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SOLUBILITY DATA SERIES

Volume 23

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SOLUBILITY DATA SERIES

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Volume 23

COPPER, SILVER, GOLD AND ZINC, CADMIUM, MERCURY OXIDES AND HYDROXIDES

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FOREWORD

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

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

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

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

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

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

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

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

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

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

The Critical Evaluation part gives the following information:

(i) a verbal text of evaluation which discusses the numerical solubility information appearing in the primary sources located in the literature. The evaluation text concerns primarily the quality of data after consideration of the purity of the materials and their characterization, the experimental method employed and the uncertainties in control of physical parameters, the reproducibility of the data, the agreement of the worker's results on accepted test systems with standard values, and finally, the fitting of data, with suitable statistical tests, to mathematical functions;

(ii) a set of recommended numerical data. Whenever possible, the set of recommended data includes weighted average and standard deviations, and a set of smoothing equations derived from the experimental data endorsed by the evaluator;

(iii) a graphical plot of recommended data.

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

The typical data sheet carries the following information:

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

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

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

This new approach to numerical data presentation, formulated at the initiation of the project and perfected as experience has accumulated, has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

Finally, the role of education is more than corollary to the efforts we are seeking. The scientific standards advocated here are necessary to strengthen science and technology, and should be regarded as a major effort in the training and formation of the next generation of scientists and engineers. Specifically, we believe that there is going to be an impact of our project on scientific-communication practices. The quality of consolidation adopted by this program offers down-to-earth guidelines, concrete examples which are bound to make primary publication services more responsive than ever before to the needs of users. The self-regulatory message to scientists of the early 1970s to refrain from unnecessary publication has not achieved much. A good fraction of the literature is still cluttered with poor-quality articles. The Weinberg report (in 'Reader in Science Information', ed. J. Sherrod and A. Hodina, Microcard Editions Books, Indian Head, Inc., 1973, p. 292) states that 'admonition to authors to restrain themselves from premature, unnecessary publication can have little effect unless the climate of the entire technical and scholarly community encourages restraint...' We think that projects of this kind translate the climate into operational terms by exerting pressure on authors to avoid submitting low-grade material. The type of our output, we hope, will encourage attention to quality as authors will increasingly realize that their work will not be suited for permanent retrievability unless it meets the standards adopted in this project. It should help to dispel confusion in the minds of many authors of what represents a permanently useful bit of information of an archival value, and what does not.

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

A. S. Kertes

PREFACE

This volume presents and evaluates solubility data for the oxides and hydroxides of two groups of transition series metals, i.e., copper, silver, gold, and zinc, cadmium, mercury, from Groups I and II of the Periodic Table.

The history of the interest in the solubilities of most of these oxides and hydroxides may be divided into approximately three periods. In the earliest period the interest was mainly in the extent to which these substances were amphoteric. They were all known to show basic characteristics, but there was a question of the extent to which they exhibited acidic behavior. The study of the solubility of these substances in strong bases or alkalies was selected as one method for detecting any such acidic behavior.

The second period occurred during and following World War II. At that time several of these metals were being used as components in an alkaline battery, e.g., mercury-zinc, nickel-cadmium, silver-zinc and silver-cadmium batteries. The study of the solubility of the oxides and hydroxides of these metals was undertaken, again in alkaline solutions but now in solutions of larger concentrations, in an effort to understand and control the electrode reactions occurring in these battery systems.

The third stage is related to interest in the environment. These metals are known to have some toxic characteristics, and it has been of interest to determine to what extent they and their compounds can enter into the environment through dissolution processes. Such studies have been accompanied by the development of analytical procedures and techniques capable of detecting very small quantities of these metals.

The main source used in the search for relevant articles was *Chemical Abstracts* from 1907 to 1984. The search for work published prior to 1907 was limited to: (a) the eighth edition of Gmelin, *Handbuch der Anorganischen Chemie;* (b) the work of Mellor (1); and (c) the references cited in each of the articles used in the preparation of this volume. However, with few exceptions, no works published before 1900 were used for preparing data sheets. The reasons for this are primarily: (a) the matter of the stability or instability of the hydroxides, particularly, was not clearly understood at that time and, as a result, the nature of the solid phases that were used was not well defined; (b) the nature of solutions of electrolytes was not well understood by comparison with today's work and "degree of ionization" was often used to evaluate ionic concentrations; (c) the solubility of the substances studied in this volume is often very small in aqueous solvents and the analytical techniques then available were generally not sensitive enough.

So far as I am aware, all the pertinent articles up to 1984 have been reviewed. A few articles were unavailable during the course of this work, but it appears that the inclusion of these articles (usually in lesser known journals of the eastern European countries) would not have changed to any significant extent the conclusions presented in this volume. However, as these articles become available they will be included in a later update volume.

On the compilation sheets the data are given with the same number of significant figures as are reported by the authors of the original article. However, when calculations are made to present the data in different units, the number of significant figures was sometimes reduced. This was done in accordance with the compiler's estimate of the reproducibility of the data. Further discussion of the validity of the data are presented in the respective Critical Evaluations.

With one exception, all the data included in this volume are for solubilities in aqueous solutions. Very little information has been published about the solubility in non-aqueous solvents of the oxides and hydroxides covered in this volume. One such article is that of Becker (2) which reports the solubility of a variety of compounds in formamide at 298 K. The experimental details are very meager. The solubility of CuO is stated to be less than 0.01 mass % while that of ZnO is merely given as 0.8 g/100 g formamide.

In another article (3) the solubility of CuO in liquid ammonia at 298 K is given as 0.00 g/100 g.

The one exception referred to above is an article dealing with the solubility of Cu_2O and CuO in acetonitrile and in methyl acetate (4). Compilation sheets have been included for this article although only a few pertinent data are given in it. However, these data are not discussed in the Critical Evaluations. The data are included because they appear to be reasonable within the limits of the experimental conditions. There is no other work with which they can be compared.

In many articles the solubility data are presented only in the form of one or more graphs. No data sheets have been prepared for these articles unless it was possible to obtain from the author(s), in a personal communication, the numerical data upon which such graphs were constructed. Thus, e.g., data for the solubility of CuO in non-aqueous media (5, 6) have been omitted from this volume. For the same reason an article dealing with the solubility of Cu_2O in solutions containing diethylenetriamine and sulfuric acid (7) has been excluded from consideration. Furthermore, this article gives no information about experimental details, analytical procedures, or quality of the materials that were used.

Where both the oxide and hydroxide of a metal exist in the solid state the solubility data for both are considered together in the Critical Evaluation. This is a matter of convenience because the dissolution of the oxide in aqueous solutions often produces the hydroxide of the metal. Furthermore, the oxide may be the more stable of the two solids. Often, the hydroxide is metastable with respect to the oxide. The difficulties associated with the preparation of stable oxides or hydroxides and with the attainment of equilibrium between solid and solution have been discussed elsewhere (8).

The transition series metals often have more than one oxidation state. However, there may be no stable oxides or hydroxides corresponding to each of the oxidation states. For the metals discussed in this volume, only copper and silver have solid oxides corresponding to more than one oxidation state. In the Critical Evaluations the solubility data for each oxidation state are discussed separately.

In the Critical Evaluations that follow, stability and formation constant values for some complexes are sometimes presented and evaluated. These values were derived from solubility data and the evaluation of them usually considers similarly derived data. The values are not necessarily compared with similar values obtained by the use of other kinds of experimental data.

The work presented in this volume was not done by one person alone. Besides those who contributed compilation sheets there were many others who helped in other ways, and whose contribution can be recognized here. Conrad Bult and Lynne Hopkins of the Calvin College Library, Drs. A. S. Kertes, J. W. Lorimer, and M. Salomon of the Solubility Data Project all provided considerable help in locating and obtaining copies of the articles that have been reviewed. Special thanks are due to the personnel of the Chemistry Department Library at Michigan State University for the freedom given me to use all their facilities in preparing the materials for this volume. Carol Dirkse and Dr. R. Van Dragt of Calvin College gave indispensable assistance by providing translations of several articles. Dr. I. Khodakovskii of the USSR Academy of Sciences graciously reviewed and commented on the solubility work done under hydrothermal conditions. And then there are the three efficient, helpful, and patient typists: Louise Null, Sue Sweetman and Jan Woudenberg. They did the tedious work of typing, retyping, and more retyping and, out of this ordeal, they have still come up smiling.

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October 1984

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.

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

Definitions

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

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

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

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

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

Quantities Used as Measures of Solubility

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

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

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

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

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

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

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

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

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

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

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

where M_A is the molar mass of the solvent.

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

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

The terms molarity and molar are not used.

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

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

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

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

Thermodynamics of Solubility

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

Activity Coefficients (1)

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

$$RT \ln(f_B x_B) = \mu_B - \mu_B^* \qquad (7)$$

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

$$\lim_{x_B \to 1} f_B = 1 \qquad (8)$$

(b) *Solutions*.

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

$$RT \ln(\gamma_B m_B) = \mu_B - (\mu_B - RT \ln m_B)^\infty \qquad (9)$$

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

$$\gamma_B^\infty = 1 \qquad (10)$$

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

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

or

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

or

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

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

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

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

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

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

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

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

(ii) *Solvent, A:*

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

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

where $\mu_A{}^*$ is the chemical potential of the pure solvent.

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

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

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

The Liquid Phase

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

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

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

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

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

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

where (7)

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

it is found that

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

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

where

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

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

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

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

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

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

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

$$\begin{aligned} nH_A + H_B - H_{AB}^* &= \Delta H_{AB} + n(H_A - H_A^*) + (H_B - H_B^*) \\ &= \Delta H_{AB} + w(nx_B^2 + x_A^2) \end{aligned} \tag{27}$$

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

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

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

$$\begin{aligned} \ln\{x_B(1-x_B)^n\} \simeq\ & \ln\{\frac{n^n}{(1+n)^{n+1}}\} - \{\frac{\Delta H_{AB}^* - T^*\Delta C_p^*}{R}\}(\frac{1}{T} - \frac{1}{T^*}) \\ & + \frac{\Delta C_p^*}{R}\ln(\frac{T}{T^*}) - \frac{w}{R}\{\frac{x_A + nx_B}{T} - \frac{n}{(n+1)T^*}\} \end{aligned} \tag{29}$$

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

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

If the solid contains only component B, n = 0 in eqn (29) and (30).
If the infinite dilution standard state is used in eqn (25), eqn (26) becomes

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

and (27) becomes

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

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

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

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

$$= \{\Delta H^\infty_{AB} + n(H_A - H_A^*) + (H_B - H_B^\infty)\}d(1/T) \quad . \tag{33}$$

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

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

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

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

(b) *Solubility as a function of composition.*

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

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

$$= (n\mu_A^* + \nu_+\mu_+^\infty + \nu_-\mu_-^\infty) + nRT\ \ln f_A x_A$$

$$+ \nu RT\ \ln \gamma_\pm m_\pm Q_\pm \tag{36}$$

for a salt hydrate A_nB which dissociates to water, (A), and a salt, B, one mole of which ionizes to give ν_+ cations and ν_- anions in a solution in which other substances (ionized or not) may be present. If the saturated solution is sufficiently dilute, $f_A = x_A = 1$, and the quantity K^0_{s0} in

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

$$= -RT\ \ln K^0_{s0}$$

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

is called the *solubility product* of the salt. (It should be noted that it is not customary to extend this definition to hydrated salts, but there is no reason why they should be excluded.) Values of the solubility product are often given on mole fraction or concentration scales. In dilute solutions, the theoretical behaviour of the activity coefficients as a function of ionic strength is often sufficiently well known that reliable extrapolations to infinite dilution can be made, and values of K^0_{s0} can be determined. In more concentrated solutions, the same problems with activity coefficients that were outlined in the section on variation of solubility with temperature still occur. If these complications do not arise, the solubility of a hydrate salt $C_{\nu_+}A_{\nu_-}\cdot nH_2O$ in the presence of other solutes is given by eqn (36) as

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

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

The Solid Phase

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

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

COMPILATIONS AND EVALUATIONS

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

Guide to the Compilations

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

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

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

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

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

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

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

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

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

Estimated Error. If these data were omitted by the original authors, and if relevant information is available, the compilers have attempted to

estimate errors from the internal consistency of data and type of apparatus used. Methods used by the compilers for estimating and reporting errors are based on the papers by Ku and Eisenhart (15).

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

References. See the above description for Original Measurements.

Guide to the Evaluations

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

Components. See the description for the Compilations.

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

Critical Evaluation

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

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

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

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

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

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

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COMPONENTS:	EVALUATOR:
(1) Copper(I) oxide; Cu_2O; [1317-39-1] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506 U.S.A. October 1984

CRITICAL EVALUATION:

The only solubility data reported for unipositive copper are for Cu_2O. There is no substantial evidence for the existence of a solid CuOH. Bevillard examined samples of Cu_2O prepared by various methods and samples of substances that might have been CuOH (1). The examination consisted of chemical analysis and X-ray diffraction measurements. The conclusion reached was that the existence of CuOH is doubtful. The preparations appeared to be Cu_2O with varying amounts of water. Color differences among various samples of Cu_2O were ascribed to differences in particle size.

Unlike investigations of the other transition series metals of Groups I and II of the Periodic Table, no attention has been given to the solubility of Cu_2O in water or in solutions of alkalies. No acidic, basic or solubility product constants have been reported on the basis of solubility measurements.

Feitknecht (2) calculated a solubility product constant value of 1.26×10^{-15} for CuOH, presumably at 298 K. The calculation was based on thermodynamic and e.m.f. data that were available. However, some of these values were revised in the process of carrying out the calculations. An attempt had been made earlier to determine the solubility product constant experimentally (3). The method involved the measurement of the e.m.f. of a cell containing a Cu_2O/Cu electrode immersed in a solution of NaOH or KOH. The value of the K_{so} reported was 1.0×10^{-14} at 290 K. This is ten times the value calculated for 298 K (2). It is evident from this that the solubility product constant for CuOH has not been determined, but it probably is of the order of 10^{-15}.

The solubility of Cu_2O in aqueous NH_3 has been measured at 298 K (4). The purpose of the work was to gather information about the composition of Cu(I)-NH_3 complexes. Considerable care was taken in making the solubility measurements, and there is no reason to consider these values as doubtful. However, there are some uncertainties in the values and the two samples of Cu_2O that were used show some differences in solubility, Figure 1. These differences may be due to differences in particle size.

Two investigations of the solubility of Cu_2O have been made because of the possibility that it may be an intermediate in the corrosion of copper. In one such study (5) the rate of dissolution of Cu_2O was measured in a variety of aqueous salt solutions, but the report contains no solubility data. Concentrations of dissolved Cu_2O were measured after two time intervals, the longer being one day, and there was no assurance that the solutions were saturated. The rate of dissolution was measured as a function of pH. Except in solutions of Na_3PO_4, the "solubility" of Cu_2O passed through a minimum at a pH of 11 to 12. The data are presented only in graphical form and no temperature is specified.

In the other solubility investigation related to the corrosion of copper (6) the solubility of Cu_2O was measured in supercritical steam at a temperature of 895 K. The pressure varied from 186×10^5 to 310×10^5 Pa. The pH range was 7.5 to 9.6, but the solubility of Cu_2O was constant in this pH range. The solubility of Cu_2O was more dependent on pressure than on the temperature. The values reported are to be considered tentative until further, similar, work is reported.

COMPONENTS:

(1) Copper(I) oxide; Cu_2O; [1317-39-1]

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

EVALUATOR:

T. P. Dirkse
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U.S.A.

October 1984

CRITICAL EVALUATION:

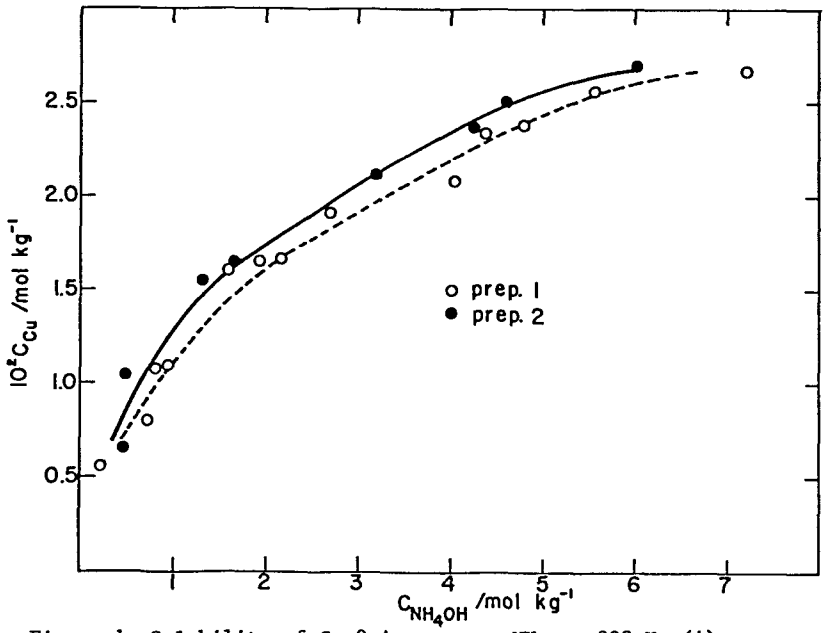

Figure 1. Solubility of Cu_2O in aqueous NH_3 at 298 K. (4). Preparation 2 contains a much larger proportion of very small microcrystalline particles than does Preparation 1.

