnote a above. Temp: precision \pm 0.05 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Vosburgh, W.C.; Cogswell, S.A.
(2) Potassium nitrate; KNO ₃ ; [7757-79-1]	J. Am. Chem. Soc. 1943, 65, 2412-3.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of potassium nitrate T/K = 298.15	H. Miyamoto

The solubility, S, of AgBrO₃ in KNO₃ solutions is given in the table below.

KNO ₃ concn	103S	
mol kg-1	mol kg-1	105K0 _{s0}
0	8.27	5.61
0.0477	9.49	5.59
0.1002	10.27	5.50
0.401	13.04	5.62

The solubility product of silver bromate was calculated from the following two equations where I is the ionic strength, and y_{\pm} is the mean molal activity coefficient.

$$K_{00}^{0} = S^{2} \gamma_{+}^{2}$$

$$-\log y_{\perp} = \frac{0.5056\sqrt{I}}{\left(1+\sqrt{I}\right)} + 0.104\sqrt{I}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The procedure was as follows (1). KNO₃ solutions were saturated with AgBrO₃ in Pyrex flasks immersed in a water bath at 25.00°C, and avoiding diffused daylight or artificial light. Samples for analyses were taken after 3-4 h, and again two or more h later to for constancy in concentrations. The aliquots were removed with a pipet to which was attached a filter either of Pyrex glass wool or Pyrex fritted glass.

Aliquots were weighed and the iodate content determined iodometrically with 0.01 mol dm⁻³ thiosulfate solution. Ammonium molybdate was used as a catalyst.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by slow precipitation from solutions of AgNO₃ and KBrO₃. Analysis for silver gave 45.70 % (calculated is 45.75 %). Potassium nitrate was of analytical reagent grade.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.05 K.

REFERENCES:

 Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. J. Am. Chem. Soc. <u>1941</u>, 63, 2670.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Ricci, J.E.; Offenbach, J.A.
(2) Potassium bromate; KBrO ₃ ; [7758-01-2]	J. Am. Chem. Soc. 1951, 73, 1597-9.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Composition T/K = 298	H. Miyamoto and M. Salomon

Composition of saturated solutions at 25°C a,b

KBrO ₃	KBrO ₃	AgBrO ₃	AgBrO ₃	density	nature of the
mass %	mol %ª	mass %	mol %ª	g cm-3	solid phaseb
0	0	0.193	0.01477*	0.9983	AgBrO ₃
3.21		not given	not given	1.022	#
5.70		*	H	1.049	H
7.03		**	**	1.050	H
7.52				1.054	AgBrO ₃ + KBrO ₃
7.57			н	1.052	H
7.56		n	н	1.053	H
7.55		*	н	1.054	Ħ
7.52ª	0.8696	0	0	1.053	KBrO ₃

^aMass % solubilities calculated by the compilers. In pure water, the compilers calculate a solubility of 0.008202 mol kg⁻¹ for AgBrO₃ and 0.4869 mol kg⁻¹ for NaBrO₃ at 25°C.

bThe authors state that the solubility of AgBrO₃ is neglibible, within experimental error, in the presence of potassium bromate.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Ternary mixtures of known composition were allowed to equilibrate at 25°C for two weeks with stirring. The solutions were analyzed for KBrO₃ simply by evaporation to dryness since the solubility of AgBrO₃ in the presence of KBrO₃ is negligible. Method for the determination of AgBrO₃ in pure water not given, but it probably involved titration with KSCN (the Volhard method).

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ was prepared by mixing dilute solutions of bromic acid and Ag₂CO₃ in the presence of HNO₃. After some heating and digestion, the solid was washed with water and dried at 110°C. Two batches analyzed for Br gave 99.93 and 99.75 % AgBrO₃ purity. Ag₂CO₃ prepd by addn of Na₂CO₃ to an excess of aqueous AgNO₃ solution. Bromic acid sln prepd from dil H₂SO₄ and solid Ba(BrO₃)₂·H₂O. KBrO₃ was 99.97 % pure.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision probably better than \pm 0.1 K (compilers).

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Potassium sulfate; K ₂ SO ₄ ; [7778-80-5] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E. J. Am. Chem. Soc. 1924, 46, 60-4.
VARIABLES: Concentration of potassium sulfate T/K = 298.15	PREPARED BY: H. Miyamoto

number of experiments	K ₂ SO ₄ concn mol kg ⁻¹	AgBrO ₃ soly mmol kg-1	av deviation %	density kg dm ⁻³
12	0	8.062	0.14	0.9990
6	0.025	9.292	0.18	1.0009
6	0.05	10.015	0.10	1.0028
3	0.10	11.092	0.05	1.0062

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Complete details given in the compilation of the paper by Dalton et al. on the analogous Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

K₂SO₄ of unknown origin was tested for halide (negative) and used as received. Other details given in the compilation cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Lel'chuk, Yu. L.
 (2) Potassium sulfate; K₂SO₄; [7778-80-5] (3) Water; H₂O; [7732-18-5] 	Zh. Neorg. Khim. 1958, 3, 2453-7: Russ. J. Inorg. Chem. (Engl. Transl.) 1958, 3, 29-35.
VARIABLES: Concentration of potassium sulfate T/K = 298.15	PREPARED BY: E. M. Woolley

EXPERIMENTAL DATA:

K ₂ SO ₄ conen mol dm-3	AgBrO ₃ soly (S) mmol dm ⁻³	$10^{5}K_{s0} = S^{2}$ mol ² dm ⁻⁶	105K0*0	ya
0	8.25	6.80	5.50	0.990
0.001	8.45	7.14	5.61	0.887
0.003	8.65	7.48	5.55	0.862
0.010	9.42	8.87	5.72	0.804
0.030	10.61	11.26	5.74	0.714
0.100	13.05	17.03	5.57	0.572
0.300	17.62	31.04	5.50	0.421

 8 K 0 8 O calculated from S 2 y 2 where y is the activity coefficient calculated from an unspecified form of the Debye-Hückel equation using an ion size parameter of 0.910 x 10⁻¹⁰ m.

AUXILIARY INFORMATION

Duplicate samples analyzed for both silver and for bromate: i.e. each solubility value in the above table is
bromate: i.e. each solubility value in the above table is
the average of four analyses as described in the
compilation of Lel'chuk's study of the analogous

METHOD/APPARATUS/PROCEDURE:

Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

 K_2SO_4 prepd from equivalent amounts of K_2CO_3 and H_2SO_2 . All remaining information given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Potassium perchlorate; KClO ₄ ; [7778-74-7] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E. J. Am. Chem. Soc. 1924, 46, 60-4.
VARIABLES: Concentration of potassium perchlorate T/K = 298.15	PREPARED BY: H. Miyamoto

number of experiments	KClO ₄ concn mol kg-1	AgBrO ₃ soly mmol kg-1	av deviation %	density kg dm- ³
12	0	8.062	0.14	0.9990
3	0.025	8.716	0.03	1.0010
2	0.05	9.190	0.03	1.0033
5	0.10	9.706	0.02	1.0074

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Complete details given in the compilation of the paper by Dalton et al. on the Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

C.p. grade KClO₄ was recrystallized and dried at 100-110°C for several hours. Other details given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Magnesium nitrate; Mg(NO ₃) ₂ ; [10377-60-3] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Tananaev, I.V.; Lel'chuk, Yu. L.; Petrovitskaya, B.K. Zh. Obshch. Khim. 1949, 19, 1207-15: J. Gen. Chem. USSR (Engl. Transl.) 1949, 19, 1201-9.
VARIABLES: Concentration of magnesium nitrate T/K = 298.2	PREPARED BY: E. M. Woolley

EXPERIMENTAL DATA:

Mg(NO ₃) ₂ concn mol dm- ³	AgBrO ₃ soly (S) mmol dm-3	$10^{5}K_{s0} = S^{2}$ mol ² dm ⁻⁶	10 ⁵ K ⁰ s0	y_{\pm}^{b}
0	8.26ª	6.83	5.50	0.990
0.001	8.56	7.33	5.82	0.981
0.003	8.72	7.60	5.75	0.870
0.01	9.28	8.61	5.78	0.820
0.03	9.81	9.62	5.36	0.746
0.1	11.1	12.3	4.95	0.634
0.3	12.7	16.1	4.56	0.532
1.0	17.3	30.0	5.5	0.428

^{*}The average soly in pure water was also given as 0.1948 g 100 cm³.

 $log y_{\pm} = -0.505I^{1/2}/(1 + 0.33 \times 2.4I^{1/2})$ and $I = 3[Mg(NO_3)_2] + S$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Each solubility value in the above table is the average of four analyses (from two separate experiments) as described in the compilation of Lel'chuk's study of the Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Mg(NO₃)₂ recrystallized twice. All remaining information given in the compilation cited on the left.

 $^{{}^{}b}K^{0}_{s0}$ calculated from $S^{2}y_{\pm}^{2}$ where

COMPONENTS:	ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E. J. Am. Chem. Soc. 1924, 46, 60-4.				
(1) Silver bromate; AgBrO₃; [7783-89-3](2) Magnesium nitrate; Mg(NO₃)₂; [10377-60-3]					
				(3) Water; H ₂ O; [7732	-18-5]
VARIABLES: Concentration of mag T/K = 298.15	nesium nitrate	····	PREPARI H. Miya		
EXPERIMENTAL DA	TA:				
number of	Mg(NO ₃) ₂ concn	AgBr	O ₃ soly	av deviation	density
experiments	mol kg-1	mmo	ol kg-1	%	kg dm ⁻³
12	0	8.06	52	0.14	0.9990
6	0.025	8.93	35	0.25	1.0003
3	0.05	9.41	14	0.05	1.0018
8	0.10	10.09	90	0.12	1.0046
	AUXII	LIARY IN	FORMAT	ION	
METHOD/APPARATUS/PROCEDURE:			SOURCE AND PURITY OF MATERIALS:		
Complete details given in the compilation of the paper			Mg(NO ₃) ₂ prepd by adding HNO ₃ to MgCO ₃ sln to		

by Dalton et al. on the Na₂SO₄-AgBrO₃-H₂O system.

neutralization. Mg analyzed as Mg₂P₂O₇.

Other details given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Magnesium sulfate; MgSO ₄ ; [7487-88-9]			ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E. J. Am. Chem. Soc. 1924, 46, 60-4.							
						(3) Water; H ₂ O; [7732-	18-5]			
						VARIABLES: Concentration of magn	nesium sulfate		PREPAR	ED BY:
T/K = 298.15			H. Miyamoto							
EXPERIMENTAL DA	TA:									
number of	MgSO ₄ concn	AgBr	O ₃ soly	av deviation						
experiments	mol kg-1	mmo	ol kg-1	%						
12	0	8.06	62	0.14						
2	0.0200	8.92	2	0.12						
3	0.0510	9.67	7	0.12						
4	0.1000	10.3		0.13						
4	0.1988	11.3	8	0.13						
	AUXI	LIARY IN	NFORMAT	TION						
METHOD/APPARATUS/PROCEDURE:			SOURCE	AND PURITY OF MATERIALS:						
Complete details given in the compilation of the paper by Dalton et al. on the KNO ₃ -AgBrO ₃ -H ₂ O system.			J	nd purity of MgSO ₄ not specified. Remaining ven in the compilation cited on the left.						

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Calcium nitrate; Ca(NO ₃) ₂ ; [10124-37-5] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Tananaev, I.V.; Lel'chuk, Yu. L.; Petrovitskaya, B.K. Zh. Obshch. Khim. 1949, 19, 1207-15: J. Gen. Chem. USSR (Engl. Transl.) 1949, 19, 1201-9.
VARIABLES: Concentration of calcium nitrate T/K = 298.2	PREPARED BY: E. M. Woolley and H. Miyamoto

EXPERIMENTAL DA	TA:				
Ca(NO ₃) ₂ concn mol dm ⁻³	AgBrO ₃ soly (S) mmol dm-3	$10^{5}K_{s0} = S^{2}$ $mol^{2} dm^{-6}$	105K0 _{s0}	y _± b	
0	8.26ª	6.83	5.50	0.990	
0.001	7.91	6.26	4.99	0.893	
0.003	8.07	6.51	4.93	0.870	
0.01	9.15	8.36	5.58	0.818	
0.03	9.88	9.74	5.35	0.741	
0.1	11.1	12.3	4.88	0.630	
0.3	13.3	17.7	4.77	0.519	
1.0	18.1	32.8	5.50	0.410	

aThe average soly in pure water was also given as 0.1948 g 100 cm3.

 $log y_{\pm} = -0.505I^{1/2}/(1 + 0.33 \times 2.19I^{1/2})$ and $I = 3[Ca(NO_3)_2] + S$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Each solubility value in the above table is the average of four analyses (from two separate experiments) as described in the compilation of Lel'chuk's study of the Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Source and purity of Ca(NO₃)₂ not given. All remaining information given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Strontium nitrate; Sr(NO ₃) ₂ ; [10042-76-9] (3) Water; H ₂ O; [7732-18-5]		Tananaev Zh. Obsh	ORIGINAL MEASUREMENTS: Tananaev, I.V.; Lel'chuk, Yu. L.; Petrovitskaya, B.K. Zh. Obshch. Khim. 1949, 19, 1207-15: J. Gen. Chem. USSR (Engl. Transl.) 1949, 19, 1201-9. PREPARED BY: E. M. Woolley and H. Miyamoto		
VARIABLES: Concentration of stror T/K = 298.2					
EXPERIMENTAL DA	TA:				
Sr(NO ₃) ₂ concn	AgBrO ₃ soly (S)	$10^5 \mathrm{K}_{*0} = \mathrm{S}^2$			
mol dm-3	mmol dm-3	mol ² dm ⁻⁶	10^{5} K $_{0}^{*0}$	У± ^а	
0	8.26	6.83	5.50	0.990	
0.001	8.40	7.06	5.60	0.890	

Sr(NO ₃) ₂ concn	Agbros soly (2)	$10 \text{ eV}^{10} = 2 \text{ s}$		
mol dm-3	mmol dm-3	mol ² dm ⁻⁶	105K0*0	У±а
0	8.26	6.83	5.50	0.990
0.001	8.40	7.06	5.60	0.890
0.003	8.59	7.38	5.55	0.867
0.01	8.96	8.03	5.34	0.815
0.03	10.0	10.0	5.41	0.736
0.1	12.2	14.9	5.45	0.605
0.3	14.3	20.4	5.10	0.500
1.0	19.4	37.6	5.50	0.382

*K0,0 calculated from S2y±2 where

 $log y_{\pm} = -0.505I^{1/2}/(1 + 0.33 \times 1.92I^{1/2})$ and $I = 3[Sr(NO_3)_2] + S$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Each solubility value in the above table is the average of four analyses (from two separate experiments) as described in the compilation of Lel'chuk's study of the Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Source and purity of Sr(NO₃)₂ not given. All remaining information given in the compilation cited on the left.

 $^{{}^{}b}K^{0}_{s0}$ calculated from $S^{2}y_{\pm}^{2}$ where

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Barium nitrate; Ba(NO ₃) ₂ ; [10022-31-8] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E. J. Am. Chem. Soc. 1924, 46, 60-4.
VARIABLES: Concentration of barium nitrate T/K = 298.15	PREPARED BY: H. Miyamoto

number of experiments	Ba(NO ₃) ₂ concn mol kg ⁻¹	AgBrO ₃ soly mmol kg-1	av deviation %	density kg dm- ³
12	0	8.062	0.14	0.9990
2	0.025	9.088	0.04	1.0018
2	0.05	9.655	0.00	1.0046
4	0.10	10.373	0.18	1.0098

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Complete details given in the compilation of the paper by Dalton et al. on the Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Ba(NO₃)₂ of unknown source dried to 100-110°C to const mass. AgNO₃ test for halides was negative.

Other details given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Barium nitrate; Ba(NO ₃) ₂ ; [10022-31-8] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Tananaev, I.V.; Lel'chuk, Yu. L.; Petrovitskaya, B.K. Zh. Obshch. Khim. 1949, 19, 1207-15: J. Gen. Chem. USSR (Engl. Transl.) 1949, 19, 1201-9.
VARIABLES: Concentration of barium nitrate T/K = 298.2	PREPARED BY: E. M. Woolley

EXPERIMENTAL DATA:

Ba(NO ₃) ₂ concn mol dm-3	AgBrO ₃ soly (S) mmol dm-3	$10^{5}K_{s0} = S^{2}$ mol ² dm ⁻⁶	102K0°0	у±р	
0	8.26*	6.83	5.50	0.990	
0.001	8.24	6.78	5.38	0.891	
0.003	8.39	7.04	5.30	0.868	
0.01	8.94	8.00	5.31	0.816	
0.03	9.91	9.82	5.31	0.736	
0.1	12.2°	14.8d	5.67	0.619	
0.3	14.9	22.2d	5.50	0.498	

aThe average soly in pure water was also given as 0.1948 g 100 cm³.

 $log y_{\pm} = -0.505I^{1/2}/(1 + 0.33 \times 1.91I^{1/2})$ and $I = 3[Ba(NO_3)_2] + S$

cThere is an apparent misprint for this solubility in the original article.

dThere are misprints of these values near the beginning of the article which, near the end, were given as these correct values.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Each solubility value in the above table is the average of four analyses (from two separate experiments) as described in the compilation of Lel'chuk's study of the Na₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Source and purity of Ba(NO₃)₂ not given. All remaining information given in the compilation cited on the left.

bK0_{s0} calculated from S2y±2 where

COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Noyes, A. A.		
(2) Silver nitrate; AgNO ₃ ; [7761-88-8]			
(3) Water; H ₂ O; [7732-18-5]	Z. Phys. Chem. 1890, 6, 241-67.		
VARIABLES:	PREPARED BY:		
Concentration of silver nitrate T/K = 297.7	E. M. Woolley and H. Miyamoto		
EXPERIMENTAL DATA:			
AgNO ₃ concn	AgBrO ₃ soly		
mmol dm-3	mmol dm-3		
0	8.10		
8.50	5.10		
34.6	2.16		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Excess AgBrO ₃ in aq AgNO ₃ slns thermostated at			
24.5°C with frequent agitation for several days. Solubility determined by iodometric titrn.	Nothing specified.		
	ESTIMATED ERROR:		
	Nothing specified.		

 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Cadmium nitrate; Cd(NO₃)₂; [10325-94-7] (3) Water; H₂O; [7732-18-5] VARIABLES: Concentration of cadmium nitrate T/K = 298 		Lel'chuk, Yu. L. Zh. Obshch. Khim. 1955, 25, 1273-7: J. Gen. Chem USSR (Engl. Transl.) 1955, 25, 1219-22.		
		PREPARED BY: E. M. Woolley and H. Miyamoto		
EXPERIMENTA	AL DATA:			
concn of Cd(NO ₃) ₂ mol dm ⁻³	soly, S, of AgBrO ₃ mmol dm ⁻³	$10^{5}K_{s0} = S^{2}$ $mol^{2} dm^{-6}$	105K°a∩	У+в
0	8.25	6.80	5.50	0.900
0.001	8.13	6.61	5.26	0.892
0.003	8,42	7.09	5.37	0.870
0.010	8.75	7.66	5.16	0.820
0.030	9.10	8.28	4.60	0.746
0.100	10.4	10.8	4.38	0.637
0.300	13.2	17.4	4.89	0.530
1.000	17.4	30.3	5.50	0.426

parameter of 2.385 x 10^{-10} m. Thermodynamic solubility product K_{00}^0 calculated from $y_{\pm}^2 K_{00}$.

METHOD/APPARATUS/PROCEDURE: Ag detd gravimetrically as AgCl. Other details identical to those given in the compilation of the paper by Lel'chuk et al. for the AgBrO₃-NaNO₃-H₂O system. SOURCE AND PURITY OF MATERIALS: C.p. grade Cd(NO₃)₂ used (nothing else specified). For details on prepn of AgBrO₃, see the compilation cited on the left. ESTIMATED ERROR: Soly: nothing specified.

Temp: precision ± 1 K.

AUXILIARY INFORMATION

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Cadmium sulfate; CdSO ₄ ; [10124-36-4] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E. J. Am. Chem. Soc. 1924, 46, 60-4.
VARIABLES: Concentration of cadmium sulfate T/K = 298.15	PREPARED BY: H. Miyamoto

number of experiments	CdSO ₄ concn mol kg-1	AgBrO ₃ soly mmol kg-1	av deviation %	density kg dm-3
12	0	8.062	0.14	0.9990
2	0.10	10.405	0.05	1.0017.
1	0.50	13.349		1.0492

AUXILIARY INFORMATION

SOURCE AND PURITY OF MATERIALS:

Complete details given in the compilation of the paper by Dalton et al. on the analogous Na₂SO₄-AgBrO₃-H₂O system.

C.p. grade 3CdSO₄·8H₂O crystals treated with a little H₂SO₄ and ignited to 350-400°C. Other details given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3]	ORIGINAL MEASUREMENTS: Lel'chuk, Yu. L.; Skripova, L.L.; Chashchina, O.V.	
(2) Cadmium sulfate; CdSO ₄ ; [10124-36-4] (3) Water; H ₂ O; [7732-18-5]	Zh. Neorg. Khim. 1961, 6, 474-75: Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 239-41.	
VARIABLES: Concentration of cadmium sulfate T/K = 298.15	PREPARED BY: E. M. Woolley	

EXPERIMENTAL DATA:

CdSO ₄ concn mol dm ⁻³	AgBrO ₃ soly (S) mmol dm-3	$10^{5}K_{s0} = S^{2}$ mol ² dm ⁻⁶	105K0,0	ya.
0.001	8.17	6.67	5.28	0.890
0.003	8.43	7.11	5.30	0.863
0.010	8.85	7.83	5.09	0.806
0.030	9.74	9.49	5.03	0.728
0.100	10.8	11.70	4.52	0.621
0.300	13.3	17.70	4.83	0.523
1.000	17.2	29.69	5.50	0.431

 8 K 0 so calculated from S 2 y 2 where y is the activity coefficient calculated from the Debye-Hückel equation using an ion size parameter of 2.608 x $^{10^{-10}}$ m.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

Duplicate samples analyzed for both silver and for bromate: i.e. each solubility value in the above table is the average of four analyses as described in the compilation of Lel'chuk's study of the analogous Na₂SO₄-AgBrO₃-H₂O system.

CdSO₄ slns prepd by diluting 1 mol dm-3 CdSO₂ slns with double dist water. All remaining information given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₅ ; [7783-89-3] (2) Zinc nitrate; Zn(NO ₅) ₂ ; [7792-88-6] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Lel'chuk, Yu. L. Zh. Obshch. Khim. <u>1955</u> , 25, 1273-7: J. Gen. Chem. USSR (Engl. Transl.) <u>1955</u> , 25, 1219-22.
VARIABLES: Concentration of zinc nitrate T/K = 298	PREPARED BY: E. M. Woolley and H. Miyamoto

IPVDFD	IMENTAL.	DATA.

Zn(NO ₃) ₂ concn	AgBrO ₃ soly (S)	$10^5 K_{s0} = S^2$	_	
mol dm-3	mmol dm-3	mol ² dm ⁻⁶	105K0*0	У±а
0	8.25	6.80	5.50	0.990
0.001	8.43	7.11	5.63	0.890
0.003	8.75	7.65	5.75	0.867
0.001	9.12	8.32	5.52	0.815
0.030	10.2	10.4	5.64	0.737
0.100	11.6	13.4	5.13	0.619
0.300	14.7	21.6	5.44	0.502
1.000	19.3	37.2	5.50	0.384

 a K 0 _{a0} calculated from S 2 y 2 where activity coefficients y calculated from extended Debye-Hückel equation using an ion size parameter of 1.94 x 10⁻¹⁰ m.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag content of satd sins detd gravimetrically as AgCl. Other details same as in the compilation of Lel'chuk's study of the Li₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Source and purity of Zn(NO₃)₂·6H₂O not given. All remaining information given in the compilation cited on the left.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 1 K.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Zinc sulfate; ZnSO ₄ ; [7446-20-0] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Lel'chuk, Yu. L.; Skripova, L.L.; Chashchina, O.V. Zh. Neorg. Khim. 1961, 6, 474-5: Russ. J. Inorg. Chem. (Engl. Transl.) 1961, 6, 239-41.
VARIABLES: Concentration of zinc sulfate	PREPARED BY:

EXPERIMENTAL DATA:

ZnSO ₄ concn	AgBrO ₃ soly (S)	$10^5 K_{s0} = S^2$		
mol dm-3	mmol dm-3	mol ² dm ⁻⁶	105K0 ₂₀	У±а
0.001	8.22	6.76	5.34	0.889
0.003	8.51	7.24	5.37	0.862
0.01	8.88	7.88	5.12	0.806
0.03	9.88	9.76	5.14	0.726
0.1	11.3	12.80	4.89	0.618
0.3	14.0	19.60	5.23	0.517
1.0	17.5	30.62	5.50	0.424

 8 K 0 80 calculated from S 2 y 2 where activity coefficients y calculated from extended Debye-Hückel equation using an ion size parameter of 2.593 x 10⁻¹⁰ m.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Each solubility value in the above table is the average of four analyses (from two separate experiments) as described in the compilation of Lel'chuk's study of the Li₂SO₄-AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

ZnSO₄ slns prepd by diluting a 1 mol dm-3 sln of ZnSO₄·7H₂O with doubly dist water. All remaining information given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Cerium nitrate; Ce(NO ₃) ₃ ; [10108-73-3]		ORIGINAL MEASUREMENTS: Dalton, R. H.; Pomeroy, R.; Weymouth, L. E.
(3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1924, 46, 60-4.
VARIABLES: Concentration of cerium nitrate T/K = 298.15	/	PREPARED BY: H. Miyamoto

Na₂SO₄-AgBrO₃-H₂O.

number of experiments	Ce(NO ₃) ₃ concn mol kg-1	AgBrO ₃ soly mmol kg-1	av deviation %	density kg dm-3
12	0	8.062	0.14	0.9990
2	0.0125	8.888	0.14	1.0002
2	0.025	9.336	0.22	1.0014

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Complete experimental details given in the compilation	A "domestic" Ce(NO ₃) ₃ hydrate was used. Other details
of the paper by these authors on the system	on materials given in the compilation cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Longi, A.
(2) Nitric acid; HNO ₃ ; [7697-37-2]	
(3) Water; H ₂ O; [7732-18-5]	Gazz. Chim. Ital. <u>1883</u> , 13, 87-9.
VARIABLES:	PREPARED BY:
T/K = 298	B. Scrosati

EXPERIMENTAL DATA:

The solubility of AgBrO₃ in a solution of 35 mass % HNO₃ (specific gravity 1.21) is one gram of AgBrO₃ in 262.83 cm³ of solution. This is equivalent to 0.0161 mol dm⁻³ (compiler).

The solubility was given as one gram of AgBrO₃ in 320.36 g solvent. This is equivalent to 0.0132 mol per kg of solvent: i.e. per kg of 35 mass % HNO₃ (compiler).

AUXILIARY IN	FORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Nothing specified, but the solubility was probably detd gravimetrically after evaporation to dryness.	Nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Lel'chuk, Yu. L.
(2) Sulfuric acid; H ₂ SO ₄ ; [7664-93-9]	Zh. Neorg. Khim. 1958, 3, 2453-7: Russ. J. Inorg.
(3) Water; H ₂ O; [7732-18-5]	Chem. (Engl. Transl.) 1958, 3, 29-35.
VARIABLES: Concentration of sulfuric acid T/K = 298.2	PREPARED BY: E. M. Woolley

H ₂ SO ₄ concn	AgBrO ₃ soly (S)	$10^5 \mathrm{K}_{s0} = \mathrm{S}^2$		
mol dm-3	mmol dm-3	mol ² dm- ⁶	102Ko*0	уa
0	8.25	6.80	5.50	0.990
0.001	8.34	6.955	5.67	0.903
0.003	8.44	7.12	5.57	0.885
0.010	8.585	7.37	5.30	0.848
0.030	9.073	8.23	5.23	0.797
0.100	9.806	9.62	5.17	0.733
0.300	10.75	11.56	5.33	0.678
1.000	11.76	13.83	5.50	0.631

 $^{{}^{}a}K^{0}{}_{a0}$ calculated from S²y² where y is the activity coefficient calculated from an unspecified form of the Debye-Hückel equation using an ion size parameter of 5.906 x 10⁻¹⁰ m.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Duplicate samples analyzed for both silver and for

bromate: i.e. each solubility value in the above table is the average of four analyses as described in the compilation of Lel'chuk's study of the analogous Li₂SO₄-AgBrO₃-H₂O system.

Complete details given in the compilation of the paper

by Ramette and Spencer on the LiClO₄-HClO₄-

AgBrO₃-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Technical grade H_2SO_4 dist from dichromate. A 1 mol dm-3 acid sln used in dilutions with doubly dist water. All remaining information given in the compilation cited on the left.

See compilation cited on the left for complete details.

ESTIMATED ERROR: Nothing specified.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Perchloric acid; HClO ₄ ; [7601-90-3] (3) Water; H ₂ O; [7732-18-5]		ORIGINAL MEASUREMENTS: Ramette, R. W.; Spencer, J. B. J. Phys. Chem. 1963, 67, 944-6.	
VARIABLES: Concentration of perchloric acid T/K = 298		PREPARED BY: H. Miyamoto	
EXPERIMENTAL DATA:			
	HClO ₄ concn	AgBrO ₃ soly	
mol kg-1		mmol kg-1	
	0	8.03	
	0.02	8.54	
	0.05	8.95	
	0.10	9.37	
	0.15	9.61	
	0.20	9.79	
	AUXILIAR	Y INFORMATION	
METHOD/APPARATUS/PROCE	DURE:	SOURCE AND PURITY OF MATERIALS:	

COMPONENTS: (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Acetic acid; C₂H₄O₂; [64-19-7] (3) Water; H₂O; [7732-18-5] VARIABLES: T/K = 298.15 ORIGINAL MEASUREMENTS: Hill, A. E. FREPARED BY: H. Miyamoto

EXPERIMENTAL DATA:

acetic acid concn	AgBrO ₃ soly		av solubility	av solubility.
mol dm-3	g/50.13 cm-3	methoda	g dm-3	mmol dm-3
0.0	0.0979	U		
	0.0977	S		
	0.0977	U		
	0.0976	S	1.9493	8.2668
0.0498	0.0975	U		
	0.0973	S	1.9429	8.2398
0.0997	0.0973	U		
	0.0970	S	1.9379	8.2187
0.1995	0.09625	U		
	0.0963	S	1.9206	8.1451
0.4988	0.09346	U		
	0.0934	S	1.863	7.9041
0.9975	0.0904	U		
	0.0902	S	1.8013	7.6392
1.8721	0.0804	U		
	0.0818	S	1.6178	6.8608

^a U: equilibrium approached from undersaturation. S: equilibrium approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgBrO₃, acetic acid and water were placed in stoppered bottles or Florence flasks. In some experiments, the bottles were rotated in a thermostat held at 25.00°C, and in other experiments glass paddles were used to stir the mixtures in the flasks for 3 days. Equilibrium was reached from both undersaturation and from supersaturation. The AgBrO₃ content in the saturated solutions was determined by evaporation of pipetted aliquots of 50.13 cm⁻³, drying at 110°C for 1 hour, and weighing.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by mixing 1 mol dm⁻³ solutions of KBrO₃ and AgNO₃. The precipitate was washed and recrystallized from boiling water. Ag content analyzed as AgCl: found 44.97 and 45.00 % (calcd 45.75 %). C.p. grade acetic acid was analyzed by titration with standard KOH solution.

ESTIMATED ERROR:

Soly: see reproducibility of data above. Temp: precision within ± 0.02 K.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3]	ORIGINAL MEASUREMENTS: Longi, A.
(2) Aqueous ammonia; NH ₃ ; [7664-41-7]	Gazz. Chim. Ital. <u>1883</u> , 13, 87-9.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
T/K = 298	B. Scrosati and H. Miyamoto
EXPERIMENTAL DATA:	
The solubility of AgBrO ₃ was determined in a solution of	of 10 mass % aqueous ammonia (specific gravity = 0.96).
The solubility is one gram of AgBrO ₃ in 2.254 cm ⁻³ of s	
(compilers).	solution. This is equivalent to 1.00 mor unit
The solubility was also reported as one gram of AgBrO ₃ kg solvent: i.e. per kg of 10 mass % aqueous ammonia so	
AUXILIARY IN	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
No information was given in the original paper. However, the author probably determined the solubility	Nothing specified.
gravimetrically by evaporating the solvent and weigh-	
ing the remaining solid.	
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Sodium nitrate; NaNO ₃ ; [7631-99-4]	ORIGINAL MEASUREMENTS: Lel'chuk, Yu. L.; Surnina, L.V.; Barkhatova, V.I.
(3) Potassium bromate; KBrO ₃ ; [7758-01-2] (2) Water; H ₂ O; [7732-18-5]	Zh. Obshch. Khim. <u>1955</u> , 25, 1685-93: J. Gen. Chem. USSR (Engl. Transl.) <u>1955</u> , 25, 1641-6.
VARIABLES: Concentrations of NaNO ₃ and KBrO ₃ T/K = 298.2	PREPARED BY: H. Miyamoto and E. M. Woolley

The solubility of AgBrO₅, S, in solutions where initial concentrations of KBrO₃ are 0.001, 0.010, and 0.100 mol dm-3 (three independent experiments were reported) are:

103S/mol dm-3 in 0.001 mol dm-3 KBrO3 NaNO₃concn 104Ka08 expt 1 expt 2 expt 3 mean mol dm-3 mol2 dm-6 0.0 7.25 7.39 7.37 7.32 0.001 7.50 7.58 7.54 0.609 7.55 0.003 7.92 7.88 7.90 7.90 0.644 0.010 8.29 8.16 8.22 0.703 8.22 0.030 8.88 8.82 8.85 8.85 0.758 0.100 9.68 9.68 9.67 9.66 0.872 0.300 11.2 11.2 11.3 11.2 1.03 1.000 13.5 13.6 13.5 13.5 1.37 1.96 103S/mol dm-3 in 0.010 mol dm-3 KBrO3 NaNO₃ concn expt 1 expt 2 expt 3 mean 104K_{s0}a mol dm-3 mol2 dm-6 0.0 3.98 4.01 3.97 3.99 0.558 0.001 4.75 4.83 4.87 4.82 0.714 0.003 4.90 4.94 4.92 0.734 0.010 5.03 5.06 5.16 5.08 0.766 0.030 5.43 5.54 5.50 0.850 5.49 0.100 6.39 6.35 6.37 6.37 1.04 0.300 7.54 7.54 7,58 7.55 1.32 1.000 11.1 11.3 11,2 2.37

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgBrO₃ crystals and the aq solutions of NaNO₃ and KBrO₃ were placed in 400-500 cm³ paraffined brown glass bottles in a thermostat at 25.00°C. The mixtures were vigorously agitated for 8 hours, and the remaining details of Ag analysis given in ref. (1) (probably gravimetric analysis as AgCl, compilers). Three experimental runs were reported (see table above).

11.2

SOURCE AND PURITY OF MATERIALS:

continued.....

AgBrO₃ prepared by mixing solutions of AgNO₃ and KBrO₃. KBrO₃ was prepared from KOH and Br₂. NaNO₃ was recrystallized twice. Doubly distilled water was used in all experiments.

ESTIMATED ERROR:

Soly: the deviations from the mean are within ± 1.5 % except for 0.1 mol dm-3 KBrO3 slns where the deviation is as high as \pm 7.5 % (compilers).

Temp: precision ± 0.1 K.

REFERENCES:

1. Lel'chuk, Yu. L.; Sasonko, S.M. Izv. Tomsk. Politekhn. Inst. 1955, 71, 52.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]
- (3) Potassium bromate; KBrO₃; [7758-01-2]
- (2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Lel'chuk, Yu. L.; Surnina, L.V.; Barkhatova, V.I.

Zh. Obshch. Khim. 1955, 25, 1685-93: J. Gen. Chem. USSR (Engl. Transl.) 1955, 25, 1641-6.

EXPERIMENTAL DATA: (continued......)

103S/mol dm-3 in 0.100 mol dm-3 KBrO3

		0-5/mor am - m c	nor am • K	rpt O3	
NaNO ₃ conen mol dm- ³	expt 1	expt 2	expt 3	mean	
0.0	0.98	1.10 ′	1.10	1.06	1.07
0.001	1.09	1.05	1.08	1.07	1.08
0.003	1.12	1.13	1.14	1.13	1.14
0.010	1.18	1.21	1.20	1.20	1.21
0.030	1.24	1.23	1.26	1.24	1.25
0.100	1.33	1.33	1.36	1,34	1.36
0.300	1.52	1.50	1.53	1.52	1.54
1.000	2.62	2.78	2.68	2.69	2.76

* The chemical solubility product is defined by the following equation:

$$K_{s0} = S([KBrO_3] + S)$$

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]
- (3) Sodium picrate; C₆H₂N₃O₇Na; [3324-58-1]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gilbert, E. C.

J. Phys. Chem. 1929, 33, 1235-46.

VARIABLES:

Concentrations of NaNO₃ and NaOC₆H₂(NO₂)₃

T/K = 293.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

Solubilities reported for 20.00°C.

NaNO ₃ concn mol dm-3	C ₆ H ₂ N ₃ O ₇ Na concn mol dm- ³	solubility (S) mmol dm-3	$10^{5}K_{*0} = S^{2}$ $mol^{2} dm^{-6}$
0.0	0.100	8.48	7.2
0.100	0.0	8.37	
0.100	0.0	8.44	7.1
0.050	0.05	8.37	
0.050	0.05	8.40	7.1

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

successive analyses gave the same solubility results. The method of analysis of AgBrO₃ in the saturated solutions was not given, but the solubility was probably determined by iodometric titration with standard thiosulfate solution.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals and solvent mixtures were rotated until AgBrO₃ was made by metathesis from "the purest materials obtainable." Sodium picrate was prepared by mixing equivalent amounts of NaOH and picric acid (Kahlbaum "Zur Analyse") in hot solution. The salt was filtered, washed, recrystallized from water, washed with alcohol, and dried. The final product was the monohydrate. NaNO₃ (Kahlbaum "Zur Analyse") was dried and not treated any further.

ESTIMATED ERROR:

Soly: precision around \pm 0.04 mmol dm⁻³ (compiler). Temp: precision ± 0.01 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Ramette, R. W.; Spencer, J. B.
(2) Lithium nitrate; LiNO ₃ ; [7790-69-4]	
(3) Perchloric acid; HClO ₄ ; [7601-90-3]	J. Phys. Chem. 1963, 67, 944-6
(4) Water; H ₂ O; [7732-18-5]	
VARIABLES: Concentration of LiNOs	PREPARED BY:
T/K = 298	H. Miyamoto
,	

The perchloric acid concentration of all solutions is 1 x 10-4 mol dm-3. The acid was added to supress hydrolysis. The authors state that there is a tendency for silver to form hydroxy complexes.

LiNO ₃ concn	AgBrO ₃ soly
mol dm-3	mmol dm-3
0.0	8.03
0.02	8.62
0.05	9.17
0.10	9.73
0.15	10.14
0.20	10.51

Using the Davies equation to estimate activity coefficients (1), the authors computed the thermodynamic solubility product: $log K_{00} = -4.271$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

LiNO₃ and HClO₄. Although equilibrium was reached in 2-3 hours, solutions were rotated in an air thermostat at 25°C for at least 24 hours, and then transferred to a water bath for final equilibration and sampling by pressure filtration. The dissolved bromate was determined by duplicate iodometric titration with thiosulfate solution.

SOURCE AND PURITY OF MATERIALS:

A large excess of AgBrO₃ was added to the solutions of AgBrO₃ prepared by slow addition of solutions of AgNO₃ and KBrO₃ to distilled water at room temperature. The product was washed, dried, and recrystallized. The purity of this product was determined gravimetrically as AgBr (99.8 %) and by iodometric titration (99.7 %).

> LiNO₃ and HClO₃ were analytical reagent grade materials.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision probably better than ± 0.1 K (compiler).

REFERENCES:

1. Davies, C. W. J. Chem. Soc. 1938, 2093.

COMPONENTS: (1) Silver bromate; AgBrO ₈ ; [7783-89-3] (2) Lithium perchlorate; LiClO ₄ ; [7791-03-9] (3) Perchloric acid; HClO ₄ ; [7601-90-3] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Ramette, R. W.; Spencer, J. B. J. Phys. Chem. <u>1963</u> , 67, 944-6
VARIABLES: Concentration of LiClO ₄ T/K = 298	PREPARED BY: H. Miyamoto

The perchloric acid concentration of all solutions is 1 x 10-4 mol dm-3. The acid was added to supress hydrolysis. The authors state that there is a tendency for silver to form hydroxy complexes.

AgBrO ₃ soly
mmol dm-3
8.03
8.55
8.97
9.39
9.70
9.94

Using the Davies equation to estimate activity coefficients (1), the authors computed the thermodynamic solubility product: $log K_{s0} = -4.271$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

LiClO₄ and HClO₄. Although equilibrium was reached in 2-3 hours, solutions were rotated in an air thermostat at 25°C for at least 24 hours, and then transferred to a water bath for final equilibration and sampling by pressure filtration. The dissolved bromate was determined by duplicate iodometric titration with thiosulfate solution.

SOURCE AND PURITY OF MATERIALS:

A large excess of AgBrO₃ was added to the solutions of AgBrO₃ prepared by slow addition of solutions of AgNO₃ and KBrO₃ to distilled water at room temperature. The product was washed, dried, and recrystallized. The purity of this product was determined gravimetrically as AgBr (99.8 %) and by iodometric titration (99.7 %).

> LiClO₄ and HClO₃ were analytical reagent grade materials.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision probably better than ± 0.1 K (compiler).

REFERENCES:

1. Davies, C. W. J. Chem. Soc. 1938, 2093.

ĺ	СО	MPON	ENTS:
	(1)	Silver	bromat

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Lithium perchlorate; LiClO₄; [7791-03-9](3) Perchloric acid; HClO₄; [7601-90-3]

(4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ramette, R. W.; Dratz, E. A.

J. Phys. Chem. 1963, 67, 940-2

VARIABLES:

Concentration of LiClO₄ T/K = 298.9, 298.2 and 308.2

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

The perchloric acid concentration of all solutions is 1 x 10-4 mol dm-3. The acid was added to supress hydrolysis.

t/ºC	LiClO ₄ conen mol dm-3	AgBrO ₃ soly mmol dm-3
14.7	0.0	5.56
	0.025	5.99
	0.050	6.26
	0.075	6.43
	0.100	6.45
25.0	0.0	8.09
	0.025	8.73
	0.050	9.09
	0.075	9.35
	0.100	9.52
35.0	0.0	11.22
	0.025	12.03
	0.050	12.48
	0.075	12.84
	0.100	13.09

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A large excess of AgBrO₃ was added to the solutions of LiClO₄ and HClO₄. The solutions were rotated in borosilicate glass bottles for two days in a thermostat at 38°C, and were then transferred to a water bath thermostated at either 35, 25 or 14.7°C. The bottles were thermostated at the desired temperature for 3 days with occasional shaking. The saturated solutions were filtered through fine porous glass by pressure, and aliquots were pipetted into titration flasks. The solutions were analyzed for bromate by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by slow addition of solutions of AgNO₃ and KBrO₃ to distilled water at room temperature. The product was washed, dried, and recrystallized. The purity of this product was determined gravimetrically as AgBr (99.8 %) and by iodometric titration (99.7 %).

LiClO₄ and HClO₄ were analytical reagent grade materials.

ESTIMATED ERROR:

Soly: nothing specified, but see next page.

Temp: precision probably better than ± 0.1 K (compiler).

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄; [7601-90-3]

ORIGINAL MEASUREMENTS:

Ramette, R. W.; Dratz, E. A.

J. Phys. Chem. 1963, 67, 940-2

(4) Water; H₂O; [7732-18-5]

EXPERIMENTAL DATA: (continued....)

The thermodynamic solubility product was evaluated from $K_{s0}^0 = S^2y^2$ where S is the solubility and y is the activity coefficient estimated from the following equations:

$$log y = -AI^{1/2}/(1 + BI^{1/2})$$

where

$$I = S + [LiClO_4] + [HClO_4]$$

The results of these calculations and the computed thermodynamic functions are given below.

	Α	В	-log K ⁰ ,0
t/ºC	mol-1/2 dm-3/2	mol-1/2 dm-3/2	± 0.006*
14.7	0.501	1.71	4.577
25.0	0.509	1.50	4.265
35.0	0.519	1.57	3.994
	ΔG^0	∆Н0	Δ\$0
t/ºC	kcal mol-1	kcal mol-1	cal K-1 mol-1
25.0	5.83 ± 0.02	12.7 ± 0.3	19.7 ± 1.2

*All ± quantities given in the above tables are uncertainties "estimated for 50 % confidence."

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Acetic acid; C₂H₄O₂; [64-19-7]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Davies, P. B.; Monk, C. B.

J. Chem. Soc. 1951, 2718-23.

VARIABLES:

Concentrations of NaOH and acetic acid

T/K = 298.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

NaOH concn mol dm-3	CH ₃ COOH concn mol dm-3	AgBrO ₃ soly mmol dm-3
0.0	0.0	8.11
0.03180	0.05418	9.28
0.03975	0.04501	9.54
0.07152	0.07760	10.24

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used. The bromate concentration in the saturated solutions was determined by addition of excess KI to about 25 cm³ aliquots followed by addition of about 15 cm³ of 1 mol dm⁻³ H₂SO₄. The aliquots were then titrated with standard thiosulfate solution to the starch endpoint.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by addition of dilute solutions of A.R. grade KBrO₃ and AgNO₃ to a large volume of hot water. The product was washed and dried.

AnalaR acetic acid was used.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.03 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Keefer, R. M.; Andrews, L. J.; Kepner, R. E.
(2) Perchloric acid; HClO ₄ ; [7601-90-3]	
(3) 2-Butanoic acid (vinylacetic acid); C ₄ H ₆ O ₂ ; [625-38-7]	J. Am. Chem. Soc. <u>1949</u> , 71, 3906-9.
(4) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration vinylacetic acid T/K = 298	H. Miyamoto
1/K = 270	H. Wilyamoto

The solubility of AgBrO₃ was determined at 25°C in solutions of constant ionic strength of 1.0 mol dm⁻³ (see below for details on preparation of these solutions).

C ₄ H ₆ O ₂ conen	AgBrO ₃ soly	K ₁
mol dm-3	102mol dm-3	mol-1 dm3
0.467	2.90	16.2
0.234	2.15	16.1
0.117	1.67	16.1
0.0585	1.37	15.8
0	1.01	

The authors reported that $K_{s0} = 1.029 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-3}$ at a constant ionic strength of 1.0 mol dm⁻³. The authors also reported that $K_{s0} = 1.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ in a solution of constant ionic strength of 0.10 mol dm⁻¹ solution using KNO₃ to adjust the ionic strength.

Values of K₁ given in the above table are based on the following equilibrium:

$$Ag^+ + C_4H_6O_2 \Leftrightarrow Ag(C_4H_6O_2)^+$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

HClO₄ was added to aqueous solutions of vinylacetic acid in sufficient quantity to maintain a constant ionic strength of 1.0 mol dm⁻³. These solutions were then added to glass-stoppered Erlenmeyer flasks containing AgBrO₃ crystals. The flasks were agitated for 4 hours at 25°C after which the excess solid was allowed to settle. Aliquots were removed and analyzed for silver by addition of NaBr followed by weighing the precipitated AgBr.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by slowly adding a dilute solution of KBrO₃ to a dilute solution of AgNO₃. The precipitate was washed, filtered, and placed in water for several days to remove suspended particles of AgBrO₃. The product was dried at 110°C and analyzed for silver: Ag found = 45.90 %, and Ag calculated = 45.75 %.

The preparation of vinylacetic acid was described elsewhere (1).

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

 Andrews, L. P.; Kepner, R. E. J. Org. Chem. 1949, 71, 2397.

ORIGINAL MEASUREMENTS:
Monk, C. B.
†
Trans. Faraday Soc. 1951, 47, 292-7.
PREPARED BY:
H. Miyamoto and E. M. Woolley
H. Wilyamoto and E. Wi. Wooney
•

NaOH concn mol dm-3	glycine concn mol dm ⁻³	AgBrO ₃ soly mol dm-3
0.0	0.0	0.00809
0.00681	0.01568	0.01112
0.01634	0.02758	0.01518
0.01777	0.04037	0.01595
0.02076	0.03645	0.01718

*Solubility in pure water based on "a number of determinations," and a value of $log~K^0_{a0} = -4.2764$ was given based on activity coefficients calculated from (1):

$$log y_{\pm}^2 = -I^{1/2}/\{1 + I^{1/2}\} - 0.2I$$

Ion pairing of AgBrO₃ was estimated and accounted for in this calculation of KO₈₀.

In addition to the thermodynamic solubility product, the following equilibrium constants were evaluated:

$$K_1 = [Ag^+][C_2H_4NO_2^-]y_\pm^2/[Ag(C_2H_4NO_2)]$$

$$K_2 = [Ag(C_2H_4NO_2)][C_2H_4NO_2^-]/[Ag(C_2H_4NO_2)_2^-]$$

For the above equilibria, the authors give $K_1 = 3.0 \times 10^{-4}$ mol dm⁻³, and $K_2 = 4.2 \times 10^{-4}$ mol dm⁻³.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used. The bromate concentration in the saturated solutions was determined by addition of excess KI to about 25 cm3 aliquots followed by addition of about 15 cm3 of 1 mol dm-3 H₂SO₄. The aliquots were then titrated with standard thiosulfate solution to the starch endpoint.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by addition of dilute solutions of A.R. grade KBrO3 and AgNO3 to a large volume of hot water. The product was washed and dried.

AR grade glycine was used after drying in a vacuum oven at 90°C for several hours.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

1. Monk, C. B. Trans. Faraday Soc. 1951, 47, 285.

COMPONENTS: (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Silver nitrate; AgNO₃; [7761-88-8] (4) Glycine; C₂H₅NO₂; [56-40-6] (5) Water; H₂O; [7732-18-5] VARIABLES: Concentrations of NaOH, AgNO₃ and glycine T/K = 298.15 ORIGINAL MEASUREMENTS: Monk, C. B. Trans. Faraday Soc. 1951, 47, 292-7. PREPARED BY: H. Miyamoto and E. M. Woolley

EXPERIMENTAL DATA:

total NaOH mol dm-3	total [AgNO ₃] mol dm-3	total [C ₂ H ₅ NO ₂] mol dm-3	AgBrO ₃ soly mol dm-3
0.0	0.0	0.0	0.00809*
0.00217	0.02971	0.03250	0.00275
0.00707	0.03243	0.03250	0.00288
0.00449	0.01883	0.01544	0.00422
0.01048	0.01462	0.02449	0.00599

*Solubility in pure water based on "a number of determinations," and a value of $log K^0_{s0} = -4.2764$ was given based on activity coefficients calculated from (1):

$$log y_{\pm}^2 = -I^{1/2}/\{1 + I^{1/2}\} - 0.2I$$

Ion pairing of AgBrO₃ was estimated and accounted for in this calculation of KO_{sO}.

In addition to the thermodynamic solubility product, the following equilibrium constant was evaluated:

$$K_1 = [Ag^+][C_2H_4NO_2^-]y_{\pm}^2/[Ag(C_2H_4NO_2)]$$

For the above equilibrium, the author reported $K_1 = 3.0 \times 10^{-4}$ mol dm⁻³.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used. The bromate concentration in the saturated solutions was determined by addition of excess KI to about 25 cm³ aliquots followed by addition of about 15 cm³ of 1 mol dm⁻³ H₂SO₄. The aliquots were then titrated with standard thiosulfate solution to the starch endpoint.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by addition of dilute solutions of A.R. grade KBrO₃ and AgNO₃ to a large volume of hot water. The product was washed and dried.

AR grade glycine was used after drying in a vacuum oven at 90°C for several hours.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

1. Monk, C. B. Trans. Faraday Soc. 1951, 47, 285.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) DL-Alanine; C₃H₇NO₂; [302-72-7] (4) Water; H₂O; [7732-18-5] 	Monk, C. B. Trans. Faraday Soc. <u>1951</u> , 47, 292-7.
VARIABLES: Concentrations of NaOH and alanine	PREPARED BY:
T/K = 298.15	H. Miyamoto

total NaOH	total [C ₃ H ₇ NO ₂]	AgBrO ₃ soly
mol dm-3	mol dm-3	mol dm-3
0.01260	0.02568	0.01363
0.01480	0.04259	0.01483
0.02076	0.03632	0.01734
0.02372	0.03378	0.01861

From the above data, the following equilibrium constants were evaluated (see the compilation by this author for the $AgBrO_3$ -NaOH-glycine- H_2O system for complete details):

 $K_1 = [Ag^+][C_3H_6NO_2^-]y_{\pm}^2/[Ag(C_3H_6NO_2)] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$

and

 $K_2 = [Ag(C_3H_6NO_2)][C_3H_6NO_2]/[Ag(C_3H_6NO_2)_2] = 2.9 \times 10^{-4} \text{ mol dm}^{-3}$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY
See the compilation by this author for the AgBrO ₃ -	Reagent grade alanine v
NaOH-glycine-H ₂ O system for complete details.	alcohol and dried in vac

SOURCE AND PURITY OF MATERIALS: Reagent grade alanine was recrystallized from aqueous alcohol and dried in vacuum for several hours at 90°C.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	
(2) Sodium hydroxide; NaOH; [1310-73-2]	Monk, C. B.
(3) Silver nitrate; AgNO ₃ ; [7761-88-8]	Trans. Faraday Soc. 1951, 47, 292-7.
(4) DL-Alanine; C ₃ H ₇ NO ₂ ; [302-72-7]	
(5) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentrations of NaOH, AgNO ₃ and DL-alanine	1
T/K = 298.15	H. Miyamoto

EXPERIMENTAL DATA:

total NaOH mol dm-3	total [AgNO ₃] mol dm-3	total [C ₃ H ₇ NO ₂] mol dm- ³	AgBrO ₃ soly mol dm-3
0.00117	0.02940	0.01535	0.00273
0.00100	0.02437	0.01535	0.00304
0.00347	0.02038	0.01535	0.00366
0.00396	0.01889	0.03098	0.00410

From the above data, the following equilibrium constant was evaluated (see the compilation by this author for the AgBrO₃-NaOH-glycine-H₂O system for complete details):

 $K_1 = [Ag^+][C_3H_6NO_2^-]y_{\pm}^2/[Ag(C_3H_6NO_2)] = 2.2 \times 10^{-4} \text{ mol dm}^{-3}$

AUXII	JARY	INFORM.	ATION	

METHOD/APPARATUS/PROCEDURE: See the compilation by this author for the AgE

See the compilation by this author for the AgBrO₃-NaOH-glycine-H₂O system for complete details.

SOURCE AND PURITY OF MATERIALS:

Reagent grade alanine was recrystallized from aqueous alcohol and dried in vacuum for several hours at 90°C.

COMPONENTS: (1) Silver bromate; AgBrO ₅ ; [7783-89-3]	ORIGINAL MEASUREMENTS:
(2) Sodium hydroxide; NaOH; [1310-73-2] (3) N-Glycyl glycine; C ₄ H ₈ N ₂ O ₃ ; [556-50-3] (4) Water; H ₂ O; [7732-18-5]	Monk, C. B. Trans. Faraday Soc. <u>1951</u> , 47, 292-7.
VARIABLES: Concentrations of NaOH and glycyl glycine T/K = 298.15	PREPARED BY: H. Miyamoto

total [NaOH] mol dm-3	total [C ₄ H ₈ N ₂ O ₃] mol dm ⁻³	AgBrO ₃ soly mol dm-3
0.0	0.0	0.00809*
0.00536	0.01346	0.01037
0.00710	0.01401	0.01111
0.00830	0.02035	0.01168
0.01524	0.02495	0.01462

*Solubility in pure water based on "a number of determinations," and a value of $log \ K^0_{s0} = -4.2764$ was given based on activity coefficients calculated from (1):

$$log y_{\pm}^2 = -I^{1/2}/\{1 + I^{1/2}\} - 0.2I$$

Ion pairing of AgBrO₃ was estimated and accounted for in this calculation of KO_{sO}.

In addition to the thermodynamic solubility product, the following equilibrium constant was evaluated:

$$K_1 = [Ag^+][C_4H_7N_2O_3^-]y_{\pm}^2/[Ag(C_4H_7N_2O_3)]$$

For the above equilibrium, the author reported $K_1 = 2.07 \times 10^{-3} \text{ mol dm}^{-3}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturating column method used. The bromate concentration in the saturated solutions was determined by addition of excess KI to about 25 cm³ aliquots followed by addition of about 15 cm³ of 1 mol dm⁻³ H₂SO₄. The aliquots were then titrated with standard thiosulfate solution to the starch endpoint.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by addition of dilute solutions of A.R. grade KBrO₃ and AgNO₃ to a large volume of hot water. The product was washed and dried.

Glycyl glycine (Roche product) was dried in a vacuum oven at 90°C for several hours.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

1. Monk, C. B. Trans. Faraday Soc. 1951, 47, 285.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Lithium nitrate; LiNO₃; [7790-69-4] (3) Perchloric acid; HClO₄; [7601-90-3] (4) Deuterium oxide (water-d₂); D₂O; [7789-20-0] 	Ramette, R. W.; Spencer, J. B. J. Phys. Chem. <u>1963</u> , 67, 944-6
VARIABLES: Concentration of LiNO ₃ T/K = 298	PREPARED BY: E. M. Woolley

The aqueous (H_2O) perchloric acid concentration of all solutions is 1 x 10-4 mol dm⁻³. The acid was added to supress hydrolysis. The authors state that there is a tendency for silver to form hydroxy complexes.

LiNO ₃ concn	AgBrO ₃ soly	
mol dm-3	mmol dm-3	
0.0	6.78	
0.075	8.20 ^b	
0.15	8.68	
0.225	9.15	
0.30	0.54	

*Using the Davies equation to estimate activity coefficients, the authors computed the thermodynamic solubility product: $log K_{0}^{\bullet} = -4.412$.

bJudging by the constancy of the ratio of the solubility of AgBrO₃ in D₂O and H₂O, the authors conclude that this data point is too high by about 1 %.

AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE: Complete details given in the compilation of these authors' study of the AgBrO ₃ -LiNO ₃ -HClO ₄ -H ₂ O system.	SOURCE AND PURITY OF MATERIALS: Heavy water (General Dynamics Corp.) was specified to be greater than 99.5 % pure.		

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Lithium perchlorate; LiClO ₄ ; [7791-03-9] (3) Perchloric acid; HClO ₄ ; [7601-90-3] (4) Deuterium oxide (water-d ₂); D ₂ O; [7789-20-0]	ORIGINAL MEASUREMENTS: Ramette, R. W.; Spencer, J. B. J. Phys. Chem. 1963, 67, 944-6
VARIABLES: Concentration of LiClO ₄ T/K = 298	PREPARED BY: E. M. Woolley

EXPERIMENTAL DATA:

The aqueous (H_2O) perchloric acid concentration of all solutions is 1 x 10-4 mol dm⁻³. The acid was added to supress hydrolysis. The authors state that there is a tendency for silver to form hydroxy complexes.

LiClO ₄ concn	AgBrO ₃ soly		
mol dm-3	mmol dm-3		
0.0	6.78		
0.03	7.46		
0.075	7.86		
0.15	8.32		
0.225	8.60		
0.30	8.84		

*Using the Davies equation to estimate activity coefficients, the authors computed the thermodynamic solubility product: $log K_{s0} = -4.412$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Complete details given in the compilation of these authors' study of the AgBrO₃-LiClO₄-HClO₄-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Heavy water (General Dynamics Corp.) was specified to be greater than 99.5 % pure.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄; [7601-90-3]
- (4) Deuterium oxide (water-d₂); D₂O; [7789-20-0]

ORIGINAL MEASUREMENTS:

Ramette, R. W.; Dratz, E. A. J. Phys. Chem. 1963, 67, 940-2

VARIABLES:

Concentration of LiClO₄ T/K = 298.9, 298.2 and 308.2

PREPARED BY:

G. Jancso and E. M. Woolley

EXPERIMENTAL DATA:

The aqueous (H_2O) perchloric acid concentration of all solutions is 1 x 10-4 mol dm-3. The acid was added to supress hydrolysis.

t/ºC	LiClO ₄ concn mol dm-3	AgBrO ₃ soly mmol dm-
14.7	0.0	4.54
	0.025	4.94
	0.050	5.16
	0.075	5.30
	0.100	5.42
25.0	0.0	6.76
	0.025	7.33
	0.050	7.65
	0.075	7.89
	0.100	8.02
35.0	0.0	9.57
	0.025	10.26
	0.050	10.62
	0.075	10.92
	0.100	11.12

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A large excess of AgBrO₃ was added to the solutions of LiClO₄ and HClO₄. The solutions were rotated in borosilicate glass bottles for two days in a thermostat at 38°C, and were then transferred to a water bath thermostated at either 35, 25 or 14.7°C. The bottles were thermostated at the desired temperature for 3 days with occasional shaking. The saturated solutions were filtered through fine porous glass by pressure, and aliquots were pipetted into titration flasks. The solutions were analyzed for bromate by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by slow addition of solutions of AgNO₃ and KBrO₃ to distilled water at room temperature. The product was washed, dried, and recrystallized. The purity of this product was determined gravimetrically as AgBr (99.8 %) and by iodometric titration (99.7 %).

LiClO₄ and HClO₄ were analytical reagent grade materials.

Heavy water was obtained from General Dynamics Corp. with a specified purity greater than 99.5 %.

ESTIMATED ERROR:

Soly: nothing specified, but see next page.

Temp: precision probably better than ± 0.1 K (compiler).

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Lithium perchlorate; LiClO₄; [7791-03-9]
- (3) Perchloric acid; HClO₄; [7601-90-3]
- (4) Deuterium oxide (water-d₂); D₂O; [7789-20-0]

ORIGINAL MEASUREMENTS:

Ramette, R. W.; Dratz, E. A. J. Phys. Chem. 1963, 67, 940-2

EXPERIMENTAL DATA: (continued....)

The thermodynamic solubility product was evaluated from $K^0_{s0} = S^2y^2$ where S is the solubility and y is the activity coefficient estimated from the following equations:

$$log y = -AI^{1/2}/(1 + BI^{1/2})$$

where

$$I = S + [LiClO_4] + [HClO_4]$$

The results of these calculations and the computed thermodynamic functions are given below.

	Α	В	-log K ⁰ *0
t/ºC	mol-1/2 dm-3/2	mol-1/2 dm-3/2	± 0.006*
14.7	0.507	1.55	4.749
25.0	0.515	1.56	4.414
35.0	0.525	1.82	4.126
	ΔG^0	ΔН0	ΔS ⁰
t/ºC	kcal mol-1	kcal mol-1	cal K-1 mol-1
25.0	6.02 ± 0.01	12.5 ± 0.4	21.8 ± 1.3

*All ± quantities given in the above tables are uncertainties "estimated for 50 % confidence."

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Methanol; CH₄O; [67-56-1]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Owen, B. B.

J. Am. Chem. Soc. 1933, 55, 1922-8.

VARIABLES:

Solvent composition

T/K = 298

PREPARED BY:

H. Miyamoto and M. Salomon

EXPERIMENTAL DATA:

methanol content		AgBrO ₃ soly	density
mass %	mol %*	mmol dm-3	kg dm-
0 .	0	8.12b	0.9987
10	5.9	5.51	0.9802
20	12.3	3.79	0.9650
30	19.4	2.65	0.9492
40	27.3	1.82	0.9318
50	36.0	1.24	0.9123
60	45.8	0.83	0.8908

aCalculated by the compiler.

bMean of four independent measurements with an average deviation of 0.004 mmol dm-3.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Three to four grams of AgBrO₃ crystals were placed in long-necked 200 to 500 cm³ flasks. Ice-cold solvent was quickly introduced into the flasks without wetting the necks, and the flasks were sealed. The flasks were rotated slowly for five or six days at 25°C. Preliminary studies indicated that equilibrium was reached within two days. After 2-3 days, the solutions became turbid.

The saturated solutions were forced through asbestosglass wool filtering mats, and 100 to 400 g samples were weighed. The Ag content was determined gravimetrically as AgBr.

For the mixed solvents, the solubilities were determined on a mass basis and converted to mol dm⁻³ units using the density values given in the table.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ was prepared from dilute solutions of Baker's "Analyzed" grade AgNO₃ and KBrO₃. Equivalent volumes of these two solutions were slowly mixed, and the resulting precipitate was washed and recrystallized from conductivity water.

Methanol, Baker's "Analyzed" grade, "absolute," was used without further purification.

ESTIMATED ERROR:

Soly: av deviation given above. Precision of all results not specified.

Temp: nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	
	Neuman, E. W.
(2) Methanol; CH ₄ O; [67-56-1]	
	J. Am. Chem. Soc. 1934, 56, 28-9.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Solvent composition	
T/K = 298	H. Miyamoto

methanol c	content	AgBrO ₃ soly
mass %	mol %ª	mmol dm-3
0	0	8.131
3.62	2.07	7.00
7.31	4.25	6.05
11.08	6.55	5.22
14.92	8.97	4.50
18.84	11.54	3.94
22.83	14.26	3.40
26.91	17.15	2.92
31.08	20.23	2.53
35.33	23.50	2.17
39.67	26.99	1.84
44.11	30.74	1.58
48.63	34.74	1.31

^{*}Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached by rotating solid AgBrO₃ with AgBrO₃ was prepared by adding a dilute solution of the mixed solvents in a thermostat at 25°C. The saturated solutions were analyzed for silver by potentiometric titration with KBr using the following type of cell:

Cu | Agar, Ba(NO₃)₂ || unknown || AgBr, Ag

SOURCE AND PURITY OF MATERIALS:

KBrO₃ to a dilute solution of AgNO₃. The precipitate was washed, filtered and suspended in water for several days to remove traces of KBrO3 and AgNO3.

The source and purity of methanol was not given.

ESTIMATED ERROR:

Nothing specified.

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Methanol; CH₄O; [67-56-1]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.

Nippon Kagaku Zasshi 1960, 81, 1376-80.

VARIABLES:

Concentration of methanol

 $T/K \approx 293.15$, 298.15 and 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

methanol content		silver bromate solubility/mmol dm-		
mass %	mol %a	20°C	25°C	30°C
0.0	0.0	7.28	8.59	10.02
6.012	3.472	5.57	6.71	7.85
9.846	5.785	4.78	5.67	6.72
19.736	12.146	3.47	4.21	4.87
29.942	19.374	2.56	2.99	3.46
33.448	22.032	2.22	2.73	3.19
43.170	29.928	1.69	2.07	2.32
55.032	40.761	1.18	1.36	1.64
69.140	55.746	0.78	0.97	1.06

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours which was sufficient time to reach equilibrium. After the solid was allowed to settle, aliquots of saturated solution were withdrawn and the solubility was determined by analysis for total silver.

To each aliquot of saturated solution, a measured excess of 0.050 mol dm-3 of NaCl solution was added, and the remaining chloride titrated with 0.025 mol dm-3 AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako Co. guaranteed reagent) to a large volume of dilute KNO₃ solution. The solution was boiled, aged, and the precipitate washed and dried under reduced presure.

Methanol (Wako Co. guaranteed reagent) was dried over CaO, refluxed over AgNO3, and distilled.

ESTIMATED ERROR:

Soly: probable error within ± 0.023 mmol dm⁻³. Temp: precision ± 0.02 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Acetic acid; C₂H₄O₂; [64-19-7]
- (4) Methanol; CH₄O; [67-56-1]
- (5) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Davies, P. B.; Monk, C. B.

J. Chem. Soc. 1951, 2718-23.

VARIABLES:

Concentrations of NaOH, CH₃COOH and CH₃OH

T/K = 298.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH ₃ OH content mass %	CH ₃ OH content ^a mol %	NaOH concn mol dm-3	CH ₃ COOH concn mol dm- ³	AgBrO ₃ soly mmol dm- ³
43.5	30.2	0	0	1.58
		0.01953	0.02272	2.13
		0.03125	0.03786	2.35
		0.03906	0.05679	2.47
53.8	39.6	0	0	1.09
		0.01953	0.02272	1.58
		0.03125	0.03563	1.78
		0.03515	0.04165	1.84

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturating column method was used. Saturated solutions were analyzed for bromate by addition of excess KI to about 25 cm³ aliquots followed by addition of about 15 cm3 of 1 mol dm-3 H₂SO₄. The aliquots were then titrated with standard thiosulfate solution using a starch indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by adding dilute solutions of (A.R. grade) KBrO₃ and AgNO₃ to a large volume of hot water. The precipitate was washed and dried.

AnalaR acetic acid was used. "Laboratory grade" methanol was used.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.03 K.

	01110	. Dionato		12.1
COMPONENTS:		ORIGINAL MEASUREMENTS:		
(1) Silver bromate; AgBrO ₃ ; [7783-	-89-3]			
(2) Ethanol; C ₂ H ₆ O; [64-17-5]		Owen, B. B.		
(3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1933, 55, 1922-8.]
VARIABLES:		PREPARED BY:		
Solvent composition				
T/K = 298		H. Miyamoto an	d M. Salomon	
EXPERIMENTAL DATA:				
CH₃CH₂OH	content	AgBrO ₃ soly	density	
mass %	mol %a	mmol dm-3	kg dm ⁻³	
o	0	8.12 ^b	0.9987	
10	4.2	5.53	0.9804	
20	8.9	3.86	0.9664	
30	14.4	2.78	0.9507	
40	20.7	1.97	0.9315	
50	28.1	1.36	0.9099	
aCalculated by the compiler.				
bMean of 4 independent determina	itions: average devi	ation reported as 0.00	04 mmol dm ⁻³ .	1
	AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:		SOURCE AND P	URITY OF MATERIALS:	
All procedures identical to those given in the compila-		- Absolute ethanol	was distilled first from KOH and	d then
tion of this author's study of the			from Ag ₂ O. See the compilation cited on the lef	
AgBrO3-CH3OH-H2O system.		other details.		

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Ethanol; C_2H_6O ; [64-17-5]		ORIGINAL MEASUREMENTS:	
		Neuman, E. W.	
(3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1934, 56, 28-9.	
VARIABLES:		PREPARED BY:	
Solvent composition T/K = 298		H. Miyamoto	
EXPERIMENTAL DATA:			
CH ₃ CH ₂ OF	I content	AgBrO ₃ solubility	
mass %	mol %ª	mmol dm ⁻³	
0	0	8.131	
3.62	1.45	7.00	
7.30	2.99	6.06	
11.06	4.64	5.27	
14.89	6.40	4.55	
18.84	8.32	3.97	
22.80	10.35	3.46	
30.79	14.82	2.63	
35.29	17.58	2.23	
39.62	20.42	1.94	
44.06	23.55	1.65	
48.59	26.99	1.40	
^a Calculated by the compiler.			
	AUXILIARY II	NFORMATION	
METHOD/APPARATUS/PROCEDURE:		SOURCE AND PURITY OF MATERIALS:	
All procedures identical to those given in the compila-		Source and purity of ethanol not given. See the	
tion of this author's study of the		compilation cited on the left for other details.	

AgBrO₃-CH₃OH-H₂O system.

COMPONENTS: (1) Silver bromat

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Ethanol; C₂H₆O; [64-17-5]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.; Koizumi, E.

Nippon Kagaku Zasshi 1956, 77, 1255-9.

VARIABLES:

Solvent composition T/K = 293.15, 298.15 and 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH₃CH₂C)H content	silver bron	nate solubility/n	nmol dm-3
mass %	mol %a	20°C	25°C	30°C
0.0	0.0	7.28	8.59	10.02
3.729	1.492	6.30	7.33	8.79
8.161	3.358	5.30	6.24	7.54
14.917	6.416	4.26	4.94	6.03
22.072	9.971	3.36	3.88	4.77
26.689	12.462	2.86	3.39	4.04
35.359	17.621	2.18	2.69	3.17
44.039	23.532	1.76	1.99	2.40
54.871	32.225	1.31	1.47	1.70
71.079	49.008	0.77	0.86	0.96
82.728	65.193	0.57	0.61	0.67

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours which was sufficient time to reach equilibrium. After the solid was allowed to settle, aliquots of saturated solution were withdrawn and the solubility was determined by analysis for total silver.

To each aliquot of saturated solution, a measured excess of 0.050 mol dm-3 of NaCl solution was added, and the remaining chloride titrated with 0.025 mol dm-3 AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Takeda Co. guaranteed reagent) to a large volume of hot dilute KNO₃ solution. The solution was boiled, aged, and the precipitate washed and dried under reduced presure. Ethanol (Japan government guaranteed reagent) was refluxed over AgNO₃ and H₂SO₄, and then distilled.

ESTIMATED ERROR:

Soly: probable error within \pm 0.04 mmol dm⁻³. Temp: precision \pm 0.02 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Acetic acid; C₂H₄O₂; [64-19-7]
- (4) Ethanol; C₂H₆O; [64-17-5]
- (5) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Davies, P. B.; Monk, C. B.

J. Chem. Soc. 1951, 2718-23.

VARIABLES:

Concentrations of NaOH, CH₃COOH and CH₃CH₂OH T/K = 298.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH ₃ CH ₂ OH mass %	content mol %ª	NaOH concn mol dm ⁻³	CH ₃ COOH concn mol dm ⁻³	AgBrO ₃ soly mmol dm ⁻³
29.5	14.0 ₆	0	0	2.69
		0.03906	0.04544	3.86
		0.06636	0.06700	4.28
	21.0 ₉	0	0	1.86
40.6		0.03906	0.04544	3.05
		0.04687	0.05301	3.20
52.2	29.9 ₃	0	0	1.14
	· ·	0.01953	0.02272	1.88
		0.03515	0.04166	2,25

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturating column method was used. Saturated solutions were analyzed for bromate by addition of excess KI to about 25 cm³ aliquots followed by addition of about 15 cm³ of 1 mol dm⁻³ H₂SO₄. The aliquots were then titrated with standard thiosulfate solution using a starch indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by adding dilute solutions of (A.R. grade) KBrO₃ and AgNO₃ to a large volume of hot water. The precipitate was washed and dried.

AnalaR acetic acid was used. "Laboratory grade" ethanol was used.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.03 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]		
(2) Sodium hydroxide; NaOH; [1310-73-2]	Davies, P. B.; Monk, C. B.	
 (3) Acetic acid; C₂H₄O₂; [64-19-7] (4) 1,2-Ethanediol (ethylene glycol); C₂H₆O₂; [107-21-1] (5) Water; H₂O; [7732-18-5] 	J. Chem. Soc. 1951, 2718-23.	
VARIABLES: Concentrations of NaOH, CH ₃ COOH and	PREPARED BY:	
HOCH ₂ CH ₂ OH T/K = 298.15	H. Miyamoto	

EXPERIMENTAL DAT	A:			
HOCH ₂ CH ₂ OH mass %	content mol %ª	NaOH concn mol dm-3	CH ₃ COOH concn mol dm ⁻³	AgBrO ₃ soly mmol dm ⁻³
39.3	15.8 ₂	0	0	5.28
		0.05676	0.1178	6.98
51.2	23.34	0	0	4.61
		0.02440	0.02840	5.52
		0.04392	0.05206	6.06
63.1	33.17	0	0	3.98
		0.02440	0.02840	4.91
aCalculated by the comp	piler.			

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Procedures identical to those in the compilation of these authors' study of the AgBrO₃-NaOH-CH₃COOH-CH₃CH₂OH-H₂O system.

SOURCE AND PURITY OF MATERIALS:
"Laboratory grade" ethylene glycol was used. Other
details given in the compilation cited on the left.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) 1,2-Ethanediol (ethylene glycol); C ₂ H ₆ O ₂ ; [107-21-1] (3) Water; H ₂ O; [7732-18-5] VARIABLES: Solvent composition T/K = 298		Owen, B B	ORIGINAL MEASUREMENTS: Owen, B B. J. Am. Chem. Soc. 1933, 55, 1922-8. PREPARED BY: H. Miyamoto and M. Salomon	
EXPERIMENTAL DATA: HOCH ₂ CH ₂ C)H content	AgBrO ₃ soly	density	
mass %	mol %ª	mmol dm-3	kg dm-3	
0	0	8.12b	0.9987	
10	3.1	7.26	1.0097	
20	6.8	6.50	1.0228	
30	11.1	5.85	1.0362	
40	16.2	5.26	1.0496	
50	22.5	4.70	1.0624	
70	40.4	3.61	1.0851	
*Calculated by the compiler.				
	AUXILI	ARY INFORMATIO	N	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Procedures identical to those in the compilation of this author's study of the $AgBrO_3-CH_3OH-H_2O$ system.

SOURCE AND PURITY OF MATERIALS:

Ethylene glycol was dried with CaO, and distilled in vacuum. Other details given in the compilation cited on the left.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) 1,2-Ethanediol (ethylene glycol); C₂H₆O₂; [107-21-1]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.

Nippon Kagaku Zasshi 1960, 81, 1801-5.

VARIABLES:

Solvent composition

T/K = 293.15, 298.15 and 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

HOCH ₂ CH ₂ OH content		silver bron	nate solubility/n	nmol dm-3
mass %	mol %a	20°C	25ºC	30°C
0.0	0.0	7.28	8.59	10.02
7.347	2.250	6.50	7.76	9.19
16.717	5.505	5.95	6.98	8.28
28.934	10.568	5.28	6.16	7.25
41.836	17.271	4.64	5.40	6.34
50.188	22.627	4.20	4.96	5.85
63.940	33.978	3.68	4.26	4.90
74.386	45.738	3.25	3.76	4.25
85.049	62,280	2.76	3.29	3.61

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours which was sufficient time to reach equilibrium. After the solid was allowed to settle, aliquots of saturated solution were withdrawn and the solubility was determined by analysis for total silver.

To each aliquot of saturated solution, a measured excess of 0.050 mol dm-3 of NaCl solution was added, and the remaining chloride titrated with 0.025 mol dm-3 AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako Co. guaranteed reagent) to a large volume of hot dilute KNO3 solution. The solution was boiled, aged, and the precipitate washed and dried under reduced presure. Ethylene glycol (Wako, Co. guaranteed reagent) was dried over Na₂SO₄, and distilled twice under reduced pressure.

ESTIMATED ERROR:

Soly: probable error within \pm 0.034 mmol dm⁻³. Temp: precision ± 0.02 K.

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) 2-Methoxyethanol; C₃H₈O₂; [109-86-4]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.; Nabata, K.

Nippon Kagaku Zasshi 1970, 91, 499-500.

VARIABLES:

Solvent composition T/K = 298.15 and 308.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

t/ºC	[C ₃ H ₈ O ₂] mass %	[C ₃ H ₈ O ₂] mol %ª	AgBrO ₃ soly mmol dm-3
25	0	0	8.59
	4.818	1.184	7.19
	10.192	2.616	6.27
	19.988	5.584	4.88
	29.872	9.161	3.88
	50.344	19.357	2.29
	70.098	35.691	1.11
	90.287	68.756	0.20
	100	100	0
35	0	0	11.62
	5.435	1.342	10.14
	10.362	2.664	8.92
	20.045	5.603	7.06
	30.393	9.369	5.56
	50.449	19.422	3.03
	69.718	35.278	1.41
	89.693	67.322	0.23
	100	100	0

^{*}Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and the mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours. After allowing excess solid to settle, aliquots of saturated solution were withdrawn and analyzed for total silver by adding a measured excess of NaCl solution followed by backtrating the excess chloride with AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako, Co. guaranteed reagent) to a large volume of a dilute KNO₃ solution. The solution was boiled and then aged. The precipitate was washed and dried under reduced pressure.

2-Methoxyethanol (Wako, Co. guaranteed reagent) was dried over Na₂CO₃ and distilled two times.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

COMPONENTS:		ORIGINAL MEA	SUREMENTS:	
(1) Silver bromate; AgBrO ₃ ; [778	3-89-3]			
 (2) 1-Propanol; C₃H₈O; [71-23-8] (3) Water; H₂O; [7732-18-5] 		Owen, B. B.		
		J. Am. Chem. S	Soc. <u>1933</u> , 55, 1922-8.	
VARIABLES:	H. C. Come	PREPARED BY:		
Solvent composition T/K = 298		H. Miyamoto a	nd M. Salomon	
EXPERIMENTAL DATA:				
CH ₃ CH ₂ CH ₂	OH content	AgBrO ₃ soly	density	
mass %	mol %ª	mmol dm-3	kg dm-3	
0	0	8.12 ^b	0.9987	
10	3.2	5.80	0.9821	
20	7.0	4.36	0.9674	
30	11.4	3.31	0.9472	
40	16.7	2.41	0.9261	
50	23.1	1.63	0.9051	
aCalculated by the compiler.				
bMean of 4 independent determine	nations: average devi	ation reported as 0.00	04 mmol dm ⁻³ .	
	AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCI	EDURE:	SOURCE AND P	SOURCE AND PURITY OF MATERIALS:	
All procedures identical to those	given in the	1-Propanol (East	1-Propanol (Eastman) was dried with Na metal and	
compilation of this author's study	of the	then fractionated	. See the compilation cited on the left	
AgBrO ₃ -CH ₃ OH-H ₂ O system.		for other details.		

COMPONENTS:		ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-	-89-3]	
(2) 1-Propanol; C ₃ H ₈ O; [71-23-8]		Neuman, E. W.
(3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1934, 56, 28-9.
VARIABLES:		PREPARED BY:
Solvent composition T/K = 298		H. Miyamoto
EXPERIMENTAL DATA:	· · · · · · · · · · · · · · · · · · ·	
CH₃CH₂OH	I content	AgBrO ₃ solubility
mass %	mol %ª	mmol dm-3
0	0	8.131
3.67	1.13	7.14
11.27	3.67	5.62
15.16	5.08	4.99
19.13	6.62	4.49
23.17	8.29	4.05
31.49	12.11	3.21
40.13	16.73	2.43
49.13	22.45	1.70
63.28	34.06	0.86
Calculated by the compiler.		
	AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEI	OURE:	SOURCE AND PURITY OF MATERIALS:
All procedures identical to those g	iven in the	Source and purity of 1-propanol not given. See the
compilation of this author's study	of the	compilation cited on the left for other details.
AgBrO ₈ -CH ₃ OH-H ₂ O system.		

COMPONENTS:		ODICI	NAT MEACHIN	ANDREC.	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) 1-Propanol; C ₃ H ₈ O; [71-23-8]			ORIGINAL MEASUREMENTS: Miyamoto, H.		
			•	.: 1050 70 1214 0	
(3) Water; H_2O ; [7732-18-5]	.0]	Мірро	n Nagaku Zassi	ii <u>1958,</u> 79, 1314-8.	
· · · · · · · · · · · · · · · · · · ·	···				
VARIABLES: Solvent composition		PREPA	RED BY:		
T/K = 293.15, 298.15 and 303	3.15	н. мі	yamoto		
EXPERIMENTAL DATA:					
CH ₃ CH ₂ CH ₂	OH content	silver bror	nate solubility/r	nmol dm-3	
mass %	mol %a	20°C	25°C	30°C	
0.0	0.0	7.28	8.59	10.02	
3.337	1.024	6.62	7.57	8.60	
6.911	2.177	5.80	6.71	7.48	
12.819	4.222	4.75	5.60	6.28	
17.680	6.049	4.20	4.96	5.47	
25.313	9.223	3.50	3.90	4.39	
30.685	11.716	3.09	3.35	3.84	
37.174	15.065	2.48	2.71	3.10	
46.754	20.838	1.87	2.07	2.23	
67.613	38.493	0.82	0.93	1.02	
73.777	45.752	0.66	0.75	0.84	
Calculated by the compiler.					
	AUXILI	ARY INFORMA	ATION		
METHOD/APPARATUS/PROC	CEDURE:	SOUR	CE AND PURIT	Y OF MATERIALS:	
All procedures identical to those given in the			1-Propanol (Kanto Kagaku Co. guaranteed reagent)		
compilation of this author's stu-	dy of the	refluxe	refluxed over CaO, distilled twice from metallic Ca,		
AgBrO ₃ -CH ₃ OH-H ₂ O system.		and the	and then distilled a third time.		