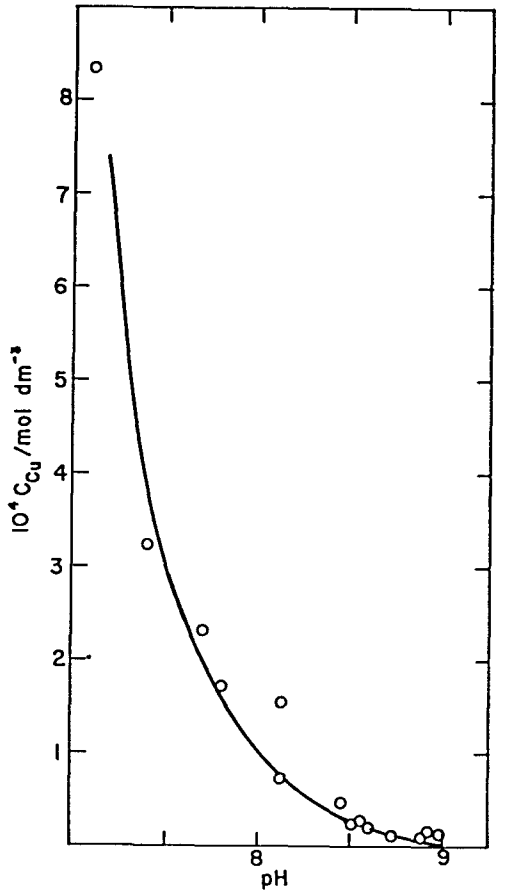

Figure 2. Solubility of Cu_2O in sea water at 298 K. (8).

COMPONENTS:	EVALUATOR:
(1) Copper(I) oxide; Cu_2O; [1317-39-1] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506 U.S.A. October 1984

CRITICAL EVALUATION:

One of the characteristics of Cu_2O is its toxicity. For this reason it can be used as a fungicide and in marine anti-fouling paints. An interest in the possible use of Cu_2O as a fungicide to treat certain seeds prompted an investigation of the effect of hydrolyzed protein material and certain amino acids on the water solubility of Cu_2O (7). The nitrogenous materials increase the water solubility of Cu_2O at 298 K. The results that were reported were qualitative in nature, and the source of the nitrogenous materials was not identified. Therefore, no data sheet was prepared for this report.

Two studies were undertaken because Cu_2O is an ingredient of marine anti-fouling paints. This application requires a knowledge of the solubility of Cu_2O in sea water. The rate of dissolution of Cu_2O in sea water was the main interest in one investigation (8), but some solubility data were also included, Figure 2. It is not evident from the report whether a natural or a synthetic sea water was used. At the pH of sea water (8.1) the solubility of Cu_2O at 298 K is given as 8.6×10^{-5} mol dm^{-3}. Ragg (9) measured the solubility of Cu_2O in Baltic Sea water (pH = 8.1). The temperature was not specified, but it probably was around 290 K. The solubility value reported was about one-tenth the value reported earlier (8). The paper by Ragg contains practically no experimental detail. The value of Ferry and Carritt (8) is to be preferred, but must be considered tentative.

Because of an interest in the processes whereby certain metals may enter the environment, Shlyapnikov and Shtern began a study of the solubility of metal oxides in NaCl solutions exposed to CO_2 at elevated pressures. The first paper (10) contains only a few data and there are inconsistencies between data in the text and in the Tables. Later a more thorough study was made of the solubility of Cu_2O under such conditions (11). The solubility of Cu_2O increases with increasing concentration of NaCl or KCl, and with increasing pressure of CO_2. Under these conditions the copper in Cu_2O is oxidized to Cu^{2+}. There is no reason to reject these values, but because they are the only ones available for these systems, they can only be considered as tentative.

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10. Shlyapnikov, D. S.; Shtern, E. K. *Dokl. Akad. Nauk SSSR* 1975, *225*, 428; *Doklady Acad. Sci. USSR, Earth Sci. Sect. (Eng. transl.)* 1975, *225*, 185.
11. Shlyapnikov, D. S.; Shtern, E. K. *Zhur. Neorg. Khim.* 1977, *22*, 1100; *Russ. J. Inorg. Chem. (Engl. transl.)* 1977, *22*, 604.

COMPONENTS:

(1) Copper(I) oxide; Cu_2O; [1317-39-1]

(2) Sea Water

ORIGINAL MEASUREMENTS:

Ferry, J. D.; Carritt, D. E. *Ind. Eng. Chem.* 1946, *38*, 612-7.

VARIABLES:

pH of the sea water at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Cu_2O in oxygen-free sea water at 25°C.

pH	$10^4 C_{Cu}$/mol dm^{-3}	pH	$10^4 C_{Cu}$/mol dm^{-3}
7.11	8.35[e]	8.51	0.26[d]
7.40	3.26[b]	8.56	0.29[d]
7.70	2.34[b]	8.60	0.22[a]
7.80	1.73[c]	8.73	0.14[a]
8.12	0.74[c]	8.88	0.11[a]
8.12	1.57[a]	8.92	0.19[a]
8.46	0.49[d]	8.96	0.14[a]

[a] CO_2 was removed from the sea water by flushing with nitrogen.

[b] HCl was added to the sea water and the pH was adjusted by adding NaOH.

[c] gaseous CO_2 was added to the sea water after it was deaerated.

[d] Same as in c except that the nitrogen was treated to remove all traces of oxygen.

[e] Same as in d, except the Cu_2O was painted on to a solid surface.

The following equation fits the data in the Table:

$$\log C_{Cu} = 4.03 - pH.$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Cu_2O was placed in a vessel that had been evacuated and then filled with N_2. Air-free sea water was forced into the vessel under nitrogen pressure. The mixtures were agitated at 25°C. After equilibration the mixtures were filtered and the pH of the filtrate was quickly measured with a glass electrode. After the cuprous copper had been air oxidized its concentration was determined colorimetrically with sodium diethyldithiocarbamate (1).

SOURCE AND PURITY OF MATERIALS:

The Cu_2O was an electrolytic preparation. Nothing is said about the composition or source of the sea water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Ketchum, B. H.; Ferry, J. D.; Redfield, A. C.; Burns, A. E. *Ind. Eng. Chem.* 1945, *37*, 456.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(I) oxide; Cu_2O; [1317-39-1] (2) Baltic Sea water.	Ragg, M. *Farbe u. Lack* 1950, *56*, 435-41.
VARIABLES: None.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES:

The solubility of Cu_2O in Baltic Sea water is given as 0.6 mg dm^{-3}. This appears to be the weight of Cu and not of Cu_2O in the solution, but this is not stated specifically. This amounts to 9.4×10^{-6} mol dm^{-3}[a].

No temperature is stated. The author deals with the solubility of different heavy-metal compounds that are used in marine anti-fouling paints. Some of these solubility values are given at 18°C and others at 15°C, so the solubility value for Cu_2O is probably one or the other of these temperatures.

The pH of the Baltic Sea water was given as 8.1 for other solubility values. It appears that the Baltic Sea water used for the Cu_2O solubility determination was at the same pH.

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Cu_2O was added to the filtered Baltic Sea water and the mixture was shaken for several hours--until saturation. The liquid phase was filtered from the solid phase. The analytical method to determine copper is not described, but later in the article a rather complete description is given of a colorimetric method using dithizone.	No information is given.
	ESTIMATED ERROR: No details are given.
	REFERENCES:

COMPONENTS:

(1) Copper(I) oxide; Cu_2O; [1317-39-1]

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

ORIGINAL MEASUREMENTS:

Pocock, F. J.; Stewart, J. F. *J. Eng. Power* 1963, *85*, 33-45.

VARIABLES:

Temperature and pressure of the steam.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Cu_2O in supercritical steam.

pH	temp/°F[a]	Pressure/psig	C_{Cu}/ppb
7.5	1148	4500	9.1
7.7	1147	4500	7.7
7.6	1152	4500	9.9
9.6	1155	4500	11.5
9.6	1149	4500	11.5
9.6	1144	4500	7.7
9.6	1149	2700	0.3
9.6	1147	3900	4.7
9.6	1118	3300	2.8

[a] Average temperature during the course of the experiment.

During these experiments some of the Cu_2O was reduced to Cu.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Five grams of Cu_2O was placed on each of six trays in an autoclave. Supercritical steam was passed through the autoclave at a rate sufficient to insure saturation equilibrium. Sampling was continued for about 3 hours. Blanks were run to measure the amount of copper extracted from the stainless steel of the autoclave. The analytical method used to determine copper content is not mentioned or described.

SOURCE AND PURITY OF MATERIALS:

Cu_2O was reagent-grade quality. It was pelletized and sintered at 1850°F under a helium atmosphere, then crushed, screened and washed to remove fines. The feedwater was demineralized and deaerated. NH_4OH was introduced to raise the pH.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(I) oxide; Cu_2O; [1317-39-1]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Donnan, F. G.; Thomas, J. S. *J. Chem. Soc.* 1912, *99*, 1788-96.

VARIABLES:

Concentration of ammonium hydroxide at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Cu_2O in aqueous NH_4OH at 25°C.

Preparation 1[a]		Preparation 2[a]	
C_{NH_4OH}/mol kg^{-1}	C_{Cu}/mol kg^{-1}	C_{NH_4OH}/mol kg^{-1}	C_{Cu}/mol kg^{-1}
0.23	0.00566	0.46	0.00665
0.71	0.00791	0.48	0.01050
0.81	0.01080	1.33	0.01555
0.95	0.01095	1.67	0.01650
1.59	0.01597	3.19	0.02127
1.92	0.01645	4.24	0.02366
2.17	0.01660	4.60	0.02510
2.69	0.01924	6.00	0.02603
4.04	0.02081		
4.36	0.02340		
4.78	0.02375		
5.56	0.02565		
7.20	0.02670		

[a] Preparation 2 was lighter in color than Preparation 1 and was considered to contain a much larger proportion of very small micro-crystalline particles.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures were prepared under a hydrogen atmosphere. The flasks were sealed and rotated in a thermostat at 25°C for 2 to 4 weeks and then were allowed to settle for a week while still in the thermostat. The total NH_3 content was determined by distilling over from an excess of alkali. The copper content was determined by electrolysis after excess of HNO_3 had been added to the sample.

SOURCE AND PURITY OF MATERIALS:

Equal weights of $CuSO_4$ and sucrose were dissolved in water, and sufficient KOH was added to redissolve all the precipitate. On standing at 70°C, Cu_2O precipitated from the solution. It was collected, washed with water and then with alcohol and ether, and dried over H_2SO_4 in a vacuum. Stock NH_4OH was prepared by distilling ordinary concentrated NH_4OH over lime and collecting the vapor in distilled water.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:
(1) Copper (I) oxide; Cu_2O; [1317-39-1]
(2) Sodium Chlordie; NaCl; [7647-14-5]
(3) Potassium chloride; KCl; [7447-40-7]
(4) Carbon dioxide; CO_2 [124-38-9]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Shlyapnikov, D. S.; Shtern, E. K. *Zh. Neorg. Khim.* 1977, *22*, 1100-6; *Russ. J. Inorg. Chem. (Engl. transl.)* 1977, *22*, 604-8.

VARIABLES:
Concentration of chlorides, pressure of CO_2, and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of Cu_2O in chloride solutions.

Salt	C_{salt}/mol dm^{-3}	20°C, pCO_2 = 50 atm C_{Cu}/g dm^{-3}	200°C, pCO_2 = 90 atm C_{Cu}/g dm^{-3}
none	0	0.40	0.047
NaCl	1	2.4127	4.8735
"	2	5.4181	10.2503
"	3	8.2000	15.0500
"	4	11.0000	19.1500
KCl	1	4.7449	5.8305
"	2	8.5429	14.7500
"	3	13.0541	21.8021
"	4	17.3600	29.4140

Some experiments were also carried out in which the total ionic strength of the solution was maintained at 4 mol dm^{-3} by adding $NaNO_3$. The solubility of Cu_2O increased with increasing Cl^- ion concentration but no numerical data are given. It was found that the cation also had an effect on the solubility of Cu_2O. Again, no numerical data are given, but a graph shows that the K^+ ion is most effective in increasing the solubility of Cu_2O under these conditions, with the other alkali metal ions being less effective.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The Cu_2O and solvent were placed in an autoclave which was shaken mechanically for 24 hours. After this time, the autoclave was inverted and the mixture was filtered through a corundum filter fitted into the autoclave. The filtrate was acidified with HCl and treated with Br_2 to oxidize the copper which was then determined by the thiosulfate method. The pressure in the autoclave was maintained by adding a calculated amount of solid CO_2.

SOURCE AND PURITY OF MATERIALS:
The chlorides were reagent grade materials and were recrystallized. The Cu_2O was also a reagent grade substance.

ESTIMATED ERROR:
No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(I) oxide; Cu_2O; [1317-39-1]
(2) Bromine; Br_2; [7726-95-6]
(3) Acetonitrile; C_2H_3N; [75-05-8]
(4) Methyl acetate; $C_3H_6O_2$; [79-20-9]

ORIGINAL MEASUREMENTS:

Busheina, I. S.; Headridge, J. B. *Analyst* 1981, *106*, 221-6.

VARIABLES:

Method of determining the solubility at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Cu_2O in organic solvent-bromine mixtures at 25°C.

	acetonitrile-bromine		methyl acetate-bromine	
	refluxing	no refluxing	refluxing	no refluxing
C_{Cu}/g per 100 ml	0.32	0.13	0.18	0.09
C_{Cu}/mol dm^{-3} [a]	0.050	0.020	0.028	0.014

[a] The mol dm^{-3} values were calculated by the compiler

The purpose of this study was to determine the feasibility of using organic solvent-bromine mixtures for removing various kinds of inclusions from metals.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvents consisted of 10 vol of organic material plus one vol of Br_2. Two methods were used; (a) With refluxing. 300 mg samples of Cu_2O were added to 30 ml of solvent. If no reaction was observed the mixture was heated under reflux for 30 min and then allowed to cool (1). (b) Without reflux. Successive portions of solid samples were added to the solvent until all noticeable reaction stopped. The mixture was then shaken mechanically for 15 min and placed in a thermostat at 25°C overnight. The phases were separated by filtration through a Whatman Glass microfiber paper, Type GF/F. A sample of filtrate was evaporated to dryness, the residue was dissolved in acid and the mixture amalyzed by atomic absorption spectrophotometry.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The solvent components were given an additional purification procedure.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Busheina, I. S.; Headridge, J. B. *Analyst* 1980, *105*, 600.

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:

For the bipositive oxidation state of copper there is both a solid oxide, CuO, and a solid hydroxide, $Cu(OH)_2$. However, in some environments the hydroxide is metastable with respect to the oxide. Such situations are discussed later in this Critical Evaluation. The hydroxide has been referred to as a hydrous oxide whose properties depend on the temperature of precipitation, the amount of alkali used, and the age of the precipitate. The degree of hydration of the precipitate decreases with increasing concentration of alkalies (1).

In addition to the metastability of the hydroxide, the possibility of the presence of colloidal CuO or $Cu(OH)_2$ must also be considered in evaluating the solubility data. Measurements of conductance (2) and viscosity (3) indicate that the hydroxide is at least partially peptized in solutions of NaOH and NH_4OH.

Solubility in water

There are a few reports that give numerical values for the solubility of CuO or $Cu(OH)_2$ in water, but the values were determined at different temperatures.

Copper oxide. Remy and Kuhlmann (4) used conductance measurements as the experimental approach to measuring the solubility of CuO in water at 293 K. The values were obtained by a conductimetric titration and by a measurement of the specific conductance of a saturated solution. The latter value was used together with accepted values for the ionic conductance of Cu^{2+} and OH^- ions to arrive at a solubility value. The average of the values obtained by these two methods was 6.8×10^{-5} mol dm^{-3}. This information was repeated in a later report (5) but no new solubility information was then given.