COMPONENTS:			ORIGINAL MEASUREMENTS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]		1	Neuman, E. W.	
(2) 2-Propanol; C ₈ H ₈ O; [67-63-0]			J. Am. Chem. Soc. 1934, 56, 28-9.	
(3) Water; H ₂ O; [7732-1	8-5]			
VARIABLES:			PREPARED BY:	
Solvent composition T/K = 298			H. Miyamoto	
EXPERIMENTAL DAT	Α.		111 111,11111111	
EALERIMENTAL DAT	A: [C ₃ H ₈ O]	[C ₅ H ₈ O]	AgBrO ₃ soly	
	mass %	mol %a	mmol dm-3	
	0	0	8.131	
	3.64	1.12	7.00	
	7.34	2.32	6.07	
	11.12	3.61	5.29	
	14.97	5.01	4.61	
	18.90	6.53	4.06	
	22.90	8.18	3.60	
	26.99	9.98	3.18	
	31.16	11.95	2.81	
	39.77	16.52	2.10	
	48.74	22.18	1.53	
*Calculated by the comp	oiler.			
		AUXILIARY I	NFORMATION	
METHOD/APPARATU	S/PROCEDURE:		SOURCE AND PURITY OF MATERIALS:	
All procedures identical	•		The source of 2-propanol was not specified. See the	
compilation of this auth	_		compilation cited on the left for other details.	
AgBrO ₃ -CH ₃ OH-H ₂ O s	ystem.			

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) 2-Propanol; C₃H₈O; [67-63-0]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.

Nippon Kagaku Zasshi 1959, 80, 110-3.

VARIABLES:

Solvent composition

T/K = 293.15, 298.15 and 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

2-propane	ol content	silver bro	nate solubility/n	nmol dm-3
mass %	mol %a	20°C	25ºC	30°C
0.0	0.0	7.28	8.59	10.02
3.072	0.941	6.57	7.58	8.67
6.361	1.996	5.82	6.74	7.84
11.946	3.908	4.83	5.53	6.30
17.931	6.147	3.98	4.52	5.00
23.856	8.586	3.39	3.85	4.31
29.241	11.023			3.51
29.458	11.126	2.99	3.27	
37.410	15.195	2.47	2.83	2.97
46.280	20.525	2.02	2.21	2.38
58.369	29.592	1.42	1.53	1.67
69.941	41.090	0.94	1.01	1.08

^{*}Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours which was sufficient time to reach equilibrium. After the solid was allowed to settle, aliquots of saturated solution were withdrawn and the solubility was determined by analysis for total silver.

To each aliquot of saturated solution, a measured excess of 0.050 mol dm-3 of NaCl solution was added, and the remaining chloride titrated with 0.025 mol dm-3 AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako Co. guaranteed reagent) to a large volume of dilute KNO₃ solution. The solution was boiled, aged, and the precipitate washed and dried under reduced presure.

2-Propanol (Kanto Kagaku Co. guaranteed reagent) was dried over CaO and distilled twice.

ESTIMATED ERROR:

Soly: probable error within \pm 0.07 mmol dm⁻³. Temp: precision \pm 0.02 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium nitrate; NaNO₃; [7631-99-4]
- (3) 2-Propanol; C₃H₈O; [67-63-0]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gross, P.; Kuzmany, P.; Wald, M.

J. Am. Chem. Soc. 1937, 59, 2692-4.

VARIABLES:

Concentration of NaNOs

T/K = 288.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

Solubility of AgBrO₃ at 15.000°C in a 79.92 % 2-propanol and 20.08 % water mixture containing NaNO₃. Nowhere in the paper do the authors define the bases of the % used to define the solvent composition. The density of the solvent was given as $d_4^{15} = 0.8402$ g cm⁻³, and the static permittivity of the solvent was given as $\epsilon = 25.4$.

NaNO ₃ concn	AgBrO ₃ soly		
104mol dm-3	104mol dm-3	-log K _{s0}	-log K ⁰ _{s0}
0	1.326	7.755	7.842
1.335	1.385	7.717	7.841
2.627	1.435	7.686	7.838
5.156	1.513	7.646	7.840
7.588	1.576	7.605	7.833
9.932	1.627	7.577	7.833
12.29	1.682	7.548	7.829
14.37	1.732	7.523	7.825
17.64	1.762	7.508	7.839
22.53	1.810	7.485	7.856

Solubility product calculated from K_{s0} = [AgBrO₃]². The thermodynamic solubility product was calculated from

 $log K_{00}^{0} = log K_{00} - 3.76(I)^{1/2}$

where I is the ionic strength.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvent composition is 79.92 % 2-propanol and 20.08 % water (% not defined, but probably was mass %). The mixed solvent with NaNO₃ and solid AgBrO₃ were placed in glass flasks. The flasks were rotated in a thermostat at 15.000°C for 12 hours which was stated to be sufficient time to insure equilibrium. For the analysis, 25 cm³ of filtered saturated solution was placed in a small flask and evaporated on a boiling water bath while N₂ was forced through the liquid. The precipitated AgBrO₃ was titrated iodometrically.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by adding AgNO₃ to a solution of KBrO₃. Both AgNO₃ and KBrO₃ were AR grade materials and recrystallized twice. NaNO₃ was the "purest commercial product," and was recrystallized from ethanol. C.p. grade 2-propanol was distilled from sulfanilic acid in a stream of N₂.

ESTIMATED ERROR:

Soly: precision probably ≤ 1 % (compiler). Temp: precision ± 0.0025 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Silver nitrate; AgNO₃; [7761-88-8]
- (3) 2-Propanol; C₃H₈O; [67-63-0]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gross, P.; Kuzmany, P.; Wald, M.

J. Am. Chem. Soc. 1937, 59, 2692-4.

VARIABLES:

Concentration of AgNO₃

T/K = 288.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

Solubility of AgBrO₃ at 15.000°C in a 79.38 % 2-propanol and 20.62 % water mixture containing NaNO₃. Nowhere in the paper do the authors define the bases of the % used to define the solvent composition. The density of the solvent was given as $d_4^{15} = 0.8415$ g cm⁻³, and the static permittivity of the solvent was given as $\epsilon = 25.6$.

AgNO ₃ concn	AgBrO ₃ soly		
104mol dm-3	104mol dm-3	-log K _{s0}	-log Ko
0	1.532	7.630	7.723
1.008	1.136	7.614	7.725
1.978	0.883	7.598	7.725
2.912	0.725	7.579	7.723
3.811	0.611	7.568	7.726
4.714	0.541	7.546	7.722
5.549	0.484	7.535	7.720
7.134	0.406	7.514	7.721
8.645	0.353	7.498	7.723

Solubility product calculated from $K_{s0} = [AgBrO_3]^2$. The thermodynamic solubility product was calculated from

 $log K_{00} = log K_{00} - 3.76(I)^{1/2}$

where I is the ionic strength.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvent composition is 79.38 % 2-propanol and 20.62 % water (% not defined, but probably was mass %). The mixed solvent with $AgNO_3$ and solid $AgBrO_3$ were placed in glass flasks. The flasks were rotated in a thermostat at 15.000°C for 12 hours which was stated to be sufficient time to insure equilibrium. For the analysis, 25 cm³ of filtered saturated solution was placed in a small flask and evaporated on a boiling water bath while N_2 was forced through the liquid. The precipitated $AgBrO_3$ was titrated iodometrically.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by adding AgNO₃ to a solution of KBrO₃. Both AgNO₃ and KBrO₃ were AR grade materials and recrystallized twice. C.p. grade 2-propanol was distilled from sulfanilic acid in a stream of N₂.

ESTIMATED ERROR:

Soly: precision probably ≤ 1 % (compiler). Temp: precision ± 0.0025 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium benzene sulfonate; C₆H₅O₃SNa; [515-42-4]
- (3) 2-Propanol; C₃H₈O; [67-63-0]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gross, P.: Kuzmany, P.: Wald, M.

J. Am. Chem. Soc. 1937, 59, 2692-4.

VARIABLES:

Concentration of C6H5O3SNa

T/K = 288.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

Solubility of AgBrO₃ at 15.000°C in a 79.04 % 2-propanol and 20.96 % water mixture containing NaNO₃. Nowhere in the paper do the authors define the bases of the % used to define the solvent composition. The density of the solvent was given as $d_4^{15} = 0.8423$ g cm⁻³, and the static permittivity of the solvent was given as $\epsilon = 25.75$.

C ₆ H ₅ O ₃ SNa concn 10 ⁴ mol dm- ³	AgBrO ₃ soly 104mol dm-3	-log Kan	-log K ⁰ n0
	•••		
0	1.788	7.495	7.600
1.009	1.482	7.469	7.596
1.981	1.889	7.447	7.595
3.816	1.963	7.414	7.595
4.728	1.980	7.406	7.601
5.564	2.003	7.396	7.603
6.786	2.025	7.387	7.610
8.675	2.045	7.379	7.625

Solubility product calculated from $K_{*0} = [AgBrO_5]^2$. The thermodynamic solubility product was calculated from

 $log K_{s0} = log K_{s0} - 3.76(I)^{1/2}$

where I is the ionic strength.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvent composition is 79.04 % 2-propanol and 20.96 % water (% not defined, but probably was mass %). The mixed solvent with $C_6H_5O_3SNa$ and solid $AgBrO_3$ were placed in glass flasks. The flasks were rotated in a thermostat at 15.000°C for 12 hours which was stated to be sufficient time to insure equilibrium. For the analysis, 25 cm³ of filtered saturated solution was placed in a small flask and evaporated on a boiling water bath while N_2 was forced through the liquid. The precipitated $AgBrO_3$ was titrated iodometrically.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by adding AgNO₃ to a solution of KBrO₃. Both AgNO₃ and KBrO₃ were AR grade materials and recrystallized twice. Sodium benzene sulfonate was made from a concentrated solution of NaOH (AR grade, Merck) and benzene sulfonic acid (Kahlbaum). The product was recystallized from ethanol. C.p. grade 2-propanol was distilled from sulfanilic acid in a stream of N₂.

ESTIMATED ERROR:

Soly: precision probably ≤ 1 % (compiler). Temp: precision \pm 0.0025 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Potassium nitrate; KNO₃; [7757-79-1]
- (3) 2-Propene-1-ol (allyl alcohol); C₃H₆O; [107-18-6]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.; Kepner, R.E.

J. Am. Chem. Soc. 1949, 71, 3906-9.

VARIABLES:

Concentration of H2CCHCH2OH

T/K = 298

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

The initial solvent was water with small amounts of H₂CCHCH₂OH, and 0.10 mol dm⁻³ KNO₃.

H ₂ CCHCH ₂ OH concn	AgBrO ₃ soly	K_1
mol dm-3	102mol dm-3	mol-1 dm ³
0.585	. 2.98	14.0
0.293	2.20	14.0
0.146	1.69	13.8
0.0732	1.38	13.6

The authors reported K_{s0} = 1.00 x 10⁻⁴ mol² dm⁻⁶ in 0.10 mol dm⁻³ KNO₃ solution. Values of K₁ in the above table are defined by:

$$K_1 = \frac{\left[Ag(C_3H_6O)^*\right]}{\left[Ag^*\right]\left[C_3H_6O\right]}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

KNO₃ was added to the solvent to adjust the ionic strength at 0.10 mol dm-3. These solutions were then added to AgBrO₃ crystals in glass-stoppered erlenmeyer flasks. The flasks were aggitated for 4 hours at 25°C. After allowing excess solid to settle, aliquots of saturated solution were withdrawn and analyzed for silver by adding a measured excess of NaCl solution, and backtitrating the excess chloride with AgNO3 using The source and purity of allyl alcohol was not given. dichlorofluorescein as an indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ was prepared by slowly adding a dilute solution of KBrO₃ to a dilute solution of AgNO₃. The precipitate was washed, filtered, suspended in water for several days, and dried at 110°C. The precipitate was analyzed for silver: found 45.90 % (calculated 45.75 %).

ESTIMATED ERROR:

Nothing specified.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Potassium nitrate; KNO₃; [7757-79-1]
- (3) 2-Methyl-2-propene-1-ol (β -methallyl alcohol); C₄H₈O; [513-42-8]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.; Kepner, R.E.

J. Am. Chem. Soc. 1949, 71, 3906-9.

VARIABLES:

Concentration of H₂CC(CH₃)CH₂OH

T/K = 298

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

The initial solvent was water with small amounts of H2CC(CH3)CH2OH, and 0.10 mol dm-3 KNO3.

H ₂ CC(CH ₃)CH ₂ OH concn	AgBrO ₃ soly	K_1
mol dm-3	102mol dm-3	mol-1 dm3
0.470	2.42	10.8
0.235	1.84	10.8
0.118	1.48	10.8
0.059	1.27	11.2

The authors reported $K_{s0} = 1.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ in 0.10 mol dm⁻³ KNO₃ solution. Values of K_1 in the above table are defined by:

$$K_1 = \frac{\left[Ag(C_4H_8O)^*\right]}{\left[Ag^*\right]\left[C_4H_8O\right]}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

KNO₃ was added to the solvent to adjust the ionic strength at 0.10 mol dm⁻³. These solutions were then added to AgBrO₃ crystals in glass-stoppered erlenmeyer flasks. The flasks were aggitated for 4 hours at 25°C. After allowing excess solid to settle, aliquots of saturated solution were withdrawn and analyzed for silver by adding a measured excess of NaCl solution, and backtitrating the excess chloride with AgNO₃ using dichlorofluorescein as an indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ was prepared by slowly adding a dilute solution of KBrO₃ to a dilute solution of AgNO₃. The precipitate was washed, filtered, suspended in water for several days, and dried at 110° C. The precipitate was analyzed for silver: found 45.90 % (calculated 45.75 %). β -Methallyl alcohol (Shell Chem. Corp.) was dried and fractionated before use.

ESTIMATED ERROR:

Nothing specified.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) 1,2,3-Propanetriol (glycerol); C₃H₈O₃; [56-81-5]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Miyamoto, H.

Nippon Kagaku Zasshi 1959, 80, 825-8.

VARIABLES:

Solvent composition

T/K = 288.15, 293.15, 298.15 and 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

glycerol	content	silv	er bromate sol	ubility/mmol dm-3	•
mass %	mol %ª	15ºC	20ºC	25°C	30°C
0.0	0.0	6.07	7.28	8.59	10.02
8.348	1.751	5.86	7.02	8.30	9.82
16.180	3.639	5.72	6.96	8.03	9.58
30.909	8.047	5.54	6.44	7.82	8.98
40.628	11.806	5.24	6.28	7.44	8.60
58.346	21.507	4.81	5.57	6.59	7.55
66.989	28.416			6.19	7.00
79.633	43.338	3.89	4.67	5.40	6.18
90.713	65.644		3.46	4.29	5.09

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours which was sufficient time to reach equilibrium. After the solid was allowed to settle, aliquots of saturated solution were withdrawn and the solubility was determined by analysis for total silver.

To each aliquot of saturated solution, a measured excess of 0.050 mol dm⁻³ of NaCl solution was added, and the remaining chloride titrated with 0.025 mol dm⁻³ AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako Co. guaranteed reagent) to a large volume of dilute KNO₃ solution. The solution was boiled, aged, and the precipitate washed and dried under reduced presure.

Glycerol (Kanto Kagaku Co. guaranteed reagent) was distilled twice under reduced pressure.

ESTIMATED ERROR:

Soly: probable error within ± 0.03 mmol dm⁻³. Temp: precision ± 0.02 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) 1,2,3-Propanetriol (glycerol); C ₃ H ₈ O ₃ ; [56-81-5]	Owen, B B.
(3) Water; H_2O ; [7732-18-5]	J. Am. Chem. Soc. 1933, 55, 1922-8.
VARIABLES:	PREPARED BY:
Solvent composition T/K = 298	II Minamata and M Calaman
EVDEDIMENTAL DATA.	H. Miyamoto and M. Salomon

EXP.	ER	IMEN	TAL	DATA:
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glycerol con	ntent	AgBrO ₃ soly	density
mass %	mol %a	mmol dm-3	kg dm-3
0	0	8.12 ^b	0.9987
10	2.1	7.80	1.0207
20	4.7	7.49	1.0453
30	7.7	7.15	1.0706
40	11.5	6.84	1.0971
50	16.4	6.48	1.1239
60	22.7	6.08	1.1511
70	31.3	5.59	1.1784
80	43.9	4.94	1.2054

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Procedures identical to those in the compilation of this author's study of the AgBrO₃-CH₃OH-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Baker's analyzed glycerol dist in vac. For glycerol content > 30 %, Kahlbaum's "purest" glycerol was used.

COMPONENTS:		OI	RIGINAL MEASUREMENT	rs:
 Silver bromate; A₁ Sodium hydroxide Acetic acid; C₂H₄ 1,2,3-Propanetriol Water; H₂O; [7732 	s; NaOH; [1310-73-2 O ₂ ; [64-19-7] I (glycerol); C ₃ H ₈ O ₃ ;		avies, P. B.; Monk, C. B. Chem. Soc. <u>1951</u> , 2718-2.	3.
VARIABLES: Concentrations of Nat I/K = 298.15	OH, CH ₃ COOH and	glycerol	EPARED BY: . Miyamoto	
EXPERIMENTAL DA	ITA:			
glycerol mass %	glycerol mol %ª	NaOH concr mol dm-3	CH ₃ COOH conen mol dm- ³	AgBrO ₃ soly mmol dm-3
31.7	8.32	0.0	0.0 0.03437	7.09 8.33
		0.03096	0.03437	0.33

AUXILIARY INFORMATION

0.02927

0.05160

METHOD/APPARATUS/PROCEDURE:

42.3

*Calculated by the compiler.

Procedures identical to those in the compilation of these authors' study of the AgBrO₃-NaOH-CH₃COOH-CH₃CH₂OH-H₂O system.

12.54

SOURCE AND PURITY OF MATERIALS:

0.03381

0.05776

"Laboratory grade" glycerol was used. Other details given in the compilation cited on the left.

6.75

8.01

8.60

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) 2-Methyl-2-propanol (t-butanol); C₄H₁₀O; [75-65-0]

(3) Water; H₂O; [7732-18-5]

VARIABLES:

Solvent composition

T/K = 293.15, 298.15 and 303.15

ORIGINAL MEASUREMENTS:

Miyamoto, H.

Nippon Kagaku Zasshi 1957, 78, 1392-6.

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

t-butanol content		silver broa	mate solubility/n	nmol dm-3
mass %	mol %a	20ºC	25ºC	30°C
0.0	0.0	7.28	8.59	10.02
2.781	0.690	6.55	7.71	9.08
4.882	1.232	6.02	7.13	8.43
10.555	2.788	4.58	6.04	7.13
15.943	4.407	3.94	4.80	5.86
20.539	5.911	3.49	4.35	5.21
25.336	7.619	3.11	3.73	4.57
30.860	9.786	2.58	3.03	3.73
38.712	13.309	2.10	2.41	2.91
48.447	18.593	1.56	1.74	2.06
58.542	25.551	1.14	1.31	1.48

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours which was sufficient time to reach equilibrium. After the solid was allowed to settle, aliquots of saturated solution were withdrawn and the solubility was determined by analysis for total silver.

To each aliquot of saturated solution, a measured excess of 0.050 mol dm⁻³ of NaCl solution was added, and the remaining chloride titrated with 0.025 mol dm⁻³ AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako Co. guaranteed reagent) to a large volume of dilute KNO₃ solution. The solution was boiled, aged, and the precipitate washed and dried under reduced presure.

t-Butanol (Kanto Kagaku Co. guaranteed reagent) was recrystallized and distilled from metallic sodium.

ESTIMATED ERROR:

Soly: probable error within \pm 0.03 mmol dm⁻³. Temp: precision \pm 0.02 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Potassium nitrate; KNO₃; [7757-79-1] (3) 2-Butene-1-ol (crotyl alcohol); C₄H₈O; [6117-91-5] (4) Water; H₂O; [7732-18-5] 	Keefer, R. M.; Andrews, L. J.; Kepner, R.E. J. Am. Chem. Soc. <u>1949</u> , 71, 3906-9.
VARIABLES: Concentration of CH ₃ CH=CHCH ₂ OH T/K = 298	PREPARED BY: H. Miyamoto

The initial solvent was water with small amounts of crotyl alcohol, and 0.10 mol dm-3 KNO₃.

CH ₃ CH=CHCH ₂ OH concn	AgBrO ₃ soly	K ₁
mol dm-3	10 ² mol dm ⁻³	mol ⁻¹ dm ³
0.702	1.87	3.6
0.527	1.73	3.9
0.351	1.54	4.0
0.176	1.30	4.0
0.0878	1 16	41

The authors reported $K_{a0} = 1.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ in 0.10 mol dm⁻³ KNO₃ solution. Values of K_1 in the above table are defined by:

 $K_1 = [Ag(C_4H_8O)^+]/[Ag^+][C_4H_8O]$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Complete details given in the compilation of these	Crotyl alcohol was prepd from 2-butenal (crotonalde-
authors' study of the AgBrO ₃ -KNO ₃ -C ₃ H ₆ O-H ₂ O sys-	hyde). Remaining details given in the compilation
tem.	cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Potassium nitrate; KNO₃; [7757-79-1] (3) 3-Butene-2-ol (methyl vinyl carbinol); C₄H₈O; [598-32-3] (4) Water; H₂O; [7732-18-5] 	Keefer, R. M.; Andrews, L. J.; Kepner, R.E. J. Am. Chem. Soc. <u>1949</u> , 71, 3906-9.
VARIABLES: Concentration of CH ₃ CH(OH)CH=CH ₂ T/K = 298	PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA:

The initial solvent was water with small amounts of CH₃CH(OH)CH=CH₂, and 0.10 mol dm-8 KNO₃.

CH ₃ CH(OH)CH=CH ₂ concn	AgBrO ₃ soly	K ₁	
mol dm ⁻³	10 ² mol dm ⁻³	mol ⁻¹ dm ³	
0.255	2.12	14.7	
0.204	1.93	14.3	
0.102	1.53	14.5	
0.051	1.28	14.9	
0.025	1.14	14.9	

The authors reported $K_{s0} = 1.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ in 0.10 mol dm⁻³ KNO₃ solution. Values of K_1 in the above table are defined by:

 $K_1 = [Ag(C_4H_8O)^+]/[Ag^+][C_4H_8O]$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Complete details given in the compilation of these authors' study of the AgBrO3-KNO3-C3H6O-H2O system.

SOURCE AND PURITY OF MATERIALS:

CH₃CHOHCH=CH₂ prepd by hydrolysis of butenyl chloride. Remaining details given in the compilation cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Potassium nitrate; KNO ₃ ; [7757-79-1] (3) 2-Methyl-2-butene-1-ol; C ₅ H ₁₀ O; [4675-87-0] (4) Water; H ₂ O; [7732-18-5]	Keefer, R. M.; Andrews, L. J.; Kepner, R.E. J. Am. Chem. Soc. <u>1949</u> , 71, 3906-9.
VARIABLES: Concentration of CH ₃ CH=C(CH ₃)CH ₂ OH T/K = 298	PREPARED BY: H. Miyamoto

The initial solvent was water with small amounts of CH₃CH=C(CH₃)CH₂OH, and 0.10 mol dm-3 KNO₃.

CH ₃ CH=C(CH ₃)CH ₂ OH concn	AgBrO ₃ soly	K_1
mol dm-3	102mol dm-3	mol-1 dm3
0.100	1.21	4.8
0.050	1.12	4.9
0.020	1.05	5.5

The authors reported $K_{80} = 1.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ in 0.10 mol dm⁻³ KNO₃ solution. Values of K_1 in the above table are defined by:

 $K_1 = [Ag(C_5H_{10}O)^+]/[Ag^+][C_5H_{10}O]$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Complete details given the compilation of these	CH ₃ CH=C(CH ₃)CH ₂ OH was supplied by Prof. W.G.
authors' study of the AgBrO ₃ -KNO ₃ -C ₃ H ₆ O-H ₂ O	Young of the UCLA. Remaining details given in the
system.	compilation cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Potassium nitrate; KNO₃; [7757-79-1] (3) 1-Penten-3-ol (ethyl vinyl carbinol); C₅H₁₀O; [616-25-1] (4) Water; H₂O; [7732-18-5] 	Keefer, R. M.; Andrews, L. J.; Kepner, R.E. J. Am. Chem. Soc. <u>1949</u> , 71, 3906-9.
VARIABLES: Concentration of C ₂ H ₅ CH(OH)CH=CH ₂ T/K = 298	PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA:

The initial solvent was water with small amounts of C₂H₆CH(OH)CH=CH₂, and 0.10 mol dm-3 KNO₃.

C ₂ H ₅ CH(OH)CH=CH ₂ concn	AgBrO ₃ soly	K ₁
mol dm-3	102mol dm-3	mol-1 dm3
0.472	2.68	13.8
0.236	2.04	14.2
0.0944	1.52	15.3
0.0472	1.28	15.2

The authors reported $K_{s0} = 1.00 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6} \text{ in 0.10 mol dm}^{-3} \text{ KNO}_3 \text{ solution.}$ Values of K_1 in the above table are defined by:

 $K_1 = [Ag(C_5H_{10}O)^+]/[Ag^+][C_5H_{10}O]$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Complete details given the compilation of these authors' study of the $AgBrO_3$ - KNO_3 - C_3H_6O - H_2O system.

SOURCE AND PURITY OF MATERIALS:

 $C_2H_5CH(OH)CH=CH_2$ prepd from ethylmagnesium bromide and acrolein (2-propenal). Remaining details given in the compilation cited on the left.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Potassium nitrate; KNO₅; [7757-79-1]
- (3) Phenol; C₆H₆O; [108-95-2]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Keefer, R. M.; Andrews, L. J.; Kepner, R.E.

J. Am. Chem. Soc. 1949, 71, 3906-9.

VARIABLES:

Concentration of C₆H₅OH

T/K = 298

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

The initial solvent was water with small amounts of C6H5OH, and 0.10 mol dm-3 KNO3.

C ₆ H ₅ OH concn	AgBrO ₃ soly	K ₁
mol dm-3	102mol dm-3	mol-1 dm ³
0.448	1.28	1.54
0.224	1.14	1.48
0.112	1.07	1.59
0	0.989	

The authors reported $K_{10} = 9.78 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$ in 0.10 mol dm⁻³ KNO₃ solution. Values of K_1 in the above table are defined by:

$$K_1 = \frac{\left[Ag(C_6H_6O)^*\right]}{\left[Ag^*\right]\left[C_6H_6O\right]}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

KNO₃ was added to the solvent to adjust the ionic strength at 0.10 mol dm⁻³. These solutions were then added to AgBrO₃ crystals in glass-stoppered erlenmeyer flasks. The flasks were aggitated for 4 hours at 25°C. After allowing excess solid to settle, aliquots of saturated solution were withdrawn and analyzed for silver by adding a measured excess of NaBr solution, and weighing the precipitated AgBr.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ was prepared by slowly adding a dilute solution of KBrO₃ to a dilute solution of AgNO₃. The precipitate was washed, filtered, suspended in water for several days, and dried at 110°C. The precipitate was analyzed for silver: found 45.90 % (calculated 45.75 %).

The source and purity of KNO₃ was not given. J.T. Baker c.p. grade phenol was distilled.

ESTIMATED ERROR:

Nothing specified.

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Mannitol; C₆H₁₄O₆; [87-78-5]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Owen, B. B.

J. Am. Chem. Soc. 1933, 55, 1922-8.

VARIABLES:

Solvent composition

T/K = 298

PREPARED BY:

H. Miyamoto and M. Salomon

EXPERIMENTAL DATA:

mannitol content		AgBrO ₃ soly	density
mass %	mol %a	mmol dm-3	kg dm-3
0	0	8.12b	0.9987
5	0.5	8.24	1.0147
10	1.1	8.38	1.0328
15	1.7	8.51	1.0513

*Calculated by the compiler.

bMean of four independent measurements with an average deviation of 0.004 mmol dm-3.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Three to four grams of AgBrO₃ crystals were placed in long-necked 200 to 500 cm³ flasks. Ice-cold solvent was quickly introduced into the flasks without wetting the necks, and the flasks were sealed. The flasks were rotated slowly for five or six days at 25°C. Preliminary studies indicated that equilibrium was reached within two days. After 2-3 days, the solutions became turbid.

The saturated solutions were forced through asbestosglass wool filtering mats, and 100 to 400 g samples were weighed. The Ag content was determined gravimetrically as AgBr.

For the mixed solvents, the solubilities were determined on a mass basis and converted to mol dm⁻³ units using the density values given in the table.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ was prepared from dilute solutions of Baker's "Analyzed" grade AgNO₃ and KBrO₃. Equivalent volumes of these two solutions were slowly mixed, and the resulting precipitate was washed and recrystallized.

Mannitol (Th. Schuchardt, Gorlitz, Germany) was recrystallized four times from conductivity water, and then dried in vacuum (1).

ESTIMATED ERROR:

Soly: av deviation given above. Precision of all results not specified.

Temp: nothing specified.

REFERENCES:

1. Akerlof, G. J. Am. Chem. Soc. 1932, 54, 4125.

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Sucrose; $C_{12}H_{22}O_{11}$; [57-50-1]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Koizumi, E.; Miyamoto, H.

Nippon Kagaku Zasshi 1956, 77, 193-6.

VARIABLES:

Concentration of sucrose

T/K = 293.15, 298.15and 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENT.	AL DATA:

BILL ENGINEE CLIEB BILLIN			
	$[C_{12}H_{22}O_{11}]$	$[C_{12}H_{22}O_{11}]$	AgBrO ₃ soly
t/ºC	mass %	mol %a	mmol dm-3
20	0	0	7.28
20	-	•	
	5.379	0.298	7.18
	9.951	0.578	7.00
	17.142	1.077	6.83
	35.197	1.742	6.61
	34.793	2.732	6.39
	46.975	4.455	5.62
25	0	0	8.59
	5.047	0.279	8.43
	10.234	0.596	8.32
	17.347	1.093	8.05
	25.221	1.744	7.87
	35.413	2.805	7.63
	46.654	4.400	6.84
30	0	0	10.02
	5.047	0.279	9.94
	9.951	0.578	9.86
	16.959	1.063	9.75
	25.194	1.742	9.39
	35.258	2.786	9.20
	47.389	4.526	8.44

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and the mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours. After allowing excess solid to settle, aliquots of saturated solution were withdrawn and analyzed for total silver by adding a measured excess of NaCl solution followed by backtrating the excess chloride with 0.025 mol dm⁻³ AgNO₃ using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako, Co. guaranteed reagent) to a large volume of hot water. The precipitate was washed, and dried under reduced pressure.

Sucrose (Kanto Kagaku Co. guaranteed reagent) was used as received.

ESTIMATED ERROR:

Soly: precision within ± 0.05 mmol dm⁻³ (compiler). Temp: precision ± 0.02 K.

COMPONENTS:		OPIC	INAL MEASUR	EMENTS:	
(1) Silver bromate; AgBrO ₃ ;	17783_89_31	1	Miyamoto, H.		
(2) 2-Propanone (acetone);	-			ı i <u>1957</u>, 78, 690-4.	
(3) Water; H ₂ O; [7732-18-5]	• • • •	1	on magnet wass.	<u>1221,</u> 70, 070 4.	•
VARIABLES:		PREF	PARED BY:	· · · · · · · · · · · · · · · · · · ·	
Solvent composition		1			
T/K = 293.15, 298.15 and	303.15	H. M	liyamoto		
EXPERIMENTAL DATA:					
CH ₃ C(0	O)CH ₃ content	silver bro	omate solubility/1	nmol dm ⁻³	
mass %	mol %ª	20°C	25°C	30°C	
0.0	0.0	7.28	8.59	10.02	
3.943	1.257	6.57	7.71	9.26	
7.977	2.618	5.84	6.88	8.19	
16.532	5.788	4.45	5.28	6.32	
22.332	8.188	3.68	4.33	5.41	
30.164	11.815	2.96	3.57	4.20	
36.898	15.353	2.42	2.79	3.49	
44.062	19.635	1.90	2.19	2.60	
54.697	27.246	1.29	1.48	1.93	
68.787	40.603	0.79	0.96	1.13	
80.470	56.103	0.51	0.65	0.80	
aCalculated by the compiler	•				
	AUXIL	IARY INFORM	IATION		
METHOD/APPARATUS/P.	ROCEDURE:	soui	RCE AND PURIT	Y OF MATERIAL	ιS:
All procedures identical to	those given in the co	mpila- C.p. g	grade acetone was	treated with AgN	O ₃ and NaOH
tion of this author's study of	f the	and t	he resulting ppt v	vas removed by fil	tration. The
AgBrO ₃ -CH ₃ OH-H ₂ O syste	m.	L L	solvent was stored over K ₂ CO ₃ , and distd from metallic sodium.		

COMPONENTS: (1) Silver bromate; AgBrO ₅ ; [7783-89-3] (2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1] (3) Water; H ₂ O; [7732-18-5]		ORIGINAL MEASUREMENTS: Owen, B. B. J. Am. Chem. Soc. 1933, 55, 1922-8.			
VARIABLES: Solvent composition T/K = 298		PREPARED BY H. Miyamoto a	': and M. Salomon		
EXPERIMENTAL DATA:					
[C ₃ H ₆ O	[C ₃ H ₆ O]	AgBrO ₃ soly	density		
mass %	mass %a	mmol dm-3	kg dm ⁻⁸		
0	0	8.12 ^b			
10	3.3	5.92	0.9845		
20	7.2	4.29	0.9700		
30	11.7	3.00	0.9537		
40	17.1	2.03	0.9355		

^aCalculated by the compiler.

bMean of 4 independent determinations with 0.004 mmol dm⁻³ average deviation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

All procedures identical to those given in the compilation of this author's study of the AgBrO₃-CH₃OH-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Acetone (Baker's "analyzed" or Eastman Kodak's product) was distilled two times. Other details given in the compilation cited on the left.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sodium hydroxide; NaOH; [1310-73-2]
- (3) Acetic acid; C₂H₄O₂; [64-19-7]
- (4) 2-Propanone (acetone); C₃H₆O; [67-64-1]
- (5) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Davies, P. B.; Monk, C. B.

J. Chem. Soc. 1951, 2718-23.

VARIABLES:

Concentrations of NaOH, CH₃COOH and CH₃C(O)CH₃ T/K = 298.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH ₃ C(O)CH ₃ mass %	contenta mol %	NaOH concn mol dm-3	CH ₃ COOH concn mol dm-3	AgBrO ₃ soly mmol dm-5
21.1	7.6 ₇	0	0	3.98
		0.02526	0.03837	4.94
		0.04210	0.05180	5.37
26.1	9.87	0	0	3.18
		0.02972	0.05790	4.32
		0.04128	0.08088	4.67
		0.06391	0.1236	5.19
38.4	16.2 ₀	0	0	2.16
		0.02526	0.03453	3.18
		0.04210	0.05084	3.70
39.5	16.84	0	0	2.07
		0.03705	0.07237	3.51
		0.04128	0.08088	3.62
		0.04954	0.1065	3.83

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturating column method was used. Saturated solutions were analyzed for bromate by addition of excess KI to about 25 cm³ aliquots followed by addition of about 15 cm³ of 1 mol dm-³ H₂SO₄. The aliquots were then titrated with standard thiosulfate solution using a starch indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ crystals were prepared by adding dilute solutions of (A.R. grade) KBrO₃ and AgNO₃ to a large volume of hot water. The precipitate was washed and dried.

AnalaR acetic acid was used. "Laboratory grade" acetone was used.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.03 K.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Tetrahydrofuran; C ₄ H ₈ O; [109-99-9] (3) Water; H ₂ O; [7732-18-5]			ORIGINAL MEASUREMENTS: Koizumi, E.; Miyamoto, H. Bull. Chem. Soc. Jpn 1956, 29, 950-3.		
VARIABLES: Solvent composition T/K = 293.15, 298.15 and 303.15			PREPARED BY: H. Miyamoto		
EXPERIMENTAL DATA:					
C₄H _i	O content	silver bron	nate solubility/n	nmol dm-3	
mass %	mol %ª	20°C	25°C	30°C	
0.0	0.0	7.28	8.59	10.02	
3.347	0.858	6.34	7.62	8.99	
6.769	1.782	5.72	6.83	8.08	
12.645	3.490	4.73	5.81	6.82	
18.770	5.458	3.97	4.88	5.62	
24.471	7.489	3.39	4.23	4.79	
29.208	9.345	2.93	3.67	4.12	
35.670	12.168	2.51	2.90	3.28	
43.537	16.153	1.90	2.31	2.55	
54.513	23.042	1.34	1.53	1.77	
64.232	30.971	0.99	1.13	1.43	
*Calculated by the compiler.					
	· AUXILI	ARY INFORMA	TION		
METHOD/APPARATUS/PROCEDURE:			SOURCE AND PURITY OF MATERIALS:		
All procedures identical to those given in the compilation of these authors' study of the AgBrO ₃ -sucrose-H ₂ O system.		1 .	Tetrahydrofuran (Badische A.G.) was purified by two fractional distillations.		by two

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) 1,4-Dioxane; C ₄ H ₈ O ₂ ; [123-91-1] (3) Water; H ₂ O; [7732-18-5]		Ko	ORIGINAL MEASUREMENTS: Koizumi, E.; Miyamoto, H. Nippon Kagaku Zasshi 1954, 75, 1302-5.			
VARIABLES: Solvent compo T/K = 293.15,	sition 298.15 and 303	.15		PARED BY: Miyamoto		
EXPERIMENT	TAL DATA:					
	C ₄ H ₈ O ₂ co	ntent	silver b	romate solubility/n	nmol dm-3	
	mass %	mol %ª	20°C	25°C	30°C	
	0.0	0.0	7.28	8.59	10.02	
	2.494	0.520	6.94	8.19	9.51	
	4.884	1.039	6.68	7.69	9.02	
	10.243	2.280	5.81	6.90	7.96	
	15.178	3.530	5.04	6.06	6.90	
	20.105	4.894	4.34	5.06	5.94	
	25.114	6.417	3.85	4.46	5.12	
	30.219	8.134	3.29	3.96	4.64	
	37.694	11.008	2.65	3.19	3.72	
aCalculated by	the compiler.					
		AUXILI	ARY INFOR	MATION		
METHOD/AP	PARATUS/PROC	EDURE:	sou	SOURCE AND PURITY OF MATERIALS:		
All procedures	identical to those	given in the	1,4-	1,4-Dioxane (Takeda Co., c.p. reagent) was recrystal-		
compilation of	these authors' stu	dy of the	lized	lized and distilled.		
AgBrO ₃ -sucros	se-H ₂ O system.					

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) 1,4-Dioxane; C ₄ H ₈ O ₂ ; [123-91-1] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Monk, C. B. J. Chem. Soc. 1951, 2723-6.
VARIABLES: Solvent composition T/K = 298	PREPARED BY: H. Miyamoto

C ₄ H ₈ O ₂ co	ntent	AgBrO ₃ soly			
mass %	ass % mol % mmol kg-1		-log Ko _{s0}	E	
10	2.2	6.24	4.496	69.7	
20	4.9	4.76	4.739	60.8	

aCalculated by the compiler.

The thermodynamic solubility product was calculated from

$$log K_{so}^{0} = 2log S - \left(\frac{78.54}{\epsilon}\right)^{3/2} \left(\frac{\sqrt{I}}{1+\sqrt{I}}\right) - 0.2I$$

where S is the solubility, I the ionic strength, and ϵ is the static permittivity of the solvent.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Procedures identical to those in the studies by Monk, and by Monk and Davies compiled throughout this

SOURCE AND PURITY OF MATERIALS:

AnalaR grade dioxane was used. Other details given in the various compilations of Monk, and Monk and Davies' studies.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	
(2) Sodium hydroxide; NaOH; [1310-73-2] (3) Acetic acid; C ₂ H ₄ O ₂ ; [64-19-7]	Davies, P. B.; Monk, C. B.
(4) 1,4-Dioxane; C ₄ H ₈ O ₂ ; [123-91-1] (5) Water; H ₂ O; [7732-18-5]	J. Chem. Soc. 1951, 2718-23.
VARIABLES: Concentrations of NaOH, CH ₃ COOH and 1,4-dioxane	PREPARED BY:
T/K = 298.15	H. Miyamoto

EXPERIMENTAL DATA:

chapter.

C ₄ H ₈ O ₂ mass %	C ₄ H ₈ O ₂ mol %*	NaOH concn mol dm-3	CH ₃ COOH concn mol dm-3	AgBrO ₃ soly mmol dm-3
15.0	3.4 ₈	0	0	5.16
		0.03906	0.03522	6.52
		0.05160	0.05776	7.07
22.5	5.6 ₀	0	0	4.03
		0.05041	0.05649	6.05
*Calculated by the con	npiler.			

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Procedures identical to those in the compilation of these authors' study of the

AgBrO₃-NaOH-CH₃COOH-CH₃CH₂OH-H₂O system.

SOURCE AND PURITY OF MATERIALS:

"Laboratory grade" ethylene glycol was used. Other details given in the compilation cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]		
	Miyamoto, H.; Watanabe, Y.	
(2) Ethylene carbonate; C ₃ H ₄ O ₃ ; [96-49-1]		
	Nippon Kagaku Zasshi <u>1967</u> , 88, 36-8.	
(3) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
Solvent composition		
T/K = 298.15 and 308.15	H. Mivamoto	

	$[C_3H_4O_3]$	$[C_3H_4O_3]$	AgBrO ₃ soly
t/ºC	mass %	mol %ª	mmol dm-3
25	0	0	8.59
	5.121	1.092	8.14
	9.935	2.207	7.80
	20.704	5.070	7.16
	29.997	8.060	6.41
	40.102	12.046	5.36
	49.997	16.981	4.40
	59.996	23.478	3.16
	79.969	44.955	1.10
35	0	0	11.62
	5.205	1.111	11.21
	10.002	2.223	10.80
	20.000	4.865	9.90
	30.194	8.129	8.66
	40.018	12.009	7.25
	50.377	17.197	5.74
	60.011	23.489	4.22
	80.058	45.093	1.36
	93.584	74.899	0.19

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ and the mixed solvent were placed into glass-stoppered bottles. The bottles were rotated in a thermostat at a given temperature for 72 hours. After allowing excess solid to settle, aliquots of saturated solution were withdrawn and analyzed for total silver by adding a measured excess of NaCl solution followed by backtrating the excess chloride with AgNO3 using dichlorofluorescein indicator.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by addition of dilute solutions of AgNO₃ and KBrO₃ (Wako, Co. guaranteed reagent) to a large volume of a dilute KNO₃ solution. The solution was boiled and then aged. The precipitate was washed and dried under reduced pressure.

Ethylene carbonate (Tokyo Kasei Co. guaranteed reagent) was distilled two times under reduced pressure.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Sulfinyl bis-methane (dimethyl sulfoxide); C₂H₆OS; [67-68-5]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Janardhanan, S.; Kalidas, C.

Bull. Chem. Soc. Jpn 1980, 53, 2363-5.

VARIABLES:

Solvent composition

T/K = 303.2

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

(CH ₃) ₂ SO	(CH ₃) ₂ SO	AgBrO ₃ soly	
mol fraction	mass %a	mol kg-1	
0	0	0.0098	
0.1	32.5	0.0080	
0.2	52.0	0.0071	
0.3	65.0	0.0087	
0.4	74.3	0.0114	
0.5	81.3	0.0140	
0.6	86.7	0.0184	
0.7	91.0	0.0227	
0.8	94.5	0.0277	
0.9	97.5	0.0333	
1.0	100.0	0.0379	

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ was vigorously shaken in $(CH_3)_2SO-H_2O$ mixtures for 24 hours, and then transferred to a thermostat maintained at 30 \pm 0.1°C. The solutions were stirred for an additional 24 hours to insure attainment of equilibrium. The mixtures were centrifuged, and aliquots analyzed for bromate by addition of excess standard aqueous KI solution followed by potentiometric titration with standard AgNO₃.

SOURCE AND PURITY OF MATERIALS:

Silver bromate was prepared by reaction of AgNO₃ with KBrO₃. The precipitate was first washed with water, then with acetone, and dried under vacuum at 70-80°C for several hours. The purity of the salt was checked by determination of its silver content.

(CH₃)₂SO (BDH, LR grade) was heated over NaOH for 2 hours at 90°C, and then flash-distilled under vacuum. Doubly distilled water was used.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.1 K.

COMPONENTS: (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Perchloric acid; HClO₄; [7601-90-3]

(3) Formamide; CH₃NO; [75-12-7]

(4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Dash, U.N.

Thermochim. Acta 1975, 11, 25-33.

VARIABLES:

Concentration of HClO₄

T/K = 298.15, 303.15 and 308.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

Note that the solubility, S, of AgBrO₃ in HClO₄/formamide solutions prepared from 70 % (in water) HClO₄.

	HClO ₄ concn	solubility
t/ºC	mol dm-3	mol dm-3
25	0.02735	0.02080
	0.03543	0.02118
	0.04645	0.02185
	0.06352	0.02291
	0.08539	0.02442
	0.09315	0.02501
	0.10420	0.02570
30	0.02876	0.02236
	0.04860	0.02338
	0.05945	0.02393
	0.09342	0.02626
	0.10812	0.02762
	0.11992	0.02858
35	0.02625	0.02344
	0.03225	0.02396
	0.05226	0.02493
	0.06180	0.02570
	0.07185	0.02637
	0.09766	0.02754

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were prepared by dissolving weighed amounts of 70 % HClO₄ in known (weighed) amounts of formamide at an ice-cold temperature to prevent decomposition of formamide upon mixing. These mixtures were placed in amber-colored glass-stoppered bottles containing excess AgBrO₃. The bottles were stoppered and heavily paraffined, and then rotated in a water thermostat at a specified temperature for 7 to 8 hours (see ref. (1)).

AgBrO₃ in the satd slns detd iodometrically using 0.01 mol dm⁻³ Na₂S₂O₃ sln and a microburet. Each solubility value is the average of "three closely agreeing results."

SOURCE AND PURITY OF MATERIALS:

Details state to be similar to those in (1). AgBrO₃ prepared by slow addition of AgNO₃ and KBrO₃ slns to distilled H₂O while stirring. The precipitate was washed and dried. HClO₄ of G.R. quality (70 % in aqueous solution) was used.

Commercial formamide was treated with CaO and distilled at reduced pressure.

ESTIMATED ERROR:

Soly: reproducibility not given, but titrns accurate to ± 0.2 %.

Temp: precision ± 0.01 K.

REFERENCES:

 Nayak, B.; Dash, U.N. Thermochim. Acta <u>1973</u>, 6, 223.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Giridhar, V. V.; Kalidas, C.

Proc. Indian Acad. Sci. 1984, 93, 795-800.

VARIABLES:

Solvent composition

T/K = 303.15

PREPARED BY:

H. Miyamoto and M. Salomon

EXPERIMENTAL DATA:

HCON(CH ₃) ₂ mole fraction	HCON(CH ₃) ₂ mass % ^a	AgBrO ₃ sol mmol kg-1	
0	0	10.2	
0.1	31.1	5.26	
0.2	50.4	3.68	
0.3	63.5	2.19	
0.4	73.0	1.83	
0.5	80.2	1.31	
0.6	85.9	0.90	
0.7	90.4	0.62	
0.8	94.2	0.52	
0.9	97.3	0.34	
1.0	100	0.21	

^{*}Mass % calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities were determined by a potentiometric method as in (1). See the compilation of the AgIO₃-(CH₃)₂SO-CH₃OH system for details on this method.

Thermodynamic solubility product constants calculated using the extended Debye-Hückel equation with an ion size parameter of 0.65 nm, but not reported in the original paper. The authors use these K^0_{s0} values to calculate Gibbs energies of transfer from water to the water-dimethylformamide mixed solvents. Values of $\Delta G^0_t(AgBrO_3)$ are given in the paper.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd as in (2): i.e. by reaction of AgNO₃ with KBrO₃. The ppt was thoroughly washed with water and then with acetone, and dried in vacuum for several hours at 70-80°C. Purity was checked by potentiometric determination of silver content. HCON(CH₃)₂ (BDH, LR) dist under vac was dried over anhydr CuSO₄ for one week, and finally distilling again under vac. The product had a b.p. of 15°C at 15 mm Hg, and at 25°C had a density of 0.9441 g cm⁻³, $n_D = 1.4268$, and an electrolytic conductance of 1.05 x 10-7 S cm⁻¹. Doubly distilled conductivity water was used in the preparation of solvent mixtures.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.1 K.

- Kalidas, C.; Sivaprasad, P. Indian J. Chem. <u>1979</u>, A17, 79.
- Janardhanan, S.; Kalidas, C. Bull. Chem. Soc. Jpn. 1980, 53, 2363.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Urea; CH ₄ N ₂ O; [57-13-6] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Miyamoto, H. Nippon Kagaku Zasshi 1960, 81, 54-7.
VARIABLES: Solvent composition	PREPARED BY:
T/K = 288.15. 293.15. 298.15 and 303.15	H. Miyamoto

H2NCONH2 content		silver bromate solubility/mmol dm-3			
mass %	mol %≥	15°C	20°C	25ºC	30ºC
0.0	0.0	6.07	7.28	8.59	10.02
10.077	3.252	8.71	10.19	11.98	13.35
20.054	6.998	11.61	13.39	15.44	16.89
29.896	11.342	14.85	16.87	19.19	20.40
39.143	16.174	18.85	21.39	23.60	25.63

*Calculated by the compiler.

AUXILIARY INFORMATION

ı	METHOD/APPARATUS/PROCEDURE:
I	All procedures identical to those given in the
1	compilation of this author's study of the
ı	AgBrO ₃ -CH ₃ OH-H ₂ O system.

SOURCE AND PURITY OF MATERIALS:

Urea (Kanto Kagaku Co. guaranteed reagent) was recrystallized three times and dried under reduced pressure.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Glycine; C ₂ H ₅ NO ₂ ; [56-40-6] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Owen, B. B. J. Am. Chem. Soc. 1933, 55, 1922-8.
VARIABLES: Concentration of glycine T/K = 298	PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA:

[C ₂ H ₅ NO ₂] mass %	[C ₂ H ₅ NO ₂] mass % ^a	AgBrO ₃ soly ^b mmol dm ⁻³	density kg dm-3
0	0	8.12¢	
5	1.2	12.9	1.0184
10	2.6	18.4	1.0395
15	4.1	24.9	1.0613

aCalculated by the compiler.

bMean of 4 independent determinations with 0.004 mmol dm-3 average deviation.

cA "heavy purplish turbidity" was noted in the equilibrated solutions, possibly indicating an undesirable reaction. The author claims the results to be qualitative because of the glycine impurities.

AUXILIARY INFORMATION

${\tt METHOD/APPARATUS/PROCEDURE:}$

All procedures identical to those given in the compilation of this author's study of the AgBrO₃-CH₃OH-H₂O system.

SOURCE AND PURITY OF MATERIALS:

Glycine, a "domestic" commercial product contained organic impurities which imparted a tan color to its solutions. See the compilation cited on the left for other details.

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Acetonitrile; C₂H₃N; [75-05-8]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Subramanian, S.; Rao, S.C.A.V.S.S.; Kalidas, C.

Indian J. Chem. Sec. A 1981, 20, 723-5.

VARIABLES:

Solvent composition

T/K = 303.2

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH ₃ CN mol fraction	CH ₃ CN mass % ^a	AgBrO ₃ soly mol kg-1
0	0	0.0102
0.1	20.2	0.0732
0.2	36.3	0.0914
0.3	49.4	0.0852
0.4	60.3	0.0696
0.5	69.5	0.0554
0.6	77.4	0.0404
0.7	84.2	0.0244
0.8	90.1	0.0127
0.9	95.4	0.00477
1.0	100.0	0.00187

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgBrO₃ was vigorously shaken in CH₃CN-H₂O mixtures for 24 hours, and then transferred to a thermostat maintained at $30 \pm 0.1^{\circ}$ C. The solutions were stirred for an additional 24 hours to insure attainment of equilibrium. The mixtures were centrifuged, and aliquots analyzed for bromate by addition of excess standard aqueous KI solution followed by potentiometric titration with standard AgNO₃.

SOURCE AND PURITY OF MATERIALS:

Silver bromate was prepared by reaction of AgNO₃ with KBrO₃. The precipitate was first washed with water, then with acetone, and dried under vacuum at 70-80°C for several hours. The purity of the salt was checked by determination of its silver content. CH₃CN (BDH, LR grade), after a preliminary distillation, was dried with anhydrous K_2CO_3 , and then further purified as described in (1): the product had a b.p. = 80° C, and at 25° C, d = 0.7766 g cm⁻³ and n_d = 1.3436. Doubly distilled water was used.

ESTIMATED ERROR:

Soly: reproducibility better than ± 1 %. Temp: precision \pm 0.1 K.

REFERENCES:

1. Jayadevappa, E. S. Indian J. Chem. 1969, 7, 1146.

COMPONENTS: (1) Silver bromate; AgBrO ₃ ; [7783-89-3] (2) Pyridine; C ₆ H ₅ N; [110-86-1] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Vosburgh, W.C.; Cogswell, S.A. J. Am. Chem. Soc. 1943, 65, 2412-3.
VARIABLES: Concentration of pyridine T/K = 298.15	PREPARED BY: H. Miyamoto

The solubility, S, of AgBrO₃ in aqueous pyridine solutions is given in the table below.

$[C_{\delta}H_{\delta}N]_{tot}$	103S
mol kg-1	mol kg-1
0	8.27
0.00597	9.80
0.00827	10.32
0.01273	11.49
0.01564	12.34

The authors computed a value of $K_1 = 0.096$ mol kg⁻¹ where K_1 is defined as follows:

$$K_1 = \frac{[Ag^*][C_5H_5N]}{[Ag(C_5H_5N)^*]}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The procedure was as follows (1). Pyridine solutions were saturated with AgBrO₃ in Pyrex flasks immersed in a water bath at 25.00°C, and avoiding diffused daylight or artificial light. Samples for analyses were taken after 3-4 h, and again two or more h later to for constancy in concentrations. The aliquots were removed with a pipet to which was attached a filter either of Pyrex glass wool or Pyrex fritted glass.

Aliquots were weighed and the iodate content determined iodometrically with 0.01 mol dm⁻³ thiosulfate solution. Ammonium molybdate was used as a catalyst.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepared by slow precipitation from solutions of AgNO₃ and KBrO₃. Analysis for silver gave 45.70 % (calculated is 45.75 %). Practical grade pyridine was refluxed over BaO and distilled through a Widmer column. A fraction within a 0.2 K boiling range was used.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.05 K.

REFERENCES:

 Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. J. Am. Chem. Soc. <u>1941</u>, 63, 2670.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	Palanivel, A.; Rajendran, G.; Kalidas, C.
(2) Pyridine; C ₅ H ₅ N; [110-86-1]	Ber. Bunsen. Ges. Phys. Chem. 1986, 90, 794-7.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES: Solvent composition	PREPARED BY:
T/K = 303.15	H. Miyamoto and M. Salomon

pyridine content		solubility	K_{s0} b
mol fraction	mass %a	mol kg-1	mol ² kg- ²
0.0	0.0	0.01	0.0000820
0.1	32.8	1.18	0.4964
0.2	52.3	1.52	0.5822
0.3	65.3	1.73	0.4958
0.4	79.5	1.93	0.3934
0.5	81.4	2.04	0.2934
0.6	86.8	1.97	0.1210
0.7	91.1	1.89	0.0493
0.8	94.6	1.78	0.0167
0.9	97.5	1.63	0.00848
1.0	100.0	1.37	0.00322

aCalculated by the compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experimental method given in reference (1). Solvent compositions are accurate to within \pm 0.02 %. All solubility measurements were carried out at least twice, and the agreement was better than \pm 0.2 %.

Thermodynamic solubility product constants calculated using the extended Debye-Hückel equation with an ion size parameter of 0.60 nm. Dielectric constants, ϵ , were detd with a DK meter 60 GK (Franz Kustner Nachf. KG, Dresden) and are accurate to within \pm 0.2 %.

mole % pyridine	€	
0.0	76.7	
0.1	62.7	
0.2	50.1	
0.3	40.0	
0.4	33.0	
0.5	28.5	
0.6	22.2	
0.7	18.2	
0.8	15.0	
0.9	13.7	
1.0	12.3	

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd by reaction of AgNO₃ with KBrO₃. The ppt was thoroughly washed with water and then with acetone, and dried in vacuum for several hours at 70-80°C. Purity of all salts checked by potentiometric determination of silver content. Pyridine was refluxed over KOH for 8 h followed by fractional distillation. The middle fraction, b.p.= 115°C at 760 mm Hg, was collected and stored over fresh KOH. At 25°C, this product had a density of 0.9787 g cm⁻³ and a viscosity of 0.885 cP. Doubly distilled conductivity water was used in the preparation of solvent mixtures.

ESTIMATED ERROR:

Soly: precision better than ± 0.2 %. Temp: precision ± 0.05 K.

- 1. Kalidas, C.; Schneider, H. Z. Phys. Chem. N.F. 1981, 10, 487.
- 2. Janardhanan, S.; Kalidas, C. Bull. Chem. Soc. Jpn. 1980, 53, 2363.

bThese are thermodynamic solubility product constants.

COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Tetraethylammonium perchlorate; C₈H₂₀NClO₄; [2567-83-1] (3) Tetraethylammonium bromate; C₈H₂₀BrO₃; [82150-35-4] (4) Nitromethane; CH₃NO₂; [75-52-5] 	 (a) Badoz-Lambling, J.; Bardin, J. C. Electrochim. Acta 1974, 19, 725-31. (b) Bardin, J. C. J. Electroanal. Chem. Interfacial Electrochem. 1970, 28, 157-76. (c) Badoz-Lambling, J.; Bardin, J. C.
	C.R. Acad. Sci. Ser. C 1968, 266, 95-9.
VARIABLES:	PREPARED BY:
T/K = 293	H. Miyamoto and E. M. Woolley

The value of $K_{s0} = [Ag^+][BrO_3^-]$ in nitromethane solution was determined from the analysis of the potentiometric titration curve for titration of $(C_2H_5)_4NBrO_3$ with $AgClO_4$. The ionic strength was probably held constant at 0.1 mol dm⁻³ using $(C_2H_5)_4NClO_4$. The authors reported the following value for the concentration solubility product at 20°C:

$$-log K_{s0} = 13.0$$

From this value, the compilers calculate $K_{a0} = 1 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$.

Thus, the solubility in nitromethane in a solution of ionic strength of 0.1 mol dm⁻³ appears to be around 3 x 10⁻⁷ mol dm⁻³ (compilers).

Note that the original values reported in 1968 (ref. (a)) were corrected in 1970 (ref. (b)), and again in the 1974 reference. The latter correction was primarily concerned with accounting for impurities in nitromethane.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potentiometric titration method using the Ag/Ag+ reference electrode. AgClO₄ was titrated into $(C_2H_5)_4NBrO_3$ solution, and from the measured e.m.f., the value of $K_{*0} = [Ag^+][BrO_3^-]$ was calculated. The standard e.m.f. for the Ag/Ag+ reference electrode was determined from measurements on dilute AgClO₄ solutions in the presence of 0.01 mol dm⁻³ HClO₄.

The potentiometric titrations were probably carried out at a constant ionic strength of 0.1 mol dm⁻³. The authors stated that the results were verified by voltammetry.

SOURCE AND PURITY OF MATERIALS:

Eastman practical grade CH₃NO₂ was thoroughly washed successively with Na₂CO₃, NaHSO₃, and H₂SO₄ aqueous solutions. It was then dried over CuSO₄ and distilled from boric acid. A center fraction collected at 110°C was dried and stored over CaSO₄ under N₂. The product contained 0.005 mol dm⁻³ water, and small amounts of C₂H₅NO₂ and C₃H₇NO₂. Electrodes were prepared according to ref. (1).

ESTIMATED ERROR:

log K_{*0}: precision ± 0.2 (authors, 1968).
Soly: nothing specified.
Temp: nothing specified.

REFERENCES:

 Cauquis, G.; Serve, D. Bull. Soc. Chim. Fr. <u>1966</u>, 302.

COMPONENTS: (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Tetrabutylammonium perchlorate; C₁₆H₃₆NClO₄; [1923-70-2] (3) Tetrabutylammonium bromate; C₁₆H₃₆BrO₃; [39692-41-6] (4) 1,2-Dimethoxyethane; C₄H₁₀O₂; [110-71-4] VARIABLES: T/K = 298 ORIGINAL MEASUREMENTS: Caillet, A.; Demange-Guerin, G. J. J. Electroanal. Chem. Interfacial Electrochem. 1972, 40, 187-96. PREPARED BY: H. Miyamoto and E. M. Woolley

EXPERIMENTAL DATA:

Complete experimental numerical data not reported, but were interpreted in terms of the following equilibria accounting for ion association (ionic strength = 0.1 mol dm⁻³):

$$AgBrO_3(s) + (C_4H_9)_4NCIO_4 \Leftrightarrow AgCIO_4 + (C_4H_9)_4NBrO_3$$
 $pK^*_{*0} = 9.8 \pm 0.5$

From this value, the compilers calculate

$$K_{40}^{\bullet} = [AgClO_4][(C_4H_9)_4NBrO_3] = 1.6 (\pm 1) \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}.$$

Correcting for ion association, the following are obtained:

$$AgBrO_3(s) \Leftrightarrow Ag^+ + BrO_3^-$$
 pK = 12.0 (authors)
 $K_{s0} = [Ag^+][BrO_3^-] = 1 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-3}$ (compilers)

The effects of ion pairing were accounted for by the equation

$$pK_{s0} = pK_{s0}^* + pK_d(AgClO_4) + pK_d((C_4H_9)_4NBrO_3)) + pK_d((C_4H_9)_4NClO_4)$$

where K_d is the dissociation constant for the indicated ion pair. The values of $pK_d = 3.8$ for AgClO₄ and 5.1 for $(C_4H_9)_4NClO_4$ are from ref. (1): $pK_d = 3.5$ for $(C_4H_9)_4NBrO_3$ was assumed by analogy. (Note that an apparent typographical error in the paper lists this last pK_d value as 4.5).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potentiometric titration method using the following cell:

Ag | MBrO₃(c₁), MClO₄(c₂), AgClO₄(c₃) \parallel ref

where M represents $(C_4H_9)_4N$, c_1 is probably 0.05 mol dm⁻³, $c_2 = 0.1$ mol dm⁻³, and c_3 is the conen of AgClO₄ titrated into the solution. The reference electrode is probably the same as in ref. (1):

$$ref = AgClO_4(c_4), MClO_4(c_2) | Ag$$

where $c_4 = 0.01$ mol dm⁻³. The equilibrium constant was calcd from the potentials along the titration curve.

SOURCE AND PURITY OF MATERIALS:

Nothing specified, but the compilers assume that the purification of 1,2-dimethoxyethane and the source of the electrolytes are similar to that described in (1). In (1), the solvent was refluxed in N₂ over Na for 4 hours, and then fractionally distilled. The water content was determined to be 0.005 mol dm⁻³.

ESTIMATED ERROR:

log K_{e0}: ± 0.5 (error not defined).
 Soly: nothing specified.
 Temp: nothing specified.

REFERENCES:

 Caillet, A.; Demange-Guerin, G. J. Electroanal. Chem. Interfacial Electrochem. <u>1972</u>, 40, 69.

T/K = 298	H. Miyamoto and E. M. Woolley
VARIABLES:	PREPARED BY:
(4) Tetrahydrofuran; C ₄ H ₈ O; [109-99-9]	
[39692-41-6]	40, 187-96.
(3) Tetrabutylammonium bromate; C ₁₆ H ₃₆ BrO ₃ ;	J. Electroanal, Chem. Interfacial Electrochem. 1972,
(2) Tetrabutylammonium perchlorate; C ₁₆ H ₃₆ NClO ₄ ; [1923-70-2]	Caillet, A.; Demange-Guerin, G. J.
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	
COMPONENTS:	ORIGINAL MEASUREMENTS:

Complete experimental numerical data not reported, but were interpreted in terms of the following equilibria accounting for ion association (ionic strength = 0.1 mol dm-3):

$$AgBrO_3(s) + (C_4H_9)_4NClO_4 \Leftrightarrow AgClO_4 + (C_4H_9)_4NBrO_3$$
 $pK^*_{s0} = 11.1 \pm 0.5$

From this value, the compilers calculate

$$K_{s0}^{*} = [AgClO_4][(C_4H_9)_4NBrO_3] = 8 (\pm 6) \times 10^{-12} \text{ mol}^2 \text{ dm}^{-6}.$$

Correcting for ion association, the following are obtained:

$$AgBrO_3(s) \Leftrightarrow Ag^+ + BrO_3^-$$
 pK = 11.2 (authors)

$$K_{s0} = [Ag+][BrO_{3}-] = 6 \times 10^{-12} \text{ mol}^2 \text{ dm}^{-3}$$
 (compilers)

The effects of ion pairing were accounted for by the equation

$$pK_{*0} = pK^{*}_{*0} + pK_{d}(AgClO_{4}) + pK_{d}((C_{4}H_{9})_{4}NBrO_{3})) + pK_{d}((C_{4}H_{9})_{4}NClO_{4})$$

where K_d is the dissociation constant for the indicated ion pair. The above pK_d values were not given. pK_d for $(C_4H_9)_4NBrO_3$ was assumed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potentiometric titration method using the following cell:

Ag
$$|MBrO_3(c_1), MClO_4(c_2), AgClO_4(c_3)||$$
 ref

where M represents $(C_4H_9)_4N$, c_1 is probably 0.05 mol dm⁻³, $c_2 = 0.1$ mol dm⁻³, and c_3 is the concn of AgClO₄ titrated into the solution. The reference electrode is probably the same as in ref. (1):

$$ref = AgClO_4(c_4), MClO_4(c_2) \mid Ag$$

where $c_4 = 0.01$ mol dm⁻³. The equilibrium constant was calcd from the potentials along the titration curve.

SOURCE AND PURITY OF MATERIALS:

Nothing specified, but the compilers assume that the purification of 1,2-dimethoxyethane and the source of the electrolytes are similar to that described in (1). In (1), the solvent was stored over K for 15 days, refluxed in N_2 over Na for 4 hours, and then fractionally distilled. The water content was determined to be 0.005 mol dm⁻³.

ESTIMATED ERROR:

 $log \ K_{s0}$: ± 0.5 (error not defined). Soly: nothing specified.

Temp: nothing specified.

REFERENCES:

 Caillet, A.; Demange-Guerin, G. J. Electroanal. Chem. Interfacial Electrochem. 1972, 40, 69.

PREPARED BY:

VARIABLES:

Concentration of NaClO₄

COMPONENTS: (1) Silver bromate; AgBrO₃; [7783-89-3] (2) Sodium perchlorate; NaClO₄; [7601-89-0] (3) Formamide; CH₃NO; [75-12-7] ORIGINAL MEASUREMENTS: Dash, U. N.; Nayak, B. Thermochim. Acta 1975, 11, 17-24.

T/K = 298.15, 303.15 and 30	08.15	H. Miyamoto and	E. M. Woolley	
EXPERIMENTAL DATA:				
	NaClO ₄ concn	AgBrO ₃ soly	-log S*	
t/ºC	mol dm-3	mol dm-3	(eq. [1])	
25	0.10420	0.01965	1.7865	
	0.09315	0.01960	1.7849	
	0.08539	0.01955	1.7840	
	0.06352	0.01950	1.7787	
	0.04645	0.01940	1.7749	
	0.03543	0.01905	1.7782	
	0.02735	0.01890	1.7778	
	0.00759	0.01862	1.7729	
30	0.11992	0.02121	1.7575	
	0.10812	0.02101	1.7590	
	0.09342	0.02086	1.7584	
	0.05945	0.02076	1.7507	
	0.04860	0.02054	1.7514	
	0.02876	0.02034	1.7475	
35	0.09766	0.02220	1.7332	
	0.07185	0.02211	1.7279	
	0.06180	0.02178	1.7312	
	0.05226	0.02170	1.7296	

AUXILIARY INFORMATION

0.02165

0.02152

0.02136

0.03225

0.02625

0.01470

METHOD/APPARATUS/PROCEDURE:

Solutions of NaClO₄ in formamide were prepared by weight and placed into amber-colored glass-stoppered bottles containing excess AgBrO₃. The stoppers were heavily paraffined, and the bottles were then rotated in a water thermostat at a given temperature for 7-8 hours (see ref. (1)). Solubilities were determined by iodometric titration of bromate using 0.01 mol dm⁻³ Na₂S₂O₃ solution in a microburet.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd by addition of solutions of AgNO₃ and KBrO₃ to mechanically-stirred distilled water at room temp for a period of 5 hours. The product was washed and dried. NaClO₄ prepd from Na₂CO₃ and a slight excess of dil HClO₄. The anhydr salt was obtained by recrystallization above 50°C, and it was dried in a current of dry air. Commercial formamide was treated with CaO and distilled under reduced pressure.

1.7227

1.7226

1,7197

continued.....

ESTIMATED ERROR:

Titrn accuracy ± 0.2 %. Soly: nothing specified. Temp: precision ± 0.01 K.

- 1. Nayak, B.; Dash, U.N. Thermochim. Acta 1973, 6,
- Agarwal, R.K.; Nayak, B. J. Phys. Chem. <u>1966</u>, 70, 2568: <u>1967</u>, 71, 2062.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver bromate; AgBrO ₃ ; [7783-89-3]	
	Dash, U. N.; Nayak, B.
(2) Sodium perchlorate; NaClO ₄ ; [7601-89-0]	
	Thermochim. Acta 1975, 11, 17-24.
(3) Formamide; CH ₃ NO; [75-12-7]	

EXPERIMENTAL DATA: (continued.....)

Values of log S* in the data tables were calculated by the authors from

$$logS' = logS - \frac{AI^{1/2}}{1 + I^{1/2}}$$
 [1]

where S is the experimental solubility, $I = S + [NaClO_4]$, and values of A were taken from ref. (1). Plots of log S* against I were linear, and the intercepts (S0) and slopes (B) are given in the table below (these calculations by the compilers).

	A	-B	S ⁰
t/ºC	mol-1/2 dm3/2	mol-1 dm3	mol dm-3
25	0.307	0.132	0.01700
30	0.308	0.125	0.01811
35	0.309	0.159	0.01927

Values of the thermodynamic solubility product, $K_{0,0} = (S^0)^2$, and the derived thermodynamic quantities were calculated by the compilers and are given in the following table.

		ΔG^0	ΔH^0	ΔS^0
t/ºC	104K0 _{s0}	kJ mol-1	kJ mol-1	J mol-1 K-1
25	2.89	20.20	19.14	-3.6
30	3.28	20,22	19.14	-3.6
35	3.71	20.24	19.14	-3.6

Finally, the compilers calculated the solubility, S, of AgBrO₃ in pure formamide in the absense of an inert electrolyte (i.e. no NaClO₄) from the following equation:

$$logS = logS^0 + \frac{AS^{1/2}}{1 + S^{1/2}} - BS$$
 [2]

Using the constants A and B in table above, the compilers used eq. [2] to compute the following solubilities in the binary AgBrO₃-HCONH₂ system.

	AgBrO ₃ soly (S)	$10^4 K_{s0} = (S)^2$
t/ºC	mol dm-3	mol ² dm- ⁸
25	0.01861	3.46
30	0.01989	3.95
35	0.02126	4.52

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) Methanol; CH₄O; [67-56-1]
- (3) Sulfinyl bis-methane (dimethyl sulfoxide); C₂H₆OS; 167-68-51

ORIGINAL MEASUREMENTS:

Janardhanan, S.; Kalidas, C.

Z. Naturforsch., T. A. Physik., Phys. Chem., Kosmophys. 1984, 39A, 600-2.

VARIABLES:

Solvent composition

T/K = 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

(CH ₃) ₂ SO	(CH ₃) ₂ SO		AgBrO ₃ soly
mole fraction	mass %a	E	102mol kg-1
0	0	31.80	0.005
0.1	21.3	35.75	0.024
0.2	37.9	38.80	0.079
0.3	51.1	41.60	0.186
0.4	61.9	44.00	0.362
0.5	70.9	45.20	0.640
0.6	78.5	46.01	1.00
0.7	85.1	46.45	1.54
0.8	90.7	46.60	2.20
0.9	95.6	46.45	3.03
1.0	100	46.00	3.79

^{*}Mass % calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities were determined by a potentiometric method as in (1). See the compilation of the AgIO₃-(CH₃)₂SO-CH₃OH system for details on this method.

Thermodynamic solubility product constants calculated using the extended Debye-Hückel equation with an ion size parameter of 0.65 nm, but not reported in the original paper. The authors use these Koao values to calculate Gibbs energies of transfer from CH₃OH to the CH₃OH-(CH₃)₂SO mixed solvents. Values of $\Delta G_{i}(AgBrO_{3})$ are given in the paper.

Dielectric constants, ϵ of the solvent mixtures at 30°C were measured, and are given in the data table above.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd as in (1): i.e. by reaction of AgNO₃ with KBrO₃. The ppt was thoroughly washed with water and then with acetone, and dried in vacuum for several hours at 70-80°C. Purity was checked by potentiometric determination of silver content. (CH₃)₂SO (BDH, LR) purified as in (2): i.e. by heating over molecular sieves for 2 h at 90°C followed by flash distillation under vac. CH₃OH (BDH, LR) purified as in (2): i.e. by refluxing over neutral alumina followed by distillation, and drying over K2SO4 followed by fractional distillation.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.1 K.

- 1. Janardhanan, S.; Kalidas, C. Bull. Chem. Soc. Jpn 1980, 53, 2363.
- 2. Janardhanan, S.; Kalidas, C. Proc. Indian Acad. Sci. 1981, 90, 89.

- (1) Silver bromate; AgBrO₃; [7783-89-3]
- (2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]
- (3) Methanol; CH₄O; [67-56-1]

ORIGINAL MEASUREMENTS:

Giridhar, V. V.; Kalidas, C.

Indian J. Chem. 1983, 22A, 224-6.

VARIABLES:

Solvent composition T/K = 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

HCON(CH ₃) ₂ mole fraction	HCON(CH ₃) ₂ mass % ^a	AgBrO ₃ soly 104mol kg-1
0	0	0.5
0.1	20	1.23
0.2	36	1.52
0.3	49	1.90
0.4	60	2.03
0.5	70	2.26
0.6	77	2.36
0.7	84	2.60
0.8	90	2.70
0.9	95	2.84
1.0	100	2.05

^{*}Mass % calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities were determined as in (1): i.e. probably a potentiometric method. See the compilation of the AgIO₃-(CH₃)₂SO-CH₃OH system for details on this method.

Thermodynamic solubility product constants calculated using the extended Debye-Hückel equation with an ion size parameter of 0.65 nm, but not reported in the original paper. The authors use these K^0_{*0} values to calculate Gibbs energies of transfer from CH₃OH to the CH₃OH-HCON(CH₃)₂ mixed solvents. Values of $\Delta G^0_{t}(AgBrO_3)$ are given in the paper.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd as in (1): i.e. by reaction of AgNO₃ with KBrO₃. The ppt was thoroughly washed with water and then with acetone, and dried in vacuum for several hours at 70-80°C. Purity was checked by potentiometric determination of silver content. HCON(CH₃)₂ (BDH, LR) dist, dried over anhydr CuSO₄ for one week, and redistilled under reduced pressure. The product had a b.p. of 15°C at 15 mm Hg, and at 25°C had a density of 0.9441 g cm⁻³, n_D = 1.4268, and an electrolytic conductance of 1.05 x 10⁻⁷ S cm⁻¹. CH₃OH dried with anhydr Na₂SO₄, distilled, refluxed over neutral alumina and fractioning: the middle fraction was saved. The product had a b.p. of 64.6°C, and at 20°C, d = 0.7914 g cm⁻³, and n_D = 1.3286.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.1 K.

REFERENCES:

 Janardhanan, S.; Kalidas, C. Bull. Chem. Soc. Jpn. 1980, 53, 2363.

COMPONENTS:

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Methanol; CH₄O; [67-56-1]

(3) Acetonitrile; C₂H₃N; [75-05-8]

ORIGINAL MEASUREMENTS:

Subramarian, S.; Kalidas, C.

Electrochim. Acta 1984, 29, 753-6.

VARIABLES:

Solvent composition

T/K = 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH ₃ CN	CH ₃ CN		AgBrO ₃ soly
mole fraction	mass %ª	E	103mol kg-1
0	0	31.8	0.098
0.1	12	32.3	1.935
0.2	24	32.6	4.39
0.3	35	33.0	6.59
0.4	46	33.3	8.39
0.5	56	33.7	9.18
0.6	66	34.0	9.37
0.7	75	34.3	8.39
0.8	84	34.8	6.49
0.9	92	35.0	4.08
1.0	100	35.5	1.87

Mass % calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method from (1). About 25 ml of solvent mixture and excess AgBrO₃ stirred in a thermostated vessel for about 12 hours. Aliquots of saturated solution filtered through a glass filter and analyzed for iodate. A defined quantity of excess KI solution added to a weighed aliquot, and the excess KI back-titrated potentiometrically with standard AgNO₃ solution using a Metrohm Multidosimate (E415) buret. All solubility determinations were carried out least twice, and the agreement was better than ± 1 %.

Dielectric constants, ϵ of the solvent mixtures at 30°C were measured, and are given in the data table above.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd by reaction of aq slns of AgNO₃ and KBrO₃. The ppt was filtered, washed with water and then with alcohol, and dried over P_2O_5 in vacuum at 80°C to const weight. Purity was checked by potentiometric determination of silver. CH₃CN (BDH, LR) distd, dried over anhydr K₂CO₃, and redistd from a few crystals of AgNO₃. The product had a b.p. of 80.0 \pm 0.1°C, and at 25°0, d = 0.7766 g cm⁻³. CH₃OH (BDH, LR) was distd, dried over anhydr Na₂SO₄, and redistd from Mg turnings. The middle fraction (64-65°) was collected, and at 25°C, d = 0.7867 g cm⁻³.

ESTIMATED ERROR:

Soly: precision better than ± 1 %. Temp: nothing specified.

REFERENCES:

 Kalidas, C.; Schneider, H. Z. Phys. Chem. <u>1980</u>, 120, 145.

COMPONENTS:

(1) Silver bromate; AgBrO₃; [7783-89-3]

(2) Ethanol; C₂H₆O; [64-17-5]

(3) Acetonitrile; C₂H₃N; [75-05-8]

ORIGINAL MEASUREMENTS:

Subramarian, S.; Kalidas, C.

Electrochim. Acta 1984, 29, 753-6.

VARIABLES:

Solvent composition

T/K = 303.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

CH₃CN	CH3CN		AgBrO ₃ soly
mole fraction	mass %ª	€	103mol kg-1
0	0	23.9	0.055
0.1	9	25.1	0.406
0.2	18	26.2	1.12
0.3	28	27.4	1.96
0.4	37	28.6	2.83
0.5	47	29.6	3.63
0.6	57	30.9	4.28
0.7	68	32.1	4.64
0.8	78	33.3	4.37
0.9	89	34.5	3.56
1.0	100	35.5	1.87

^{*}Mass % calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method from (1). About 25 ml of solvent mixture and excess AgBrO₃ stirred in a thermostated vessel for about 12 hours. Aliquots of saturated solution filtered through a glass filter and analyzed for iodate. A defined quantity of excess KI solution added to a weighed aliquot, and the excess KI back-titrated potentiometrically with standard AgNO₃ solution using a Metrohm Multidosimate (E415) buret. All solubility determinations were carried out at least twice, and the agreement was better than ± 1 %.

Dielectric constants, ϵ of the solvent mixtures at 30°C were measured, and are given in the data table above.

SOURCE AND PURITY OF MATERIALS:

AgBrO₃ prepd by reaction of aq slns of AgNO₃ and KBrO₃. The ppt was filtered, washed with water and then with alcohol, and dried over P_2O_5 in vacuum at 80°C to const weight. Purity was checked by potentiometric determination of silver. CH₃CN (BDH, LR) distd, dried over anhydr K₂CO₃, and redistd from a few crystals of AgNO₃. The product had a b.p. of 80.0 \pm 0.1°C, and at 25°, d = 0.7766 g cm⁻³. CH₃CH₂OH (BDH, LR) was distilled from magnesium and iodine as recommended in (2).

ESTIMATED ERROR:

Soly: precision better than ± 1 %. Temp: nothing specified.

- Kalidas, C.; Schneider, H. Z. Phys. Chem. <u>1980</u>, 120, 145.
- Vogel, A.I. Practical Organic Chemistry. 3rd ed., Longmans, London, 1975: page 167.

COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University)
(2) Water; H ₂ O; [7732-18-5]	M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

THE BINARY SYSTEM

Data for the solubility of silver iodate in pure water have been reported in 21 publications (1-21). In eight of these publications (1, 8, 11, 12, 18-21) the solubilities were reported in units of mol kg⁻¹, and in 16 publications (1 - 10, 12 - 17) the solubilities were reported in units of mol dm⁻³. There are no indications of the existence of any hydrates. Experimentally, the solubilities in binary and multicomponent systems are all based on isothermal methods with varying analytical procedures: the gravimetric method (1, 2, 5, 29), conductometric method (3, 4), potentiometric method (18, 19, 22 -24, 24, 32), colorimetric method (6), volumetric (iodometric) methods (7 -17, 20, 28, 30, 31, 34), and radioassay methods (26, 33).

Data at 298.15 K

The solubility data for $AgIO_3$ at 298.15 K are summarized in Table 1. The solubility value of 1.793 x 10^{-4} mol dm⁻³ for $AgIO_3$ in an aqueous solution containing 1 x 10^{-4} mol dm⁻³ HClO₄ (26) is not included in Table 1.

Table 1. Experimental solubilities in the binary AgIO₃-H₂O system at 298.15 K (mol dm⁻³ units)

solubility	number of	
mol dm ⁻³	measurements	reference
1.27 × 10 ^{-4a}	1	1
1.764 x 10 ⁻⁴ (av)	17	8
1.746 x 10 ⁻⁴	extrapolated	12
1.78×10^{-4} (av)	2	5
1.78×10^{-4}	1	13
1.785 x 10 ^{-4b} (av)	3	10
1.80×10^{-4} (av)	6	14
1.89 x 10 ^{-4a} (av)	10	2
1.92 x 10-4a (av)	3	15 - 17

^{*}Rejected data points.

bSee the compilation of this paper indicating that there might be some confusion as to the true units of these three solubility values.

The average value for the solubility of $AgIO_3$ at 298.15 K for the 30 acceptable independent measurements listed in Table 1 is 1.774×10^{-4} ($\pm 0.007 \times 10^{-4}$) mol dm⁻³, and this is designated as the recommended solubility at 298.15 K. In deriving this recommended value, those solubility values which differed by more than two times the standard deviation (σ) were rejected, and the uncertainty is based on a Student's t analysis for the 98 % confidence level (for the 30 acceptable data points in Table 1, Student's t = 2.462 for 29 degrees of freedom, the standard deviation is 0.0155, and the standard deviation of the mean is 0.0028). The standard deviation is defined in the usual manner as

$$\sigma^2 = \frac{\sum_{i=1}^{N} (c_i - \bar{c})^2}{N - 1}$$
 [1]

The standard deviation of the mean is defined as $\sigma_m = \sigma/\sqrt{N}$ and the uncertainty is therefore calculated from $t\sigma_m$.

COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University)
(2) Water; H ₂ O; [7732-18-5]	M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

Data at other temperatures

Table 2. Experimental solubilities as a function of temperature

T/K	$10^4c_1/\mathrm{mol~dm^{-3a}}$	$10^4m_1/\text{mol kg}^{-1a}$	reference
282.58	0.97		4
283.2	0.97 (3)		9
291.2	1.36		4
291.5	1.38		4
293.1	1.52 ^b (17)		3
293.2	1.38 ^b		6
293.2	1.463 (3)		9
298.2	1.27 ^b	1.28 ^b	1
298.2	1.746	1.754	12
298.2	1.764 (17)		8
298.2	1.78 (2)		5
298.2	1.78		13
298.2	1.785 (3)		9,10
298.2	1.80 (6)		14
298.2	1.89 ^b		2
298.2	1.92 ^b		15-17
298.2		1.794	11
298.2		1.8	20
299.8	1.91	as es as	4
303.2	2.152 (3)		9,10
303.2		2.34	19
303.2		3.22b	21
303.2		3.3 ^b	18
308.2	2.587 (3)		9,10
308.2	2.65		15
308.2	2.66		16
318.2	3.52		14
348.2		8.40 (25)	7

^{*}When specificially stated by the authors, the numbers of independent solubility measurements are given in parenthesis.

The solubility data for AgIO₃ for various temperatures are given in Table 2 in which 17 acceptable data points are indicated. Assigning equal weights to all 17 data points, the following smoothing equation was obtained by the method of relative least squares

$$\ln(c_1/\text{mol dm}^{-3}) = -1838.31 + 2477.69/(T/100\text{K}) + 1683.72 \ln(T/100\text{K}) - 281.966(T/100\text{K})$$
 [2]

The standard error of estimate for the calculated - observed solubilities from eq. [2] is $\sigma = 2.3 \times 10^{-6}$.

bRejected data points on the basis that the difference between observed and calculated solubilities exceeded 20.

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Silver Iodate

COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University)
(2) Water; H ₂ O; [7732-18-5]	M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

Table 3. Tentative solubilities calculated from the smoothing equation and corresponding thermodynamic solubility products

$10^4c_1/\mathrm{mol~dm^{-3}}$	$10^8 K_{\rm s0}/{ m mol^2~dm^{-6c}}$
0.985	0.961
1.119	1.406
1.457	2.097
1.786 ^b	3.147 ^d
2.175	4.661
2.613	6.716
3.079	9.311
3.534	12.248
	0.985 1.119 1.457 1.786 ^b 2.175 2.613 3.079

^{*}Total uncertainty in these tentative values at the 98 % confidence level is ± 0.7 %.

Table 3 contains the results for tentative thermodynamic solublity products, K_{a0} , calculated from

$$K_{s0} = c_1^2 \gamma_{\bullet}^2 \tag{3}$$

where the mean molar activity coefficients (γ_{\pm}) were calculated from the Davies equation (36) using the dielectric constants (ϵ) tabulated by Robinson and Stokes (37):

$$-\ln \gamma_* = \frac{1.8246 \times 10^6}{(\epsilon T)^{3/2}} \left(\frac{c_1^{1/2}}{1 + c_1^{1/2}} - 0.3c_1 \right)$$
 [4]

The smoothed solubilities given in Table 3 are designated as tentative solubilities on the basis that there is a small difference between the smoothed solubility of 1.786 x 10^{-4} mol dm⁻³ and the recommended value of 1.774 x 10^{-4} mol dm⁻³ obtained from the weighted average method discussed above. Of the four e.m.f. studies (22, 23, 27 and 38) which employ cells with liquid junctions to determine the solubility product, only the data of Kolthoff and Chantooni are close to the tentative value at 298.2 K given in Table 3. The K_{s0} values of ~7 x 10^{-8} mol² dm⁻⁶, 1.096 x 10^{-8} mol² dm⁻⁶ and 1.122 x 10^{-8} mol² dm⁻⁶ at 298.2 K from references 22, 23 and 38 are obviously in error and must be rejected (note that the data from reference 38 was not compiled). Using the K_{s0} data in Table 3 except for 298.2 K for which we use the recommended solubility product, standard thermodynamic quantities were computed for the reaction $AgIO_3(s) \leftrightarrow Ag^+(sIn) + IO_3^-(sIn)$ by the least squares method resulting in

$$\ln\left\langle \frac{K_{s0}}{K_{s0}(298)} \right\rangle = 22.4613 - \frac{6695.889}{T/K}$$
 [5]

For this relation, the standard deviations of the intercept and slope are, respectively, 0.26 and 76.6, and for the correlation coefficient, $r^2 = 0.9991$. The enthalpy calculated from -R(slope) = $\Delta H_{aln} = 55.67$ kJ mol⁻¹, and at 298.2 K the entropy $\Delta S_{aln} = 42.96$ J K⁻¹ mol⁻¹. These thermodynamic quantities are designated as tentative values.

^bNote that the data from Table 1 led the evaluators to propose a recommended solubility of 1.774×10^{-4} ($\pm 0.007 \times 10^{-4}$) mol dm⁻³ for the solubility at 298.2 K.

^eThermodynamic solubility product (see description below).

^dThe recommended thermodynamic solubility product using the recommended solubility of 1.774 x 10⁻⁴ mol dm⁻³ is 3.105 x 10⁻⁸ mol² dm⁻⁶.

Silver Iodate 167

COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University)
	E.M. Woolley (Brigham Young University)
(2) Water; H ₂ O; [7732-18-5]	M. Salomon (US Army ETDL)
	September 1989

CRITICAL EVALUATION:

For solubilities in mol kg⁻¹ units, the data in Table 2 are taken as tentative values. Standard thermodynamic quantities based on these units can be computed from tabulated density values and the data given in Table 3.

The solubilities reported by Ramette (26) in 99.5+ % D₂O containing 1 x 10⁻⁴ mol dm⁻³ HClO₄ are given in the compilations and these data are designated as tentative.

TERNARY SYSTEMS

Systems With One Saturating Component

The solubility of Ag(IO₃) in KNO₃ solutions has been reported in four publications (7-9, 12). Li and Lo (9) studied the solubilities at 283 K, 293 K, 298 K, 303 K and 308 K, and Baxter (7) employed the single temperature of 348 K. All other studies were carried out at 298 K. Derr et al. (12) reported only graphical data along with smoothing equations for the solubility as a function of ionic strength (mol kg⁻¹ units), and these smoothing equations can be found in the compilation of this study. The solubility data based on mol dm⁻³ units at 298 K from references (8 and 9) are given in Table 4 below.

Table 4. Experimental solubilities of AgIO₃ as a function of KNO₃ concentration at 298.2 K

KNO ₃ concn	AgIO ₃ soly	
mol dm ⁻³	104mol dm ⁻³	reference
0	1.774ª	
0.001301	1.823	8
0.001301	1.827	9
0.003252	1.870	8
0.003252	1.868	9
0.006503	1.914	8
0.006503	1.913	9
0.01410	1.994	8
0.01410	2.002	9
0.07050	2.301	8
0.07050	2.304	9
0.1213	2.454	9
0.1998	2.665	8
0.2528	2.793	9
0.4995	3.314	8
0.5050	3.330	9
0.8738	3.904	9
0.9989	4.086	8

^BRecommended solubility in pure water.

The agreement between these two studies of (8 and 9) appear to be excellent, and where solubilities are reported at the same concentration of KNO₃, the average value can be taken as the recommended solubility. Over the entire range of 0 - 1 mol dm⁻³ KNO₃, the data were fitted by the relative least squares method to the following simple smoothing equation:

$$c_1 = 1.764 \cdot 10^{-4} + 1.87590 \cdot 10^{-4} c_2^{1/2} + 3.60711 \cdot 10^{-5} c_2 + 9.24915 \cdot 10^{-6} c_2^{1.5}$$
 [6]

The standard deviation for the solubility c_1 is 1.0×10^{-6} which leads the evaluators to propose that solubilities calculated from this smoothing equation are precise to three significant figures and are therefore designated as tentative solubilities.

COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University)
(2) Water; H ₂ O; [7732-18-5]	M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

Systems With One Saturating Component, continued.

The solubility of Ag(IO₃) in solutions containing salts other than KNO₃ has been reported in five publications (7, 8, 14, 25, 30). Baxter (7) studied the solubility in solutions of potassium perchlorate, and in aqueous sulfate solutions of potassium, magnesium and barium at 348.2 K. Both Baxter (7) and Kolthoff and Lingane (8) reported solubilities in barium nitrate solutions at 348.2 K and 298.2 K, respectively, and Kolthoff and Lingane also studied the AgIO₃-TINO₃-H₂O system at 298.2 K. Shchigol (30) reported solubilities in aqueous solutions of KIO₃ at ~293 K to ~295 K, and Ricci and Amron (14) studied solubilities in aqueous AgNO₃ solutions at 298.2 K. Rainier and Martin (25) reported solubilities in solutions containing lithium iodate at temperatures of 298.2, 308.2, and 323.2 K.

Solubility in Acids and Bases

The solubility of AgIO₃ in nitric acid solutions has been reported by Longi (1), Hill and Simmons (5) and by Li and Lo (10). For HNO₃ concentrations above 8 mol dm⁻³, Hill and Simmons state that there is iodate decomposition, and Li and Lo stated that even at nitric acid concentrations below 1 mol dm⁻³, the increasing solubility of AgIO₃ as the HNO₃ concentration increases is due to incomplete dissociation of iodic acid formed by double decomposition between silver iodate and nitric acid. In fact the evaluators had difficulty in fitting these solubility data to a smoothing equation for nitric acid concentrations greater than 2 mol dm⁻³ (see below). The experimental solubilities of AgIO₃ in HNO₃ solutions at 298.2 K are given in Table 5 below.

Table 5. Experimental solubilities of AgIO₃ as a function of HNO₃ concentration at 298.2 K

HNO ₃ concn	AgIO ₃ soly	
mol dm ⁻³	10 ³ mol dm ⁻³	reference
0	0.1774ª	
0.001301	0.18297	10 _P
0.006503	0.1949	10
0.01410	0.2070	10
0.07050	0.2660	10
0.1213	0.3040	10
0.125	0.304	5¢
0.250	0.379	5
0.2528	0.3828	10
0.500	0.499	5
0.5050	0.5027	10
0.8738	0.6522	10
1.00	0.731	5
2.00	1.174	5
4.00	2.469	5
6.72	4.113	1
8.00	5.608	5

^{*}Recommended solubility. bData from reference 10 are averages from three determinations.

The evaluators could not obtain a satisfactory fit to an empirical smoothing equation using all 16 data points in Table 5. We were able to obtain a satisfactory fit to the thirteen most dilute data points omitting the solubility of 0.6522 x 10⁻⁴ mol dm⁻³ in aqueous HNO₃ solution of 0.8738 mol dm⁻³ (rejected data point from ref. 10). The necessity of rejecting this data point is clearly seen in the figure on the top of the following page, and based on the remaining data points for HNO₃ concentrations up to 2.0 mol dm⁻³, the following smoothing equation was obtained by the relative least squares method:

Data from reference 5 are averages from two determinations from under- and supersaturation.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Water; H₂O; [7732-18-5] EVALUATORS: H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University) M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

Solubility in Acids and Bases, continued

$$c_1 = 1.738 \cdot 10^{-4} + 2.7609 \cdot 10^{-4} c_2^{1/2} + 2.37186 \cdot 10^{-4} c_2 + 4.61745 \cdot 10^{-5} c_2^{15}$$
 [7]

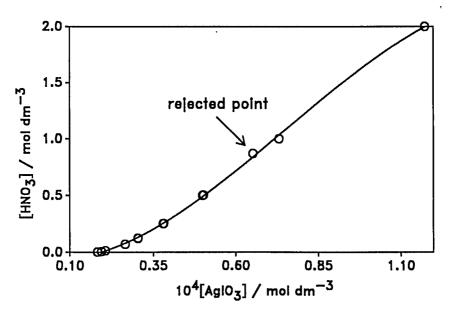


Figure 1. Solubility of AgiO₃ in Aqueous HNO₃ Solutions

Over the HNO₃ concentration range of 0 - 2.0 mol dm⁻³, the solubilities of AgIO₃ calculated from equation [7] are designated as tentative solubilities. In view of the uncertanties in the chemisty of the AgIO₃-HNO₃-H₂O system for nitric acid concentrations greater than 2 mol dm⁻³, and in view of our inability to satisfactorily fit the solubility data to HNO₃ concentrations greater than 2 mol dm⁻³, we designate the smoothed solubilities calculated from eq. [7] as tentative values, and all experimental solubilities for HNO₃ concentrations greater than 2 mol dm⁻³ are considered to be uncertain.

Ricci and Amron (14) studied the AgIO₃-I₂O₅-H₂O system at 298.2 K and 318.2 K, and report the incongruently soluble pyro-iodate AgIO₃·I₂O₅ at both temperatures. The study failed to detect AgIO₃ in solution, but both anhydrous and monohyrate AgIO₃·I₂O₅ complexes were detected in the solid phases.

Two studies report solubilities in the AgIO₃-NH₃-H₂O system (1, 12), and we assign much greater accuracy to the results of Derr, Stockdale and Vosburgh (12). These latter authors reported the singular complex [Ag(NH₃)₂]⁺, and report a value of 1.65 x 10⁷ mol⁻¹ dm³ for the formation constant of this complex. In a subsequent publication on the quaternary AgIO₃-NH₄NO₃-NH₃(aq)-H₂O system, Vosburgh and McClure (28) reported a formation constant of 2.5 x 10⁴ mol dm⁻³ for the Ag(NH₃)⁺ complex.

Ternary Systems with Two Saturating Components

Shklovskaya, Arkhipov, Kidyarov, Vdovkina and Poleva (20) studied the $AgIO_3-LiIO_3-H_2O$ system by the isothermal method at 298.2 K. The compilation of this paper can be found in Volume 30 of the IUPAC Solubility Data Series (35). The system is characterized by the formation of a series of solid solutions involving polymorphic LiIO₃ and α -LiIO₃, and details on the solid phases of LiIO₃ can also be found in (35).

170 Silver lodate

COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University)
(2) Organic solvents	M. Salomon (US Army ETDL) September 1989
(3) Water; H ₂ O; [7732-18-5]	· ·

CRITICAL EVALUATION:

Ternary Systems with Two Saturating Components, continued

Ricci and Amron (14) studied the four systems given below, and in which the concentration of AgIO₃ was not detected in solutions containing the second salt. Even qualitative tests for silver in these solutions were negative. In contrast to these studies, it should be noted that Shklovskaya et al. (20) were able to detect AgIO₃ in LiIO₃ solutions: e.g. for LiIO₃ concentrations of 7 to 43 mass %, AgIO₃ solubilities ranging from 0.00012 to 0.00047 mass % were reported with varying solid phase composition (see previous page).

$$AgIO_3 - LiIO_3 - H_2O$$
 $AgIO_3 - NaIO_3 - H_2O$
 $AgIO_3 - KIO_3 - H_2O$
 $AgIO_3 - NH_4IO_3 - H_2O$

QUATERNARY AND QUINTERNARY SYSTEMS

While there are insufficient data to allow for comparisons and data evaluation, it is noted that in all studies on quaternary (12, 25, 28 29) and quinternary (29, 33, 34) systems, AgIO₃ is the only saturating component.

SOLUBILITIES IN AQUEOUS-ORGANIC MIXTURES

The solubility of AgIO₃ in aqueous-organic mixtures has been reported in 11 publications (11, 15-19, 21, 23, 24, 31, 32). The study by Dash et al. (32) actually does not involve the determination of solubilities, but employs standard half-cell e.m.f. data to compute thermodynamic solubility products in 1,4-dioxane - water mixtures at temperatures of 278K, 283 K, 288 K, 293 K and 298 K. Similarly, for glycerol-water mixtures (23) and urea-water mixtures (24), no solubility data were measured, but instead thermodynamic solubility products were computed from standard half-cell e.m.f. values.

Keefer and Reiber (11) determined solubilities in aqueous glycine and alanine solutions and found increasing solubilities for increasing amino acid concentration. The slope of the plot of log (solubility) as a function of amino acid concentration was found to be abnormal and explained by assuming complexation between silver and glycinate or alanate ions.

Solubilities in pryidine-water mixtures at 298 K (25) were interpreted in terms of $AgPy^+$ and $AgPy_2^+$ complexes. At 303 K (21), the solubility was found to reach a maximum in a solution contain 0.1 pyridine mole fraction, and these data interpreted in terms of preferencial solvation of silver ions by pyridine and preferential solvation of iodate ions by water. Vosburg and Cogswell (25) used a maximum of ~0.03 pyridine mole fraction and the existence of the solubility maximum was therefore not observed by these authors.

Miyamoto and co-workers determined the solubility of AgIO₃ in ethylene carbonate-water mixtures (15), 2-methoxyethanol-water mixtures (16), and tetrahydrofuran-water mixtures (17). Jannardhana and Kalidas (18) determined the solubility of AgIO₃ in dimethyl sulfoxide-water mixtures, and a common feature in all four of these systems is the monotonic decrease in solubility as the concentration of the organic component increases: i.e. no maxima or minima were observed.

Subramanian, Rao and Kalidas (19) determined the solubility of AgIO₃ in acetonitrile-water mixtures and again find a maximum at an acetonitrile concentration of 0.1 mole fraction. These results were interpreted in terms of selective solvation similar to those in the pyridine-water mixtures discussed above.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University) M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

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COMPONENTS:	EVALUATORS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) E.M. Woolley (Brigham Young University)
(2) Water; H ₂ O; [7732-18-5]	M. Salomon (US Army ETDL) September 1989

CRITICAL EVALUATION:

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COMPONENTS:	EVALUATORS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	H. Miyamoto (Niigata University) M. Salomon (US Army ETDL)	
(2) Organic Solvents	September 1989	

CRITICAL EVALUATION:

SOLUBILITIES IN NONAQUEOUS MEDIA

The solubility of AgIO₃ in both protic and aprotic organic solvents was reported in nine independent studies (1-9) which are briefly reviewed below. Complete details can be found in the compilations.

Kolthoff and Chantooni (1) determined the solubility of $AgIO_3$ in pure methanol containing $(C_2H_5)_4NCI$ and $(C_2H_5)_4NIO_3$ (see compilation for numerical values) at 298 K. From these solubilities they calculate a solubility product of 2.0 x 10^{-13} mol² dm⁻⁶ for $AgIO_3$. This same paper reports the determination of the concentration solubility product, K_{s0} , by the e.m.f. method, and from two data points an average value of 2.7 x 10^{-13} mol² dm⁻⁶ was calculated. A subsequent study at 298.2 K by Kalidas and Schneider (3) employed the e.m.f. to determine solubilities which in turn yielded a value of 1.16×10^{-11} mol² dm⁻³ for the concentration solubility product K_{s0} . According to Subramanian and Kalidas (9), these large differences in K_{s0} values may, presumably, be attributed to irreversible behavior of the $Ag,AgIO_3$ electrode used by Kolthoff and Chantooni. At 303 K, Kalidas et al. (2, 9) used the e.m.f. method to determine solubilities in pure methanol and report the identical value of 1.92×10^{-11} mol² kg⁻² for the concentration solubility product.

For the solubility of $AgIO_3$ in pure acetonitrile, Kolthoff and Chantooni (1) report an average value (2 data points) of 2.3 x 10^{-11} mol² dm⁻⁶ for K_{s0} at 298 K. At 303 K, Kalidas et al. report concentration solubility product constants of 3.8 x 10^{-9} mol² kg⁻² (calculated by the evaluators), and 4.17 x 10^{-10} mol² kg⁻² in (5 and 9), respectively.

Similar disagreement can be found for K_{80} values in references (1, 2 and 4): 1.6 x 10^{-10} mol² dm⁻⁶, 8.53 x 10^{-11} mol² kg⁻² and 6.4 x 10^{-11} mol² kg⁻², repectively (the latter value calculated by the evaluators from the solubility data in the compilation).

- 1. Kolthoff, I.M.; Chantooni, M.K. J. Phys. Chem. 1973, 77, 523.
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COMPONENTS:

(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Noyes, A.A.; Kohr, D.A.

J. Am. Chem. Soc. 1902, 24, 1141-8.

VARIABLES:

T/K = 298

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

solubility from undersaturation

solubility from supersaturation

g	AgIO ₃ in		g	AgIO ₃ in	
2	50 cm ³ sln	104mol dm-3a	25	0 cm³ sin	104mol dm-3a
	0.0109	1.86		0.0112	1.91
	0.0107	1.82		0.0113	1.93
	0.0112	1.91		0.0117	1.99
	0.0108	1.84		0.0106	1.81
	0.0111	1.89		0.0114	1.94
averages:	0.01094	1.86	averages:	0.01122	1.92

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgIO₃ and pure water were rotated in a thermostat at 25°C for 4 or 5 hours. Saturation was approached from both undersaturation and from supersaturation. After allowing the solid particles to settle for a short time, the solutions were filtered by suction. AgI was precipitated from the saturated solutions by addition of KI. The precipitate was collected in a platinum Gooch crucible upon a layer of finely divided Pt, dried at 160°C, and weighed.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ was precipitated from solutions of (recrystallized) Ag₂SO₄ and KIO₃. The precipitate was washed with hot water.

ESTIMATED ERROR:

Soly: standard deviation about 4 %. Temp: nothing specified.

ന	MD	ON	ΙĽΝ	ITS:
···	1711	•		

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Böttger, W.

Z. Phys. Chem. 1903, 46, 521-619.

VARIABLES:

T/K = 293.1

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

	equilibration	κ(sln)	κ(water)
t/ºC	time (hours)	10 ⁶ S cm ⁻¹	10 ⁶ S cm ⁻
19.96	36	14.14	0.770
19.96	69	14.09	0.770
19.96	67	14.11	0.770
19.94	15	14.06	1.18
19.94	5	13.91	1.18
19.94	87	13.88	1.18
19.94	7	14.02	1.18
19.94	8	14.00	1.18
19.94	34	14.15	1.06
19.94	43	14.12	1.06
19.94	37	14.11	1.06
19.95	26	14.36ª	1.32
19.95	92	14.36a	1.32
19.95	36	14.38ª	1.32
19.94	51	14.72ª	1.302
19.94	42	14.31ª	1.27
19.94	35	14.29ª	1,27

^aAverage $\kappa(\sin) = 1.405 \times 10^{-5} \text{ S cm}^{-1}$ not including these values. Using this average and molar conductances of 57.0 and 35.5 S cm² mol⁻¹ for λ^{∞} for Ag⁺ and IO₃⁻, respectively, the author computes a solubility of 1.51₉ x 10⁻⁴ mol dm⁻³ from eqs. [1] and [2]. $K_{80} = S^2 = 2.31 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$.

$$\kappa(AgIO_3) = \kappa(sln) - \kappa(water)$$
 [1]

 $S = 1000 \kappa(AgIO_3)/\{\lambda^{\infty}(Ag^+) + \lambda^{\infty}(IO_3^-)\}$ [2]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility was determined by conductivity measurements. The condictivity cells which employed Pt electrodes were designed to prevent entrapment of air bubbles. After sealing, the entire cell was immersed in a water bath and rotated in the dark. Equilibrium was taken when the electrolytic conductivity was constant within experimental error (usually within 20 to 30 minutes). The bridge and the thermometer were calibrated, and the cell constants determined by using 0.010 mol dm⁻³ KCl solution.

SOURCE AND PURITY OF MATERIALS:

Analytically pure chemicals (Merck) were used. AgIO₃ was precipitated from cold AgNO₃ and KIO₃ solutions. Part of the precipitate was washed several times in diffused daylight, and the residual parts were filtered off, dried, and stored. KCl was purified by precipitation from a saturated aqueous solution with alcohol. Laboratory distilled water was redistilled from a tin-plated still and stored in a flask fitted with a drying tube with NaOH and CaO.

ESTIMATED ERROR:

 κ : precision $\pm 1 \times 10^{-6}$ S cm⁻¹ (compilers). Soly: precision ± 20 % (compilers).

Temp: accuracy ± 0.02 K.

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3]	ORIGINAL MEASUREMENTS: Sammet, V.
(2) Water; H ₂ O; [7732-18-5]	Z. Phys. Chem. 1905, 53, 641-91.
VARIABLES:	PREPARED BY:
T/K = 298 and 333 K	H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

Solubility products were calculated from emf measurements on the following cell:

 $Ag \mid AgNO_3(c_1) \parallel KNO_3(c_1) \parallel KIO_3(c_2) \mid AgIO_3, Ag$ [1]

	c ₁	C ₂	E ₁	108K _{s0} a	108K _{a0} b
t/ºC	mol dm-3	mol dm-3	volts	mol ² dm ⁻⁶	mol ² dm ⁻⁶
25	0.1	0.01	0.249	4.49	6.2
	0.1	0.01	0.250	4.34	6.0
	0.1	0.01	0.248	4.72	6.5
	0.1	0.1	0.303	4.60	7.6
	0.1	0.1	0.297	5.70	9.6
	0.1	0.1	0.305	4.36	7.0
60	0.1	0.01	0.214	42.94	58
	0.1	0.01	0.213	44.00	60
	0.1	0.01	0.213	44.00	60
	0.1	0.1	0.279	40.70	60
	0.1	0.1	0.278	42.19	62

^{*}Author's values, evidently including activity coefficients.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Emf measurements on cell [1] were not described in detail. Corrections for liquid junction potentials were not made. Activity corrections were made by the method of incomplete dissociation of AgNO ₃ and KIO ₃ solutions.	Nothing specified.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

bCompilers' calculations for concentration solubility products from $\ln K_{s0} = -E_1 F/RT + \ln(c_1 c_2)$.

COMPONENTS:

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kohlrausch, F.

Z. Phys. Chem. 1908, 64, 129-69.

VARIABLES:

PREPARED BY:

T/K = 282.4, 291.1, 291.5 and 299.8

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

	κ(AgIO ₃)	soly	soly	κ*(AgIO ₃)
t/ºC	106S cm-1	104mol dm-3	g dm-3	106S cm-1
9.43	8.48	0.971	0.0275	6.86
18.00	11.90	1.363	0.0385	11.90
18.37	12.07	1.382	0.0391	12.17
26.60	16.61	1.90 ₆	0.0539	20.02

For pure water the author states that $\kappa(\text{water}) = 1.10$ to 1.23 x 10⁶S cm⁻¹, but individual values for each temperature are not given. There is some confusion as to the significance of $\kappa^*(\text{AgIO}_3)$ values. The solubilities were calculated from the corrected $\kappa(\text{AgIO}_3)$ values (eqs. [1] and [2] below), and the $\kappa^*(\text{AgIO}_3)$ values are probably the actual measured values subject to corrections for temperature changes in the molar conductivities. The effect of temperature on the electrolytic conductivities is given in eq. [3] below.

At 18°C, the molar conductivities (infinite dilution) of Ag⁺ and IO₃⁻ are 54.3 and 33.9 S cm² mol⁻¹, respectively, and individual values corrected for finite concentrations for each temperature are given below. Eqs. [1] and [2] were used to calculate the solubilities.

$$\kappa(AgIO_3) = \kappa(sln) - \kappa(water)$$

solubility = $1000 \kappa (AgIO_3)/\lambda$ [2]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

SOURCE AND PURITY OF MATERIALS:

[1]

Temperature dependencies were calculated from

 $\kappa_{\rm t} = \kappa_{18}[1 + \alpha(t - 18) + \beta(t - 18)^2]$ [3]

where $\alpha = 0.0231$ and $\beta = 0.00009$. The data given in the above table are not fully explained by this equation

AgIO₃ was prepared from solutions of AgNO₃ and NaIO₃. The precipitate was dried and powdered in the dark.

The molar conductances corrected for finite concentrations are given below (A units are S cm² mol⁻¹).

entra-	ESTIMATED	ERROR:

t/ºC	Λ
9.43	87.4

18.00 87.3

18.37 87.3 26.60 87.1 Nothing specified.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Water; H₂O; [7732-18-5] VARIABLES: T/K = 293 ORIGINAL MEASUREMENTS: Whitby, G.S. Z. Anorg. Chem. 1910, 67, 62-4 and 107-9. H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

The solubility of AgIO₃ in water at 20°C was given as 0.039 g dm-3.

From this value, the compilers calculate a solubility of 1.38 x 10-4 mol dm-3.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturated solutions were analyzed by diluting a portion to a known volume. To a 50 cm³ portion of the diluted solution were added several drops of concentrated NaOH solution, and the resulting solution was placed in a boiling water bath for 2 minutes. 6 drops of 1 mol dm-³ NaOH solution were added along with a small amount of sucrose, and the mixture heated 20 to 30 seconds, cooled, and the resulting yellowish color intensity measured colorimetrically. The intensity of these solutions were compared to the intensity of standard AgNO3 solutions treated in an identical manner. The author states that the detection limit for silver is 4 x 10-5 g dm-³.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Soly: precision ± 5 % (compilers). Temp: nothing specified.

COMPONENTS:
(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Water; H₂O; [7732-18-5]

VARIABLES:

ORIGINAL MEASUREMENTS:
Baxter, W.P.

J. Am. Chem. Soc. 1926, 48, 615-21.

E.M. Woolley

EXPERIMENTAL DATA:

T/K = 348.15

	solubility	No. of	deviations f	from the mean	method of
detmn No.	103mol kg-1	expts	max/%	average/%	AgIO ₃ prepr
1	0.8415	4	0.17		1 .
2	0.8414	3	0.12		1
3	0.8411	4	0.39		2
4	0.8395	5	0.43		3
5	0.8371	5	0.43		4
6	0.8403	9		0.07	?
7	0.8416	3		0.04	?
8	0.8403	9		0.07	?
9	0.8373	5		0.08	?
10 .	0.8417	4		0.06	?
11	0.8417	4		0.06	?

Determinations 6 to 11 are specified as referring to "weighed in air." Buoyancy corrections would make the resulting solubilities smaller by less than about 0.1 %. Determinations 1 to 5 are specified as referring to mmol per "1000 g solution," whereas determinations 6 to 11 refer to mmol per "1000 g water." This would make only about 0.024 % difference in the solubilities reported by these two methods. Determinations 10 and 11 appear to refer to the same experiments as do determinations 6 and 8. The average of all values (except 8 and 11) is 0.839₆ x 10-3 mol kg-1 with a standard deviation of 0.001₇.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

1.5 g AgIO₃ crystals were rotated with 350 cm³ water in bottles made of Pyrex tubing and were sealed. The bottles were rotated in a thermostat maintained at 75.00°C for 20 to 100 hours, and equilibrium was approached from both above and below. The bottles were then placed in a rack in the thermostat, the tip of a side tube broken off, and a hole blown in the top neck through which a heated delivery tube was introduced. The tube contained a wad of asbestos fibers. A sample of 240-300 g of satd sln was removed by using compressed air to force the sln through the delivery tube and the asbestos filter. These aliquots were delivered into weighed glass-stoppered flasks containing 10 cm3 of dil HCl. After weighing, the contents of the flask were cooled, 2 g KI added, and the liberated I2 titrated with standardized Na2S2O3.

SOURCE AND PURITY OF MATERIALS:

Initial prepn of AgIO₃ by mixing slns of AgNO₃ and slight excess of warm 0.15 mol dm-³ KIO₃. The ppt was washed with cold water, 6-8 liters of hot water, and dried at 110°C for 2 hours. The following correspond to the preparation number given in the above table.

Prepn 1 and 2: the initial AgIO₃ was divided into 2 parts (i.e. they are the same).

Prepn 3. The initial ppt was dissolved in dil NH₃ solution, pptd with HNO₃, and washed and dried as above.

Prepn 4. These were solid residues from soly determinations using AgIO₃ from prepns 1-3. These residues were dissolved in dil NH₃ and treated as in 3 above.

Ordinary distd water was redistd from Ag₂SO₄ sln and then distd once more.

ESTIMATED ERROR:

Soly: reproducibility within 0.2 %. Temp: precision ± 0.02 K.

COMPONENTS:

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kolthoff, I.M.; Lingane, J.J.

J. Phys. Chem. 1938, 42, 133-40.

VARIABLES:

T/K = 298.15

PREPARED BY:

E.M. Woolley

EXPERIMENTAL DATA:

initial mass of AgIO ₃ grams	numb of expts	average total silver content mmol dm-3	average total iodate content mmol dm-3	108K _{s0} a mol² dm-6	calcd soly $(K_{s0})^{1/2}$ mmol dm ⁻³
0.05	4	0.1633	0.1839	3.00	0.173
5.0	3	0.1630	0.1910	3.11	0.176
0.05	1p	0.176	0.180	3.17	0.178
0.1	5ь	0.1750	0.1796	3.143	0.1773
3.0	IР	0.176	0.181	3.18	0.179
0.3	3ь	0.1761	0.1780	3.13	0.177¢

a Solublity product K_{s0} calculated from $[Ag^+]_{total}[IO_3^-]_{total}$

cThe authors give an "extrapolated" value of 1.744 x 10-4 mol dm-3 for the solubility at zero ionic strength. The extrapolation was based on this data point and the solubilities in KNO₃ solutions (see the compilation of the AgIO₃-KNO₃-H₂O system by these authors). Based on the extrapolated solubility at zero ionic strength, the authors computed the thermodynamic solubility product $K_{\pm 0}^0 = 3.04 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgIO₃ crystals and 200 cm³ water placed in either plain or paraffin-coated brown glass bottles stoppered with paraffined corks. The bottles were rotated for 3 h in a thermostat at 25°C. Analyses showed that equilibrium was established within one hour. 100 cm³ samples were withdrawn through a filter pipet with cotton affixed to the tip. The first portion of solution that was withdrawn was discarded, and about 100 cm³ analyzed for both silver and iodate. Silver was determined by potentiometric titration with 0.001 mol dm⁻³ KI solution delivered from a calibrated 10-ml microburet. Iodate was determined by iodometric titration with freshly prepared and standardized 0.01 mol dm⁻³ thiosulfate using a calibrated microburet.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by rapid precipitation using dilute KIO₃ (slight excess) and AgNO₃ solutions. KIO₃ was recrystallized three times. AgNO₃ was "pure." The precipitate was aged for 4 days in the mother solution, and then washed twelve times with conductivity water. It was dried in a vacuum oven for 10 hours at 55°C. The AgIO₃ was then recrystallized from 1 mol dm⁻³ HNO₃. Conductivity water had an electrolytic conductance of 1.4 x 10⁻⁶ S cm⁻¹.

ESTIMATED ERROR:

Titrns: precision \pm 0.2 % for Ag and \pm 0.3 % for iodate. Temp: precision \pm 0.02 K.

bParaffin-coated bottles used.

COMPONENTS:

(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ricci, J.E.; Amron, I.

J. Am. Chem. Soc. 1951, 73, 3613-8.

VARIABLES:

T/K = 298 and 318

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

t/ºC	solubility g dm ⁻³	solubilitya 104mol dm-3
25	0.0506	1.79
25	0.0506	1.79
25	0.0512	1.81
25	0.0511	1.81
25	0.0507	1.79
25	0.0509	1.80
average 25	0.0508	1.80
45	0.0995	3.52
45	0.0997	3.53
average 45	0.0996	3.52

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess silver iodate and freshly boiled, distilled water were placed in Pyrex bottles and rotated in a large constant temperature water bath. At 25°C the bottles were rotated for 7 days and 5 months, and at 45°C, the bottles were rotated for 2 days. After allowing the solid to settle, the saturated solutions were sampled with calibrated delivery pipets fitted with filter paper tips. Solutions analyzed for iodate with sodium thiosulfate.

SOURCE AND PURITY OF MATERIALS:

Commercial AgIO₃ was purified by recrystallization or by washing with warm dilute nitric acid and water. The product was dried at 100°C. The purity of the solid was determined by both iodometric titration (99.9-100.0 %) and by gravimetric silver determination (99.6 %).

ESTIMATED ERROR:

Soly: precision \pm 0.8 % deviation from the mean. Temp: precision probably \pm 0.05 K (compiler).

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Potassium iodate; KIO₃; [7758-05-6] (3) Water; H₂O; [7732-18-5] VARIABLES: Concentration of KIO₃ Room temperature: T/K ~ 293 to ~ 295 CONIGINAL MEASUREMENTS: Shchigol, M.B. Zh. Obshch. Khim. 1952, 22, 721-30: J. Gen. Chem. USSR (Engl. Transl.) 1952, 22, 787-94. PREPARED BY: E.M. Woolley and H. Miyamoto

EXPERIMENTAL DATA:

KIO ₃ concn mol dm ⁻³	AgIO ₃ solubility mol dm ⁻³
0.005	6.0 x 10 ⁻⁵
0.025	5.0 x 10-4
0.050	8.3 x 10-4

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Precipitated AgIO₃ placed in 100 cm³ flasks to which were added 25 cm³ water and KIO₃. The volume was adjusted to 100 cm³ by additions of water. The solutions were agitated for 24 hours, filtered, and the iodate content of the filtrate determined iodometrically. Only the mean value of three determinations was given. Presumably the solubility was determined as the difference between the measured total iodate concentration and the initial KIO₃ concentration.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Potassium nitrate; KNO₃; [7757-79-1]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kolthoff, I.M.; Lingane, J.J.

J. Phys. Chem. 1938, 42, 133-40.

VARIABLES:

Concentration of potassium nitrate

T/K = 298.15

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

KNO ₃ conen mol dm ⁻³	total silver content mmol dm ⁻³	total iodate content mmol dm ⁻³	average solubility mmol dm-
0	0.1761=	0.1780a	0.1771
0.001301	0.1813	0.1832	0.1823
0.003252	0.1863	0.1877	0.1870
0.006503	0.1908	0.1919	0.1914
0.01410	0.1991	0.1996	0.1994
0.07050	0.2302	0.2300	0.2301
0.1995	0.2668	0.2663	0.2665
0.4995	0.3345	0.3284	0.3314
0.9989	0.4087	0.4086	0.4086

^aAverage of 3 experiments (see the compilation on the AgIO₃-H₂O system by these authors).

The authors give an "extrapolated" value of 1.744 x 10^{-4} mol dm⁻³ for the solubility at zero ionic strength. Based on this extrapolated solubility, the authors computed the thermodynamic solubility product $K_{s0}^0 = 3.04 \text{ x}$ 10^{-8} mol² dm⁻⁶.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgIO₃ crystals and 200 cm³ KNO₃ solution placed in paraffin-coated brown glass bottles stoppered with paraffined corks. The bottles were rotated for 3 h in a thermostat at 25°C. Analyses showed that equilibrium was established within one hour. 100 cm³ samples were withdrawn through a filter pipet with cotton affixed to the tip. The first portion of solution that was withdrawn was discarded, and about 100 cm³ analyzed for both silver and iodate. Silver was determined by potentiometric titration with 0.001 mol dm⁻³ KI solution delivered from a calibrated 10-ml microburet. Iodate was determined by iodometric titration with freshly prepared and standardized 0.01 mol dm⁻³ thiosulfate using a calibrated microburet.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by rapid precipitation using dilute KIO₃ (slight excess) and AgNO₃ solutions. KIO₃ was recrystallized three times. AgNO₃ was "pure." The precipitate was aged for 4 days in the mother solution, and then washed twelve times with conductivity water. It was dried in a vacuum oven for 10 hours at 55°C. The AgIO₃ was then recrystallized from 1 mol dm⁻³ HNO₃. KNO₃ was recrystallized several times and shown to be free from chloride. Conductivity water had an electrolytic conductance of 1.4 x 10⁻⁶ S cm⁻¹.

ESTIMATED ERROR:

Titrns: precision \pm 0.2 % for Ag and \pm 0.3 % for iodate. Temp: precision \pm 0.02 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C.
(3) Potassium nitrate; KNO ₃ ; [7757-79-1]	J. Am. Chem. Soc. 1941, 63, 2670-4.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of KNO ₃ T/K = 298	E.M. Woolley

EXPERIMENTAL DATA:

The solubility of silver iodate in aqueous potassium nitrate solutions was determined by iodometric titration, and all results were presented graphically. The authors found the solubility to follow the equations given below where S is the solubility in mol dm-3 units (Sc) or mol kg-1 units (Sm).

Based on mol dm-3 units.

$$- log S_c = - log S_c^0 - \{0.5056 I_c^{1/2}/(1 + I_c^{1/2}) + 0.150 I_c\}$$
[1]

where

$$I_c = [KNO_3] + S_c$$
 and $S_c^0 = 1.746 \times 10^{-4} \text{ mol dm}^{-3}$ [2]

Based on the results of eq. [2], the compiler calculates $K_{s0} = (S_c^0)^2 = 3.049 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$.

Based on mol kg-1 units.

$$- log S^{m} = - log S_{m}^{0} - \{0.5056 I_{m}^{1/2}/(1 + I_{m}^{1/2}) + 0.160 I_{m}\}$$
 [3]

where

$$I_m = \{KNO_3\} + S_m \text{ and } S_m^0 = 1.754 \text{ x } 10^{-4} \text{ mol kg}^{-1}$$
 [4]

The authors gave $K_{s0} = (S_m^0)^2 = 3.076 \times 10^{-8} \text{ mol}^2 \text{ kg}^{-1}$.

The measured solubilities were stated to fit eqs. [1]-[4] within 0.4 % maximum deviation, and within 0.17 % average deviation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Silver iodate crystals and aqueous KNO3 were stirred in AgIO3 prepared by slowly adding solutions of AgNO3 Pyrex flasks immersed in a water bat at 25°C for two or more hours. Saturation was verified by subsequent analysis. 200 cm³ samples of the saturated solutions were removed by forcing the solution through a filter and into a pipet by air pressure. The iodate content of weighed samples was determined iodometrically with standardized 0.01 mol dm-3 thiosulfate solution.

SOURCE AND PURITY OF MATERIALS:

and KIO3 to a large volume of water in the dark with continuous stirring. The precipitate was washed and dried in air. Analysis was consistent with the stoichiometry. KNO₃ of reagent grade was recrystallized and dried at 110°C.