The solubility of CuO in water was also measured at 298 K (6). The solubility value, 2.9×10^{-5} mol dm^{-3}, was obtained by chemical analysis of a saturated solution. This value is the better of the two just mentioned because it was determined by direct analysis. However, the value is classed as tentative because of lack of supporting work and because the authors had difficulty preparing saturated solutions that contained no colloidal CuO.

Copper hydroxide. The solubility of $Cu(OH)_2$ in water is reported to be 3×10^{-6} mol dm^{-3} (7). This value was obtained in the course of a study of the treatment of sewage and industrial wastes. It is marred by the fact that there is a lack of precision in the work and no temperature is specified. This is true also of other reports. The solubility of $Cu(OH)_2$ in distilled water is said to be about 4×10^{-6} mol dm^{-3} at room temperature. The article (8), however, gives practically no experimental details and presents the data only in graphical form.

Makarov, et al. (9) determined the solubility of $Cu(OH)_2$ in solutions of hydrogen peroxide and, as an extension of that work, report a value of 2.9×10^{-6} mol kg^{-1} for the solubility of $Cu(OH)_2$ in water at 273 K. But, again, very few experimental details are given.

Another report on solubility (10) merely uses information already in the literature at that time and presents no new experimental data.

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A.
(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

Because of the lack of experimental details, and the few values reported, the solubility of $Cu(OH)_2$ in water can only be given as about 10^{-6} mol dm^{-3} in the temperature range 273-300 K.

Solubilities in acids

Aqueous HF. Only one report is available for this system (11). The solubility values were measured at 298 K, but they cannot be considered reliable because there is practically no information about the experimental details of this investigation.

Aqueous HNO_3. There has been one investigation of the solubility of CuO in aqueous HNO_3 (12). The temperature varied from 298 to 301 K and only a few dilute solutions of HNO_3 were used. The values reported can only be classified as tentative because of the absence of corroborating work.

Aqueous H_3BO_3. Only one paper (13) gives information on the $Cu(OH)_2$-H_3BO_3-H_2O system but the interest in the study was to determine the nature and composition of the solid phases that were present in this system at room temperature. No solubility data are included.

Solubilities in alkalies

Aqueous NaOH. Early in this century it had been shown that $Cu(OH)_2$ was slightly soluble in aqueous NaOH or KOH solutions without the presence of other substances (14). However, such solutions were shown to be metastable (15). A thorough investigation of this system was made by Muller. In two preliminary publications he verified the metastability and noted that the solubility of $Cu(OH)_2$ was dependent on the method used for the preparation of the $Cu(OH)_2$ (16), and he presented a phase diagram for the system (17). He later published a more complete account of the results of his investigations (18). The conclusion of this thorough investigation was that $Cu(OH)_2$ does dissolve to a significant extent in aqueous NaOH and the solubility increases markedly with increasing concentration of NaOH, Figure 1. However, these solutions are metastable. The copper content decreases on standing and the undissolved solid phase undergoes a change in color. The chemically-bound water content (or the $Cu(OH)_2$ content) of the solid phase is dependent on the copper concentration in the solution phase. In no instance did the chemically-bound water content become zero, i.e., the solid phase did not change completely to CuO. On the other hand, CuO had a lower solubility in the aqueous NaOH solutions than did the solutions of $Cu(OH)_2$ after they had ceased to decrease in copper content on standing. That is, with $Cu(OH)_2$ dissolved in aqueous NaOH, the solid phase approached but did not reach the composition CuO. Likewise, the solution decreased in copper content but the value did not reach the value of a saturated solution of CuO in aqueous NaOH. Thus, on the basis of the work of Muller, a solubility value for a saturated solution of $Cu(OH)_2$ in aqueous NaOH (or KOH) is meaningless. The most that can be said for such values is that they are minimum values. This agrees with earlier work (15).

The metastability of solutions of $Cu(OH)_2$ in aqueous NaOH has also been noted at 298 K by others (19). This group found that the solubility of

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:

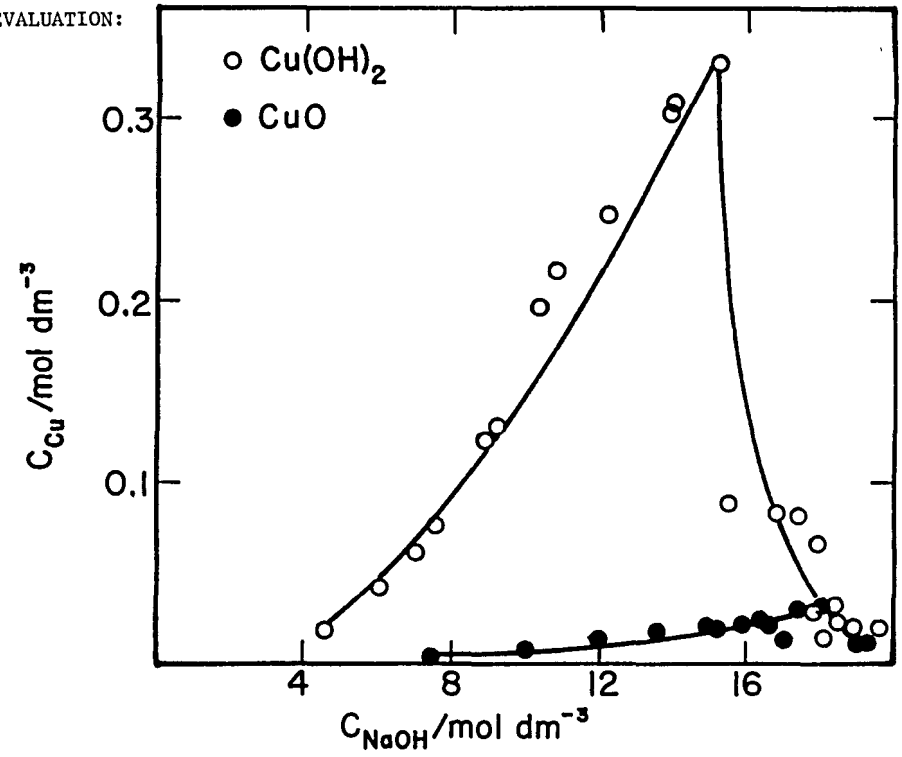

Figure 1. Solubility of $Cu(OH)_2$ and CuO in aqueous NaOH at 291 K, ref. (18).

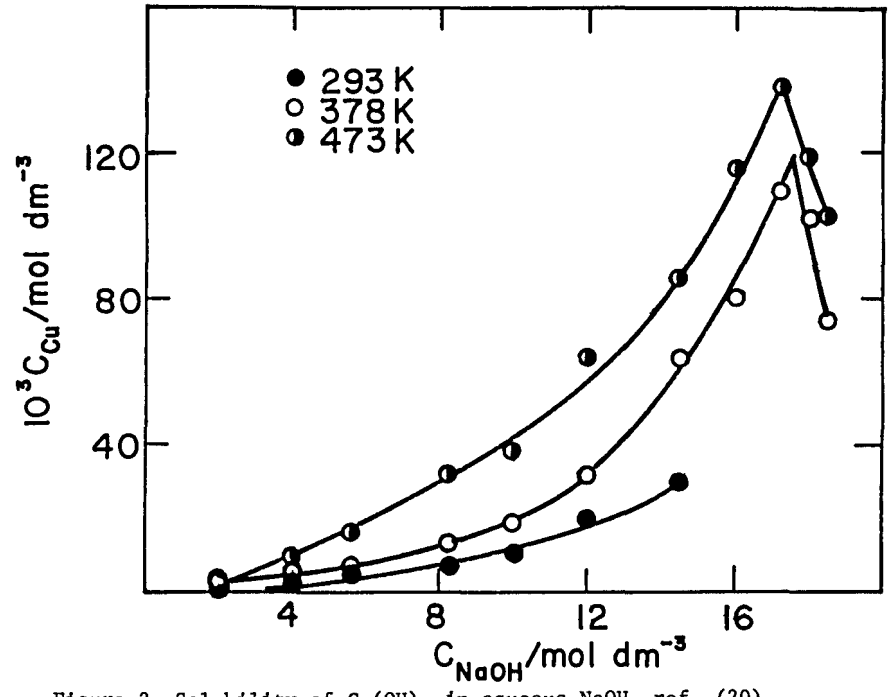

Figure 2. Solubility of $Cu(OH)_2$ in aqueous NaOH, ref. (20).

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A.
(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

$Cu(OH)_2$ decreased with aging. They also found that the amount of $Cu(OH)_2$ dissolved in a 7.5 mol dm^{-3} solution of NaOH increased for about the first hour after the components were mixed, but then decreased over the period of a month. No equilibrium solubility values are given in this paper. The solubility values recorded after a month of standing are about 10% of those shown on Figure 1. The data obtained by some members of this research group (20) are shown on Figure 2. The solubility of $Cu(OH)_2$ increases with increasing temperature and shows the same variation with increasing NaOH concentration as do the results on Figure 1, but the solubility values given on Figure 2 are much smaller than those shown on Figure 1. This may be due to the preparation of $Cu(OH)_2$ that was used (19).

In larger concentrations of NaOH (above 16 mol dm^{-3}) the solubility of $Cu(OH)_2$ and of CuO decrease markedly. This is due to the fact that the solid phase changes to Na_2CuO_2.

The difference in solubility of $Cu(OH)_2$ and CuO in aqueous NaOH was noted by Feitknecht (21) who presented no new solubility data but observed that the free energy content of CuO is about 1.62 kcal mol^{-1} less than that of $Cu(OH)_2$. Another report (22) mentions that freshly precipitated $Cu(OH)_2$ is more soluble in aqueous solutions of alkalies than is CuO, but no numerical solubility data are given.

Solubility values for solutions of $Cu(OH)_2$ in NaOH solutions more dilute than those shown on Figure 1 have also been reported (23). The three papers (15, 18, 23) that report solubility values for $Cu(OH)_2$ in aqueous NaOH (all at approximately the same temperature) give different solubility values for the NaOH concentration range that is common to all of them. This is to be expected when dealing with a metastable system. Another set of solubility values for $Cu(OH)_2$ in aqueous NaOH at 298 K (24) resemble more nearly the solubility values for CuO that were reported by Muller (18).

Solubility values for solutions of CuO in aqueous NaOH (18) can be accepted as equilibrium values because such solutions were stable. Solubility values for this same system have also been reported by others (6) and are shown on Figure 3. There are differences that should be noted. In one report (6) the concentrations are given as mol kg^{-1} while in the other (18) they are given as mol dm^{-3}. The temperatures differ by 7 K. Yet, in spite of these differences the data support each other in the alkali concentration regions that are common to both. Furthermore, solubilities in NaOH and in KOH are about the same. The values of Akhmetov, et al. (24) are somewhat larger. There are too few data to recommend solubility values or an equation that expresses the solubility of CuO in aqueous NaOH. Therefore, for temperatures around room temperature the data on Figure 3 (6, 18) are classified as tentative, but there is no reason to doubt their validity. They are preferred to those of ref. (24) because in that work no information is given about the CuO that was used in making the measurements. A value of 4.2×10^{-3} mol dm^{-3} was mentioned as a solubility value of CuO in a 7.5 mol dm^{-3} NaOH solution at 298 K (19). This value was not reported as an equilibrium value but it is in good agreement with the values shown on Figure 3.

The solubility of CuO in aqueous NaOH at higher temperatures has also been reported (25) and is shown on Figure 4. The values are considerably

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:

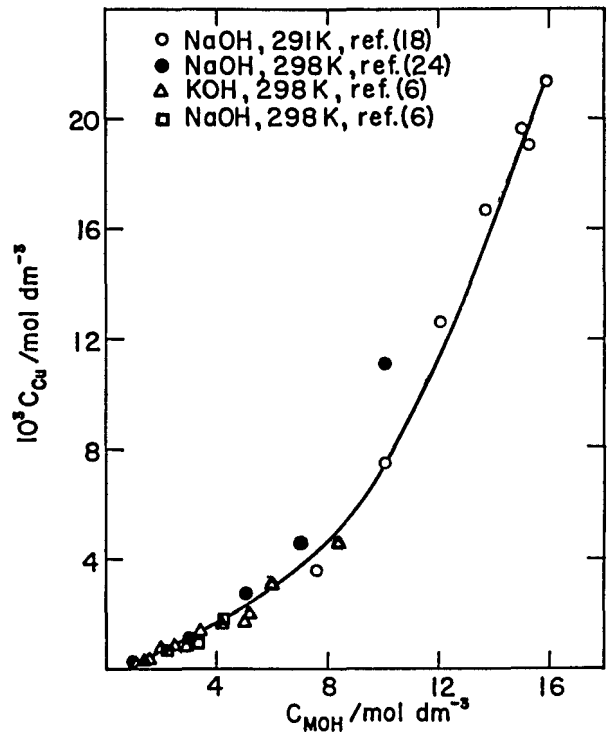

Figure 3. Solubility of CuO in aqueous NaOH and KOH solutions. For ref. (6) the units on the axe are mol kg^{-1}.

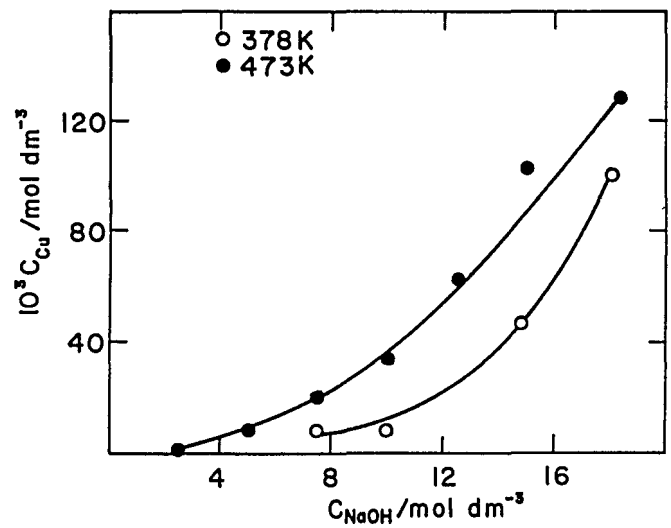

Figure 4. Solubility of CuO in aqueous NaOH, ref. (25).

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A.
(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

larger than those shown on Figure 2. This may be due to the higher temperature, but these values can only be accepted tentatively until further work is reported.

Aqueous KOH. Traube (26) has reported some solubility values for solutions of $Cu(OH)_2$ in aqueous KOH containing polyhydroxy compounds. These data were not entered on a data sheet because no temperature was specified and there is no information about the source and purity of the materials that were used. The solubility data are expressed as ratios. The main objective of the work was not to measure solubilities but to ascertain the mechanism whereby $Cu(OH)_2$ dissolves in such mixtures. The discussion of the mechanism of dissolution was continued in two later reports (27, 28) but no additional solubility information was given.

Solubility constants

The dissolution of $Cu(OH)_2$ and CuO in aqueous solutions may proceed by one or more of reactions (1) to (4).

$$Cu(OH)_2(s) = Cu(OH)_2(sln) \quad (1)$$

$$CuO(s) + H_2O = Cu(OH)_2(sln) \quad (1a)$$

$$Cu(OH)_2(s) = Cu^{2+} + 2OH^- \quad (2)$$

$$CuO(s) + H_2O = Cu^{2+} + 2OH^- \quad (2a)$$

$$Cu(OH)_2(s) + OH^- = Cu(OH)_3^- \quad (3)$$

$$CuO(s) + H_2O + OH^- = Cu(OH)_3^- \quad (3a)$$

$$Cu(OH)_2(s) + 2OH^- = Cu(OH)_4^{2-} \quad (4)$$

$$CuO(s) + H_2O + 2OH^- = Cu(OH)_4^{2-} \quad (4a)$$

Reactions (1) and (1a) have received practically no attention. In a review containing values for a variety of constants and reactions (29), the value of the equilibrium constant for reaction (1) is given as 3.3×10^{-5} at 298 K. However, this value was deduced from thermodynamic data found in the literature, but no indication is given as to the source of this information. On the other hand, the solubility of undissociated $Cu(OH)_2$ in aqueous solutions was estimated to be about 10^{-9} mol dm^{-3} at 298 K (6). The solubility is too small to be determined precisely, and its contribution to the total solubility of $Cu(OH)_2$ is considered to be negligible.