ESTIMATED ERROR:

Soly: nothing specified, but the precision in the fit to eqs. [1]-[4] is given above.

Temp: nothing specified.

COMPONENTS: (1) Silver iodate;

(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Potassium nitrate; KNO₃; [7757-79-1]

(2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Li, N.C.C.; Lo, Y.-T.

J. Am. Chem. Soc. 1941, 63, 394-7.

VARIABLES:

Concentration of potassium nitrate T/K = 283, 293, 298, 303 and 308

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

KNO ₃ conen/mol dm-	3 solubility	of AgIO ₃ (104n	nol dm- ^{3a}) as a fu	nction of temper	ature
	10°C	20°C	25°C	30°C	35°C
0р	0.9605b	1.442b	1.748 ^b	2.119b	2.541b
0.0	0.97	1.463	1.785	2.152	2.587
0.001301			1.827		
0.001326	1.0016	1.508		2.212	2.663
0.003252			1.868		
0.003263	1.023	1.543		2.263	2.714
0.006464	1.054	1.582		2.324	2.786
0.006503			1.913		
0.01404	1.104	1.656		2.419	2.920
0.01410			2.002		
0.07032	1.279	1.943		2.844	3.381
0.07050			2.304		
0.1213			2.454	3.041	
0.2003					3.908
0.2528			2.793	3.428	
0.4987					4.803
0.5050			3.330	4.035	
0.8378			3.904		

alt is not entirely clear whether these values are expressed as mol dm-3 or mol kg-1, and although the differences would be small, the authors apparently have (incorrectly?) compared and combined their

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgIO₃ crystals and KNO₃ solutions were placed in brown glass bottles coated inside with paraffin and closed with paraffined corks. The bottles were rotated in a thermostat at specified temperatures, and three solubility determinations were made for each KNO₃ solution at each temperature. The solubility of AgIO₃ was determined iodometrically by titration of 100 cm³ aliquots of filtered saturated solution with 0.01 mol dm⁻³ Na₂S₂O₃ solutions which were frequently standardized by titration into potassium dichromate according to (1).

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by mixing dil solutions of c.p. grade AgNO₃ and twice recrystallized KIO₃. The ppt was aged for several days, washed repeatedly with conductivity water, and dried under vacuum at 60°C. KNO₃ was recrystallized three times.

ESTIMATED ERROR:

Titrations accurate to ± 0.3 %.
Soly: reproducibility not specified.
Temp: precision ± 0.05 K.

REFERENCES:

 Kolthoff, I.M.; Lingane, J.J. J. Phys. Chem. <u>1938</u>, 42, 133.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Potassium nitrate; KNO₃; [7757-79-1] (2) Water; H₂O; [7732-18-5] ORIGINAL MEASUREMENTS: Li, N.C.C.; Lo, Y.-T. J. Am. Chem. Soc. 1941, 63, 394-7.

EXPERIMENTAL DATA: (continued.....)

results directly with other work based on mol kg-1 concentration units.

bThese are "extrapolated" thermodynamic values, based on an extended Debye-Hückel formula. The extrapolated solubilities are designated as S⁰.

Based on the extrapolated "thermodynamic solubilities," the solubility products at various temperatures were computed from $K_{s0} = (S^0)^2$, and the results are given below.

t/ºC	10	20	25	30	35
$10^8 { m K_{80}}^{ m c,d}$	0.923	2.078	3.055	4.490	6.456
108K ₈₀ c,e	0.923	2.079	3.056	4.490	6.457

cBased on mol dm-3 units.

Using the above compilers' values, the compilers fitted the K_{s0} values to eq. [1] by the method of least squares, and the results were used to compute the thermodynamic parameters given below.

$$ln K_{s0} = a + b/(T/K)$$
 [1]

a = 5.4878

 $b = -6.79344 \times 10^3 \text{ K}$

 $\Delta H = -Rb + RT^2(d\ln \rho^0/dT) = 14418$ cal mol-1.

 $\Delta S(298.15 \text{ K}) = 10.87 \text{ cal mol}^{-1} \text{ K}^{-1}$.

In the relation for ΔH , ρ^0 is the density of pure water. The standard deviation for the fit to eq. [1] is 0.0048 which corresponds to about 0.5 % error in K_{s0} , or about 0.3 % error in the measured solubilities.

dAuthors' calculations.

[«]Compilers' calculations.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Potassium nitrate; KNO₃; [7757-79-1] (3) Water; H₂O; [7732-18-5] J. Am.

ORIGINAL MEASUREMENTS: Baxter, W.P.

J. Am. Chem. Soc. 1926, 48, 615-21.

VARIABLES:

Concentration of potassium nitrate T/K = 348.15

PREPARED BY:

E.M. Woolley and H. Miyamoto

EXPERIMENTAL DATA:

KNO ₃ concn ^a mol kg ⁻¹	solubility ^a 10 ³ mol kg ⁻¹	No. of expts	average deviation from the mean (%)
0.0	0.8416	3	0.04
0.001	0.8547	2	0.16
0.002	0.8660	2	0.10
0.005	0.8875	2	0.02
0.010	0.9158	2	0.04
0.020	0.9570	1	
0.050	1.0365	2	0.07
0.100	1.1258	2	0.11

^aThese are specified as referring to masses "weighed in air." Buoyancy corections would make the resulting concentrations smaller by less than about 0.1 %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

1.5 g AgIO₃ crystals were rotated with 350 cm³ KNO₃ solution in bottles made of Pyrex tubing and were sealed. The bottles were rotated in a thermostat maintained at 75.00°C for 20 to 100 hours, and equilibrium was approached from both above and below. The bottles were then placed in a rack in the thermostat, the tip of a side tube broken off, and a hole blown in the top neck through which a heated delivery tube was introduced. The tube contained a wad of asbestos fibers. A sample of 240-300 g of satd sln was removed by using compressed air to force the sln through the delivery tube and the asbestos filter. These aliquots were delivered into weighed glass-stoppered flasks containing 10 cm3 of dil HCl. After weighing, the contents of the flask were cooled, 2 g KI added, and the liberated I2 titrated with standardized Na₂S₂O₃.

SOURCE AND PURITY OF MATERIALS:

Initial prepn of AgIO₃ by mixing sins of AgNO₃ and slight excess of warm 0.15 mol dm⁻³ KIO₃. The ppt was washed with cold water, 6-8 liters of hot water, and dried at 110°C for 2 hours. The following defines the four prepns, but the author does not specify which prepn was used in the present study.

Prepn 1 and 2: the initial AgIO₃ was divided into 2 parts (i.e. they are the same).

Prepn 3. The initial ppt was dissolved in dil NH₃ solution, pptd with HNO₃, and washed and dried as above.

Prepn 4. These were solid residues from soly determinations using AgIO₃ from prepns 1-3. These residues were dissolved in dil NH₃ and treated as in 3 above.

Ordinary distilled water was redistilled from a Ag₂SO₄ solution and then redistilled.

C.p. grade KNO₃ was recrystallized 1 to 3 times, washed free of chloride and dried at 120°C for five or more hours.

ESTIMATED ERROR:

Soly: reproducibility within 0.2 %. Temp: precision ± 0.02 K.

188		er lodate		
COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97		ORIGINAL MEASUREMENTS: Baxter, W.P.		
(2) Potassium perchlorate; KClO ₄ ; [7778-74-7] (3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1926, 48, 615-21.		
VARIABLES: Concentration of potassium perchlorate T/K = 348.15		PREPARED BY: E.M. Woolley and H. Miyamoto		
EXPERIMENTAL DATA: KClO ₄ concn ^a	solubilitya	No. of	average deviation	
mol kg-1	103mol kg-1	expts	from the mean (%)	

EXPERIMENTAL DATA:			
KClO ₄ concn	solubility ^a	No. of	average deviation
mol kg-1	103mol kg-1	expts	from the mean (%)
0.0	0.8403	9	0.07
0.002	0.8661	3	0.09
0.005	0.8900	2	0.03
0.010	0.9143	2	0.06
0.020	0.9503	2	0.08
0.050	1.0183	2	0.04
0.100	1.0882	2	0.04

aThese are specified as referring to masses "weighed in air." Buoyancy corections would make the resulting concentrations smaller by less than about 0.1 %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

See the AgIO₃-KNO₃-H₂O compilation by this author for complete experimental details and estimated errors.

SOURCE AND PURITY OF MATERIALS:

See previous compilations of this author's publication for details on prepn of AgIO₃. C.p. grade KClO₄ was recrystallized, washed and dried at 120°C for five or more hours.

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3] (2) Potassium sulfate; K ₂ SO ₄ ; [7778-80-5] (3) Water; H ₂ O; [7732-18-5]		ORIGINAL MEASUREMENTS: Baxter, W.P. J. Am. Chem. Soc. <u>1926</u> , 48, 615-21.		
VARIABLES: Concentration of potassium sulfate T/K = 348.15		PREPARED BY: E.M. Woolley and H. Miyamoto		
EXPERIMENTAL DATA:				
K₂SO ₄ concn ^a	solubilitya	No. of	average deviation	
mol kg-1	103mol kg-1	expts	from the mean (%)	
0.0	0.8403	9	0.07	
0.0	0.8373	5	0.08	
0.0005	0.8555	2	0.08	
0.001	0.8760	2	0.04	
0.002	0.9024	2	0.12	
0.005	0.9603	2	0.07	
0.010	1.0241	2	0.04	
0.020	1.1110	2	0.06	
0.050	1.2932	2	0.26	
^a These are specified as referring concentrations smaller by less the	_	in air." Buoyanc	y corections would make the resulting	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

See the AgIO₃-KNO₃-H₂O compilation by this author for complete experimental details and estimated errors.

SOURCE AND PURITY OF MATERIALS:

See previous compilations of this author's publication for details on prepn of AgIO₃. C.p. grade K₂SO₄ was recrystallized, washed and dried at 120°C for five or more hours.

ORIGINAL MEASUREMENTS:

COMI ONENIS.		1	EADOREMENTO.	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]		Baxter, W.P.		
(2) Magnesium sulfate; MgSO ₄ ; [7487-88-9]				
(3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1926, 48, 615-21.		
VARIABLES:		PREPARED	BY:	
Concentration of magnesium sulfate	•			
T/K = 348.15		E.M. Woolley and H. Miyamoto		
EXPERIMENTAL DATA:				
MgSO ₄ concn ^a	solubilitya	No. of	average deviation	
mol kg-1	103mol kg-1	expts	from the mean (%)	
0.0	0.8417	4	0.06	•
0.0002	0.8522	2	0.00	
0.0005	0.8698	1	,	
0.001	0.8855	2	0.04	
0.002	0.9111	2	0.03	
0.005	0.9629	1		
0.010	1.0201	2	0.01	
0.020	1.0928	2	0.35	
		_		:
aThese are specified as referring to		air. Buoyanc	corections would make the result	mg
concentrations smaller by less than	about 0.1 %.			
	AUXILIARY II	NFORMATION		
METHOD (APPLAD ATTIC (PROCED)		7		
METHOD/APPARATUS/PROCED		1	D PURITY OF MATERIALS:	41
See the AgIO ₃ -KNO ₃ -H ₂ O compilation by this author			compilations of this author's public	
for complete experimental details and estimated errors.			prepn of AgIO ₃ . "Very pure" Mg	
			, and the Mg content detd gravime	trically
as Mg ₂ P ₂ O ₇ .				
COMPONENTS:		ORIGINAL I	MEASUREMENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3	3]	Baxter, W.P.		
(2) Barium nitrate; Ba(NO ₃) ₂ ; [1002	2-31-8]			
(3) Water; H ₂ O; [7732-18-5]		J. Am. Chem. Soc. 1926, 48, 615-21.		
VARIABLES:		PREPARED	BY:	
Concentration of barium nitrate T/K = 348.15		E.M. Woolley and H. Miyamoto		
EXPERIMENTAL DATA:			, u.u. 111 111 111 111 111 111 111 111 11	
	solubilitya	No. of	average deviction	
Ba(NO ₃) ₂ concn ^a			average deviation	
mol kg-1	103mol kg-1	expts	from the mean (%)	
0.0	0.8417	4	0.06	
0.0005	0.8646	2	0.02	
0.001	0.8717	2	0.05	
0.002	0.8973	1		
0.005	0.9322	1	••	
0.010	0.9664	2	0.15	
These are specified as referring to			y corections would make the result	ting
concentrations smaller by less than		Duoyuno	, Joseph would make the lesun	0
concentrations smaller by less than				
1				

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

COMPONENTS:

See the $AgIO_3$ - KNO_3 - H_2O compilation by this author for complete experimental details and estimated errors.

SOURCE AND PURITY OF MATERIALS:

See previous compilations of this author's publication for details on prepn of AgIO₃. C.p. grade Ba(NO₃)₂ recrystallized 1-3 times, washed and dried at 120°C for five or more hours.

190 Silver Iodate

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kolthoff, I.M.; Lingane, J.J.
(2) Barium nitrate; Ba(NO ₃) ₂ ; [10022-31-8]	
(3) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. 1938, 42, 133-40.
VARIABLES:	PREPARED BY:
Ba(NO ₃) ₂ concentration fixed at 0.01 mol dm ⁻³ .	
T/K = 298.15	H. Miyamoto

Note that the concentration of barium nitrate is fixed at 0.01 mol dm⁻³.

initial mass	total Ag	total IO ₃ -	
of AgIO ₃	content	content	$10^8 K_{s0}^a$
grams	mmol dm-3	mmol dm-3	mol ² dm ⁻⁶
0.05	0.211	0.214	4.52
3.0	0.220	0.208	4.58

a Solubility product calculated from $K_{s0} = [Ag^+]_{total}[IO_3^-]_{total}$.

AUXILIARY INFORMATION

	METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
	AgIO ₃ crystals added to 0.01 mol dm ⁻³ Ba(NO ₃) ₂	Ba(NO ₃) ₂ recrystallized several times and shown to be
i	solutions, and remaining details identical to those in the	free from chloride. Remaining details in compilation
	compilation on the AgIO ₃ -KNO ₃ -H ₂ O system by these	cited on the left.
	authors.	

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kolthoff, I.M.; Lingane, J.J.
(2) Thallium nitrate; TINO ₃ ; [10102-45-1]	
(3) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. 1938, 42, 133-40.
VARIABLES:	PREPARED BY:
$TINO_3$ concentration fixed at 0.01 mol dm ⁻³ . T/K = 298.15	H. Miyamoto

EXPERIMENTAL DATA:

Note that the concentration of thallium nitrate is fixed at 0.01 mol dm-3.

initial mass	total Ag	total IO ₃ -	
of AgIO ₃	content	content	108K ₈₀ a
grams	mmol dm-3	mmol dm-3	mol ² dm ⁻⁶
0.05	0.200	0.198	3.96
3.0	0.205	0.191	3.92

a Solubility product calculated from $K_{s0} = [Ag^+]_{total}[IO_3^-]_{total}$.

AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
AgIO ₃ crystals added to 0.01 mol dm ⁻³ TINO ₃ solutions, and remaining details identical to those in the compilation on the AgIO ₃ -KNO ₃ -H ₂ O system by these authors.	,			

COMPONENTS: (1) Silver iodate;

(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Silver nitrate; AgNO₃; [7761-88-8]

(3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Ricci, J.E.; Amron, I.

J. Am. Chem. Soc. 1951, 73, 3613-8.

VARIABLES:

Silver nitrate concentration

T/K = 298

PREPARED BY:

H. Miyamoto and M. Salomon

EXPERIMENTAL DATA:

silver	nitrate	concentrationa	
211461	mmate	concentration*	

silver iodate solubilitya

mass %	mol kg-1	mass %	mol kg-1
22.65	1.72	0.009	0.41
48.47	5.54	0.006	0.41
70.43	14.02	0.035	4.2
71.84	15.04	0.040 to 0.043	5.0 to 5.4

^aMolalities calculated by the compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess silver iodate and AgNO₃ solution prepared with freshly boiled distilled water were placed in Pyrex bottles and rotated in a large constant temperature water bath. The total solid was determined by evaporation to dryness after addition of a drop of concd HNO₃, which apparently by preventing reduction of silver, always gave pure white residues. The final weighed residue was taken up in water for determination of AgIO₃, whereupon AgNO₃ was calculated by difference.

For iodate determination, the solution of the residue was treated with HCl to precipitate AgCl and the filtrate was titrated with 0.01 N sodium thiosulfate.

The isotherm was of the simplest type: i.e. neither hydrates nor double salts were formed.

SOURCE AND PURITY OF MATERIALS:

Commercial AgIO₃ was purified by recrystallization or by washing with warm dilute nitric acid and water. The product was dried at 100°C. The purity of the solid was determined by both iodometric titration (99.9-100.0 %) and by gravimetric silver determination (99.6 %).

C.p. grade AgNO₃ was dried and not treated any further.

ESTIMATED ERROR:

Soly: precision ± 0.003 mass %.

Temp: precision probably ± 0.05 K (compiler).

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3] (2) Nitric acid; HNO ₃ ; [7697-37-2] (3) Water; H ₂ O; [7732-18-5]	Longi, A. Gazz. Chim. Ital. <u>1883</u> , 13, 87-9.
VARIABLES: Concentration of nitric acid	PREPARED BY:
T/K = 298	B. Scrosati

EXPERIMENTAL DATA:

In pure water, the solubility of AgIO₃ was given as:

1 g in 27728.94 g $\rm H_2O$ $\,$ (1.28 x 10⁻⁴ mol kg⁻¹, compiler) and

1 g in 27821.88 cm³ sln (1.27 x 10⁻⁴ mol dm⁻³, compiler).

In an aqueous solution of 35 mass % HNO₃ (specific gravity = 1.21), the solubility is

1 g in 859.81 cm³ sln (4.11 x 10⁻³ mol dm⁻³, compiler).

AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: Nothing specified. Solubility probably determined by evaporation and weighing. SOURCE AND PURITY OF MATERIALS: Nothing specified.

COMPONE	NTS:		ORIGINAL MEA	SUREMENTS:	
(2) Ammoni	date; AgIO ₃ ; [7783-97-3 a; NH ₃ ; [7664-41-7] 5 ₂ O; [7732-18-5]	1	Longi, A. Gazz. Chim. Ital	. <u>1883,</u> 13, 87-9).
	S: on of ammonia		PREPARED BY:		
T/K = 298			B. Scrosati		
EXPERIME	NTAL DATA:				
aq ammor	nia sin composition		AgIO ₃ solub	ility at 25°C	
mass %	specific gravity	cm ³ sln/g	mol dm-3a	g sln/g	mol kg-1a
0.5	0.998	42.73	0.0828	42.39	0.0834
10	0.96	2.383	1.48	2.202	1.61
ªCalculat	ed by the compiler.				
•		AUXILIARY II	NFORMATION		**************************************
METHOD/A	PPARATUS/PROCEDU	JRE:	SOURCE AND P	URITY OF MAT	TERIALS:
	cified. Solubility probal and weighing.	oly determined by	Nothing specifed.		

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Silver iodate; AgIO₃; [7783-97-3] Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. (2) Aqueous ammonia; NH₃ (aq); [7664-41-7] J. Am. Chem. Soc. 1941, 63, 2670-4. (3) Water; H₂O; [7732-18-5] VARIABLES: PREPARED BY: Concentration of ammonia T/K = 298H. Miyamoto

EXPERIMENTAL DATA:

total NH ₃ concn mol kg-1	solubility ^a mmol kg-1	density kg dm-3	ionic strength mmol dm-3	108K _I b _, mol ² dm ⁻⁶
0.01241	3.665	0.997	3.98	6.07
0.01267	3.752	0.997	4.06	5.99
0.01845	5.488	0.997	5.87	6.13
0.02481	7.430	0.998	7.88	6.13
0.03085	9.358	0.997	9.86	5.92
0.06180	19.01	1.003	19.74	6.11
0.1028	32.23	1.003	33.2	6.04
0.1249	39.32	1.005	40.4	6.18
0.1847	59.37	1.009	60.7	6.05
0.2487	81.25	1.014	82.8	5.97

aNote that the solubilities were determined by the total iodate concentration.

bThe data were interpreted in terms of the the following:

 $Ag(NH_3)_2^+ = Ag^+ + 2NH_3(aq)$ K_{I}

where

 $K_I = [Ag+][NH_3]^2/[Ag(NH_3)_2+]$

 K_I was calculated from a value of the thermodynamic solubility product of $K_{a0} = 3.076 \times 10^{-8}$, activity coefficients, NH₃ ionization, and material balance equations.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ammonia solutions were stirred in Pyrex flasks immersed in a water bath at 25°C for two or more hours. Saturation was verified by subsequent analyses. 200 cm3 aliquots of equilibrated solutions removed by forcing the solution through a filter and into a pipet by air pressure to avoid loss of NH3. The weighed solutions were delivered into excess standardized 0.1 mol dm-3 HCl, and the excess acid titrated with standardized 0.1 mol dm-3 NaOH with methyl red indicator.

The solubility was determined by analysis of the iodate | ESTIMATED ERROR: concentration by iodometric titration with standardized 0.01 mol dm-3 thiosulfate solution.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by slowly adding solutions of AgNO₃ and KIO₃ to a large volume of water in the dark with continuous stirring. The precipitate was washed and dried in air. Analysis was consistant with the stoichiometry. A stock solution of ammonia was prepared by dilution of a concentrated solution that was shown by analysis to contain a negligible amount of carbonate.

Nothing specifed.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Hill, A.E.; Simmons, J.P.
(2) Nitric acid; HNO ₃ ; [7697-37-2]	J. Am. Chem. Soc. 1909, 31, 821-39.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of nitric acid T/K = 298	H. Miyamoto

EXPERIMENTAL DATA:

Ag(IO₃) solubility

	116(103)	Jointaling	
HNO ₃ concn	from supersatn	from undersatn	averagesa
mol dm-3	g dm-3	g dm ⁻³	103mol dm-3
0.000	0.0506	0.0500	0.178
0.125	0.0876	0.0852	0.304
0.250	0.1065	0.1084	0.379
0.500	0.1433	0.1394	0.499
1.00	0.2069	0.2065	0.731
2.00	0.3328	0.3310	1.174
4.00	0.7057	0.6913	2.469
8.00 ^b	1.585	1.590	5.608

^{*}Authors' values based on average g dm-3 solubilities (compiler).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgIO₃ was added to HNO₃ solutions, and the mixtures stirred for one or two days in a thermostat at 25°C. Equilibrium was approached from both the supersaturated and undersaturated sides. The solutions were analyzed by reduction of AgIO₃ to AgI by means of SO₂. The precipitated AgI was filtered in a Gooch crucible and dried to constant weight at 120°C. Great care was taken to be sure that the AgI coagulated.

The authors noted that when AgIO₃ was reprecipitated from dilute HNO₃, an amorphous solid formed having a considerably higher solubility than the crystalline form. This amorphous form gradually reverted to the crystalline form upon equilibration of the HNO₃ solutions.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ was precipitated from solutions of (recrystallized) Ag₂SO₄ and KIO₃. The precipitate was washed with hot water.

ESTIMATED ERROR:

Soly: precision less than 2 % (compiler). Temp: nothing specified.

bIn solutions where HNO₃ concn is greater than 8.00 mol dm-3, the iodate decomposed.

COMPONENTS: (1) Silver iodate:

(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Nitric acid; HNO₃; [7697-37-2]

(2) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Li, N.C.C.; Lo, Y.-T.

J. Am. Chem. Soc. 1941, 63, 394-7.

VARIABLES:

Concentration of nitric acid T/K = 298, 303 and 308

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

HNO ₃ concn/mol dm-3	solubility of A	gIO ₃ (104mol dm-	3) as a function of temperatu	ire
	25°C	30°C	35°C	
0	1.785	2.152	2.587	
0.001301	1.8297			
0.006503	1.949	2.373	2.844	
0.01410	2.070	2.520	3.045	
0.07050	2.660	3.256	3.922	
0.1213	3.040	3.750	4.537	
0.2528	3.820	4.738	5.688	
0.5050	5.027	6.350	7.718	
0.8738	6.522			

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

AgIO₃ crystals and HNO₃ solutions were placed in brown glass bottles coated inside with paraffin and closed with paraffined corks. The bottles were rotated in a thermostat at specified temperatures, and three solubility determinations were made for each HNO₃ solution at each temperature. The solubility of AgIO₃ was determined iodometrically by titration of 100 cm³ aliquots of filtered saturated solution with 0.01 mol dm⁻³ Na₂S₂O₃ solutions which were frequently standardized by titration into potassium dichromate according to (1).

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by mixing dil solutions of c.p. grade AgNO₃ and twice recrystallized KIO₃. The ppt was aged for several days, washed repeatedly with conductivity water, and dried under vacuum at 60°C. HNO₃ slns were made by a series of dilutions from a stock sln standardized against pure sodium carbonate using methyl orange indicator.

ESTIMATED ERROR:

Titrations accurate to ± 0.3 %.

Soly: reproducibility not specified.

Temp: precision ± 0.05 K.

REFERENCES:

 Kolthoff, I.M.; Lingane, J.J. J. Phys. Chem. <u>1938</u>, 42, 133. 196 Silver lodate

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Ramette, R.W.
(2) Perchloric acid; HClO ₄ ; [7601-90-3]	J. Chem. Eng. Data 1972, 17, 195-6.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
T/K = 275 to 323	H. Miyamoto, G. Jancso, E.M. Woolley and M. Salomon

EXPERIMENTAL DATA:

All solubilities (S) determined in solutions containing 1 x 10-4 mol dm-3 HClO₄.

	solubility	
t/ºC	103mol dm-3	-log K _{s0} ^s
2	0.0667	8.364
11	0.1005	8.010
20	0.1457	7.689
25	0.1793	7.510
30	0.2148	7.354
40.2	0.3090	7.041
49.1	0.4121	6.794

 $[^]a$ $K_{s0} = S^2 y_{\pm}^2$ using the relation $\log y_{\pm} = AI^{1}/(1 + I^{1})$ where the ionic strength is I = S + 0.0001. These K_{s0} data were fitted by least squares to the following smoothing equation.

$$log K_{s0} = 8.9270 - 0.010953(T/K) - 3298.4/(T/K)$$

Based on this smoothing equation, the following thermodynamic quantities were calculated.

t/ºC	ΔG kcal mol ⁻¹	ΔH kcal mol ⁻¹	ΔS cal mol ⁻¹ K ⁻¹	ΔC _p cal mol ⁻¹ K ⁻¹
0	10.577	14.236	13.47	-27
25	10.252	13.520	10.96	-30
50	10.009	12.741	8.45	-32

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A column 3 cm high in a 4-mm i.d. tube was prepared from 4 g AgIO₃ crystals labeled with Ag¹¹⁰. This column was jacketed with a larger tube carrying circulating water from a constant temperature bath. A solution of 0.0001 mol dm-3 HClO4 was forced through the column, and a test tube was used to collect about 1 gram of saturated solution which was then weighed and counted. Background was about 200 cpm, and samples for analyses were counted to give 105 to 106 total counts (10 to 100 minutes). The analyses were carried out on a weight basis, and conversion to volume units made by use of literature densities (1) for pure H_2O . Thermometers checked against NBS calibrated thermometers. All volumetric glassware was calibrated. Standards for gamma counting were taken by weight from stock solutions prepd by weighing dried samples of the radioactive ppt followed by dissolving in NaCN solution. Counting times were accurate to ± 0.1 seconds. Authors state that repeated solubility determinations at each temperature gave assurance of reproducibility, but numerical information not given.

SOURCE AND PURITY OF MATERIALS:

Crystalline AgIO₃ prepared by pptn from the following solutions: AgNO₃ labeled with Ag¹¹⁰, NH₄OH, KIO₃, and 2-hydroxyethylacetate. This mixture was allowed to stand for 2 weeks, the AgIO₃ redissolved in aq NH₃, and pptd with addn of HClO₄. All chemicals were A.R. grade, and water was redistilled and stored in borosilicate glass 'jugs.'

ESTIMATED ERROR:

Soly: nothing specified.

Temp: accuracy probably ± 0.1 K (compilers).

REFERENCES:

 Chang, T.; Chien, J. J. Am. Chem. Soc. <u>1941</u>, 63, 1709.

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3]	ORIGINAL MEASUREMENTS: Ricci, J.E.; Amron, I.
(2) Iodine oxide; I ₂ O ₅ ; [12029-98-0]	J. Am. Chem. Soc. 1951, 73, 3613-8.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Composition T/K = 298 and 318	M. Salomon

EXPERIMENTAL DATA:

The AgIO₃-I₂O₅-H₂O system at 25.0°C

mass % I ₂ O ₅	sln density/g cm ⁻³	solid phase*
19.51	1.203	Α
36.89	1.455	Α
48.64		Α
52.11		A, A·B
52.09		A, A·B
54.12		A•B
55.20	1.864	A•B
59.78	1.99 ₉	A•B
63.04	2.12	A•B
63.72		A•B
64.69	2.18	A•B
65.70	2.22	A•B
67.82		A•B
68.85		A•B
69.86		A•B
71.00	2.45	A•B
71.42		A•B
71.54b	2.48	A•B, B•W
71.55		B•W

a Solid phases: $A = AgIO_3$, $B = I_2O_5$, $W = H_2O$

bThis is point b on the phase diagram given on the next page and is the average of four.

continued....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Solutions prepd from AgIO₃, HIO₃ and H₂O and equilibrated for one week as described in the compilation of these authors' study of the AgIO₃-AgNO₃-H₂O system. Solutions sampled with delivery pipets at low concns and with specific gravity pipets at high concns. Analyses of total acid and total iodate yielded identical results (within 1/1000) indicating the absence of AgIO₃ in the satd solutions. The phase diagram for 298.2 K is given on the following page, and the 318.2 K phase diagram is very similar.

From the phase diagram the formation of the 1:1 complex is clear and formed more rapidly near point b (congruently satd with the compound and HIO₃) than near point a (the solution incongruently satd with AgIO₃ and the compound). This difference is due to poly-iodate ions whose concn increases with HIO₃ concn.

SOURCE AND PURITY OF MATERIALS:

Commercial AgIO₃ was purified by recrystallization or by washing with warm dilute nitric acid and water. The product was dried at 100°C. The purity of the solid was determined by both iodometric titration (99.9-100.0 %) and by gravimetric silver determination (99.6 %).

HIO₃ (source not specified) ground, dried at room temp for 1 week over anhydrone, and analyzed as 100.0 % pure by iodometric titrn and by titrn with stnd NaOH solution.

ESTIMATED ERROR:

Soly: precision ± 0.01 mass % (compiler). Temp: precision probably ± 0.05 K (compiler). 198 Silver Iodate

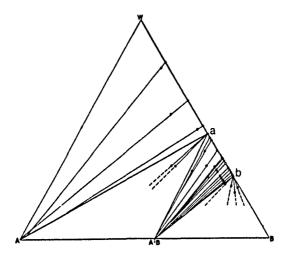
COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3]	ORIGINAL MEASUREMENTS: Ricci, J.E.; Amron, I.
(2) Iodine oxide; I ₂ O ₅ ; [12029-98-0]	J. Am. Chem. Soc. 1951, 73, 3613-8.
(3) Water; H ₂ O; [7732-18-5]	

EXPERIMENTAL DATA: (continued.....)

The $AgIO_3$ - I_2O_5 - H_2O system at $45.0^{\circ}C$

mass % I ₂ O ₅	sin density/g cm ⁻³	solid phase
34.55	1.410	Α
40.40	1.512	Α
46.43	1.637	Α
47.44	1.653	Α
48.42	1.681	Α
49.53	1.702	Α
49.95		A, A·B
49.94		A, A•B
49.94		A, A•B
50.45	1.727	A•B
50.99	1.737	A•B
51.55		A•B
52.73		A•B
54.24	1.82 ₀	A•B
55.30	1.849	A•B
56.29	-	A•B
57.44	1.911	A•B
61.10	<u>-</u>	A•B
66.74		A•B
70.64	2.42	A•B
71.69	2.47	A•B
72.05		A•B
73.24	2.54	A•B
74.02	2.58	A•B, B•W
73.89		B•W

^aSolid phases: $A = AgIO_3$, $B = I_2O_5$, $W = H_2O$



COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kolthoff, I.M.; Chantooni, M.K.
(2) Tetraethylammonium iodate; C ₈ H ₂₀ NIO ₃ ; [61327-93-3]	J. Phys. Chem. <u>1973</u> , 77, 523-6.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of $(C_2H_5)_4NIO_3$ T/K = 298	H. Miyamoto

(1) Results based on potentiometric measurements.

concn of (C ₂ H ₅) ₄ NIO ₃	E ₁	-log K _{s0}	108K0 _{a0} a
mol dm-3	mV		mol ² dm ⁻⁶
0.00115	-152	7.5 ₅	2.82
0.00290	-172	7.54	2.88
0.00483	-185	7.4 ₈	3.31
0.00870	-190	7.3 ₇	4.27
	averages:	7.5	3.3

aCalculated by compiler.

(2) Results based on conductometric measurements.

The authors reported $-log K_{s0} = 7.5_5$ from a measured electrolytic conductance of $1.5_3 \times 10^{-5}$ S cm⁻¹. The compiler calculates $K_{s0} = 2.8 \times 10^{-8}$ from this value.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility product of AgIO₃ in water was determined potentiometrically by measuring emf values of the following cell:

$$Ag,AgIO_3 \mid salt(c_1) \parallel AgNO_3(c_2) \mid Ag$$
 [1]

In the above eqn, "salt" = tetraethylammonium iodate at concentration c_1 , $c_2 = 0.00947$ mol dm⁻³, and \parallel is a salt bridge containing 0.01 mol dm⁻³ tetraethylammonium picrate.

Details of the conductivity cell and method are given in reference (2).

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared in the "conventional way." Tetraethy-lammonium iodate prepd by neutralization of aq (C₂H₅)₄NOH with Merck reagent grade HIO₃. The resulting solution was evaporated to dryness, and the solid recrystallized from ethyl acetate. The purity of the product was 99.3 % (detd iodometrically).

Salts were dried in vacuum at 70°C for 3 hours. Electrodes were prepared electrolytically (1).

ESTIMATED ERROR:

Emf values: precision within ± 2 mV. Temp: not given.

- Kolthoff, I.M.; Chantooni, M.K. J. Am. Chem. Soc. 1965, 87, 4428: Ives, D.J.; Janz, G.J. Reference Electrodes. Academic Press, NY. 1961, page 207.
- Kolthoff, I.M.; Bruckenstein, S.; Chantooni, M.K.
 J. Am. Chem. Soc. <u>1961</u>, 83, 3927.

200 Silver lodate

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3]	ORIGINAL MEASUREMENTS: Keefer, R.M.; Reiber, H.G.
(2) Glycine; C ₂ H ₅ NO ₂ ; [56-40-6] (3) Water; H ₂ O; [7732-18-5]	J. Am. Chem. Soc. <u>1941</u> , 63, 689-92.
VARIABLES: Concentration of glycine T/K = 298	PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA:

glycine content	solubility
mol kg-1a	103mol kg-1
0	0.1704b
0	0.1794b
0.02510	0.1859
0.03768	0.1880
0.05026	0.1916
0.07536	0.1971
0.08234	0.1979
0.10075	0.2020
0.1238	0.2082
0.1654	0.2181
0.2042	0.2223

^aProbably moles of glycine per kg water, but not explicity stated.

bAuthors give a reproducibility of ± 4 x 10-7 mol kg-1 for this data point.

The above solubility data were interpreted in terms of the following equilibrium.

$$Ag(C_2H_5NO_2)^+ = Ag^+ + C_2H_5NO_2$$
 K_d

The thermodynamic dissociation constant K_d was given as 5.28 x 10-5 (probably based on mol kg-1 units).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The procedure followed is described in ref. (1). An excess of air-dried AgIO₃ was placed in glass-stoppered Pyrex flasks, and 200 cm³ of the glycine solution added. The flasks were placed in a thermostat at 25°C and rotated for at least 12 hours. Aliquots for analyses were removed with a pipet by applying pressure. The pipets were fitted with an asbestos filter. The solubility of AgIO₃ was determined by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by dropwise addition of 0.15 mol dm-3 solutions of AgNO₃ and KIO₃ into 200 cm³ of water. The precipitate was allowed to stand in the mother liquor for three days and then filtered, washed, and dried at room temperature. C.p. grade glycine was recrystallized twice from water by the addition of ethanol (1)

ESTIMATED ERROR:

Soly: see footnote b above.

Temp: precision probably ± 0.01 K (compiler).

REFERENCES:

 Keefer, R.M.; Reiber, H.G.; Bisson, C.S. J. Am. Chem. Soc. <u>1940</u>, 62, 2951.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Keefer, R.M.; Reiber, H.G.
(2) DL-Alanine; C ₃ H ₇ NO ₂ ; [302-72-7]	J. Am. Chem. Soc. 1941, 63, 689-92.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES: Concentration of alanine	PREPARED BY:
T/K = 298	H. Miyamoto

alanine content mol kg-1a	solubility 10 ³ mol kg- ¹	
0	0.1794ь	
0.02511	0.1892	
0.03740	0.1924	
0.05616	0.2001	
0.07557	0.2064	
0.10092	0.2155	

aProbably moles of glycine per kg water, but not explicity stated. bAuthors give a reproducibility of ± 4 x 10-7 mol kg-1 for this data point.

The above solubility data were interpreted in terms of the following equilibrium.

$$Ag(C_3H_7NO_2)^+ = Ag^+ + C_3H_7NO_2$$
 K_d

The thermodynamic dissociation constant K_d was given as 1.37 x 10-5 (probably based on mol kg-1 units).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The procedure followed is described in ref. (1). An excess of air-dried AgIO₃ was placed in glass-stop-pered Pyrex flasks, and 200 cm³ of the alanine solution added. The flasks were placed in a thermostat at 25°C and rotated for at least 12 hours. Aliquots for analyses were removed with a pipet by applying pressure. The pipets were fitted with an asbestos filter. The solubility of AgIO₃ was determined by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by dropwise addition of 0.15 mol dm⁻³ solutions of AgNO₃ and KIO₃ into 200 cm³ of water. The precipitate was allowed to stand in the mother liquor for three days and then filtered, washed, and dried at room temperature. C.p. grade *DL*-alanine was recrystallized twice from water by the addition of ethanol (1).

ESTIMATED ERROR:

Soly: see footnote b above.

Temp: precision probably ± 0.01 K (compiler).

REFERENCES:

 Keefer, R.M.; Reiber, H.G.; Bisson, C.S. J. Am. Chem. Soc. <u>1940</u>, 62, 2951.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Vosburgh, W.C.; McClure, R.S.	
(2) Ammonium nitrate; NH ₄ NO ₃ ; [6484-52-2]		
(3) Aqueous ammonia; NH ₃ (aq); [7664-41-7]	J. Am. Chem. Soc. <u>1943</u> , 65, 1060-3.	
(4) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
Conens of NH ₃ and NH ₄ NO ₃		
T/K = 298	H. Miyamoto	

NH ₄ NO ₃ concn mmol kg ⁻¹	total NH ₃ concn mmol kg ⁻¹	AgIO ₃ solubility mmol kg-1	
0.1018	0.126	0.225	
0.1018	0.194	0.239	
	0.842	0.343	
0.0501	4.10	1.302	
0.1020	8.23	2.59	

The dissociation constant, K_d, for

 $Ag(NH_3)^+ = Ag^+ + NH_3$

was calculated by the authors who reported $K_d = 4 \times 10^{-5}$ mol dm⁻³.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: For complete details on calculation of K_n and experimental techniques, see the compilation by Derr and Vosburgh for the following system.	SOURCE AND PURITY OF MATERIALS: Complete details given in the compilation by Derr and Vosburgh cited at left.
AgIO ₃ -Ni(NO ₃) ₂ -NH ₄ NO ₃ -NH ₃ -water	

М	lottola, A.		7.
0 .	0	0	0.730
0.418	0.240	0.192	0.204
0.1367	0.0769	0.0612	0.0769a
ion given and	the mass of Ag	gCI weighed.	
ILIARY INFO	RMATION		
_	PR E. 0	Mottola, A. Chimica (Milan) PREPARED BY: E.M. Woolley 0 0 0.418 0.240 0.1367 0.0769	Chimica (Milan). 1949, 4, 422-7 PREPARED BY: E.M. Woolley 0 0 0 0.418 0.240 0.192 0.1367 0.0769 0.0612 ion given and the mass of AgCl weighed.

AgIO₃-Ni(NO₃)₂-NH₄NO₃-NH₃-water

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3] (2) Lithium perchlorate: LiClO ₄ ; [7791-03-9] (3) Lithium iodate; LiIO ₃ ; [13765-03-2] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Renier, J.J.; Martin, D.S. J. Am. Chem. Soc. <u>1956</u> , 78, 1833-7: U.S. Atomic Energy Comm. ISC-688, <u>1955</u> , 1-43.
VARIABLES: Concentrations of LiIO ₃ and LiClO ₄ T/K = 298.2, 308.2 and 323.2	PREPARED BY: H. Miyamoto

The solubility, S, of AgIO₃ in LiIO₃ solutions is given in the table below.