Reactions (2) and (2a) represent the solubility product reaction, for which the equilibrium constants are:

$$K_2^o = K_{so}^o = (a_{Cu^{2+}}) \cdot (a_{OH^-})^2 \quad (5)$$

$$K_{2a}^o = K_{so}^o = (a_{Cu^{2+}}) \cdot (a_{OH^-})^2/(a_{H_2O}) \quad (5a)$$

COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A.
(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

In spite of the fact that the solubility of $Cu(OH)_2$ in aqueous solutions of alkalies is indeterminable because of the instability of the system, there are many reports in which K_2^o has been evaluated. Two attempts have been made to evaluate this constant by measuring the e.m.f. of an appropriate cell (30, 31). A value of 1.7×10^{-13} mol^3 dm^{-9} was obtained as a concentration product at 292 K (30) and 1.0×10^{-19} mol^3 dm^{-9} was reported at 290 K (31). In neither investigation was the reproducibility very good, because of the instability of the $Cu(OH)_2/Cu$ electrode.

In four investigations the experimental method consisted of a potentiometric titration of a copper salt with aqueous NaOH or LiOH, but slightly different temperatures were used. A concentration product of 3.72×10^{-10} mol^3 dm^{-9} was reported at 293 K (32). However, there is a legitimate doubt whether equilibrium was established in this work. A value of 1.3×10^{-20} was reported for K_2^o at an unspecified temperature (22), although the data were probably obtained at room temperature. Oka (33) reported values of 1.1×10^{-19} and 9.3×10^{-19} mol^3 dm^{-9} at 298 K, depending on whether the copper salt was $Cu(NO_3)_2$ or $CuCl_2$, respectively. However, these values are rejected because of insufficient information about the experimental details and the method of treating the experimental data. An approximate value of 3.9×10^{-19} mol^3 dm^{-9} for a concentration product was reported at 298 K (34).

In two investigations the pH of a saturated solution of $Cu(OH)_2$ was measured and the copper concentration in the solution was determined by analysis. The nature of the solid phase is uncertain in one of the reports (35). Little information is given about the experimental procedure and the author's calculations could not be reproduced. In the other report (36) the saturated solution of $Cu(OH)_2$ was prepared by pouring a 0.2 mol dm^{-3} solution of $NaClO_4$ through a column containing $Cu(OH)_2$. A value of 4.78×10^{-20} was obtained for K_2^o at 298 K. This value is the most reliable of those reported but it is classified as tentative because of the instability of the $Cu(OH)_2$-alkali system and because there is no other work to substantiate it.

In a somewhat similar approach, solid $Cu(OH)_2$ was dissolved in solutions of $CuSO_4$ at 291 K (37). The pH of the resulting solutions was measured and an analysis was made for copper content (no analytical method is mentioned). On the basis of these measurements a value of K_2 was calculated for each solution. The K_2 values for the most dilute $CuSO_4$ solutions were then extrapolated to zero ionic strength. The extrapolated value, 1.31×10^{-20}, was proposed as a value for K_2^o at 291 K. One assumption implicit in this method is that the copper content of the solution is assumed to be completely in the form of Cu^{2+} ions. This has not been substantiated and, therefore, the value suggested must be accepted with some reservations.

Values for K_2^o have been calculated on the basis of theoretical considerations, such as thermodynamic values. A value of 1.6×10^{-19} at 291 K was derived in one work (21). Maijs (38) suggested that the value is between 10^{-12} and 10^{-20}, but no temperature was specified. The values suggested by Maijs are rejected because of lack of information as to the basis on which the values were calculated.

There is one report of a value of K_2^o for 348 K (39). The value is 1.26×10^{-20}. The article contains many curves for potentiometric titrations and it

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(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

is not clear exactly which experiments led to the value reported. The work may have been carried out in a way very similar to that of Akselrud and Fialkov (37). pH and copper content values for the solutions are given and apparently were manipulated in the same way. The value for K_2^o is subject to the same reservations as those expressed for the work of Akselrud and Fialkov (37). Because of the uncertainties that have been expressed, the work was not entered on a data sheet.

Because of the instability of the $Cu(OH)_2$-alkali system all values for K_2 or K_2^o are considered to be of questionable merit. More reliable values are to be expected for K_{2a}^o because reaction (2a) reaches a stable equilibrium condition. The value of K_{2a}^o is expected to be smaller than that for K_2^o because CuO is less soluble than $Cu(OH)_2$. Feitknecht (21) calculated a value of 1.0×10^{-20} at 291 K on the basis of free energy data. This is to be compared with the value of 1.6×10^{-19} calculated for K_2^o by the same author.

In one investigation (12) a value for K_{2a}^o was calculated from measurements of the solubility of CuO in HNO_3 solutions at a temperature of about 300 K. An average value of 1.5×10^{-20} was reported but the individual values of K_{2a}^o decreased as the concentration of HNO_3 increased.

The earliest reported value for K_{2a} at 298 K, based on solubility measurements, was 2.24×10^{-20} $mol^3\ dm^{-9}$ (40). The value was obtained by measuring the pH of saturated solutions in equilibrium with both CuO and basic copper(II) perchlorate. The K_{so}^o of the basic copper(II) perchlorate had been evaluated in a separate work. The total ionic strength of the solutions varied from 0.009 to 0.058 mol dm^{-3}. Later a value of 3.09×10^{-20} mol dm^{-3} was reported for K_{2a} at 298 K in solutions having a total ionic strength of 0.2 mol dm^{-3} (36). The use of activity coefficients led to a value of 4.47×10^{-21} for K_{2a}^o at 298 K.

In a third investigation (41) the solubility of CuO was measured in solutions containing NH_3 and varying in pH. The total ionic strength of all solutions was 1.0 mol dm^{-3}. The value of K_{2a} at 298 K calculated from these results was 7.94×10^{-20} $mol^3\ dm^{-9}$.

The above results are all consistent with each other. The value of K_{2a} increases with increasing total ionic strength. The one value of K_{2a}^o at 298 K must, however, be considered tentative because no other work has attempted to duplicate it.

No values, based on solubility data, have been reported for the equilibrium constant of reaction (3).

A value of 10.3×10^{-6} has been suggested for K_{3a}^o at 298 K (6), but the authors considered the copper-containing anion to be $HCuO_2^-$ rather than $Cu(OH)_3^-$.

$$K_{3a}^o = (a_{Cu(OH)_3^-})/(a_{H_2O}) \cdot (a_{OH^-}) \qquad (6)$$

The only other value reported for K_{3a}^o at 298 K is 1.2×10^{-4} (24). This value, however, was based on the solubility of $Cu(OH)_2$ (not CuO) in NaOH solutions. Therefore, the value of McDowell and Johnston (6) is to be preferred and is accepted tentatively.

COMPONENTS:	EVALUATOR:
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(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

The only value for K^o_{4a} based on solubility data is 81 x 10^{-6} at 298 K (6) but here the copper-containing anion is assumed to be CuO_2^{2-} rather than

$$K^o_{4a} = (a_{Cu(OH)_4^{2-}})/(a_{H_2O}) \cdot (a_{OH^-})^2 \qquad (7)$$

$Cu(OH)_4^{2-}$. Feitknecht (16) arrived at a value of 1.6 x 10^{-4} at 291 K. The value was calculated from free energy data and was not based on solubility measurements. A value of 7.6 x 10^{-5} has also been reported for 298 K (24), but this value was based on solubility of the $Cu(OH)_2$-aqueous NaOH system and not for the CuO-aqueous NaOH system. Therefore, the value of 81 x 10^{-6} (6) is to be preferred because it was based on solubility measurements for CuO. The value can only be classified as tentative, at best.

The cation $CuOH^+$ has also been considered to be a solute species in solutions of CuO or $Cu(OH)_2$ in aqueous alkalies. Evidence for this ion was found at 298 K but not at 323 K (42). Its presence has also been suggested by others (22, 43), but in both these reports the experimental evidence for this conclusion is not given in adequate detail.

Solubility in aqueous NH_3

Copper(II) hydroxide. An early attempt to measure the solubility of $Cu(OH)_2$ in solutions of NH_4OH failed to give reproducible results (44). The explanation given was that the solid $Cu(OH)_2$ was not a pure compound but possibly a mixture. Shortly after this attempt a report on the solubility of $Cu(OH)_2$ in NH_4OH solutions was published (45). There is no indication as to the reproducibility of the results, which were obtained at 291 K. The effect of $(NH_4)_2SO_4$ and Na_2SO_4 on the solubility of $Cu(OH)_2$ in NH_4OH was also measured and it was observed that the addition of these salts increased the solubility of $Cu(OH)_2$. The addition of NaOH and $Ba(OH)_2$ either singly or together was found to decrease the solubility of $Cu(OH)_2$ in a given concentration of NH_4OH. Later, Arkhipov and co-workers published several papers dealing with the solubility of $Cu(OH)_2$ in aqueous NH_3, generally at 292-293 K. In one paper (23) a wide range of NH_3 concentrations was used and the solubility values reported are larger than those reported by Dawson (45), Figure 5. In another paper (46) the effect of a series of polyhydroxy compounds on the solubility of $Cu(OH)_2$ in aqueous NH_3 was discussed but no numerical solubility data were given. In the first paper of this series (47) the objective was to ascertain the effect of a variety of compounds, e.g., alcohols, salts, amines, sugars, etc., on the solubility of $Cu(OH)_2$ in aqueous ammonia. The values do not agree with the values reported later (23), Figure 5. The divergence increases as the concentration of NH_3 increases. Arkhipov summarized much of this work in a later paper (48) but presented no new solubility information. The solubility of $Cu(OH)_2$ in aqueous ammonia was investigated by one other group (49), but the results are admittedly qualitative. No numerical data are given nor is any temperature specified.

In summary, there are no reliable data for the solubility of $Cu(OH)_2$ in aqueous ammonia. All the results that have been reported can only be classified as doubtful.

Copper(II) oxide. There are fewer reports on the solubility of CuO in aqueous NH_3 in spite of the fact that CuO is a more stable phase than is $Cu(OH)_2$. One

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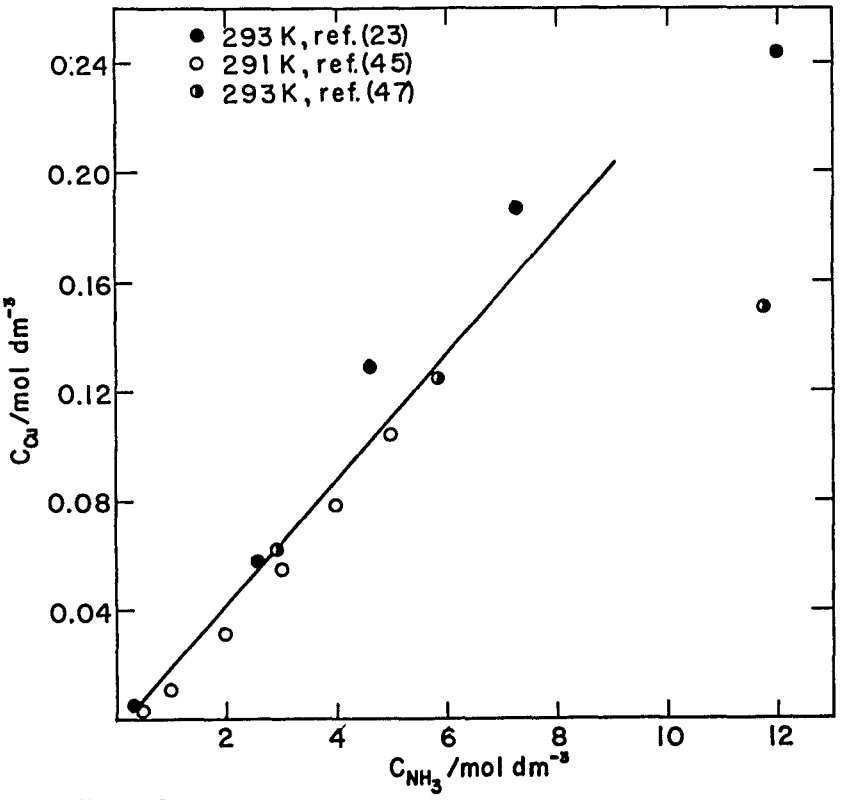

Figure 5. Solubility of $Cu(OH)_2$ in aqueous NH_3.

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(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

study was made at 298 K but no numerical solubility data are included in the report (50). This is also true of the report of Ganz, et al., (51). Only two reports give numerical solubility data for this system (41, 52). The solubility of CuO is much less than that of $Cu(OH)_2$. The solubility was measured at 298 K and is a function of the pH of the solution as well as of the concentration of NH_3 (41). There is one reservation about the pH values reported. The values were obtained by the use of a glass electrode and there is no indication whether corrections were made for the high alkalinity or whether a special high-alkaline glass electrode was used. No data sheet has been made for the work reported in ref. (52) because no temperature is specified and no information is given about the experimental procedure nor about the quality of the materials that were used.

There are no other numerical data for the solubility of CuO in aqueous ammonia. Therefore, the data of Gubeli, et al. (41) can only be classified as tentative.

Solubility in acidic oxides

Chromium oxides. Three investigations have been reported on these systems, but in none of them is any numerical solubility data given. Knoche (53) studied the effect of $Cr(OH)_3$ on the induced solubility of insoluble metal hydroxides in solutions of alkalies. $Cu(OH)_2$ was included in this study and was found to be peptized under these conditions. Hayek (54) investigated the $CuO-CrO_3-H_2O$ system at 313 K. However, his interest was to identify the basic salts that were formed. The study was made in alkaline solutions. This same system has been studied in acidic solutions at 303 K (55). The interest here was primarily in the solid phases that separate from such a system. Some solubility data are given but there is no assurance that the solutions were saturated with respect to CuO.

Phosphorus(V) oxide. Only two investigations have been made of this system. One of these (56) reports a study of the system at 291 and 333 K. The report discusses the solid phases that were formed, but no solubility data are presented. In the other investigation (57) the system was studied at 298 K, but it was studied by using copper phosphate as the solid phase and not CuO or $Cu(OH)_2$. Thus, there is no assurance that the solutions were saturated with respect to either CuO or $Cu(OH)_2$.

Selenium oxides. One investigation was made of the $Cu(OH)_2-SeO_2-H_2O$ system, but only at 373 K (58). The values are classified as tentative because there are no other values with which they can be compared. Baroni (59) studied the $CuO-SeO_3-H_2O$ system at 303 K, but the solubility data are expressed as ratios, e.g., mol H_2O:mol SeO_3, and not as absolute values. Therefore, a solubility table cannot be compiled.

Sulfur oxides. While there are many reports that discuss systems involving CuO or $Cu(OH)_2$ in aqueous solutions of sulfur oxides, they contain very little information about solubility values. Only one paper discusses the system that involves SO_2 (60). This investigation was carried out in connection with a

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(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

study of the leaching of metallic ores. Only a small phase diagram is included. It shows increasing solubility of CuO with increasing concentration of SO_2.

The studies of the $CuO-SO_3-H_2O$ system were motivated primarily by a desire to determine the composition of the solid phases that precipitated from this system. Bell and Taber studied the system at 298 K (61), but the analytical methods are not described nor is there any information about the composition of the original mixtures. Furthermore, no solubility data are included. This same system was studied in the temperature range of 322-473 K (62). The interest, again, was in the composition of the solid phases that were produced, but a few solubility data are also given. Additional solubility data were given in a later paper (63). All the data are shown on Figure 6. Another study of this system was made at 295 K (64). In this study $Cu(OH)_2$ was used as the copper compound rather than CuO. When the SO_3 was introduced as $CuSO_4$ rather then as H_2SO_4, the solubility of $Cu(OH)_2$ was practically unaffected, Figure 7. These results are all consistent with each other. The main difference is the extent of the hydration of the solid phases. This difference is probably related to the relatively imprecise methods of analysis. The values in refs. (62, 63, 64) serve to complement each other. They do not duplicate each other. Therefore all the values in these reports are accepted tentatively.

Solubility in sea water

In spite of the fact that copper compounds are used in marine anti-fouling paints, there are practically no data for the solubility of CuO or $Cu(OH)_2$ in sea water. On the basis of calculations (not on a solubility study) the solubility of $Cu(OH)_2$ in sea water is said to be 2.1×10^{-7} mol dm^{-3} and that of CuO is 1.4×10^{-8} mol dm^{-3} (65). These calculations assumed a value of 5.6×10^{-20} for the solubility product constant of $Cu(OH)_2$, and a value of 0.63 mol dm^{-3} for the ionic strength of sea water. The experimental measurement of the solubility of CuO in Baltic Sea water (66) gave a value of 1.3×10^{-6} mol dm^{-3} at about 290 K. Apparently, the solubility of $Cu(OH)_2$ or CuO in sea water is so small that it is difficult to measure precisely, and the values that have been suggested are not to be considered as reliable.