/0 C	106S	[IO ₃ -] _{tot}	4	1/0:	106Scalcd
/ºC	mol dm-3	mol dm-3	y_{\pm}^{b}	-1/2log K _{s0} c	(eq. [8])
25.0	37.0*	0.000722	0.968	3.80	45,2
	18.1ª	0.00187	0.951	3.76	18.2
	7.03	0.00421	0.933	3.79	8.46
	6.85a	0.00493	0.928	3.77	7.34
	4.29	0.0101	0.903	3.72	3.86
	3.30	0.0110	0.899	3.77	3.59
	3.05	0.0151	0.807	3.72	2.73
	2.12	0.0249	0.863	3.70	1.84
	1.13	0.0353	0.845	3.77	1.43
	1.11	0.0848	0.795	3.61	1.00
	0.978	0.1023	0.782	3.61	0.865
	0.993	0.1180	0.776	3.58	0.845
	0.835	0.1540	0.761	3.57	0.849
	0.915	0.2042	0.747	3.49	0.892
	1.04	0.2580	0.733	3.43	0.975
5.0	87.5	0.000693	0.970	3.62	99.7
	28.0	0.00272	0.943	3.59	27.2
	15.1	0.00435	0.932	3.62	17.5
	8.66a	0.00780	0.914	3.63	10.4
	7.68	0.0114	0.900	3.58	7.58
	4.09	0.0266	0.860	3.55	3.80
	2.71	0.0398	0.837	3.56	2.90
	2.46	0.0520	0.821	3.54	2.48
	1.99	0.0836	0.795	3.49	1.99
	1.73	0.1203	0.782	3.49	1.88
	1.89	0.1068	0.781	3.46	1.86
	1.69	0.1279	0.771	3.44	1.81
	1.80	0.1682	0.757	3.38	1.80
	1.74	0.2292	0.740	3.33	1.91
	1.66	0.2523	0.737	3.32	1.96
	1.97	0.2700	0.732	3.28	2.01
0.0	217	0.00914	0.966	3.37	206
	65.6	0.00283	0.942	3.40	70.9
	23.0a	0.00800	0.911	3.40	27.8
	19.9a	0.0109	0.899	3.38	21.5
	13.7	0.0177	0.880	3.37	14.4
	7.26	0.0395	0.837	3.35	8.15
	3.64	0.1008	0.783	3.33	5.12
	4.05	0.1317	0.770	3.25	4.75
	4.24	0.1580	0.760	3.21	4.62
	4.34	0.2660	0.732	3.11	4.70

^{*}These values were obtained with silver of specific activity of 1.98×10^5 counts/min mg. All other values were obtained with silver of specific activity of 2.89×10^5 counts/min mg.

^cFrom $K_{s0} = S[IO_3]_{tot}y_{\pm}^2$.

continued.....

bThese values are mean ionic activity coefficients for singly charged ions obtained by interpolation from the table of y_{\pm} values presented by Crouthamel and Martin (1).

- Silver iodate; AgIO₃; [7783-97-3]
 Lithium perchlorate: LiClO₄; [7791-03-9]
- (3) Lithium iodate; LilO₃; [13765-03-2]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Renier, J.J.; Martin, D.S.

J. Am. Chem. Soc. 1956, 78, 1833-7: U.S. Atomic

Energy Comm. ISC-688, 1955, 1-43.

EXPERIMENTAL DATA: (continued.....)

The solubility, S, of AgIO₃ in aqueous LiIO₃ + LiClO₄ solutions of constant ionic strength = 1.00 mol dm⁻³ is given in the table below.

	10 ⁶ S	[IO ₃ -] _{tot}	106Scaled
t/ºC	mol dm-3	mol dm-3	(eq. [8])
25.0	90.2	0.000940	89.5
	35.4	0.00248	34.0
	14.5	0.00540	15.6
	9.05	0.0103	8.30
	1.96	0.0501	1.93
	1.68	0.0634	1.60
	1.38	0.1001	1.21
	0.885	0.2000	1.04
	1.04	0.298	1.13
	1.14	0.400	1.31
	1.33	0.492	1.49
	1.44	0.596	1.71
	2.27	0.699	1.94
	2.48	0.754	2.06
	2.30	0.998	2.63
35.0	198	0.000900	193
	64.3	0.00265	66.1
	34.4	0.00544	32.4
	15.9	0.0110	16.3
	6.52	0.0263	7.13
	4.65	0.0400	4.93
	4.15	0.0505	4.06
	3.30	0.0659	3.33 2.56
	2.58	0.101	
	2.52 2.43	0.200 0.305	2.14 2.28
	2.21	0.404	2.57
	2.50	0.501	2.81
	3.67	0.605	3.29
	4.19	0.707	3.78
	3.48	0.772	3.95
50.0	409	0.00107	400
	146	0.00285	151
	71.5	0.00583	74.7
	40.1	0.0110	40.4
	18.3	0.0253	18.6
	11.3	0.0414	12.1
	9.72	0.0515	10.2
	7.95	0.0694	8.22
	6.21	0.1030	6.22
	5.31	0.207	5.12
	6.35	0.322	5.21
	5.73	0.412	5.56
	5.96	0.507	6.05
	7.30	0.745	7.49
	8.35	0.800	7.84
	7.34	0.810	7.91
	8.96	0.998	9.16

continued.....

- (1) Silver iodate; AgIOs; [7783-97-3]
- (2) Lithium perchlorate: LiClO₄; [7791-03-9]
- (3) Lithium iodate; LiIO₅; [13765-03-2]
- (4) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Renier, J.J.; Martin, D.S.

J. Am. Chem. Soc. 1956, 78, 1833-7: U.S. Atomic

Energy Comm. ISC-688, 1955, 1-43.

COLUMNIC AND CON ADDITIONA

COMMENTS AND/OR ADDITIONAL DATA:

(continued.....)

The saturated solutions are satisfactorily described in terms of the following equilibria:

$$AgIO_{3}(s) = Ag^{+} + IO_{3}^{-}$$

$$K_{80} = [Ag^{+}][IO_{3}^{-}]$$

[3]

$$Ag^+ + IO_3^- = AgIO_3(sln)$$

$$\beta_1 = [AgIO_3(sln)]/[Ag^+][IO_3^-]$$

$$Ag^{+} + 2IO_{3}^{-} = Ag(IO_{3})_{2}^{-}$$

$$\beta_2 = [Ag(IO_3)_2^-]/[Ag^+][IO_3^-]^2$$

The thermodynamic equilibrium constants are defined by

$$K_{s0}^0 = K_{s0} y_{\pm}^2$$

$$\beta_1^0 = \beta_1 y_0 / K_{s0}^0$$

$$\beta_2^0 = \beta_2 y_2 / \{ [IO_3^-] K_{s0}^0 \}$$

The total solubility of silver iodate is

$$S = [Ag^+ + [AgIO_3(sin)] + [Ag(IO_3)_2^-]$$

[7]

Substituting the equilibrium constants, eq. [7] becomes

$$S = K_{s0}/[IO_3^-] + \beta_1 K_{s0} + \beta_2 K_{s0}[IO_3^-]$$

[8]

Assuming [IO₃-]tot = [IO₃-] in the LiIO₃ solutions, eq. [8] can now be written as

$$log\{S[IO_3^-]_{tot}\}^{1/2} = log\{K_{s0}^0 + \beta_1 K_{s0}^0 [IO_3^-]_{tot} + \beta_2 K_{s0}^0 [IO_3^-]_{tot}\}^{1/2}$$

[9]

[10]

Plotting the left hand side of eq. [9] against $[IO_3-]^{1/2}$ gives an intercept of $log(K_{10}O)^{1/2}$.

For the solubility of AgIO₃ in the solutions of constant ionic strength of 1.00 mol dm⁻³, the total solubility is treated similarly to eq. [9], but in the following form:

$$log\{S[IO_3^-]_{tot}\}^{1/2} = log\{K_{s0} + \beta_1 K_{s0}[IO_3^-]_{tot} + \beta_2 K_{s0}[IO_3^-]_{tot}\}^{1/2}$$

The solubility product K_{*0} is obtained from eq. [10] by the plot described above. In these LiIO₃ + LiClO₄ solutions, the formation constants were obtained from a least squares treatment of eq. [11] (obtained from eq. [8] above).

$$\{S - K_{e0}/[IO_3]\} = \beta_1 K_{e0} + \beta_2 K_{e0}[IO_3]$$
 [11]

Values of the solubility products and formation constants obtained from eqs. [9]-[11] are given below. The ± values represent "probable errors."

	108K*0	$10^{7} \rm{K_{s0}}$	$10^7 \beta_1 K_{s0}$	$10^{6}\beta_{2}K_{*0}$
	(eq. [9])	(eq. [10])	(eq. [11])	(eq. [11])
t/ºC		mol ² dm ⁻⁶	mol-1 dm3	mol-2 dm ⁶
25.0	3.0 ± 0.15	0.84 ± 0.02	1.3 ± 0.8	2.42 ± 0.16
35.0	6.3 ± 0.3	1.74 ± 0.04	4.1 ± 1.2	4.29 ± 0.28
50.0	17.4 ± 1.0	4.26 ± 0.10	15.8 ± 1.8	7.16 ± 0.33

The authors also estimate that $\Delta H_1^0 = 5.14 \pm 4.54$ kcal mol⁻¹ for equilibrium [2] above, and $\Delta H_2^0 = -5.20 \pm$ for equilibrium [3].

continued.....

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Lithium perchlorate: LiClO₄; [7791-03-9]
- (3) Lithium iodate; LiIO₃; [13765-03-2]
- (4) Water; H₂O; [7732-18-5]

continued.....

ORIGINAL MEASUREMENTS:

Renier, J.J.; Martin, D.S.

J. Am. Chem. Soc. <u>1956</u>, 78, 1833-7: U.S. Atomic Energy Comm. ISC-688, <u>1955</u>, 1-43.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess tagged AgIO₃ and the various LiIO₃ or LiIO₃ + LiClO₄ solutions placed in flasks which were sealed with paraffin wax, placed in a constant temperature bath, and continuously agitated. Mixtures were allowed to equilibrate for one week. The filtering apparatus, brought to the equilibrium temperature, was inserted into the flask and pressure applied until a suitable amount of clear liquid filtrate was obtained for analyses. The total concentration of iodate was determined by iodometric titration. The solubility of silver iodate was determined by a radioassay technique for ¹¹⁰Ag.

SOURCE AND PURITY OF MATERIALS:

LiIO₃ prepared by mixing aqueous solutions of Li₂CO₃ and HIO₃. Carbon dioxide was driven off by heating, and the precipitate recrystallized, filtered, washed and dried at 120°C for 24 hours. LiClO₄ was reagent grade (G.F. Smith Chem. Co.).

110Ag was obtained from Oak Ridge National Laboratory. The irradiated Ag had been dissolved in 1.4 ml of 2 mol dm⁻³ HNO₃, and the radiochemical purity was in excess of 98 %. Stock solutions containing silver of a definite specific activity were prepared by adding aliquots of the original solution to dilute nitric acid solutions containing inactive AgNO₃. The solutions were scavenged with Fe(OH)₃ and evaporated to dryness with an excess of HNO₃. The tagged silver nitrate was then precipitated as AgCl, filtered and dissolved in concentrated ammonia solution. The silver was then electroplated on a platinum gauze cathode, and the entire purification cycle was repeated. The silver was then dissolved in nitric acid, and tagged AgIO₃ prepared by mixing this purified AgNO₃ solution with aqueous LiIO₃.

ESTIMATED ERROR:

Soly: nothing specified, but "probable errors" in equilibrium constants given in the table on the previous page.

Temp: precision ± 0.1 K.

REFERENCES:

 Crouthamel, C.E.; Martin, D.S. J. Am. Chem. Soc. 1951, 73, 569.

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Sodium chloride; NaCl; [7647-14-5]
- (3) Sodium nitrate; NaNO₃; [7631-99-4]
- (4) Sulfuric acid; H₂SO₄; [7664-93-9]
- (5) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Erdey, L.; Banyai, E.; Szabadvary, F.

Acta Chim. Acad. Sci. Hung. 1961, 26, 211-8.

VARIABLES:

Concentrations of NaCl and H_2SO_4 : concn of NaNO₃ fixed at ~ 0.2 % (mass % ?). T/K = 298

VARIABLES:

PREPARED BY:

E.M. Woolley and H. Miyamoto

EXPERIMENTAL DATA:

AgIO₃ was equilibrated with H₂SO₄ solutions containing a fixed amount of NaNO₃ (approximately 0.2 %) and the indicated amounts of NaCl.

$[H_2SO_4]^a$	$[NaCl]_{tot}$	10 ⁵ [C1-] _{meas}	[IO ₃ -] _{tot}	10 ⁵ [Ag+]	108K*0p
mol dm-3	mol dm-3	mol dm-3	mol dm-3	mol dm-3	mol ² dm-
0	0.020000	11.4	0.019888	0.2	4
	0.010000	5.8	0.009946	0.4	4
	0.004000	2.4	0.003986	1.0	4.0
	0.002000	1.2	0.002002	1.4	2.8
	0.001000	0.9	0.001003	4.2	4.2
0.005	0.020000	11.7	0.019887	0.4	8
	0.010000	5.4	0.009953	0.7	7
	0.004000	2.2	0.003990	1.2	4.8
0.05	0.020000	7.4	0.019931	0.5	10
	0.010000	3.8	0.009970	0.8	8
	0.004000	0.9	0.004003	1.2	5
0.5	0.020000	2.8	0.019982	1.0	20
	0.010000	2.3	0.009990	1.3	13
	0.004000	0.7	0.004034	4.1	16

^{*}Assumed by the compilers to be one half the original values of n (normality).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An excess of AgIO₃ tagged with ¹¹⁰Ag and 0.1 mol dm⁻³ NaCl solution tagged with ³⁶Cl were added to vials. The volume was adjusted to 50 cm³ with distilled water. One cm³ of 10 % (by mass?) NaNO₃ solution was added, and the mixtures equilibrated in a shaking thermostat, with intermittent vigorous agitation, for 2 to 3 hours. Equilibrated solutions were centrifuged and the liquid was counted with a liquid scintillation counting apparatus. Standards for radioactive comparison were made from the same tagged AgIO₃ and NaCl samples that were used in the experiments.

SOURCE AND PURITY OF MATERIALS:

Tagged AgIO₃ was prepared by mixing AgNO₃ and KIO₃ solutions and washing the precipitate with distilled water. No further details given.

ESTIMATED ERROR:

Nothing specified.

 $^{^{}b}$ Calculated by the compilers from $K_{s0} = [Ag^{+}][IO_{3}^{-}]_{tot}$; i.e. assuming other complexes such as HIO_{3} do not form.

208 Silver lodate

208		Silver	lodate				
COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3] (2) Potassium nitrate; KNO ₃ ; [7757-79-1] (3) Aqueous ammonia; NH ₃ (aq); [7664-41-7] (4) Water; H ₂ O; [7732-18-5]			ORIGINAL MEASUREMENTS: Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. J. Am. Chem. Soc. <u>1941</u> , 63, 2670-4.				
VARIABLES: Concentrations of N T/K = 298	IH ₃ and KNO ₃		PREPARED BY: H. Miyamoto				
EXPERIMENTAL I	DATA:						
total NH ₃ concn mol kg ⁻¹	KNO ₃ concn mol kg ⁻¹	solubilitya mmol kg-1	density kg dm ⁻³	ionic strength mol dm ⁻³	108K _I b mol ² dm ⁻⁶		
0.03619 0.01245 0.03628	0.0403 0.0998 0.1424	11.48 4.049 12.12	1.001 1.003 1.007	0.0524 0.1042 0.1551	5.99 5.83 5.94		
	ined by analyses of ζ_{I} , see reference bel		entration.				
		AUXILIARY I	NFORMATION				
METHOD/APPARATUS/PROCEDURE: Complete details on the definition and computation of K _I and all experimental information given in the compilation of these authors' study of the following system:			Reagent grade K	PURITY OF MATER NO ₃ was recrystallizational details, see the	ed and dried at		
AgIO ₃ -NH	I ₃ (aq)-water						

(3) Aqueous ammor	ate; NH ₄ NO ₃ ; [6484- nia; NH ₃ (aq); [7664-4	-	ORIGINAL MEASUREMENTS: Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. J. Am. Chem. Soc. 1941, 63, 2670-4.		
(4) Water; H ₂ O; [77 VARIABLES:	32-18-5]		PREPARED BY:		
Concentrations of N T/K = 298	NH ₃ and NH ₄ NO ₃		H. Miyamoto		
EXPERIMENTAL I	DATA:				
total NH ₃ concn	NH ₃ NO ₃ concn	solubilitya	density	ionic strength	108K1P
mol kg-1	mol kg ⁻¹	mmol kg-1	kg dm-3	mol dm-3	mol ² dm ⁻⁶
0.03677	0.0099	11.54	0.999	0.0214	6.17
0.03599	0.0102	11.25	0.998	0.0215	6.05
0.01277	0.0200	4.002	0.997	0.0240	6.18
0.01403	0.0503	4.515	0.998	0.0548	6.17
0.03615	0.0694	11.87	1.001	0.0813	6.01
0.01347	0.1301	4.544	1.001	0.1346	6.02
0.03626	0.1241	12.20	1.002	0.1363	6.03

SOURCE AND PURITY OF MATERIALS:

the system given on the left.

Reagent grade NH₄NO₃ was recrystallized and dried at

110°C. For additional details, see the compilation of

METHOD/APPARATUS/PROCEDURE:

AgIO3-NH3(aq)-water

system:

Complete details on the definition and computation of $\mathbf{K}_{\mathbf{I}}$ and all experimental information given in the

compilation of these authors' study of the following

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Derr, P.F.; Vosburgh, W.C.	
(2) Magnesium nitrate; Mg(NO ₃) ₂ ; [10377-60-3]		ļ
(3) Ammonium nitrate; NH ₄ NO ₃ ; [6484-52-2]	J. Am. Chem. Soc. <u>1943</u> , 65, 2408-11.	
(4) Aqueous ammonia; NH ₃ (aq); [7664-41-7]		
(5) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
Concus of NH ₃ , NH ₄ NO ₃ and Mg(NO ₃) ₂		
T/K = 298	H. Miyamoto and E.M. Woolley	

NH ₄ NO ₃ conen mmol kg ⁻¹	total NH ₃ concn mmol kg ⁻¹	total Mg(NO ₃) ₂ concn mmol kg ⁻¹	AgIO ₃ solubility mmol kg ⁻¹
3.89	3.561	1.005	1.165
7.94	8.09	4.028	2.780
4.00	16.17	4.028	5.52

Only the monammine complex $Mg(NH_3)^{++}$ was assumed to form, and the equilibrium constant for the dissociation of this complex, K_1 , is "in the vicinity of unity." Actual calculations based on known equilibrium constants for dissociation of $Ag(NH_3)_+$, $Ag(NH_3)_2$ and $AgIO_3(sln)$ along with material balance equations gives $K_1 = 1.2$, 1.6 and 1.2 mol kg⁻¹, respectively, for the above three measured solubilities.

AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: For complete details on calculation of K_n and experimental techniques, see the compilation by Derr and Vosburgh for the following system. AgIO₃-Ni(NO₃)₂-NH₄NO₃-NH₃-water SOURCE AND PURITY OF MATERIALS: AR grade Mg(NO₃)₂ used to prep a stock sln which was analyzed with 8-hydroxyquinoline. Additional details given in the compilation of Derr and Vosburgh's study cited on the left.

COMPONENTS:	ORIGINA	AL MEASURE	MENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Mottola,	Α.		
(2) Magnesium sulfate; MgSO ₄ ; [7487-88-9] (3) Ammonium sulfate; (NH ₄) ₂ SO ₄ ; [7783-20-2]	Chimica (Milan). <u>1949</u> , 4, 422-7.			
(4) Aqueous ammonia; NH ₃ (aq); [7664-41-7]		` -		
(5) Water; H ₂ O; [7732-18-5]				
VARIABLES:	PREPAR	ED BY:		
Concn of NH ₃ at fixed concns of MgSO ₄ and (NH ₄) ₂ SO ₄ T/K = 298	E.M. Woolley and H. Miyamoto			
EXPERIMENTAL DATA:				
concentration of MgSO ₄ /mol dm ⁻³	0.125	0.125	0.125	
concentration of (NH ₄) ₂ SO ₄ /mol dm ⁻³	0.125	0.125	0.125	
total NH ₃ concentration/mol dm ⁻³	0.251	0.167	0.0836	
AgIO ₃ solubility/mol dm-3	0.0923	0.0576	0.0310	

AUXILIARY INFORMATION

For complete details, see compilation of this author's study of the following 5-component system:

AgIO3-Ni(NO3)2-NH4NO3-NH3-water

210	Silver	lodate)		
COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3] (2) Nickel nitrate; Ni(NO ₃) ₂ ; [13138-45-9] (3) Ammonium nitrate; NH ₄ NO ₃ ; [6484-52-2] (4) Aqueous ammonia; NH ₃ (aq); [7664-41-7] (5) Water; H ₂ O; [7732-18-5]		Motto	INAL MEASUREM ola, A. ica (Milan) <u>1949,</u> 4		
VARIABLES: Concns of NH ₃ , NH ₄ NO ₃ and Ni(NO ₃) ₂ T/K = 298			ARED BY:	***************************************	-
EXPERIMENTAL DATA:		•			
concentration of Ni(NO ₃) ₂ /mol dm ⁻³	0.2	78	0.171	0.340	
concentration of NH ₄ NO ₃ /mol dm ⁻³	0.2	15	0.763	0.763	

1.777

0,2445

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

total NH₃ concentration/mol dm-3

silver iodate solubility/mol dm-3

AgIO₃ crystals and a volume of NH₄NO₃ solution containing Ni(NO₃)₂ were placed in a bottle, and the ammonia solution added dropwise into the bottle from a burette. The dropping of ammonia was stopped at the point of disappearence of the solid AgIO₃. A portion of this solution and excess AgIO₃ were placed in smaller rubber-stoppered flasks. These flasks were shaken in a thermostat for 2 h. For determination of total silver concentration, the sample solution was precipitated with NH₄Cl and the AgCl precipitate collected in a Gooch crucible, dried at 100°C, and weighed.

SOURCE AND PURITY OF MATERIALS:

0.505

0.0481

1.446

0.0442

AgIO₃ prepared by mixing dilute solutions of AgNO₃ and KIO₃. No other details given.

ESTIMATED ERROR:

Nothing specified.

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Nickel nitrate; Ni(NO₃)₂; [13138-45-9]
- (3) Ammonium nitrate; NH₄NO₃; [6484-52-2]
- (4) Aqueous ammonia; NH₃ (aq); [7664-41-7]
- (5) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Derr, P.F.; Vosburgh, W.C.

J. Am. Chem. Soc. 1943, 65, 2408-11.

VARIABLES:

Concns of NH₃, NH₄NO₃ and Ni(NO₃)₂ T/K = 298

PREPARED BY:

H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

NH ₄ NO ₃ concn mmol kg ⁻¹	total NH ₃ concn mmol kg ⁻¹	total Ni(NO ₃) ₂ concn mmol kg ⁻¹	AgIO ₃ solubility mmol kg-1
116.1	5.28	9.97	0.806
105.4	7.83	9.96	1.175
107.7	10.41	9.97	1.597
102.5	15.69	9.96	2.511
70.5	21.00	9.96	3.591
100.9	21.13	9.96	3.643
100.9	21.19	9.96	3.684
101.1	41.77	19.98	5.525
101.0	31.27	9.96	5.956
101.1	41.69	9.97	8.565
101.1	42.73	9.97	8.822
101.2	53.15	9.98	9.782
109.7	64.50	9.97	14.29
110.6	71.1	9.98	16.17
107.5	96.5	9.98	23.34
115.7	128.2	20.00	25.60
104.6	128.1	9.99	32:91

a This solution also contained 0.01014 mol kg-1 KIO₃.

continued.....

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions prepared by dilution of stock Ni(NO₃)₂ solution, stock NH₃ solution, a weighed quantity of NH₄NO₃, and excess AgIO₃. Remaining procedure as in (1). 200 cm³ aliquots of equilibrated solutions removed by forcing the solution through a filter and into a pipet by air pressure to avoid loss of NH₃. The aliquots were delivered into excess standardized 0.1 mol dm⁻³ HCl, and the excess HCl titrated with standardized 0.1 mol dm⁻³ NaOH using methyl red indicator. The iodate content was determined iodometrically by titration with 0.01 mol dm⁻³ thiosulfate solution.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by slow addition of AgNO₃ and KIO₃ solutions to water. After digestion on a hot plate for 24 h, the precipitate was washed and dried in air. Analysis after drying at 110°C agreed with the stoichiometry. Analytical reagent grade Ni(NO₃)₂ stock solution analyzed with dimethylglyoxime. Reagent grade NH₄NO₃ dried in a vacuum desiccator. Ammonia solutions were prepared by dilution.

ESTIMATED ERROR:

Soly: reproducibility less than 0.2 %. Temp: not specified.

REFERENCES:

 Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. J. Am. Chem. Soc. <u>1941</u>, 63, 2670.

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Nickel nitrate; Ni(NO₃)₂; [13138-45-9]
- (3) Ammonium nitrate; NH₄NO₃; [6484-52-2]
- (4) Aqueous ammonia; NH₃ (aq); [7664-41-7]
- (5) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Derr, P.F.; Vosburgh, W.C.

J. Am. Chem. Soc. 1943, 65, 2408-11.

EXPERIMENTAL DATA: (continued.....)

Equilibrium constants, Kn, for reactions of the type

$$Ni(NH_3)^{**}_n = Ni(NH_3)^{**}_{n-1} + NH_3$$

were calculated from material balance equations, and from equilibrium constants for formation of $Ag(NH_3)^+$, $Ag(NH_3)_2^+$, $NiOH^+$, and $AgIO_3(sin)$. The following values of K_n were given.

n	K _n /mol kg-1
1	0.0016
2	0.009
3	0.022
4	0.05b
5	0.07ь
6	С

bThese values were "assumed" in order to give satisfactory constancy in K1, K2, and K3.

cNi(NH₃)₆++ not formed in large enough amounts to allow estimation of K₆.

COMPONENTS:	ORIGIN	AL MEASURE	MENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Mottola,	, A.		
(2) Copper sulfate; CuSO ₄ ; [7758-98-7] (3) Ammonium nitrate; NH ₄ NO ₃ ; [6484-52-2]	Chimica	ı (Milan) 1949	. 4. 422-7.	
(4) Aqueous ammonia; NH ₃ (aq); [7664-41-7] (5) Water; H ₂ O; [7732-18-5]		. (, ,, ,==	
VARIABLES:	PREPAR	ED BY:		
Concns of NH ₃ , NH ₄ NO ₃ and CuSO ₄ $T/K = 298$	H. Miya	moto and E.M	. Woolley	
EXPERIMENTAL DATA:				
concentration of CuSO ₄ /mol dm ⁻³	0.100	0.0625	0.125	0.0637
concentration of NH ₄ NO ₃ /mol dm ⁻³	0	0	0.730	0.730
total NH ₃ concentration/mol dm-3	0.432	0.347	0.540	0.347
AgIO ₃ solubility/mol dm ⁻³	0.0755	0.073	0.0374	0.0460

AUXILIARY INFORMATION

For complete details, see compilation of this author's study of the following 5-component system:

 $AgIO_3\text{-Ni}(NO_3)_2\text{-NH}_4NO_3\text{-NH}_3\text{-water}$

COMPONENTS:	ORIGIN	AL MEASURE	MENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Mottola	, A.		
(2) Zinc sulfate; ZnSO ₄ ; [7733-02-0]				
(3) Ammonium nitrate; NH ₄ NO ₃ ; [6484-52-2]	Chimica	(Milan) <u>1949</u>	, 4, 422-7.	
(4) Aqueous ammonia; NH ₃ (aq); [7664-41-7]				
(5) Water; H ₂ O; [7732-18-5]				
VARIABLES:	PREPAR	ED BY:		
Concns of NH ₃ and ZnSO ₄ at fixed NH ₄ NO ₃ concn T/K = 298	E.M. W	oolley and H.	Miyamoto	
EXPERIMENTAL DATA:				
concentration of ZnSO ₄ /mol dm ⁻³	0.125	0.0625	0.0313	
concentration of NH ₄ NO ₃ /mol dm ⁻³	0.734	0.734	0.734	
total NH ₃ concentration/mol dm ⁻³	0.627	0.293	0.1515	
AgIO ₃ solubility/mol dm-3	0.0640	0.0362	0.0206	
AUXILIARY	INFORMAT	TION		

For complete details, see compilation of this author's study of the following 5-component system:

 $AgIO_3\text{-}Ni(NO_3)_2\text{-}NH_4NO_3\text{-}NH_3\text{-}water$

214 Silver Iodate

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Derr, P.F.; Vosburgh, W.C.
(2) Cadmium nitrate; Cd(NO ₃) ₂ ; [10325-94-7]	
(3) Ammonium nitrate; NH ₄ NO ₃ ; [6484-52-2]	J. Am. Chem. Soc. 1943, 65, 2408-11.
(4) Aqueous ammonia; NH ₃ (aq); [7664-41-7]	
(5) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concus of NH ₃ and NH ₄ NO ₃	
T/K = 298	H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

NH ₄ NO ₃ concn mmol kg ⁻¹	total NH ₃ concn mmol kg ⁻¹	total Cd(NO ₃) ₂ conen mmol kg ⁻¹	AgIO ₃ solubility mmol kg ⁻¹
99.6	5.34	10.32	0.9185
104.3	7.95	10.32	1.370
107.3	10.55	10.32	1.847
97.3	20.87	10.32	3.942

Total $NH_3 > 0.2$ mol dm-3 led to a change in the solid phase. Equilibrium constants, K_n , for

 $Cd(NH_3)_{n++} = Cd(NH_3)_{n-1}++ NH_3$

calculated from materials balance equations (see below). Reported values in mol kg⁻¹ units are $K_1 = 0.0027$, $K_2 = 0.010$, and $K_3 = 0.025$ (values of K_2 and K_3 assumed in order to obtain constancy in K_1).

AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: For complete details on calculation of K_n and experimental techniques, see the compilation by Derr and Vosburgh for the following system. AgIO₃-Ni(NO₃)₂-NH₄NO₃-NH₃-water SOURCE AND PURITY OF MATERIALS: AR grade Cd(NO₃)₂ used to prep stock sln which was analyzed by evapn with excess H₂SO₄ and weighing the CdSO₄. Additional details given in the compilation of Derr and Vosburgh's study cited on the left.

COMPONENTS:	ORIGIN	AL MEASURE	MENTS:	
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Mottola, A.			
 (2) Cadmium sulfate; CdSO₄; [10124-36-4] (3) Aqueous ammonia; NH₃ (aq); [7664-41-7] (4) Water; H₂O; [7732-18-5] 	Chimica (Milan). <u>1949</u> , 4, 422-7.			
VARIABLES: Concns of NH ₃ and CdSO ₄ T/K = 298	PREPARED BY: E.M. Woolley			
EXPERIMENTAL DATA:				
concentration of CdSO ₄ a/mol dm ⁻³	0.164	0.125	0.0566	
total NH ₃ concentration/mol dm-3	1.343	1.20	0.712	
AgIO ₃ solubility/mol dm ⁻³	0.201	0.1028	0.1365	

AUXILIARY INFORMATION

For complete details, see compilation of this author's study of the following 5-component system:

The author did not explicity state that CdSO₄ was the salt used.

AgIO₃-Ni(NO₃)₂-NH₄NO₃-NH₃-water

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Monk, C.B.
 (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Glycine; C₂H₅NO₂; [56-40-6] (4) Water; H₂O; [7732-18-5] 	Trans. Faraday Soc. <u>1951</u> , 46, 292-7.
VARIABLES: Concentrations of NaOH and glycine	PREPARED BY:
T/K = 298.15	H. Miyamoto and E.M. Woolley

total glycine concn	total NaOH concn	solubility
mol dm-3	mol dm ⁻³	mol dm-3
0	0	1.78 x 10-4a
0.01001	0.00213	6.53 x 10-4
0.02244	0.02104	5.45 x 10-3
0.04252	0.04286	10.23 x 10-3

^aBased on the solubility in pure water, the author reported the solubility product K_{s0} as $-log K_{s0} = 7.5089$ (based on mol dm-³ units). The solubility product was calculated from $K_{s0} = [Ag^+][IO_3^-]y_{\pm}^2$ where the activity coefficient was calculated from eq. [1] below.

$$log y_{\pm}^2 = -I^{1/2}/\{1 + I^{1/2}\} - 0.2I$$
 [1]

where I is the ionic strength (note that the author did not include the Debye-Hückel constant A in eq. [1] (see also ref. (1)).

Values of $K_2 = [Ag(C_2H_5NO_2)][C_2H_4NO_2^-]/[Ag(C_2H_4NO_2)_2^-]$ were determined from the experimental solubility data, and the final value of K_2 was given as 4.1 x 10⁻⁴ mol dm⁻³.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturating column method was used where the basic glycine solution was passed through a column containing AgIO₃. The iodate estimations were made by addition of excess solid KI to about 25 cm³ of the saturated solution followed by a large addition of acid. The solution was then titrated with standard thiosulfate solution to a starch endpoint.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ crystals were formed by the slow addition of dilute solutions of KIO₃ and AgNO₃ to a large volume of hot water. The product was washed, dissolved in a minimun quantity of dilute NH₄OH, and evaporated to dryness on a water bath. The granular crystals were washed with dil HNO₃ and water. A.R. grade glycine was dried in a vacuum oven at 90°C for several hours.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

1. Monk, C.B. Trans. Faraday Soc. 1951, 47, 285.

216 Silver Iodate

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Monk, C.B.
(2) Sodium hydroxide; NaOH; [1310-73-2]	
(3) DL-Alanine; C ₃ H ₇ NO ₃ ; [302-72-7]	Trans. Faraday Soc. 1951, 46, 292-7.
(4) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentrations of NaOH and alanine T/K = 298.15	H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

total alanine concn	total NaOH concn	solubility
mol dm ⁻³	mol dm-3	mol dm-3
0	0	1.78 x 10-4a
0.01007	0.00397	1.306 x 10-3
0.01792	0.01512	4.75 x 10-3
0.02742	0.02742	8.38 x 10-3

aBased on the solubility in pure water, the author reported the solubility product K_{s0} as $-log K_{s0} = 7.5089$ (based on mol dm⁻³ units). The solubility product was calculated from $K_{s0} = [Ag+][IO_3-]y_{\pm}^2$ where the activity coefficient was calculated from eq. [1] below.

$$log y_{\pm}^2 = -I^{1/2}/\{1 + I^{1/2}\} - 0.2I$$
 [1]

where I is the ionic strength (note that the author did not include the Debye-Hückel constant A in eq. [1] (see also ref. (1)).

Values of $K_2 = [Ag(C_3H_6NO_2)][C_3H_6NO_2]/[Ag(C_3H_6NO_2)_2^-]$ were determined from the experimental solubility data, and the final value for K_2 was given as 2.5 x 10-4 mol dm-3.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturating column method was used where the basic alanine solution was passed through a column containing AgIO₃. The iodate estimations were made by addition of excess solid KI to about 25 cm³ of the saturated solution followed by a large addition of acid. The solution was then titrated with standard thiosulfate solution to a starch endpoint.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ crystals were formed by the slow addition of dilute solutions of KIO₃ and AgNO₃ to a large volume of hot water. The product was washed, dissolved in a minimun quantity of dilute NH₄OH, and evaporated to dryness on a water bath. The granular crystals were washed with dil HNO₃ and water. Laboratory reagent grade alanine was recystallized from aqueous alcohol, and dried in a vacuum oven at 90°C for several hours.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

REFERENCES:

1. Monk, C.B. Trans. Faraday Soc. 1951, 47, 285.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Perchloric acid; HClO₄; [7601-90-3] (3) Deuterum oxide (water-d₂); D₂O; [7789-20-0] VARIABLES: T/K = 278 to 323 ORIGINAL MEASUREMENTS: Ramette, R.W. J. Chem. Eng. Data 1972, 17, 195-6. PREPARED BY: G. Jancso, E.M. Woolley and M. Salomon

EXPERIMENTAL DATA:

All solubilities (S) determined in solutions containing 1 x 10-4 mol dm-3 HClO₄.

t/ºC	10 ³ mol dm ⁻³	-log K _{s0} ^s
5	0.608	8.45
15	0.953	8.05
25	1.411	7.72
35	2.06	7.39
50.3	3.45	6.95

 a K_{s0} = S²y_±² using the relation log y_± = AI¹/(1 + I¹) where the ionic strength is I = S + 0.0001. These K_{s0} data were fitted by least squares to the following smoothing equation.

$$log K_{a0} = 8.8255 - 0.010970(T/K) - 3955.2/(T/K)$$

Based on this smoothing equation, the following thermodynamic quantities were calculated.

t/ºC	ΔG kcal mol ⁻¹	ΔΗ kcal mol ⁻¹	ΔS cal mol ⁻¹ K ⁻¹	ΔC _p cal mol ⁻¹ K ⁻¹
0	10.812	14.365	12.96	-27
25	10.520	13.635	10.45	-30
50	10.290	12.856	7945	-32

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A column 3 cm high in a 4-mm i.d. tube was prepared from 4 g AgIO₃ crystals labeled with Ag¹¹⁰. This column was jacketed with a larger tube carrying circulating water from a constant temperature bath. A solution of 0.0001 mol dm-3 HClO₄ in D₂O was forced through the column, and a test tube was used to collect about 1 gram of saturated solution which was then weighed and counted. Background was about 200 cpm, and samples for analyses were counted to give 105 to 106 total counts. The analyses were carried out on a weight basis, and conversion to volume units made by use of literature densities (1) for pure D₂O. Thermometers checked against NBS calibrated thermometers. All volumetric glassware was calibrated. Standards for gamma counting were taken by weight from stock solutions prepd by weighing dried samples of the radioactive ppt followed by dissolving in NaCN solution. Counting times (10-100 min) were accurate to ± 0.1 seconds. Authors state that repeated solubility determinations at each temperature gave assurance of reproducibility, but numerical information not given.

SOURCE AND PURITY OF MATERIALS:

Crystalline AgIO₃ prepared by pptn from the following solutions: AgNO₃ labeled with Ag¹¹⁰, NH₄OH, KIO₃, and 2-hydroxyethylacetate. This mixture was allowed to stand for 2 weeks, the AgIO₃ redissolved in aq NH₃, and pptd with addn of HClO₄. All chemicals were A.R. grade, and D₂O of purity greater than 99.5 % was used as received from the Liquid Carbonic Divsion of General Dynamics Corporation.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: accuracy probably ± 0.1 K (compilers).

REFERENCES:

 Chang, T.; Chien, J. J. Am. Chem. Soc. <u>1941</u>, 63, 1709.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Miyamoto, H.; Watanabe, Y.
(2) 2-Methoxyethanol; C ₃ H ₈ O ₂ ; [109-86-4]	Nippon Kagaku Zasshi <u>1970</u> , 91, 499-500.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES: Solvent composition	PREPARED BY:
T/K = 298.15 and 308.15	H. Miyamoto

PERIMENTAL		hanol content	solubility	
t/ºC	mass %	mole %b	103mol dm-3	
25	0.	0.	0.192	
	5.090	1.254	0.148	
	9.988	2.560	0.123	
	20.697	5.819	0.085	
	30.150	9.271	0.060	
	49.739	18.982	0.024	
	69.705	35.263	0.008	
	89.707	67.356	0.001	
	100.	100.	0	
35	0.	0.	0.266	
	5.374	1.327	0.214	
	12.279	3.208	0.166	
	20.122	5.628	0.125	
	30.056	9.234	0.084	
	49.596	18.894	0.035	
	69.741	35.302	0.010	
	89.901	67.820	100.0	
	100.	100.	0	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgIO₃ and solvent mixtures were placed in glass-stoppered bottles and rotated in a thermostat at the desired temperature for 48 hours. After the excess solid had settled, aliquots of the saturated solutions were withdrawn and were analyzed for iodate by iodometric titration

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by addition of dilute solutions of AgNO₃ and KIO₃ to a large volume of a dilute KNO₃ solution. This solution was then heated to boiling. The precipitate was washed and dried under reduced pressure.

2-Methoxyethanol was distilled twice.

All Chemicals were from Wako Co., and were guaranteed reagents.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3]	ORIGINAL MEASUREMENTS: Dash, U.N.; Das, B.B.; Biswal, U.K.; Panda, T.
(2) 1,2,3-Propanetriol (glycerol); C ₄ H ₈ O ₂ ; [123-91-1] (3) Water; H ₂ O; [7732-18-5]	Thermochim. Acta 1985, 89, 281-94.
VARIABLES: Solvent composition T/K = 278 to 308	PREPARED BY: H. Miyamoto and U.N. Dash

EXPERIMENTAL DATA: No solubility data measured. K_{s0}/mol^2 dm⁻⁶ values calculated from cells with liquid junctions. These solubility products then used to calculate K_{s0}/mol^2 kg⁻² using literature density values (these data are given in the original paper).

glycerol content mass %	glycerol content mol %	108K _{s0} (298 K) mol ₂ dm ⁻⁶	eq. [1] const -A	eq. [1] const 10 ⁸ B	
0	0	1.096		•	
5	1.0	2.958	3190.0023	3174.6885	
10	2.1	2.969	3018.0472	2599.209	
20	4.7	3.148	3091.5334	2867.3791	
30	7,7	2,958	3064.0415	2751.1164	

The thermodynamic solubility products were fitted to eq. [1], and values of the constants A and B are given in the above table (standard deviation for all smoothing eqs = 0.1).

$$log K_{s0} = A/(T/K) + B$$
 [1]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility products calculated from standard potentials of the following type cells:

Ag,AgCl $| KCl(c) | KIO_3(c) |$ [2]

See the compilation for the AgIO₃-dioxane-water system for complete details.

SOURCE AND PURITY OF MATERIALS:

Glycerol (BDH, AnalaR) distilled in vac. For other details, see the AgIO₃-dioxane-water compilation.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Dash, U.N.; Das, B.B.; Biswal, U.K.; Panda, T.
(2) Urea; CH ₄ N ₂ O; [57-13-6]	}
(3) Water; H ₂ O; [7732-18-5]	Thermochim. Acta 1985, 91, 329-36.
VARIABLES:	PREPARED BY:
Solvent composition	
T/K = 278 to 308	H. Miyamoto and U.N. Dash

EXPERIMENTAL DATA: No solubility data measured. K_{s0}/mol^2 dm⁻⁶ values calculated from cells with liquid junctions. These solubility products then used to calculate K_{s0}/mol^2 kg⁻² using literature density values (these data are given in the original paper).

urea content	urea content	108K _{s0} (298 K)	eq. [1] const	eq. [1] const
mass %	mol %	mol ₂ dm ⁻⁶	Α	103B
0	0	1.096		
11.52	3.759	10.73	-1668.9855	-1367.884
20.31	7.102	10.95	-1541.5161	-1777.5977
29.64	11.22	17.25	-1850.6464	-563.74
36.83	14.89	17,52	-1592.2064	-1410.288

The thermodynamic solubility products were fitted to eq. [1], and values of the constants A and B are given in the above table (standard deviation for all smoothing eqs = 0.05).

$$log K_{s0} \approx A/(T/K) + B$$
 [1]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility products calculated from standard potentials as described in the compilation for the AgIO₃-dioxanewater system.