Solubility under hydrothermal conditions

The solubility of CuO in water under hydrothermal conditions has been measured in connection with a study of the cause of deposits on a high-pressure turbine used in an electric power generator (67). The amounts of CuO that dissolved were very small and there is no information about the analytical procedure that was used to measure these small quantities. In another study of this system (68) lower temperatures and higher pressures were used. The analytical method was described. Hearn, et al. (68) state that their results are almost ten times those of Pocock and Stewart (67). This is difficult to ascertain because the conditions of temperature and pressure are not exactly duplicated in the two papers. Neither set of data can be recommended but that of Hearn, et al. (68) is tentatively accepted at this time because in that work more attention was paid to experimental detail and reproducibility of results.

Marshall and co-workers have investigated complex systems involving $CuO-SO_3$ and other metal oxides, such as NiO (69) and UO_3 (70) at elevated

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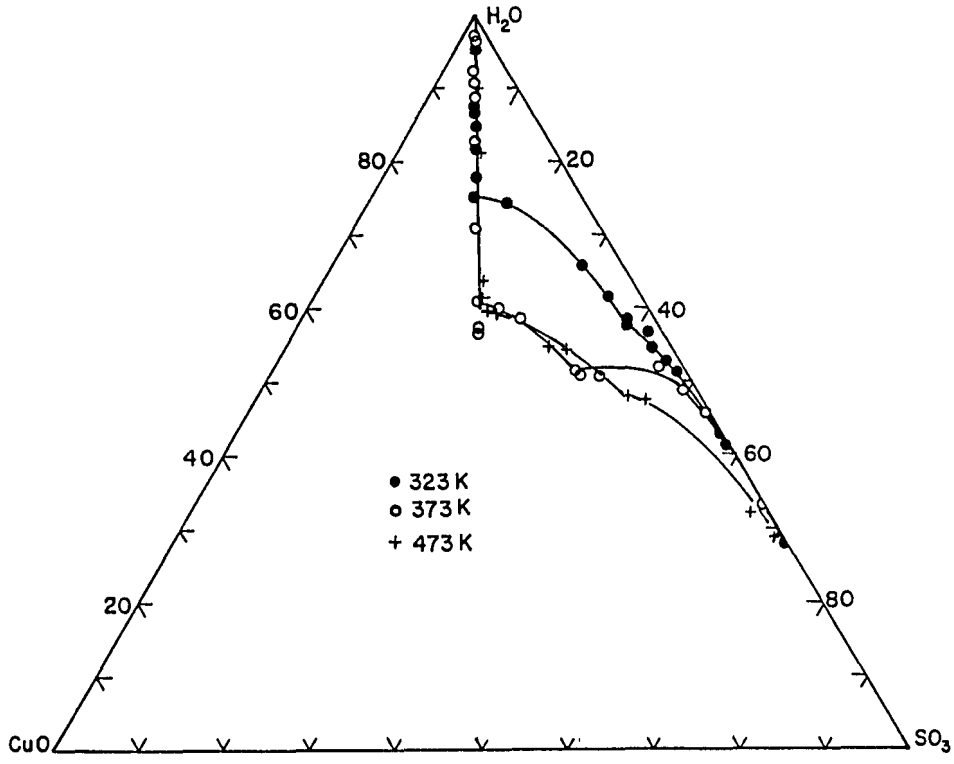
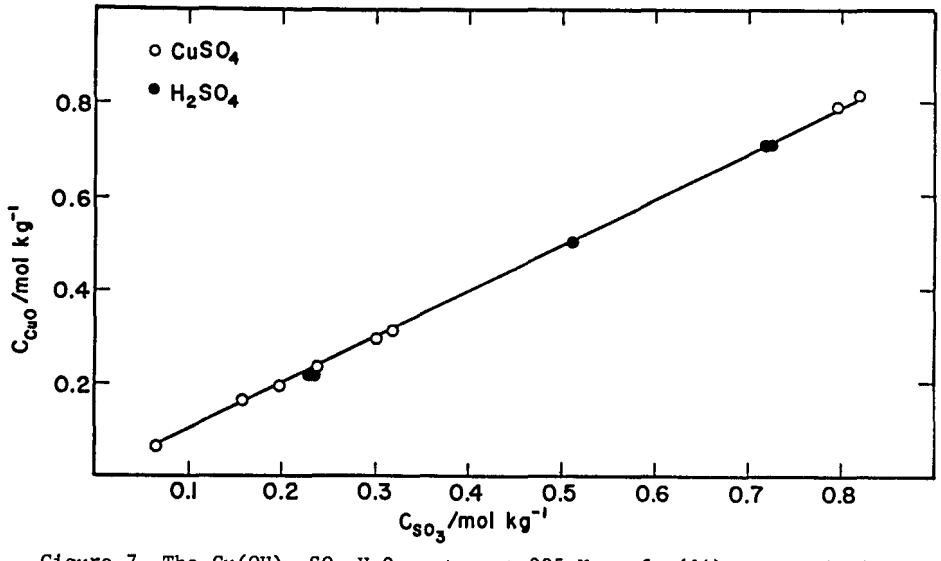


Figure 6. The $CuO-SO_3-H_2O$ system, refs. (62, 63). The scale units are in mass %.



Gigure 7. The $Cu(OH)_2-SO_3-H_2O$ system at 295 K, ref. (64): open circles, SO_3 introduced as $CuSO_4$; closed circles, SO_3 introduced as H_2SO_4.

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(2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]	
(3) Water; H_2O; [7732-18-5]	October 1984

CRITICAL EVALUATION:

temperatures, but they studied the solubility of complex copper compounds rather than CuO in these systems. The tabular data indicate the temperature at which liquid-liquid immiscibility appears but include no analysis of the liquid phases (71).

Because of an interest in the leaching and deposition of minerals in the earth, a study was made of the solubility of CuO in some salt solutions in contact with CO_2 at elevated pressures. The first report (72) contained very few data and there are inconsistencies between data in the text and in the Tables. A more complete report was published later (73). The data in this later report can only be accepted as tentative values because no other work similar to it has been reported.

There is a report of the solubility of $Cu(OH)_2$ in boiling water at 459 and 631 K (74). However, the data are presented only in graphical form and the article includes very few experimental details. The solubility decreases with increasing pH up to a value of pH = 7 and then is constant in the pH range 7 to 12. The solubility in this range is 17 - 25 μg kg^{-1} when the temperature is 631 K and the pressure is about 1.9×10^7 Pa.

The solubility of CuO in aqueous NaOH was measured at temperatures up to 473 K (24). They are the only solubility data reported under such conditions. There is no reason to doubt these values, but because they have not been duplicated they must be classified as tentative. As a result of this work equations are given for the equilibrium constants of reactions (3a) and (4a). They are:

$$\log K_{3a} = \frac{691.74}{T/K} - 1.568 \qquad (8)$$

$$\log K_{4a} = -\frac{558.40}{T/K} - 2.257 \qquad (9)$$

Solubilities in aqueous salt solutions

One investigation has been made of the solubility of CuO in solutions of sodium citrate and sodium oxalate, with and without NaOH (75). The study was made at room temperature. The results that were reported were preliminary and qualitative. One conclusion of the study was that the rate and extent of the dissolution of CuO was controlled by the OH^- ions.

Lamure (76) investigated the $Cu(OH)_2$-$HgCl_2$-H_2O system in the temperature range 290 to 373 K. However, he merely reported the composition of the solid phases that were formed, and included no solubility data.

The system $Cu(OH)_2$-$CuCl_2$-H_2O was studied at 298 and 473 K by Walter-Levy and Goreaud (77, 78), but the only data given in the articles are about the solid phases. No data are given for the liquid phases.

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CRITICAL EVALUATION:

A study has been made of the solubility of $Cu(OH)_2$ in solutions of NaCl and Na_2SO_4 (8) but no experimental details are given and the results are presented only in graphical form.

Solubility in other systems

Solutions of hydrogen peroxide. One report deals with this system and the primary interest appears to have been the isolation of copper(II) peroxides (9). The study was made over the temperature range 237 to 293 K but the copper content of the saturated solutions is given only for two temperatures: 253 and 273 K. Very few experimental details are included. Consequently, the results must be considered doubtful.

Solutions of 2, 2', 2''-nitrilotriethanol (triethanolamine). Only one report discusses this system (79). Only two data are given (for the solubility of CuO) but these are rejected because no temperature is specified, there is no assurance of saturation, and nothing is stated about the quality of the materials that were used.

Table I. Tentative values for equilibria at 298 K.

Reaction	Value
solubility of CuO in H_2O	2.9×10^{-5} mol dm^{-3}
$CuO(s) + H_2O = Cu^{2+} + 2OH^-$	$K^o_{2a} = 4.47 \times 10^{-21}$
$CuO(s) + H_2O + OH^- = Cu(OH)_3^-$	$K^o_{3a} = 10.3 \times 10^{-6}$
$CuO(s) + H_2O + 2OH^- = Cu(OH)_4^{2-}$	$K^o_{4a} = 81 \times 10^{-6}$
$Cu(OH)_2(s) = Cu^{2+} + 2OH^-$	$K^o_2 = K^o_{so} = 4.8 \times 10^{-20}$

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CRITICAL EVALUATION:

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COMPONENTS:	EVALUATOR:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1984

CRITICAL EVALUATION:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Water; H_2O; [7732-18-5]	Remy, H.; Kuhlmann, A. Z. *Anal. Chem.* 1924, *65*, 161-81.
VARIABLES: Method of measuring solubility of CuO in water.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in water.

Method	C_{CuO}/mg dm^{-3}	C_{CuO}/mol dm^{-3}
conductimetric titration	5.46	6.86×10^{-5}
specific conductance	5.39	6.77×10^{-5}

One of the purposes of this work was to devise a method to correct the measured specific conductance for the presence of CO_2. A Table was constructed to give these corrections for various conditions. The specific conductance was measured at 19.2°C, but was corrected to 18°C to calculate the solubility of CuO. Because of these corrections, the solubility determined from specific conductance measurements must be considered the less accurate of these two values.

The solubility value determined from a conductimetric titration has the disadvantage that small volumes and dilute solutions were used. There is at least a 1% uncertainty in these values.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Hot CuO was added to conductivity water. The mixture was shaken, and after shaking for about 3 hours the electrical conductivity became constant. The specific conductance was measured, corrected for the presence of CO_2, and the solubility of CuO was calculated from this value and the accepted literature values for individual ionic conductances. The above saturated solution was filtered and subjected to a conductimetric titration. The solution was first titrated with dilute H_2SO_4 and then back titrated with dilute KOH. From these values, the OH^- ion content and the solubility of CuO were calculated.	Conductivity water was used. The CuO was prepared by dissolving recrystallized pure $Cu(NO_3)_2$ in conductivity water, adding NH_4OH, carefully washing the precipitate, and then heating the precipitate.
	ESTIMATED ERROR: No details are given. The temperature varied from 19.0 to 21.3°C during the measurements.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Baltic Sea water.	Ragg, M. *Farbe u. Lack* 1950, *56*, 435-41.
VARIABLES: None.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES:

The solubility of CuO in Baltic Sea water is 0.08 mg dm^{-3}, i.e., 1.3×10^{-6} mol dm^{-3}[a]. The weight is that of copper and not of the oxide.

The article also gives solubility values for other compounds that are used in marine anti-fouling paints. The solubilities of these compounds is expressed as the weight of the metal dm^{-3}. For some of these other determinations the pH of the Baltic Sea water was 8.1, for some the temperature was 15°C, for others it was 18°C. Nothing specific is said about the temperature and the pH of the Baltic Sea water in which the solubility of CuO was measured.

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
One-half gram of CuO was added to filtered Baltic Sea water and the mixture was shaken for several hours until equilibrium was attained. After filtration, the copper content of the filtrate was determined, but the analytical method is not described. The temperature was probably either 15 or 18°C.	No indication is given.
	ESTIMATED ERROR: No details are given.
	REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

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

ORIGINAL MEASUREMENTS:

Pocock, F. J.; Stewart, J. F. *J. Eng. Power* 1963, *85*, 33-45.

VARIABLES:

Temperature and pressure of the steam.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of CuO in supercritical steam, pH = 7.5

Pressure/psig	temp/°F[a]	C_{Cu}/ppb
4500	1090	2.4
4500	994	5.8
1850	907	0.5
1850	931	-0.4[b]
2700	1006	2.9
3200	1053	2.9
4500	1153	18.4
4500	1143	15.2
1850	911	0.9
4500	1035	6.2
4500	1068	6.3
4500	1005	8.2
4500	976	11.5
4500	1152	12.3
3900	1136	11.3
4500	963	11.8
4500	1150	15.6
2700	1134	3.3

[a] Average temperature during the entire procedure.

[b] The authors suspect the blank correction was too large.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of CuO were placed in a stainless steel autoclave and the superheated steam was passed through the autoclave at the desired pressure. Sampling was continued until 3 liters of condensate had passed through the sample. This required 2.5 to 3 hours. Blank runs were made to measure the amount of copper extracted from the metal in the apparatus under the test conditions. The method used to determine copper content is not mentioned. Additional runs were made to ensure that equilibrium conditions had been attained.

SOURCE AND PURITY OF MATERIALS:

CuO was a reagent grade material that was washed with deionized water to free it of fines. The feedwater was demineralized and deaerated. Some NH_4OH was added to raise the pH.

ESTIMATED ERROR:

No details are given

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO, [1317-38-0]

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

ORIGINAL MEASUREMENTS:

Pocock, F. J.; Stewart, J. F. *J. Eng. Power* 1963, *85*, 33-45.

EXPERIMENTAL VALUES: Solubility of CuO in supercritical steam, pH ∿ 9.5.

Pressure/psig	temp/°F[a]	C_{Cu}/ppb
1750	904	-1.5[b]
2700	1015	1.1
3200	1033	4.0
2700	1135	4.2
3300	1161	12.9
4500	1164	17.1
4500	1144	15.1
4500	1159	17.0
4500	1007	23.0
4500	1053	21.1
4500	927	14.9
4500	1012	15.9
2700	1158	5.4
4500	1126	17.6
4500	898	18.4
4500	1063	13.0
4500	1089	20.2

[a] Average temperature during the procedure.

[b] This is considered to be due to too large a blank correction.

After the experiments had been concluded, an X-ray diffraction pattern was taken of the solid phase. This indicated that Cu_2O was present, possibly due to reduction of CuO by H_2 formed as a result of corrosion of the stainless steel.

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Jenkins, S. H.; Keight, D. G.; Humphreys, R. E. *Air Water Pollution* 1964, *8*, 537-56.

VARIABLES:

Source of the water.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Table I. Solubility of $Cu(OH)_2$ in distilled water.[a]

Sample number	1	2	3	4	5	6
C_{Cu}/ppm	0.22	0.19	0.18	0.25	0.13	0.16

[a] No temperature is given. The results are those obtained after four extractions.

Table II. Solubility of $Cu(OH)_2$ in CO_2-free distilled water.[a]

Sample number	1	2	3
pH of solvent	6.20	6.20	6.20
pH of sln	7.20	7.13	7.09
C_{Cu}/ppm	0.23	0.23	0.39
t/°C	18.8	18.8	18.8

[a] These results are for the eighth, and final, extraction.

Table III. Solubility of $Cu(OH)_2$ in Birmingham tap water.[a]

Number of extractions	pH of water	t/°C	Sample 1 pH	Sample 1 C_{Cu}/ppm	Sample 2 pH	Sample 2 C_{Cu}/ppm	Sample 3 pH	Sample 3 C_{Cu}/ppm
10	7.25	22.0	7.88	0.31	7.95	0.27	7.90	0.22
11	7.60	20.0	7.58	0.12	7.68	0.12	7.41	0.25
12	7.41	20.0	8.03	0.25	7.92	0.31	7.82	0.27
13	7.72	17.0	7.53	0.06	7.59	0.04	7.50	0.06
14	7.60	16.5	7.56	0.12	7.62	0.15	7.59	0.15
15	7.20	17.5	7.25	0.19	7.50	0.23	7.18	0.26
16	7.00	19.0	7.25	0.19	7.30	0.15	7.30	0.17
17	7.52	19.5	7.58	0.19	7.51	0.23	7.50	0.19

[a] After several washings the brown cupric hydroxide began to turn black.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The $Cu(OH)_2$ was washed several times, then added to the water. The mixtures were shaken mechanically, but there is no indication as to how long they were shaken. After some time was allowed for settling, the mixtures were filtered through a Millipore HA filter. Further extractions were made by adding more water and repeating the process for each such extraction. The copper content of the filtrate was determined colorimetrically using the bis-cyclohexanone oxalyldihydrazone (1).

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was of reagent grade quality. Distilled water and Birmingham (England) tap water were used as solvents.