SOURCE AND PURITY OF MATERIALS:

Urea (guaranteed grade) used as received. For other details, see the AgIO₃-dioxane-water compilation.

COMPONENTS: (1) Silver iodate; AgIO ₈ ; [7783-97-3] (2) 1,4-Dioxane; C ₄ H ₈ O ₂ ; [123-91-1] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Dash, U.N., Das, B.B.; Biswal, U.K., Panda, T.; Purohit, N.K.; Rath, D.K.; Bhattachary, S. Thermochim. Acta 1983, 71, 199-207.
VARIABLES: Solvent composition T/K = 278 to 298	PREPARED BY: H. Miyamoto and U.N. Dash

EXPERIMENTAL DATA: No solubility data measured. $K_{s0}/mol^2 dm^{-6}$ values calculated from cells with liquid junctions. These solubility products then used to calculate $K_{s0}/mol^2 kg^{-2}$ using literature density values.

t/ºC	dioxane composition mass %	dioxane composition mol %	10 ⁹ K _{s0} mol ² dm ⁻⁶	10 ⁹ K _{s0} mol ² kg- ²
5	10	2.2	3.420	3.280
	20	4.9	2.951	2.803
	30	8.1	1.570	1.455
	40	12.0	0.789	0.728
10	10	2.2	6.100	5.930
	20	4.9	4.052	3.858
	30	1.8	2.035	1.905
	40	12.0	1.091	1.006
15	10	2.2	10.530	10.248
	20	4.9	5.551	5.310
	30	8.1	2.561	2.422
	40	12.0	1.411	1.318
20	10	2.2	17.350	17.080
	20	4.9	7.408	7.148
	30	8.1	3.192	3.040
	40	12.0	1.839	1.733
25	10	2.2	27.050	26.740
	20	4.9	9.754	9.493
	30	8.1	3.491	3.345
	40	12.0	2.338	2.206

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility products calculated from standard potentials of cells employing water-dioxane mixed solvents. The following cells with liquid junctions were used.

$$Ag,AgCl \mid KCl(c) \parallel KIO_3(c) \mid$$
[1]

Emf values of cell [1] obtained from ref. (1). The solubility product of AgIO₃ was caculated from

$$ln K_{s0} = \{E^{0}(1) - E^{0}(2)\}F/RT$$
 [3]

After correcting emf values for cells [1] and [2] for liquid junction potentials using the Henderson equation, E^0 values obtained by extrapolation to infinite dilution using the extended Debye-Hückel equation. E_{lj} varied from 0.1 to 0.3 mV for all cases.

SOURCE AND PURITY OF MATERIALS:

A.R. grade chemicals were dried and not treated any further. Dioxane (G.R. Merck) purified by treatment with beads of NaOH followed by refluxing for 48 hours and distillation. This product was then refluxed over metallic Na for 6 hours. The Na-treated solvent was redistilled just prior to use.

ESTIMATED ERROR:

Emf measurements reproducible to around \pm 0.2 mV. Temp: precision \pm 0.1 K.

REFERENCES:

 Dash, U.N.; Padhi, M.C.; Thermochim. Acta <u>1982</u>, 56, 113.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Tetrahydrofuran; C₄H₈O; [109-99-9] (3) Water; H₂O; [7732-18-5] VARIABLES: Solvent composition T/K = 298.15 ORIGINAL MEASUREMENTS: Miyamoto, H. Nippon Kagaku Kaishi 1972, 659-61 PREPARED BY: H. Miyamoto

EXPERIMENTAL DATA:

ether content	of solvent	solubility
mass %	mol %ª	10 ³ mol dm ⁻³
0	0	0.192
5	1.3	0.146
10	2.7	0.109
15	4.2	0.077
20	5.9	0.051
25	7.7	0.031
30	9.7	0.019

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Water-ether mixtures and excess AgIO₃ were placed in glass-stoppered bottles. The bottles were sealed and rotated in a thermostat regulated at 25°C. After 48 hours the concentration of AgIO₃ was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ was prepared by mixing solutions of AgNO₃ and KIO₃. The product was filtered, washed, and dried under reduced pressure.

The ether tetrahydrofuran was distilled over NaOH and then redistilled over metallic Na.

All Chemicals used were reagent grade.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Ethylene carbonate; C₃H₄O₃; [96-49-1] (3) Water; H₂O; [7732-18-5] ORIGINAL MEASUREMENTS: Miyamoto, H.; Watanabe, Y. Nippon Kagaku Zasshi 1967, 88, 36-8.

VARIABLES: Solvent composition T/K = 298.15 and 308.15 PREPARED BY:

H. Miyamoto

		onate content	solubility	
t/ºC	mass %	mole %b	103mol dm-3	
25	0.	0.	0.192	
	5.472	1.170	0.171	
	10.110	2.239	0.154	
	19.991	4.863	0.126	
	30.013	8.065	0.085	
	39.360	11.839	0.060	
	50.102	17.041	0.041	
	60.208	23.637	0.021	
	79.855	44.780	0.008	
35	0.	0.	0.265	
	4.933	1.050	0.237	
	10.049	2.234	0.215	
	20.063	4.884	0.170	
	30.209	8.135	0.134	
	40.231	12.103	0.097	
	50.141	17.063	0.071	
	60.159	23.600	0.047	
	79.802	44.698	0.014	
	93.598	74.943	0.006	

AUXILIARY INFORMATION

${\tt METHOD/APPARATUS/PROCEDURE:}$

Excess AgIO₃ and solvent mixtures were placed in glass-stoppered bottles and rotated in a thermostat at the desired temperature for 72 hours. Aft the excess solid had settled, aliquots of the saturated solutions were withdrawn and were analyzed for iodate by iodometric titration

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by addition of dilute solutions of AgNO₃ and KIO₃ (Wako Co., guaranteed reagent) to a large volume of a dilute KNO₃ solution. This solution was then heated to boiling. After aging, the precipitate was washed and dried under reduced pressure.

Ethylene carbonate (Tokyo Kasei Co., guaranteed reagent) was distilled twice under reduced pressure.

ESTIMATED ERROR:

Soly: nothing specified. Temp: precision ± 0.02 K.

COMPONENTS: (1) Silver iodate; AgIO₃; [7783-97-3] (2) Sulfinyl bis-methane (dimethyl sulfoxide); C₂H₆OS; [67-68-5] (3) Water; H₂O; [7732-18-5] VARIABLES: Solvent composition T/K = 303 ORIGINAL MEASUREMENTS: Janardhanan, S.; Kalidas, C. Bull. Chem. Soc. Jpn. 1980, 53, 2363-5.

EXPERIMENTAL DATA:

dimethyl sulfox	ide content	solubility
mol fraction	mass %a	104 mol kg-1
0.0	0.0	3.3
0.1	32.5	3.0
0.2	52.0	2.8
0.3	65.0	2.4
0.4	74.3	2.1
0.5	81.3	0.73
0.6	86.7	0.46
0.7	91.0	0.40
0.8	94.5	0.25
0.9	97.5	0.18
1.0	100.0	0.08

^aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgIO₃ was placed in mixtures of $C_2H_6OS-H_2O$ which were vigorously stirred for 24 hours. These solutions were then transferred to a thermostat maintained at 30 \pm 0.1°C. Stirring was continued for another 24 hours after which time the equilibrated solution and solid were separated by centrifugation. The silver content in the saturated solutions was determined by addition of excess standard aqueous KI, followed by potentiometric titration with standard aqueous AgNO₃ solution. No oxidation of I- was observed.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ was prepared by mixing solutions of AgNO₃ and KIO₃. The product was first washed with water and then with acetone and then dried in vacuum at 70 - 80°C for several hours. The purity of the salt was checked by determination of silver content.

Dimethyl sulfoxide (BDH, AR grade) was heated to 90°C over NaOH for 2 hours. amd then flash-distilled under vacuum.

Doubly distilled water was used.

ESTIMATED ERROR:

Soly: nothing specified.
Temp: precision ± 0.1 K.

COMPONENTS: (1) Silver iodate; AgIO₅; [7783-97-3] (2) Perchloric acid; HClO₄; [7601-90-3] (3) Formamide; CH₃NO; [75-12-7] (4) Water; H₂O; [7732-18-5] VARIABLES: Concentration of HClO₄ T/K = 298.15, 303.15 and 308.15 ORIGINAL MEASUREMENTS: Dash, U.N. Phermochim. Acta 1975, 11, 25-33.

Silver Iodate

EXPERIMENTAL DATA:

Note that the solubility, S, of AgIO₃ in HClO₄/formamide solutions prepared from 70 % (in water) HClO₄.

92 2.511 36 2.540
36 2.540
20 255
00 2.656
12 2.984
89 3.015
68 3.452
65 2.849
80 3.027
34 3.053
18 4.166
40 5.028
29 3.273
29 3.475
26 4.133
96 4.363
68 4.732
29 29 26

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were prepared by dissolving weighed amounts of HClO₄ in known (weighed) amounts of formamide at an ice-cold temperature to prevent decomposition of formamide upon mixing. These mixtures were placed in amber-colored glass-stoppered bottles containing excess AglO₃. The bottles were stoppered and heavily paraffined, and then rotated in a water thermostat at a specified temperature for 7 to 8 hours (see ref. (1)).

 $AgIO_3$ in the satd slns detd iodometrically using 0.01 mol dm-3 $Na_2S_2O_3$ sln and a microburet. Each solubility value is the average of "three closely agreeing results."

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by mixing dil solutions of c.p. grade AgNO₃ and twice-recrystalized KIO₃. The ppt was aged for several days in the mother sln, washed, and dried in a vacuum oven at 60°C. HClO₄ of G.R. quality (70 %) was used.

Commercial formamide was treated with CaO and distilled at reduced pressure.

ESTIMATED ERROR:

Soly: reproducibility not given, but titrns accurate to ± 0.2 %.

Temp: precision ± 0.01 K.

REFERENCES:

 Nayak, B.; Dash, U.N. Thermochim. Acta <u>1973</u>, 6, 223.

- (1) Silver iodate; AgIO₃; [7783-97-3]
- (2) Acetonitrile; C₂H₃N; [75-05-8]
- (3) Water; H₂O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Subramanian, S.; Rao, S.C.A.V.S.S.; Kalidas, C.

Indian J. Chem. A, 1981, 20, 723-5.

VARIABLES:

Solvent composition

T/K = 303

PREPARED BY:

H. Miyamoto

EXPERIMENTAL DATA:

acetonitrile c	ontent	solubility
mol fraction	mass %*	10 ⁴ mol kg ⁻¹
0.0	0.0	3.24
0.1	20.2	9.84
0.2	36.3	9.34
0.3	49.4	7.26
0.4	60.3	5.26
0.5	69.5	3.27
0.6	77.4	1.89
0.7	84.2	0.981
0.8	90.1	0.578
0.9	95.4	0.541
1.0	100.0	0.619

aCalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess AgIO₃ was placed in mixtures of $C_2H_3N-H_2O$ which were vigorously stirred for 24 hours. These solutions were then transferred to a thermostat maintained at $30 \pm 0.1^{\circ}C$. Stirring was continued for another 24 hours after which time the equilibrated solution and solid were separated by centrifugation. The silver content in the saturated solutions was determined by addition of excess standard aqueous KI, followed by potentiometric titration with standard aqueous AgNO₃ solution.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ was prepared by mixing solutions of AgNO₃ and KIO₃. The product was first washed with water and then with acetone and then dried in vacuum at 70 - 80°C for several hours. The purity of the salt was checked by determination of silver content.

Acetonitrile (BDH, LR) dried over anhydrous K_2CO_3 and distilled was further purified as in (1): bp = 80° C, $d_{25} = 0.7766$ g cm⁻³, $n_d^{25} = 1.3436$.

Doubly distilled water was used.

ESTIMATED ERROR:

Soly: accuracy within ± 1%. Temp: precision ± 0.1 K.

REFERENCES:

1. Jayadevappa, E.S. Indian J. Chem. <u>1969</u>, 7, 1146.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Vosburgh, W.C.; Cogswell, S.A.
(2) Pyridine; C ₅ H ₅ N; [110-86-1]	J. Am. Chem. Soc. 1943, 65, 2412-3.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Concentration of pyridine T/K = 298.15	H. Miyamoto

pyridine content	103(solubility)
mol kg-1	mol kg-1
0.0497	1.082
0.0547	1.180
0.0571	1.232
0.0997	2.084
0.1013	2.130
0.1075	2.244
0.1493	3.089
0.1498	3.122
0.2018	4.173
0.2061	4.189
0.3026	6.27
0.409	8.46
0.409	8.47
0.516	10.66
0.516	10.72
0.728	15.05
0.853	17.62

For the equilibrium $Ag^+ + 2Py = AgPy_2^+$, the authors used the more dilute solubility data to compute an equilibrium constant of 7.8 x 10⁻⁵ mol² kg⁻² (note that the equilibrium constant K was defined as $(Ag^+)(Py)^2/(AgPy_2^+)$).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The procedure was as follows (1). Pyridine solutions were saturated with AgIO₃ in Pyrex flasks immersed in a water bath at 25.00°C, and avoiding diffused daylight or artificial light. Samples for analyses were taken after 3-4 h, and again two or more h later to for constancy in concentrations. The aliquots were removed with a pipet to which was attached a filter either of Pyrex glass wool or Pyrex fritted glass.

Aliquots were weighed and the iodate content determined iodometrically with 0.01 mol dm-3 thiosulfate solution. Ammonium molybdate was used as a catalyst.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared by mixing solutions of AgNO₃ and KIO₃ in the dark with continuous stirring. After digestion for 24 h, the precipitate was washed and dried at 110°C. Practical grade pyridine was refluxed over BaO and distilled through a Widmer column. A fraction within a boiling range of 0.2 K was taken.

ESTIMATED ERROR:

Soly: nothing specified.

Temp: precision ± 0.05 K.

REFERENCES:

 Derr, P.F.; Stockdale, R.M.; Vosburgh, W.C. J. Am. Chem. Soc. <u>1941</u>, 63, 2670.

COMPONENTS: (1) Silver iodate; AgIO ₃ ; [7783-97-3]	ORIGINAL MEASUREMENTS: Palanivel, A.; Rajendran, G.; Kalidas, C.
(2) Pyridine; C ₅ H ₅ N; [110-86-1]	Ber. Bunsen. Ges. Phys. Chem. 1986, 90, 794-7.
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES: Solvent composition	PREPARED BY:
T/K = 303.15	H. Miyamoto and M. Salomon

pyridine co	ontent	solubility	K_{s0} b
mol fraction	mass %ª	103mol kg-1	mol ² kg- ²
0.0	0.0	0.322	9.91 x 10 ⁻⁸
0.1	32.8	56.94	1.99 x 10-3
0.2	52.3	45.76	1.13 x 10 ⁻³
0.3	65.3	26.39	3.49 x 10-4
0.4	79.5	15.72	1.17 x 10-4
0.5	81.4	8.80	3.70 x 10-5
0.6	86.8	4.80	1.01 x 10-5
0.7	91.1	2.50	2.70 x 10-6
0.8	94.6	1.09	5.45 x 10 ⁻⁷
0.9	97.5	0.565	1.64 x 10-7
1.0	100.0	0.259	3.88 x 10-8

aCalculated by the compilers.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experimental method given in reference (1). Solvent compositions are accurate to within \pm 0.02 %. All solubility measurements were carried out at least twice, and the agreement was better than \pm 0.2 %.

Thermodynamic solubility product constants calculated using the extended Debye-Hückel equation with an ion size parameter a = 0.65 nm. Dielectric constants, ϵ , were detd with a DK meter 60 GK (Franz Kustner Nachf. KG, Dresden) and are accurate to within \pm 0.2%.

mole % pyridine	€	
0.0	76.7	
0.1	62.7	
0.2	50.1	
0.3	40.0	
0.4	33.0	
0.5	28.5	
0.6	22.2	
0.7	18.2	
0.8	15.0	
0.9	13.7	
1.0	12.3	

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared as in (2). Purity of all salts checked by potentiometric determination of silver content.

Pyridine was refluxed over KOH for 8 h followed by fractional distillation. The middle fraction, b.p.= 115°C at 760 mm Hg, was collected and stored over fresh KOH. At 25°C, this product had a density of 0.9787 g cm⁻³ and a viscosity of 0.885 cP.

Doubly distilled conductivity water was used in the preparation of solvent mixtures.

ESTIMATED ERROR:

Soly: precision better than ± 0.2 %. Temp: precision ± 0.05 K.

- 1. Kalidas, C.; Schneider, H. Z. Phys. Chem. N.F. 1981, 10, 487.
- 2. Janardhanan, S.; Kalidas, C. Bull. Chem. Soc. Jpn. 1980, 53, 2363.

bThese are thermodynamic solubility product constants.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kolthoff, I.M.; Chantooni, M.K.
(2) Tetraethylammonium iodate; C ₈ H ₂₀ NIO ₃ ; [61327-93-3] (3) Methanol; CH ₄ O; [67-56-1]	J. Phys. Chem. <u>1973</u> , 77, 523-6.
VARIABLES: Concentration of (C ₂ H ₅) ₄ NIO ₃ T/K = 298	PREPARED BY: H. Miyamoto, E.M. Woolley and M. Salomon

(1) Results based on potentiometric measurements.

conen of (C ₂ H ₅) ₄ NIO ₃ mol dm-3	E ₁ mV	-log K _{s0}	1013K _{s0} a mol² dm-6
0.00216	-444	12.50	3.16
0.0216	-507	12.65	2.24
	averages:	12.6	2.7

^BCalculated by compiler.

(2) From the equilibrium given in reaction 2 below, the solubility product of AgIO₃ was calculated from:

$$\frac{K_{*0}(AgIO_3)}{K_{*0}(AgCl)} = \frac{[IO_3]}{[Cl]}$$

Taking $log K_{s0}(AgCl) = -13.2$ in methanol (2), an average value of $log K_{s0}(AgIO_3) = -12.7$ is obtained from the above equation. This gives $K_{s0}(AgIO_3) = 2.0 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$ (compilers).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility product of AgIO₃ in water was determined potentiometrically by measuring emf values of the following cell:

$$Ag,AgIO_3 \mid salt(c_1) \parallel AgNO_3(c_2) \mid Ag$$
 [1]

In the above eqn, "salt" = tetraethylammonium iodate at concentration c_1 , $c_2 = 0.01$ mol dm⁻³, and \parallel is a salt bridge containing 0.01 mol dm⁻³ tetraethylammonium picrate.

In a second method to determine K_{a0} , the authors studied the exchange equilibrium

$$(C_2H_5)_4NCl(sin) + AgIO_3(s) \Leftrightarrow (C_2H_5)_4NIO_3(sin) + AgCl(s)$$
 [2]

Two measurements were made starting with solutions of initial (C₂H₅)₄NCI concentrations of 0.00785 and 0.0144 mol dm⁻³. After equilibration with solid AgIO₃, the iodate concentrations in the above two chloride solutions were determined iodometrically and found to be 0.002 and 0.00384 mol dm⁻³, respectively.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepared in the "conventional way." Tetraethy-lammonium iodate prepd by neutralization of aq (C₂H₅)₄NOH with Merck reagent grade HIO₃. The resulting solution was evaporated to dryness, and the solid recrystallized from ethyl acetate. The purity of the product was 99.3 % (detd iodometrically).

Salts were dried in vacuum at 70°C for 3 hours. Electrodes were prepared electrolytically (1), and methanol (Matheson, "Spectroquality") was distilled once from Mg turnings: water content was less than 0.01 %.

ESTIMATED ERROR:

Emf values: precision within ± 2 mV. Temp: not given.

- Kolthoff, I.M.; Chantooni, M.K. J. Am. Chem. Soc. 1965, 87, 4428: Ives, D.J.; Janz, G.J. Reference Electrodes. Academic Press, NY. 1961, page 207.
- 2. Buckley, P.; Hartley, H. Phil. Mag. 1929, 8, 320.

COMPONENTS: (1) Silver iodate; AglO₃; [7783-97-3] (2) Dimethyl sulfoxide (sulfinyl bis-methane); C₂H₆OS; [67-68-5] (3) Methanol; CH₄O; [67-56-1] VARIABLES: Solvent composition ORIGINAL MEASUREMENTS: Janardhanan, S.; Kalidas, C. Proc. Indian Acad. Sci. Sec. A 1981, 90, 89-92.

H. Miyamoto

EXPERIMENTAL DATA:

T/K = 303.15

dimethyl sulfor	kide content	solubility	10 ¹⁰ K ₈₀ a
mol fraction	mass %b	10 ⁵ mol kg ⁻¹	mol ² kg ⁻²
0	0	0.438	0.192
0.1	21	0.256	0.0655
0.2	38	0.465	0.216
0.3	51	0.530	0.281
0.4	62	0.960	0.922
0.5	71	1.03	1.06
0.6	79	1.08	1.17
0.7	85	2.15	4.62
0.8	91	2.47	6.10
0.9	96	2.66	7.08
1.0	100	2.92	8.53

^aCompilers assume this is a concentration solubility product since authors do not indicate that activity coefficients were employed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A potentiometric method was employed using the following concentration cell:

$$Ag \mid AgIO_3(c_1) \parallel AgNO_3(c_2) \mid Ag$$

where c_1 is the satd sln, $c_2 = 0.005$ mol dm⁻³, and \parallel is a salt bridge containing 0.1 mol dm⁻³ tetraethylammonium picrate in the same solvent. The emf of this cell is related to the activities of silver ion in the saturated solution and the reference solution by

$$E = RT/F \ln\{(a_{Ag}+)_2/(a_{Ag}+)_1\}$$

 $K_{s0} = [Ag^+][IO_3^-]$ was probably calculated by assuming $[Ag^+] = [IO_3^-]$, and by neglecting ionic activity coefficient effects.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by mixing solutions of AR grade AgNO₃ and KIO₃. The product was repeatedly washed with water and then with acetone, and then dried in vacuum at 70-80°C for several hours.

C₂H₆OS (BDH, LR) was heated to 90°C over NaOH for 2 h, and then flash-distilled under vacuum. The product was dried over molecular sieves. Methanol (BDH, LR) was refluxed over neutral alumina and distilled, dried over Na₂SO₄, and finally fractionally distilled.

ESTIMATED ERROR:

K_{s0}: nothing specified. Temp: precision ± 0.02 K.

bCalculated by the compiler.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kalidas, C.; Schneider, H.
	Electrochim. Acta 1982, 27, 477-9:
(2) N-Methylformamide; C ₂ H ₅ NO; [123-39-7]	Proc. Intern. Symp. Ind. Oriented Basic Electrochem. 2nd. Madras, India, 1980. Tech. Session V. No.
(3) Methanol; CH ₄ O; [67-56-1]	5.10.1-6.
VARIABLES:	PREPARED BY:
Solvent composition T/K = 298.15	H. Miyamoto and E.M. Woolley

namide content	$10^{12} \mathrm{K_{s0}^{a}}$
mass %b	mol ² dm- ⁶
0.	0.116
17.	0.185
32.	1.69
44.	3.69
55.	14.1
65.	22.6
73.	41.7
81.	78.7
88.	87.8
94.	125.
100.	247.
	mass %b 0. 17. 32. 44. 55. 65. 73. 81. 88. 94.

^aCompilers assume this is a concentration solubility product since authors do not indicate that activity coefficients were employed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Satd sins of silver iodate in the various solvent mixtures prepd by stirring about 25 cm³ of solvent with excess salt in a thermostat for 12 hours. A potentiometric method was employed using the following cell:

$$Ag \mid AgIO_3(c_1) \parallel AgNO_3(c_2) \mid Ag$$

where c_1 is the satd sln, $c_2 = 0.005$ mol dm⁻³, and \parallel is a salt bridge containing 0.1 mol dm⁻³ tetraethylammonium picrate in the same solvent. The emf of this cell is given by

$$E = RT/F \ln\{(a_{Ag}+)_2/(a_{Ag}+)_1\}$$

The silver electrodes were prepd electrolytically and were reproducible to ± 1 mV. $K_{00} = [Ag^{+}][IO_{3}^{-}]$ probably calcd assuming $[Ag^{+}] = [IO_{3}^{-}]$ and by neglecting activity coefficient effects.

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by mixing stoichiometric slns of AR grade AgNO₃ and KIO₃. The product was repeatedly washed with distd water and then with alcohol and then dried in vacuum at 70°C for 12 hours.

 C_2H_5NO was shaken with P_2O_5 , filtered through glass wool and vacuum distilled. This was repeated three times followed by two more vacuum distillations without P_2O_5 . The electrolytic conductance of the product at 25°C was 1 x 10⁻⁵ S cm⁻¹.

ESTIMATED ERROR:

K_{s0}: nothing specified. Temp: precision ± 0.02 K.

bCalculated by the compilers.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Subramanian, S.; Kalidas, C.
(2) Methanol; CH ₄ O; [67-56-1]	Fluid Phase Equilib. <u>1987</u> , 32, 205-10.
(3) Acetonitrile; C ₂ H ₈ N; [75-05-8]	
VARIABLES:	PREPARED BY:
Solvent composition T/K = 303	H. Miyamoto

acetonitrile cor	centration	solubility	109K ₄₀
mole fraction	mass %	mol kg-1	mol ² kg- ²
0.0	0.0	0.442	0.0192
0.1	12.5	4.054	1.556
0.2	24.3	10.696	10.500
0.3	35.4	13.127	15.720
0.4	46.1	10.404	9.976
0.5	56.2	9.300	8.021
0.6	65.8	7.674	5.495
0.7	74.9	6.087	3.486
0.8	83.7	5.029	2.394
0.9	92.0	3.417	1.117
1.0	100.0	2.078	0.417

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potentiometric method as in (1). All measurements carried out at 30°C using the cell:

$$Ag/AgIO_3(m_1) \parallel AgNO_3(m_2)/Ag$$

where m_1 is the molality of the satd sln, $m_2 = 0.005$ mol kg⁻¹, and \parallel is a salt bridge containing 0.1 mol kg⁻¹ tetraethylammonium picrate (Et₄NPic) in the same solvent. The silver ion activity in the saturated solution is obtained from the e.m.f. data using the following equation:

$$E = (RT/F) \ln \{(a_{Ag}+)_{ref}/(a_{Ag}+)_{satd sln}\}$$

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by double decomposition using aqueous AgNO₃ and KIO₃ slns. Purity of the salt confirmed by potentiometric titrn of silver.

Acetonitrile (LR BDH) was distilled, dried over anhydr K_2CO_3 , and distilled again in the presence of $AgNO_3$ crystals: b.p. $80 \pm 0.1^{\circ}C$, and $d^{25} = 0.7766$ g cm⁻³. Methanol (LR BDH) was distilled, dried over anhydr Na_2SO_4 , and then distilled from Mg turnings. The middle fraction boiling at $64-65^{\circ}$ was collected: $d^{25} = 0.7867$ g cm⁻³ (ref. (2)).

REFERENCES:

- (1) Kalidas, C.; Schneider, H. Electrochim. Acta 1982, 27, 477.
- (2) Subramanian, S.; Kalidas, C. Electrochim. Acta 1984, 29, 753.

ESTIMATED ERROR:

Soly: the average deviation does not exceed \pm 0.5 %.

Temp: precision ± 0.1 K.

COMPONENTS: ORIGINAL MEASUREMENTS: (1) Silver iodate; AgIO₃; [7783-97-3] Subramanian, S.; Kalidas, C. Fluid Phase Equilib. <u>1987</u>, 32, 205-10. (2) Ethanol; C₂H₆O; [64-17-5] (3) Acetonitrile; C₂H₃N; [75-05-8] VARIABLES: PREPARED BY: Solvent composition T/K = 303

H. Miyamoto

EXPERIMENTAL DATA:

acetonitrile cond	entration	solubility	10 ¹⁰ K ₈₀
mole fraction	mass %	mol kg ⁻¹	mol ² kg ⁻²
0.0	0.0	0.187	0.0343
0.1	9.0	0.741	0.531
0.2	18.2	1.186	1.351
0.3	27.6	1.874	3.352
0.4	37.3	2,483	5.861
0.5	47.1	2.958	8,301
0.6	57.2	3.396	10.948
0.7	67.5	3.175	9.603
0.8	78.1	2.764	7.322
0.9	88.9	2.301	5.106
1.0	100.0	2.078	4.173

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Potentiometric method as in (1). All measurements carried out at 30°C using the cell:

 $Ag/AgIO_3(m_1) \parallel AgNO_3(m_2)/Ag$

where m_1 is the molality of the satd sln, $m_2 = 0.005$ mol kg⁻¹, and | is a salt bridge containing 0.1 mol kg-1 tetraethylammonium picrate (Et₄NPic) in the same solvent. The silver ion activity in the saturated solution is obtained from the e.m.f. data using the following equation:

 $E = (RT/F) \ln \{(a_{Ag}+)_{ref}/(a_{Ag}+)_{satd sln}\}$

SOURCE AND PURITY OF MATERIALS:

AgIO₃ prepd by double decomposition using aqueous AgNO₃ and KIO₃ sins. Purity of the salt confirmed by potentiometric titrn of silver.

Acetonitrile (LR BDH) was distilled, dried over anhydr K₂CO₃, and distilled again in the presence of AgNO₃ crystals: b.p. $80 \pm 0.1^{\circ}$ C, and $d^{25} = 0.7766$ g cm⁻³.

Ethanol was purified using magnesium and iodine as described in ref. (2).

REFERENCES:

- (1) Kalidas, C.; Schneider, H. Electrochim. Acta <u>1982</u>, Soly: the average deviation does not exceed ± 0.5 %.
- (2) Subramanian, S.; Kalidas, C. Electrochim. Acta 1984, 29, 753.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kolthoff, I.M.; Chantooni, M.K.
 (2) Tetraethylammonium iodate; C₈H₂₀NIO₃; [61327-93-3] (3) Acetonitrile; C₂H₃N; [75-05-8] 	J. Phys. Chem. <u>1973</u> , 77, 523-6.
VARIABLES: Concentration of (C ₂ H ₅) ₄ NIO ₃	PREPARED BY:
T/K = 298	H. Miyamoto

Results based on potentiometric measurements (for details see compilations cited below).

conen of (C ₂ H ₅) ₄ NIO ₃ mol dm ⁻³	E ₁ mV	-log K _{s0}	mol² dm-6
0.00317	-338	10.57	2.69
0.00951	-370	10.70	2.00
	averages:	10.6	2.3

aCalculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

K_{s0} values based on emf measurements on the cell:

 $Ag,AgIO_3 \mid salt(c_1) \parallel AgNO_3(c_2) \mid Ag$ [1]

For complete details, see the compilations of the $AgIO_3-(C_2H_5)_4NIO_3$ -water (or methanol) systems by these authors.

SOURCE AND PURITY OF MATERIALS:

Acetonitrile was obtained and purified as described in ref. 2 of the compilation cited on the left. Additional details are also given in this compilation.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₃ ; [7783-97-3]	Kolthoff, I.M.; Chantooni, M.K.
(2) Tetraethylammonium iodate; C ₈ H ₂₀ NIO ₃ ;	
[61327-93-3]	J. Phys. Chem. 1973, 77, 523-6.
(3) Sulfinyl bismethane (dimethyl sulfoxide); C ₂ H ₆ OS;	
[67-68-5]	
VARIABLES:	PREPARED BY:
Concentration of (C ₂ H ₅) ₄ NIO ₃	
T/K = 298	H. Miyamoto

EXPERIMENTAL DATA:

Results based on potentiometric measurements (for details see compilations cited below).

concn of	*	loo V	1010720 -
(C ₂ H ₅) ₄ NIO ₃ mol dm ⁻³	E ₁ mV	-log K _{s0}	1010K0 _{s0} a mol² dm-6
0.00432	-312	9.82	1.51
0.0216	-347	9.77	1.70
	averages:	9.8	1.6
har committee			

^aCalculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

 K_{so} values based on emf measurements on the cell: $Ag,AgIO_3 \mid salt(c_1) \parallel AgNO_3(c_2) \mid Ag$ [1]

For complete details, see the compilations of the $AgIO_3-(C_2H_5)_4NIO_3$ -water (or methanol) systems by these authors.

SOURCE AND PURITY OF MATERIALS:

Dimethyl sulfoxide was obtained and purified as described in J. Am. Chem. Soc. 1968, 90, 23. Other details given in the compilation cited on the left.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver iodate; AgIO ₈ ; [7783-97-3]	Nayak, B.; Dash, U.N.
 (2) Sodium perchlorate; NaClO₄; [7601-89-0] (3) Formamide; CH₃NO; [75-12-7] 	Thermochim. Acta <u>1973</u> , 6, 223-9.
VARIABLES:	PREPARED BY:
Concentration of NaClO ₄ T/K = 298.15, 303.15 and 308.15	H. Miyamoto and E.M. Woolley

EXPERIMENTAL DATA:

The tables below list the solubility of AgIO₃, S, in NaClO₄/formamide solutions.

	NaClO ₄ concn	104S	-log S*
t/ºC	mol dm-3	mol dm-3	(eq. [1] below)
25	0.14040	2.692	3.6536
	0.09568	2.585	3.6601
	0.06089	2.490	3.6647
	0.05912	2.471	3.6672
	0.03200	2.388	3.6686
	0.01836	2.371	3.6619
	0.01592	2.360	3.6617
30	0.14240	3.383	3.5551
	0.09918	3.133	3.5780
	0.04964	2.944	3.5873
	0.03134	2.862	3.5898
	0.02980	2.788	3.6002
	0.01665	2.690	3.6059
	0.00893	2.500	3.6289

continued......

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were prepared by dissolving weighed amounts AgIO₃ prepd by mixing dil solutions of c.p. grade of NaClO₄ in known (weighed) amounts of formamide. These mixtures were placed in amber-colored glass-stoppered bottles containing excess AgIO3. The bottles were stoppered and heavily paraffined, and then rotated in a water thermostat at a specified temperature. Saturation was reached within 7 to 8 hours as confirmed by analyses.

AgIO₃ in the satd slns detd iodometrically using 0.01 mol dm-3 Na₂S₂O₃ sln and a calibrated buret. The Na₂S₂O₃ slns were standardized with K₂Cr₂O₇.

SOURCE AND PURITY OF MATERIALS:

AgNO₃ and twice-recrystalized KIO₃. The ppt was aged for several days in the mother sln, washed, and dried in a vacuum oven at 60°C. NaClO₄ prepd from pure Na₂CO₃ and a slight excess of dil HClO₄ followed by recrystallization above 50°C. The product was dried in a current of dry air at 250°C. Commercial formamide was treated with CaO and distilled at reduced pressure.

ESTIMATED ERROR:

Soly: titrns accurate to \pm 0.2 %. Temp: precision ± 0.01 K.

REFERENCES:

1. Agarwal, R.K.; Nayak, B. J. Phys. Chem. 1966, 80, 2568: <u>1967</u>, 71, 2062.

COMPONENTS:

(1) Silver iodate; AgIO₃; [7783-97-3]

(2) Sodium perchlorate; NaClO₄; [7601-89-0]

(3) Formamide; CH₃NO; [75-12-7]

ORIGINAL MEASUREMENTS:

Nayak, B.; Dash, U.N.

Thermochim. Acta 1973, 6, 223-9.

EXPERIMENTAL DATA: (continued......)

	NaClO ₄ concn	104S	-log S*
t/ºC	mol dm-3	mol dm-3	(eq. [1] below)
35	0.17470	3.784	3.5132
	0.09668	3.545	3.5238
	0.08196	3.492	3.5258
	0.06726	3.416	3.5302
	0.05254	3.347	3.5382
	0.02629	3.208	3.5371
	0.01183	3.153	3.5320
	0.01029	3.142	3.5316

The solubility data were fitted to eq. [1] where values of A were taken from ref. (1).

$$log S^* = log S - AI^{1/2}/(1 + I^{1/2}) = log S^0 - BI$$
 [1]

In eq. [1], $I = [NaClO_4] + S$, and values of the slope B, $log S^0$, and the extrapolated solubility of AgIO₃ in pure formamide are given in the table below. Values of $log S^*$ are give in the data tables above.

t/ºC	soly in pure CH ₃ NO 104mol dm ⁻³	108(soly)2a mol ² dm ⁻⁶	from equ B/dm³ mol		$10^8 K_{80} = (S^0)^2$ mol ² dm ⁻⁶
25	2.169	4.705	-0.0899	3.6683	4.606
30	2.488	6.190	-0.3331	3.6090	6.053
35	2.943	8.661	-0.1393	3.5366	8.448

aCompilers' calculations.

The authors also give "standard" thermodynamic values for the dissolution of AgIO₃ in formamide based on the following relations.

$$(dln K_{s0}/dT)_p = \Delta H/RT^2$$

$$\Delta G = -RT ln K_{a0}$$

$$\Delta S = (\Delta H - \Delta G)/T$$

The values of these thermodynamic parameters are given below.

	ΔG	ΔH	ΔS
t/ºC	kcal mol-1	kcal mol-1	cal K-1 mol-1
25	10.00	11.16	3.89
30	10.00	11.16	3.81
35	9.97	11.16	3.88

Bromic acid, silver salt
+ water + water-d2 Bromic acid, silver salt (aqueous) + acetic acid E75 99 152
Bromic acid, silver salt (aqueous) 99 + acetic acid 152
+ acetic acid 152
+ acetic acid 152
+ acetonitrile 100
+ ammonia 85, 88
+ bromic acid, potassium salt 80, 81
+ bromic acid, sodium salt 145, 146
+ 1,4-dioxane 147
+ 1,3-dioxolan-2-one 150
+ N,N-dimethylformamide E72, 125
+ 1,2-ethanediol E72, 121, 122
+ ethanol 151
+ glycine 141
+ mannitol E72, 117-119
+ methanol 126
+ 2-methoxyethanol 137
+ 2-methyl-2-propanol 93
+ nitric acid, barium salt 92
+ nitric acid, calcium salt 97
+ nitric acid, cerium salt 91
+ nitric acid, magnesium salt E71, 86, 87
+ nitric acid, potassium salt 94
+ nitric acid, silver salt 82
+ nitric acid, sodium salt 96
+ nitric acid, zinc salt 90
+ perchloric acid, potassium salt 158
+ perchloric acid, sodium salt E73, 135, 136
+ 1,2,3-propanetriol E73, 143
+ 2-propanone E72, 127, 128
+ 1-propanol E73, 128, 129
+ 2-propanol 153, 154
+ pyridine 142
+ sucrose 148
+ sulfinylbismethane 98
+ sulfuric acid 95
+ sulfuric acid, cadmium salt 79
+ sulfuric acid, lithium salt 89
+ sulfuric acid, potassium salt 83, 84
+ sulfuric acid, sodium salt 145
+ tetrahydrofuran 151
+ urea
Bromic acid, silver salt (multicomponent) 108, 120, 123, 124,
+ acetic acid 136, 144, 146
162, 163
+ acetonitrile 112
+ DL-alanine 132
+ benzenesulfonic acid, sodium salt 101, 102
+ bromic acid, potassium salt 109
+ 2-butaneoic acid 138
+ 3-butene-2-ol 138
+ 2-butene-1-ol 161
+ N,N-dimethylformamide 146
+ 1,4-dioxane 124
+ 1,2-ethanediol 123, 163

	+ ethanol	149, 158, 159
	+ formamide	110, 111
	+ glycine	120, 160 - 162
	+ methanol	139
	+ 2-methyl-2-butene-1-ol	134
	+ 2-methyl-2-propene-1-ol	104, 114- 116
	+ nitric acid, lithium salt	133, 134, 138 - 140
	+ nitric acid, potassium salt	101 - 103, 130, 131
	+ nitric acid, sodium salt	111
	+ nitric acid, silver salt	140
	+ phenol	139
	+ 1-pentene-3-ol	104-107, 109,
	+ perchloric acid	114-116, 149
	+ percinone acid	105 - 107
	+ perchloric acid, lithium salt	158, 159
	+ perchloric acid, ittilidin sait + perchloric acid, sodium salt	136
	+ 1,2,3-propanetriol	144
		130 - 132
	+ 2-propanone	
	+ 2-propanol	133
	+ 2-propene-1-ol	108, 110 - 113,
	+ sodium hydroxide	120, 123, 124, 136,
		144, 146
		160
	+ sulfinylbismethane	156, 157
	 + N,N,N-tributylbutanaminium bromate 	156, 157
	 + N,N,N-tributylbutanaminium perchlorate 	155
	 + N,N,N-triethylethanaminium bromate 	155
	 + N,N,N-triethylethanaminium perchlorate 	103
	 + 2,4,6-trinitrophenol, sodium salt 	113
	+ DL-tyrosine	114-116
l	+ water-d2	
	iso-Butyric acid	
	see 2-methylpropanoic acid	
	Caproic acid	
	see hexanoic acid	
Ì	Chloric acid, copper salt	E1, E2, 3
	+ water	
	Chloric acid, silver salt	E61, 62
	+ water	
1	Chloric acid, silver salt (aqueous)	E61, 63
	+ chloric acid, sodium salt	E61, 64, 65
	+ 1,3,5,7-tetrazatricyclo[3.3.1.13,7]-decane	66
	+ water-d2	
i	Chloric acid, silver salt (multicomponent)	67
	+ methanol	67
	+ 1,3,5,7-tetraazotricyclo[3.3.1.1 ^{3,7}]decane	
Ì	Copper bromate	
I	see bromic acid, copper salt	
	Copper lodate	
	see iodic acid, copper salt	
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