ESTIMATED ERROR:

No details are given but from the results given in the paper it appears that the average deviation from the mean value was about 15%.

REFERENCES:

1. Williams, T. R.; Morgan, R. R. T. *Chem. & Ind. (Rev.)* 1954, *16*, 461.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

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

ORIGINAL MEASUREMENTS:

Hearn, B.; Hunt, M. R.; Hayward, A. *J. Chem. Eng. Data* 1969, *14*, 442-7.

VARIABLES:

Temperature and pressure of the water.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in superheated steam.

t/°C	p/psig	$C_{Cu}/10^{-6}$ g kg^{-1}
57 ± 1	1730 ± 25	12.4 ± 0.3
69 ± 2	1200 ± 100	16 ± 2
81 ± 2	1100 ± 100	23 ± 2
87 ± 2	3830 ± 25	23.5 ± 1
88 ± 1	3850 ± 15	21.5 ± 1
89 ± 1	3950 ± 75	17 ± 1
110 ± 2	3300 ± 80	23.5 ± 1
117 ± 2	3700 ± 45	29 ± 1
121 ± 2	3520 ± 40	38 ± 1
122 ± 3	3450 ± 65	23 ± 1
133 ± 2	1200 ± 100	26 ± 1
154 ± 2	1200 ± 100	52 ± 2
181 ± 2	2640 ± 35	198 ± 5
187 ± 1	2005 ± 20	143 ± 3
207 ± 3	1900 ± 100	212 ± 2
232 ± 1	3025 ± 30	281 ± 5
234 ± 2	3870 ± 45	289 ± 6
249 ± 2	2900 ± 100	360 ± 4
252 ± 1	3020 ± 35	391 ± 5
260 ± 1	3780 ± 55	393 ± 7
260 ± 1	3900 ± 115	378 ± 8
260 ± 2	4135 ± 30	395 ± 5
273 ± 2	3200 ± 50	444 ± 10

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

About 500 g of CuO was placed in the equilibrator, which was then flushed with cold water to remove fine particles of CuO. Steam at the prescribed temperature and pressure was passed through the equilibrator After it had passed through the equilibrator the steam was condensed and about 450 ml was taken for analysis, which was done colorimetrically, using CCl_4 and dibenzyldithiocarbamate (1).

SOURCE AND PURITY OF MATERIALS:

The water was deionized, distilled and deaerated. No information is given about the CuO.

ESTIMATED ERROR:

The copper analysis had a standard deviation of 0.15 to 0.7 μg of Cu kg^{-1}.

REFERENCES:

1. Wilson, A. L. *Analyst* 1962, *87*, 884.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

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

ORIGINAL MEASUREMENTS:

Hearn, B.; Hunt, M. R.; Hayward, A. *J. Chem. Eng. Data* 1969, *14*, 442-7.

EXPERIMENTAL VALUES, contd.

t/°C	p/psig	$C_{Cu}/10^{-6}$ g kg^{-1}
291 ± 1	4055 ± 20	503 ± 5
298 ± 2	3225 ± 50	516 ± 6
307 ± 2	4200 ± 100	547 ± 10
322 ± 3	3270 ± 40	610 ± 32
331 ± 2	4200 ± 35	600 ± 6
350 ± 1	4000 ± 65	462 ± 10
350 ± 1	6000 ± 65	570 ± 10
374 ± 4	3500 ± 65	234 ± 10
379 ± 2	3950 ± 100	137 ± 6
376 ± 2	4000 ± 100	194 ± 6
389 ± 1	4055 ± 15	233 ± 8
389 ± 1	3995 ± 20	227 ± 8
381 ± 2	4000 ± 65	331 ± 10
378 ± 2	4500 ± 65	337 ± 10
381 ± 2	5000 ± 65	320 ± 10
381 ± 2	5500 ± 65	350 ± 10
382 ± 2	6000 ± 65	486 ± 10
386 ± 2	4050 ± 100	89 ± 6
388 ± 2	4600 ± 100	151 ± 6
401 ± 1	4305 ± 20	117 ± 1
408 ± 2	4925 ± 40	129 ± 1
401 ± 3	5100 ± 100	170 ± 1
401 ± 2	5000 ± 65	182 ± 1
405 ± 1	5375 ± 30	214 ± 1
405 ± 1	6070 ± 25	406 ± 6
420 ± 2	3840 ± 60	46 ± 1
422 ± 1	4035 ± 50	90 ± 1
421 ± 2	4435 ± 50	64 ± 1
440 ± 2	4970 ± 65	92 ± 1
430 ± 1	5060 ± 45	100 ± 1
431 ± 2	5500 ± 65	153 ± 2
434 ± 2	6000 ± 130	315 ± 5
440 ± 1	3455 ± 30	77 ± 1
448 ± 2	5990 ± 105	299 ± 2
460 ± 2	3500 ± 80	56 ± 1
460 ± 1	3500 ± 65	81 ± 1
455 ± 2	4010 ± 75	101 ± 1
469 ± 2	4520 ± 65	80 ± 1
468 ± 2	5060 ± 45	108 ± 2
463 ± 2	5490 ± 75	139 ± 4
462 ± 2	6000 ± 115	126 ± 4
461 ± 2	6050 ± 70	184 ± 6
497 ± 1	3465 ± 50	113 ± 1
497 ± 1	4065 ± 25	121 ± 1
502 ± 1	4465 ± 40	145 ± 1
501 ± 2	5045 ± 30	148 ± 1
500 ± 2	5425 ± 40	138 ± 2
503 ± 2	5980 ± 95	178 ± 2
550 ± 1	3530 ± 45	115 ± 1
550 ± 1	4050 ± 35	100 ± 1
551 ± 2	4575 ± 35	133 ± 1
551 ± 1	5050 ± 40	165 ± 1
550 ± 1	5510 ± 35	172 ± 2
550 ± 1	5980 ± 40	159 ± 2

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Melbye, G. S. *Medd. Vetenskapakad. Nobelinst.* 1922, *4*,1-11.

VARIABLES:

Concentration of NaOH at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ [a] in aqueous NaOH at room temperature.

C_{NaOH}/equiv dm^{-3}	$C_{Cu(OH)_2}$/equiv dm^{-3}
2.65	0.028
2.75	0.030
3.25	0.058
3.45	0.058
4.15	0.088
4.80	0.108
5.10	0.127
5.15	0.143
5.35	0.135
5.45	0.154
5.75	0.166
5.80	0.181
6.00	0.187
6.60	0.195
7.1	0.238

[a] This is an equilibrium involving a metastable solid, possibly $Cu(OH)_2$. The solubility values reported for $Cu(OH)_2$ are the largest values obtained in replicate determinations.

The data in the above Table can be expressed as follows:

$$C_{Cu(OH)_2} = 0.0450 \cdot C_{NaOH} - 0.095$$

This equation agrees with the data to within 1.4%.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A solution of $CuSO_4$ was very slowly titrated down a glass rod into a NaOH solution. Care was taken to avoid the formation of a precipitate in the solution. This titration was carried out until the solution became turbid. The solution was then allowed to stand before being filtered. The aim was to dissolve the $Cu(OH)_2$ as it formed rather than by dissolution of solid $Cu(OH)_2$. A sample of the filtrate was diluted to about 1/25 with CO_2-free water. The precipitate was filtered off, dissolved in HCl and then titrated iodometrically to determine the copper content. The NaOH content of the filtrate was determined by titration. The work was all carried out at room temperature, about 22°C.

SOURCE AND PURITY OF MATERIALS:

No details are given.

ESTIMATED ERROR:

The titration values for NaOH have an uncertainty of about 0.025 equiv dm^{-3}.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Muller, E. *Z. Physik. Chem.* 1923, *105*, 73-118.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of CuO in aqueous NaOH at 18°C.

C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}	C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}
7.55	0.0036	16.63	0.0229
10.00	0.0075	17.04	0.0132
12.00	0.0127	17.41	0.0302
13.54	0.0167	17.98	0.0291
14.85	0.0197	18.92	0.0115
15.22	0.0191	19.05	0.0119
15.88	0.0214	19.32	0.0112
16.20	0.0246	20.01	0.0098

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The CuO was added to the NaOH solutions and the mixtures were shaken at least 5 weeks at the prescribed temperature. The liquid phase was separated from the solid phase by filtering or by centrifuging. The copper content of the liquid phase was determined by electrolysis.

SOURCE AND PURITY OF MATERIALS:

The NaOH was prepared from metallic sodium. The CuO was prepared by heating $Cu(OH)_2$ at 300°C.

ESTIMATED ERROR:

Nothing is stated, and no duplicate results are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO, [1317-38-0]
(2) Sodium hydroxide, NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Muller, E. *Z. Physik. Chem.* 1923, *105*, 73-118.

EXPERIMENTAL VALUES, cont'd.

Table II. Solubility of CuO in aqueous NaOH at 70°C.

C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}	color of solid phase
11.79	0.0167	black
12.79	0.0219	"
14.13	0.0319	"
14.94	0.0377	"
16.75	0.0471	"
19.28	0.0167	"
19.37	0.0138	blue
20.52	0.0098	"

Table III. Solubility of CuO in aqueous NaOH at 80°C.

C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}
7.55	0.0067
10.00	0.0155
12.00	0.0243
13.54	0.0349
14.88	0.0411
16.20	0.0555

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Muller, E. *Z. Physik. Chem.* 1923, *105*, 73-118.

VARIABLES:

Concentration of NaOH at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of $Cu(OH)_2$ in aqueous NaOH.[a]

C_{NaOH}/mol dm^{-3}	days of shaking	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [b]
12.36	2	2.98	0.0469
	8	2.26	0.0356
	37	1.52	0.0239
	76	1.22	0.0192
	83	1.20	0.0189
9.80	2	3.06	0.0482
	8	1.60	0.0252
	37	0.62	0.0098
	76	0.78	0.0123
	84	0.78	0.0123
6.85	2	1.42	0.0223
	8	0.64	0.0101
	38	0.54	0.0085
	84	0.37	0.0058
3.94	2	0.72	0.0113
	8	0.31	0.0049
	38	0.18	0.0028
	84	0.13	0.0020

[a] No temperature is mentioned but from the rest of the article the temperature appears to have been around 18°C.
[b] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were shaken at the prescribed temperature. The filtrate was separated from the solid phase by filtering or by centrifuging. The copper content of the filtrate was determined by electrolysis.

SOURCE AND PURITY OF MATERIALS:

The NaOH was prepared from metallic sodium. The $Cu(OH)_2$ was a commercially available product which was stirred thoroughly with a 5% NaOH solution, then diluted with water, filtered, washed and dried.

ESTIMATED ERROR:

Nothing is said about this and there is no indication as to how reproducible the results were.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Muller, E. *Z. Physik. Chem.* 1923, *105*, 73-118.

EXPERIMENTAL VALUES, contd.

In the span of time during which the mixtures were shaken, the solid phase, which was blue originally, changed to a brownish-black color. Much of the paper then deals with the mechanism of this process. The rate of loss of copper from the solution increased with increasing temperature. The conclusion of all the work is that the $Cu(OH)_2$ in contact with the NaOH solutions undergoes a change forming solid solutions of CuO with $Cu(OH)_2$. The composition of this solid solution is dependent on the concentration of copper in the liquid phase. The process does not form CuO as the end product. The author does not arrive at a completely satisfying (to himself) explanation or mechanism for this process. But the fact raises questions as to what solid is in equilibrium with the saturated solution. This question suggests that there may be various values given for the composition of solutions "saturated" with $Cu(OH)_2$.

The following results were obtained in an effort to determine the solubility of $Cu(OH)_2$ (before decomposition sets in).
The experiments were carried out very quickly and copper determinations were made only when - as shown by color - the solid phase had undergone no change.

Table II. Solubility of $Cu(OH)_2$ in aqueous NaOH at 18°C.

C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}	C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}
6.09	0.041	4.62	0.019
6.96	0.061	6.97	0.059
7.60	0.076	9.23	0.130
8.86	0.121	12.94	0.308
10.3	0.197	15.19	0.328
10.8	0.216	17.78	0.028[c]
12.2	0.248		
13.9	0.302		
15.5	0.087[c]		
18.1	0.013[c]		

[c] In these mixtures the solid phase remained blue. It was later identified as Na_2CuO_2.

Table III. Solubility of $Cu(OH)_2$ in concentrated solutions of NaOH at 18°C.

C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3} sample 1	sample 2
16.82	0.0821	0.0799
17.37	0.0788	0.0821
17.94	0.0651	0.0659
18.37	0.0322	0.0308
18.46	0.0243	0.0229
18.91	0.0212	0.0217
19.63	0.0201	- - - -

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Jellinek, K.; Gordon, H. *Z. Physik. Chem.* 1924, *112*, 207-49.

VARIABLES:

Concentration of NaOH at 19°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of freshly prepared $Cu(OH)_2$.

t/°C	e.m.f./mV	$C_{Cu^{2+}}$/mol dm^{-3} [a]	C_{OH^-}/mol dm^{-3}	$C_{Cu^{2+}} \cdot (C_{OH^-})^2$ [a]
19	-265	7.7×10^{-12}	0.156	1.9×10^{-13}
19	-252	2.2×10^{-11}	0.117	2.9×10^{-13}
19	-262	9.8×10^{-12}	0.0817	6.5×10^{-14}
19	-246	3.5×10^{-11}	0.0789	2.2×10^{-13}
19	-252	2.2×10^{-11}	0.0824	1.5×10^{-13}
19	-242	4.8×10^{-11}	0.0483	1.1×10^{-13}
19	-227	1.6×10^{-10}	0.0208	6.8×10^{-14}
19	-207	7.7×10^{-10}	0.0168	2.2×10^{-13}
19	-183	5.2×10^{-9}	0.0065	2.2×10^{-13}

The average value for K_s^o is 1.7×10^{-13} mol^3 dm^{-9}

[a] These values have been recalculated by the compiler.

Attempts were also made to determine K_s^o for CuO using the same experimental approach as used in the Table above, but the measured e.m.f. values were not constant.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A suspension of $Cu(OH)_2$ in water was added to a measured amount of NaOH solution. The mixture was stirred one hour under a N_2 atmosphere. Then a Cu electrode was inserted in the solution and its potential was measured vs a calomel electrode. This e.m.f. was compared to that of a Cu electrode in a 0.05 mol dm^{-3} $CuSO_4$ solution (assumed to be 40% dissociated). The concentration of copper ion was calculated from this comparison as follows:

$$0.008 - \text{e.m.f.} = 0.029 \log (0.02)/[Cu^{2+}]$$

The OH^- ion concentration was determined by titration and it was assumed that the NaOH was completely dissociated. No corrections were made for junction potentials.

SOURCE AND PURITY OF MATERIALS:

The purest available materials were used. $Cu(OH)_2$ was prepared by adding aqueous NaOH to a solution of $CuSO_4$. The precipitate was washed 7 times with water. Care was taken to exclude CO_2 in all procedures.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Sulfuric acid; H_2SO_4; [7664-93-9]

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

ORIGINAL MEASUREMENTS:

Posnjak, E.; Tunell, G. *Am. J. Sci.* 1929, *18*, 1-34.

VARIABLES:

Concentration of H_2SO_4 in the temperature range 50-200°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of CuO in H_2SO_4 solutions at 200°C.

C_{CuO}/mass %	C_{SO_3}/mass %	C_{CuO}/mol kg^{-1} [a]	C_{SO_3}/mol kg^{-1} [a]	Solid phase [b]
0.02	0.05	0.0025	0.0062	A
0.17	0.30	0.021	0.038	"
2.37	2.96	0.315	0.391	"
4.57	5.58	0.639	0.776	"
8.58	10.08	1.33	1.55	"
11.93	13.03	2.00	2.16	"
17.16	18.94	3.38	3.70	"
18.46	19.83	3.76	4.01	A + B
18.72	21.65	3.95	4.54	B
18.02	22.73	3.82	4.79	"
14.36	30.99	3.30	7.08	"
13.36	33.36	3.15	7.82	"
8.21	43.62	2.14	11.3	"
6.35	45.81	1.67	12.0	"
2.14	65.48	0.831	25.3	"
1.00	70.00	0.434	30.1	C

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = $3CuO \cdot SO_3 \cdot 2H_2O$; B = $CuO \cdot SO_3 \cdot H_2O$; C = $CuO \cdot SO_3$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were sealed in combustion tubes and placed in an air thermostat at 50 ± 1°C for at least a year. At higher temperatures the tubes were heated in steel bombs kept at 100 ± 3°C for at least 4 months, or kept at 200 ± 7°C for at least 2 weeks. After equilibration, the mixtures were filtered through an alundum filtration crucible. The copper content was determined electrolytically and the SO_3 content was determined gravimetrically as $BaSO_4$.

SOURCE AND PURITY OF MATERIALS:

The CuO was prepared by adding dilute NaOH to a solution of $CuSO_4$. The precipitate was washed with hot water. No information is given about the purity or quality of the H_2SO_4 or of the water.

ESTIMATED ERROR:

Nothing is stated about the reproducibility of the results.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Copper(II) oxide; CuO; [1317-38-0] (2) Sulfuric acid; H_2SO_4; [7664-93-9] (3) Water; H_2O; [7732-18-5]	Posnjak, E.; Tunell, G. *Am. J. Sci.* 1929, *18*, 1-34.

EXPERIMENTAL VALUES, contd:

Table II. Solubility of CuO in H_2SO_4 solutions at 100°C.

C_{CuO}/mass %	C_{SO_3}/mass %	C_{CuO}/mol kg^{-1} [a]	C_{SO_3}/mol kg^{-1} [a]	Solid phase [b]
0.38	0.40	0.048	0.050	A
0.71	0.80	0.091	0.101	"
1.16	1.24	0.149	0.159	"
1.46	1.58	0.189	0.204	"
3.69	3.87	0.502	0.523	"
4.56	4.72	0.632	0.650	"
5.55	5.73	0.786	0.807	"
5.61	5.81	0.796	0.819	"
8.62	8.69	1.31	1.31	"
14.57	14.82	2.59	2.62	"
19.35	19.70	3.99	4.04	"
21.07	21.44	4.61	4.66	A + D
21.14	21.52	4.64	4.72	D
21.37	21.74	4.72	4.77	D + E
17.92	22.73	3.80	4.78	E
15.89	25.44	3.41	5.42	"
12.60	31.40	2.83	7.00	B + E
12.78	30.81	2.85	6.82	"
10.49	33.67	2.36	7.53	B
2.92	45.04	0.705	10.8	"
1.64	49.20	0.419	12.5	"
0.84	53.60	0.232	14.7	"
0.29	66.20	0.109	24.7	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = $3CuO \cdot SO_3 \cdot 2H_2O$; B = $CuO \cdot SO_3 \cdot H_2O$; C = $CuO \cdot SO_3$; D = $3CuO \cdot 2SO_3 \cdot 5H_2O$; E = $CuO \cdot SO_3 \cdot 3H_2O$.

Table III. Solubility of CuO in H_2SO_4 solutions at 50°C.

C_{CuO}/mass %	C_{SO_3}/mass %	C_{CuO}/mol kg^{-1} [a]	C_{SO_3}/mol kg^{-1} [a]	Solid phase [b]
7.53	7.57	1.12	1.10	A
8.98	9.06	1.38	1.38	"
9.88	9.97	1.55	1.56	"
10.98	11.02	1.77	1.76	"
10.98	11.08	1.77	1.78	"
12.44	12.52	2.08	2.08	A + F
9.34	16.12	1.55	2.66	F
4.74	29.28	0.903	5.54	"
3.83	34.46	0.780	6.97	"
3.53	37.58	0.754	7.97	E
1.80	41.45	0.399	9.12	B
1.09	47.43	0.266	11.5	"
0.23	56.81	0.067	16.5	"
0.22	57.11	0.065	16.7	"
0.16	71.42	0.071	31.4	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = $3CuO \cdot SO_3 \cdot 2H_2O$; B = $CuO \cdot SO_3 \cdot H_2O$; E = $CuO \cdot SO_3 \cdot 3H_2O$; F = $CuO \cdot SO_3 \cdot 5H_2O$.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Sulfuric acid; H_2SO_4; [7664-93-9]

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

ORIGINAL MEASUREMENTS:

Tunell, G.; Posnjak, E. *J. Phys. Chem.* 1931, 35, 929-46.

VARIABLES:

Concentrations of H_2SO_4 at 50°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in H_2SO_4 solutions at 50°C.

C_{CuO}/mass %	C_{SO_3}/mass %	C_{CuO}/mol kg^{-1} [a]	C_{SO_3}/mol kg^{-1} [a]	Solid phase [b]
0.05	0.05	0.0063	0.0063	A
0.13	0.13	0.0164	0.0163	"
2.20	2.22	0.289	0.290	A + B
4.73	4.75	0.657	0.655	"
5.93	5.96	0.846	0.845	"
6.52	6.57	0.943	0.944	"
3.28	38.50	0.708	8.26	C
2.35	43.04	0.541	9.84	D
1.54	45.40	0.365	10.7	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = $4CuO \cdot SO_3 \cdot 3H_2O$; B = $3CuO \cdot SO_3 \cdot 2H_2O$; C = $CuO \cdot SO_3 \cdot 3H_2O$; D = $CuO \cdot SO_3 \cdot H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were sealed in Jena combustion tubes and placed in an air thermostat at 50 ± 1°C for one to three years. The mixtures were shaken daily. After equilibration, the mixtures were filtered through a dense Jena glass filter. The copper content was determined by electrolysis and the SO_3 content was determined gravimetrically as $BaSO_4$.

SOURCE AND PURITY OF MATERIALS:

CuO was prepared by adding dilute NaOH to a solution of $CuSO_4$. The precipitate was washed with hot water. Nothing is stated about the other materials.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Sulfuric acid; H_2SO_4; [7664-93-9]

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

ORIGINAL MEASUREMENTS:

Binder, O. *Ann. Chim.* (11) 1936, 5, 337-409.

VARIABLES:

Concentration of H_2SO_4 at 22°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in H_2SO_4 solutions at 22°C.

C_{SO_3}/mass%	C_{CuO}/mass%	C_{H_2O}/mass%	C_{SO_3}/mol kg^{-1} [a]	C_{CuO}/mol kg^{-1} [a]	Solid phase [b]
1.82	1.68	96.50	0.236	0.219	A
1.79	1.67	96.54	0.232	0.217	"
1.79	1.69	96.52	0.232	0.220	"
3.79	3.69	92.52	0.512	0.501	"
3.78	3.68	92.54	0.510	0.500	"
3.77	3.66	92.57	0.509	0.497	"
5.16	5.07	89.77	0.718	0.710	"
5.15	5.05	89.80	0.716	0.707	"
5.20	5.06	89.74	0.724	0.709	"
7.19	7.04	85.77	1.05	1.03	"
7.22	7.05	85.73	1.05	1.03	"
7.29	7.11	85.60	1.06	1.04	"
8.20	8.12	83.68	1.22	1.22	"
8.28	8.14	83.58	1.24	1.22	"
8.43	8.30	83.27	1.26	1.25	"
8.94	8.77	82.29	1.36	1.34	A + B
8.90	8.77	82.33	1.35	1.34	"
8.93	8.77	82.30	1.36	1.34	"
10.95	7.59	81.46	1.68	1.17	B
11.32	7.87	80.91	1.75	1.22	"
12.03	7.26	80.71	1.86	1.13	"
13.21	6.53	80.26	2.06	1.02	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cu(OH)_2$ and sulfuric acid solutions were mixed and shaken frequently in a thermostat until the copper concentration in the liquid phase became constant. The mixtures were then filtered through a glass frit and analyzed. Copper analysis was by electrolytic deposition. Sulfate was determined gravimetrically as $BaSO_4$.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding NH_4OH to aqueous $CuSO_4$ only in a quantity sufficient to dissolve the precipitate that formed. The solution was cooled to 0°C and added gradually to a solution of NaOH. The precipitate was washed with water until it was free of sulfate ions, then with alcohol, and finally with ether. It was dried in a vacuum. No other details are given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide, $Cu(OH)_2$; [20427-59-2]

(2) Sulfuric acid, H_2SO_4; [7664-93-9]

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

ORIGINAL MEASUREMENTS:

Binder, O. *Ann. Chim.* (*11*) 1936, 5, 337-409.

EXPERIMENTAL VALUES con'td:

Solubility of $Cu(OH)_2$ in H_2SO_4 solutions at 22°C.

C_{SO_3}/mass%	C_{CuO}/mass%	C_{H_2O}/mass%	C_{SO_3}/mol kg^{-1} [a]	C_{CuO}/mol kg^{-1} [a]	Solid phase [b]
15.23	5.72	79.05	2.41	0.910	B
17.07	5.21	77.72	2.74	0.843	"
17.54	4.92	77.54	2.83	0.798	"
20.09	4.08	75.83	3.31	0.676	"
22.54	3.54	73.92	3.81	0.602	"
24.26	3.07	72.67	4.17	0.531	"
26.31	2.49	71.20	4.62	0.440	"
27.54	2.09	70.37	4.89	0.373	"
28.62	1.79	69.59	5.14	0.323	"
32.21	1.29	66.50	6.05	0.244	"
34.26	1.26	64.48	6.64	0.246	"
37.36	1.26	61.38	7.60	0.258	"
39.29	1.24	59.47	8.25	0.262	"
40.25	1.23	58.52	8.59	0.264	"
42.13	1.19	56.68	9.28	0.264	"
42.25	1.17	56.58	9.33	0.260	"
44.08	1.12	54.80	10.05	0.257	C
45.16	0.82	54.02	10.44	0.191	"
46.61	0.79	52.60	11.07	0.189	"
48.31	0.73	50.96	11.84	0.180	"
49.02	0.75	50.23	11.78	0.188	D
51.52	0.09	48.39	13.30	0.023	"
54.22	0.08	45.70	14.82	0.022	"
57.28	0.09	42.63	16.78	0.027	"
63.34	0.07	36.59	21.62	0.024	"
67.49	0.06	32.45	25.98	0.023	"
72.00	0.09	28.91	31.11	0.039	D + E
72.52	0.12	27.36	33.11	0.055	E
74.02	0.13	25.85	35.77	0.063	"
75.29	0.11	24.60	38.23	0.056	"
76.52	0.19	23.29	41.04	0.083	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] A = $SO_3 \cdot 4CuO \cdot 4H_2O$, B = $SO_3 \cdot CuO \cdot 5H_2O$; C = $SO_3 \cdot CuO \cdot 3H_2O$; D = $SO_3 \cdot CuO \cdot H_2O$; E = $SO_3 \cdot CuO$.

Some work was also done at 100°C but the solubility data obtained at that temperature are not included in the article.

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Copper(II) sulfate; $CuSO_4$; [7758-98-7]

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

ORIGINAL MEASUREMENTS:

Binder, O. *Ann. Chim.* (*11*) 1936, 5,337-409.

VARIABLES:

Concentration of $CuSO_4$ at 22°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous $CuSO_4$ at 22°C.

C_{SO_3}/mass%	C_{CuO}/mass%	C_{H_2O}/mass%	solid phase	C_{SO_3}/mol kg^{-1} [a]	C_{CuO}/mol kg^{-1} [a]
5.80	5.72	88.47	$SO_3 \cdot 4CuO \cdot 4H_2O$	0.819	0.813
5.65	5.58	88.77	"	0.795	0.790
2.43	2.38	95.19	"	0.319	0.314
2.30	2.25	95.45	"	0.301	0.296
1.84	1.80	96.36	"	0.239	0.235
1.55	1.52	96.93	"	0.200	0.197
1.24	1.22	97.54	"	0.159	0.162
0.52	0.50	98.98	"	0.066	0.064

[a] The mol/kg H_2O values were calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cu(OH)_2$ and solvent were mixed and shaken frequently in a thermostat until the concentration of the copper in the liquid phase became constant. The mixtures were then filtered through a glass frit and analyzed. Copper was determined by electrolytic deposition. Sulfate was determined gravimetrically as $BaSO_4$.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding NH_4OH to aqueous $CuSO_4$ only in a quantity sufficient to dissolve the precipitate that was formed. The solution was cooled to 0°C and added gradually to a solution of NaOH. The precipitate was washed with water until free of sulfate ions, then with alcohol, and finally with ether. It was dried in a vacuum. No other information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

McDowell, L. A.; Johnston, H. L. *J. Am. Chem. Soc.* 1936, *58*, 2009-14.

VARIABLES:

Concentration of NaOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in aqueous NaOH at 25°C.

C_{NaOH}/mol kg^{-1}	$10^5 C_{Cu}$/mol kg^{-1} from undersaturation	$10^5 C_{Cu}$/mol kg^{-1} from supersaturation
2.212	70.1	71.4
3.247	92.5	- - -
4.227	185	176

The solubility of CuO in conductivity water at 25°C was determined to be

2.5×10^{-5} mol dm^{-3}
3.5×10^{-5} mol dm^{-3}
3.7×10^{-5} mol dm^{-3}
1.7×10^{-5} mol dm^{-3}

mean value is 2.9×10^{-5} mol dm^{-3}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached from under and from supersaturation. Mixtures of CuO and alkali were shaken in a thermostat for at least 2 weeks, then allowed to sediment for a week. The clear liquid was then siphoned off and filtered. Copper content was determined by electrometric titration with $K_4Fe(CN)_6$ using a Pt electrode. Total alkalinity was determined by titration with H_2SO_4.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used throughout. CuO was prepared by adding dilute aqueous $CuSO_4$ and KOH to boiling water. The precipitate was washed until free of SO_4^{2-} ions. NaOH solutions were prepared from reagent grade solid.

ESTIMATED ERROR:

The authors give no estimate.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

McDowell, L.A.; Johnston, H. L. *J. Am. Chem. Soc.* 1936, *58*, 2009-14.

VARIABLES:

Concentration of KOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in aqueous KOH at 25°C

C_{KOH}/mol kg^{-1}	$10^5 C_{Cu}$/mol kg^{-1} from undersaturation	$10^5 C_{Cu}$/mol kg^{-1} from supersaturation
0.0417	0.07	0.07
0.0513	0.08	0.08
0.0586	0.151	0.158
0.0600	0.132	0.241
0.0741	0.196	0.189
0.0832	0.172	0.162
0.0932	0.409	0.414
0.0968	0.302	0.282
0.1027	0.145	0.184
0.1150	0.324	0.308
0.1175	0.300	0.273
0.1385	0.398	0.371
0.1608	0.489	0.604
0.1705	0.608	0.563
0.1772	0.534	0.518
0.2035	1.02	0.83
0.2165	0.96	0.73
0.2238	0.93	0.84
0.2637	1.34	1.25
0.2761	----	1.56
0.3163	4.04	3.72

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

CuO and the KOH solutions were mixed and shaken in a thermostat for at least 2 weeks, then allowed to sediment for one week. The clear filtrate was then siphoned off and filtered. Equilibrium was approached from both undersaturation and from supersaturation. Copper content was determined by electrometric titration with $K_4Fe(CN)_6$ using a Pt electrode. Total alkalinity was determined by titration with H_2SO_4.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used throughout. The KOH solutions were prepared from a potassium amalgam or from reagent grade solid. The CuO was prepared by adding $CuSO_4$ and KOH simultaneously to boiling water. The precipitate was washed repeatedly until all traces of sulfate ion were removed.

ESTIMATED ERROR:

The authors do not discuss this.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

McDowell, L. A.; Johnston, H. L. *J. Am. Chem. Soc.* 1936, *58*, 2009-14.

EXPERIMENTAL VALUES:

Solubility of CuO in aqueous KOH at 25°C (con't)

C_{KOH}/mol kg^{-1}	$10^5 C_{Cu}$/mol kg^{-1} from undersaturation	$10^5 C_{Cu}$/mol kg^{-1} from supersaturation
0.3244	4.66	3.44
0.544	4.91	5.36
0.650	4.66	3.72
0.753	11.7	11.0
0.860	11.2	9.8
1.000	16.1	16.2
1.337	26.1	24.4
1.633	32.4	34.3
1.963	71.0	65.7
2.333	82.7	79.6
2.495	80.1	73.1
2.848	91.8	94.1
3.180	117.2	121.4
3.380	132	87.0
4.015	171	144
4.151	144	150
4.227	164	156
5.065	184	167
5.253	203	181
6.05	297	---
8.38	---	435

The authors develop the following equation to fit the data. The concentrations are expressed as mol/kg H_2O.

$$C_{Cu} = 10.3 \times 10^{-6} C_{OH^-} + 81 \times 10^{-6} (C_{OH^-})^2 / a_{H_2O} \, (\gamma_{KOH})^2$$

COMPONENTS:

(1) Copper(II) hydroxide; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH at 15, 20 and 25°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions.[a]

Amount $Cu(OH)_2$ added/ g dm^{-3}	Period of standing, in hours	t/°C	C_{Cu}/g dm^{-3} A	B	C	C_{Cu}/mol dm^{-3} [b] A	B	C
15	18	20	3.56	7.70	8.90	0.056	0.121	0.140
20	18	20	3.75	7.90	9.40	0.059	0.124	0.148
30	18	20	3.87	8.20	10.40	0.061	0.129	0.164
40	18	20	3.94	8.40	11.00	0.062	0.132	0.173
50	18	20	- - -	- - -	13.58	- - -	- - -	0.214
80	18	20	- - -	- - -	13.80	- - -	- - -	0.217
120	18	20	- - -	- - -	14.33	- - -	- - -	0.225
20	3	20	3.99	8.10	9.90	0.063	0.127	0.156
20	6	20	4.13	7.70	9.60	0.065	0.121	0.151
20	18	20	3.99	8.00	9.60	0.063	0.126	0.151
20	48	20	3.99	8.00	8.60	0.063	0.126	0.135
20	72	20	3.99	7.90	8.80	0.063	0.124	0.138
20	6	15	- - -	8.20	9.80	- - -	0.129	0.154
20	6	20	- - -	7.90	9.70	- - -	0.124	0.153
20	6	25	- - -	7.50	9.40	- - -	0.118	0.148

[a] The concentrations of NH_3 are as follows: Columns A, 50 g dm^{-3}; columns B, 100 g dm^{-3}; columns C, 200 g dm^{-3}.

[b] Calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of $Cu(OH)_2$ and NH_4OH solution were shaken, allowed to stand for some time, then shaken again and filtered. The copper content of the filtrate was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried in a desiccator. No information is given about any of the other materials.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Copper(II) sulfate; $CuSO_4$; [7758-98-7]

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

ORIGINAL MEASUREMENTS:

Akselrud, N.V.; Fialkov, Ya.A. *Ukr. Khim. Zhur.* 1950, *16*, 283-95.

VARIABLES:

Concentration of $CuSO_4$ at 18.0°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility product constant of $Cu(OH)_2$ in aqueous $CuSO_4$ at 18.0°C.

C_{Cu}/mol dm^{-3}	pH	$-\log K_s o$ [a]
0		19.8820 [b]
0.0100	5.08	20.1000
0.0300	4.75	20.2829
0.1810	4.25	20.4483
0.2854	4.16	20.4695
0.5235	4.03	20.4841
0.8725	3.94	20.4383
1.1411	3.91	20.3842
1.2412	3.11	20.3851

[a] These values were calculated from the following equation:

$$-\log K_s o = -\log Cu^{2+} - 2 \log K_w - 2pH.$$

[b] This value was apparently obtained by extrapolating the first several values to zero ionic strength. It is considered to be the thermodynamic solubility product constant value.

Editor's note: The value used for K_w is not given, and it is impossible to reproduce the calculations of the $-\log K_s o$ values using the same value for K_w in all instances.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid $Cu(OH)_2$ was added to solutions of $CuSO_4$. The mixtures were stirred vigorously at 18.0 ± 0.1°C. The pH of the solutions was determined potentiometrically using a hydrogen electrode. The method used to analyze for copper is not described.

SOURCE AND PURITY OF MATERIALS:

The $CuSO_4$ was chemically pure and was recrystallized twice from water. The $Cu(OH)_2$ was prepared by treating a 5% $CuSO_4$ solution, containing 0.75 ml of glycerine per liter of solution, with dilute aqueous NaOH. The precipitate was washed repeatedly with water until there was no further evidence for the presence of sulfate ions.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I.; Pakshver, A. B.; Podbornova N. I. *Zhur. Priklad Khim.* 1950, *23*, 650-6; *J. Applied Chem. USSR (Engl. transl.)* 1950 *23*, 685-91.

VARIABLES:

Concentration of NH_4OH at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in NH_4OH solutions at 20°C.

C_{NH_3}/g dm^{-3}	C_{NH_3}/mol dm^{-3} [a]	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [a]
43.9	2.58	3.75	0.059
78.2	4.60	8.2	0.129
123.7	7.28	11.9	0.187
204.0	12.0	15.5	0.244

The above solutions were diluted with water to give the following equilibria.

0.248	0.0052
0.309	0.0062
0.353	0.0070
0.233	0.0026

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solid $Cu(OH)_2$ (dried at room temperature) was added to a large excess of solvent at 20°C. The mixtures were allowed to stand for 24 hours at 20°C. They were then filtered and the copper content of the filtrate was determined iodometrically (1). Some of the saturated solutions were carefully diluted with water until $Cu(OH)_2$ precipitated. The solutions were then set aside in the dark for two days at 20°C before the filtrate was analyzed for copper content.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by a method described earlier (2). No further information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Bruhns, G. Z. *Anal. Chem.* 1920, 59, 337.

2. Arkhipov, M. *J. Applied Chem. USSR* 1948, *21*, 11,1107.

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I.; Pakshver, A. B; Podbornova, N. I. *Zhur. Prikład Khim.* 1950, *23*, 650-6; *J. Applied Chem. USSR (Engl. transl.)* 1950, *23*, 685-91.

VARIABLES:

Sodium hydroxide concentration and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$

Table I. Solubility of $Cu(OH)_2$ in aqueous NaOH at 15°C.

C_{NaOH}/g dm^{-3}	C_{NaOH}/mol dm^{-3} [a]	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [a]
56.4	1.41	0.10	0.0016
120.8	3.02	0.31	0.0049
172.8	4.32	0.89	0.0140
209.6	5.24	1.19	0.0187
240.0	6.00	2.61	0.0411

Table II. Solubility of $Cu(OH)_2$ in aqueous NaOH at 20°C.

C_{NaOH}/g dm^{-3}	C_{NaOH}/mol dm^{-3} [a]	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [a]
68.4	1.71	0.25	0.0039
132.0	3.30	0.82	0.0129
202.0	5.05	2.87	0.0452
360.0	9.00	10.4	0.164

The above solutions were diluted with water to give the following equilibria.

0.051	0
0.203	0.0006
1.210	0.0071
4.180	0.0376

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The $Cu(OH)_2$ was dried at room temperature, added to an excess of NaOH solution, allowed to stand 24 hours, then filtered. The copper content of the filtrate was determined iodometrically (1). Some of the saturated solutions were also diluted with water until $Cu(OH)_2$ began to precipitate. These mixtures were set aside in the dark for 2 days and the solution was then analyzed for copper content.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by a method described earlier (2). Nothing is said about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Bruhns, G. *Z. Anal. Chem.* 1920, *59*, 337.

2. Arkhipov, M. *J. Applied Chem. USSR* 1948, *21*, 11, 1107.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Sircar, S. C.; Prasad, B. *J. Indian Chem. Soc.* 1956, *33*, 361-2.

VARIABLES:

Concentration of nitric acid at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility product of CuO in aqueous HNO_3.

C_{HNO_3}/mol dm^{-3}	C_{Cu}/mol dm^{-3}	pH	$10^{20}K_s^o$
0.0201	0.0100	5.28	1.9
0.0402	0.0200	5.20	2.3
0.0604	0.0301	5.11	1.9
0.0805	0.0384	5.02	1.5
0.1006	0.0482	4.95	1.6
0.1207	0.0580	4.84	0.8
0.1408	0.0676	4.74	0.6

The average value for K_s^o is 1.5×10^{-20}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of solid CuO and aqueous HNO_3 were shaken for 8 days, then filtered. The pH of the filtrate was measured with a pH meter. The copper content of the filtrate was determined iodometrically. The experiments were carried out in triplicate at 25-28°C. The copper in the filtrate was assumed to be present as Cu^{2+} ion and the activity coefficient of this ion was calculated using a principle described earlier (1).

SOURCE AND PURITY OF MATERIALS:

CuO was prepared by adding NaOH to aqueous $CuCl_2$, washing the precipitate and drying it at 110-115°C for 15 hours. There is no indication about the quality of the HNO_3.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Das, N. K.; Aditya, S.; Prasad, B. *J. Indian Chem. Soc.* 1952, *29*, 169.

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Hydrogen peroxide; H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S.Z.; Arnol'd, T.I.; Stasevich, N.H.; Shorina, E.V. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1960, 1913-20.

VARIABLES:

Temperature and concentration of hydrogen peroxide.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Table I. Solubility of $Cu(OH)_2$ in aqueous hydrogen peroxide at -20°C.

$C_{H_2O_2}$/mass %	$10^4 C_{CuO}$/mass %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^5 C_{CuO}$/mol kg^{-1} [a]	Solid phase [b]
24.4	3.88	9.49	6.5	A + B
31.54	1.35	13.5	2.5	B
34.4	2.00	15.4	3.8	"
34.4	1.9	15.4	3.6	"
40.14	1.68	19.7	3.5	"
41.23[c]	8.76	20.6	1.9	B + C
44.54	1.03	23.6	2.3	C
51.1	0.51	30.7	1.3	"
52.7[c]	0.80	32.8	2.1	"
75.1	1.05	88.7	5.3	"
84.1	1.04	156	8.2	C + D

[a] The mol/kg H_2O values were calculated by the Editor.

[b] The solid phases are: A = ice; B = $CuO_2 \cdot H_2O$; C = $CuO_2 \cdot H_2O_2 \cdot H_2O$; D = H_2O_2.

[c] These values are in error in the original paper.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions of H_2O_2 and solid $Cu(OH)_2$ were brought to equilibrium isothermally. Active oxygen was determined by titration with $KMnO_4$ in the presence of boric acid. The copper content of the solid phase was determined by electrolysis; that of the liquid phase was determined colorimetrically using dithizone.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding aqueous NaOH to a solution of $CuSO_4$ in the presence of glycerine. The precipitate was then washed with distilled water. The H_2O_2 was purified by vacuum distillation.

ESTIMATED ERROR:

No details are given as to temperature control, precision of analyses, or any other part of the procedure.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Hydrogen peroxide; H_2O_2 [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S.Z.; Arnol'd, T.I.; Stasevich, N.H.; Shorina, E.V. *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk* 1960, 1913-20.

EXPERIMENTAL VALUES, cont'd:

Table II. Solubility of $Cu(OH)_2$ in aqueous hydrogen peroxide at 0°C.

$C_{H_2O_2}$/mass %	$10^4 C_{CuO}$/mass %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^5 C_{CuO}$/mol kg^{-1} [a]	Solid phase [b]
0	0.23	0	0.29	A
2.47	0.55	0.74	0.71	"
4.82	7.77	1.49	10	"
8.26	11.6	2.65	16	B
25.75	5.65	10.2	9.6	"
33.51	4.4	14.8	8.3	"
40.50	1.5	20.0	3.2	"
46.13	1.55	25.2	3.6	"
46.66	1.5	25.7	3.5	"
49.51	2.25	28.8	5.6	"
50.57	9.51	30.1	24	B + C
55.70[c]	1.79	37.0	5.1	C
63.68	0.59	51.5	2.0	"
72.52	0.85	77.6	3.9	"

[a] The mol/kg H_2O values were calculated by the Editor.

[b] The solid phases are: A = $Cu(OH)_2$; B = $CuO_2 \cdot H_2O$; C = $CuO_2 \cdot H_2O_2 \cdot H_2O$.

[c] This is a corrected value. The value in the original paper is in error.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

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

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

ORIGINAL MEASUREMENTS:

Schindler, P.; Althaus, H.; Hofer, F.; Minder, W. *Helv. Chim. Acta* 1965, *48*, 1204-15.

VARIABLES:

Molar surface area of the CuO.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility product of CuO at 25°C.[a]

S/m^2 [b]	$\log {}^*K_{so}$ [c]
4340	8.27 ± 0.01
4210	8.22 ± 0.03
3760	8.18 ± 0.02
2530	8.08 ± 0.04
1790	8.04 ± 0.03
1210	7.97 ± 0.03
230	7.91 ± 0.02

[a] Each result is the average of 2 to 4 determinations.

[b] S is the molar surface area.

[c] ${}^*K_{so} = K_{so}/(K_w)^2$.

The use of linear regression analysis gives (with a 90% certainty) the following equation for the above data:

$$\log {}^*K_{so} = (7.89 \pm 0.05) + (8.0 \pm 1.7) \times 10^{-5}\ S.$$

From this, $\log K_{so}$ is calculated to be -19.51 ± 0.05 at 25°C.

Using the method of Davies (1), $\log K^{\circ}_{so}$ then is -20.35 ± 0.06 at 25°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The CuO was placed in a column and the solvent (water containing 0.2 mol $NaClO_4$ dm^{-3}) was forced through the column 10 to 20 times until the pH of the solution became constant. Then a sample of the solution was removed and analyzed for copper content by a compleximetric titration. The pH was determined by measuring the e.m.f. across a glass and an AgCl/Ag electrode placed in the solution. All measurements were made at 25.0 ± 0.5°C.

SOURCE AND PURITY OF MATERIALS:

CuO was prepared by adding an aqueous solution of $CuCl_2 \cdot 2H_2O$ and a methanol solution of KOH simultaneously to boiling water. The precipitated CuO was washed and then dried at 80°C over P_2O_5 in a vacuum.

ESTIMATED ERROR:

This is indicated in the reported results.

REFERENCES:

1. Davies, C. W. *Ion Association*, Butterworths, London 1960, p. 41.

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

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

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

ORIGINAL MEASUREMENTS:

Schindler, P.; Althaus, H.; Hofer, F.; Minder, W. *Helv. Chim. Acta* 1965, *48*, 1204-15.

VARIABLES:

Particle size and molar surface area of the solid phase.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility product of $Cu(OH)_2$ at 25°C.[a]

S/m^2 [b]	$\log {}^*K_s o$ [c]
250	8.91 ± 0.06
1340	9.00 ± 0.02
1910	9.00 ± 0.02
2940	9.06 ± 0.01
4570	9.12 ± 0.02

[a] Each result is the average of 4 to 8 determinations.

[b] S is the molar surface area.

[c] ${}^*K_s o = K_s o/(K_w)^2$.

The data above can be represented by the following equation:

$$\log {}^*K_s o = (8.92 \pm 0.04) + (4.8 \pm 1.5) \times 10^{-5}\ S.$$

$\log K_s o$ for $Cu(OH)_2$ is calculated to be -18.48 ± 0.04 at 25°C, and $\log K_s^\circ o$ = -19.32 ± 0.05 at 25°C in 0.2 mol $NaClO_4$ dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The equilibration was accomplished in a column containing the $Cu(OH)_2$. The solvent was forced through the column 10 to 20 times and the pH of the solution was determined by measuring the e.m.f. across a glass electrode and an AgCl/Ag electrode immersed in the solution. After the pH became constant a sample of the solution was removed and analyzed for copper content by a compleximetric titration. The solvent was a 0.2 mol dm^{-3} solution of $NaClO_4$. All measurements were made at 25.0 ± 0.05°C. The method of Davies (1) was used to obtain the thermodynamic solubility product constant.

SOURCE AND PURITY OF MATERIALS:

The larger particle sized $Cu(OH)_2$ was prepared by the method of Oswald and Jaggi (2). The finely divided $Cu(OH)_2$ was prepared by treating an aqueous solution of $Cu(NO_3)_2 \cdot 3Cu(OH)_2$ with aqueous NaOH. The particle size was determined by the concentration of NaOH and the time allowed for the reaction.

ESTIMATED ERROR:

The uncertainty is included in the reported results.

REFERENCES:

1. Davies, C. W. *Ion Association*, Butterworths, London 1960, p. 41.
2. Oswald, H. R.; Jaggi, H. *Chimia* 1960, *14*, 22.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Akhmetov, K. M.; Buketov, E. A.; Ugorets, M. I. *Tr. Khim.-Met. Inst., Akad. Nauk Kaz, SSR* 1967,3, 119-28.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of CuO in aqueous NaOH.[a]

t/°C	$10^5 c_{Cu}$/mol dm^{-3} A	B	C	D	E	F
25	24.10	70.86	106.01	275.52	472.14	1122.67
50	39.86	111.21	178.36	403.94	653.12	1384.95
75	52.45	157.38	238.43	498.34	880.86	1542.33
125	88.13	224.00	346.23	771.16	1007.22	2014.38
150	103.87	258.10	416.56	876.08	1356.40	2360.71
175	125.90	311.61	459.55	971.04	1495.20	2650.74
200	154.23	336.79	582.30	1117.43	1731.16	3116.14

[a] The NaOH concentration (mol dm^{-3}) is: Column A = 1; Column B = 2.25; Column C = 3; Column D = 5; Column E = 7; Column F = 10.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of CuO and NaOH solutions were placed in Teflon containers. At temperatures below 100°C the mixtures were kept in a thermostat for 20-30 days. At higher temperatures the mixtures were placed in an autoclave for about 10 hours. The concentration of NaOH was determined by titration. The copper content was measured colorimetrically. Each value reported is the average of 2 to 4 determinations. The temperature was controlled to within 2°C in the autoclave and to within 0.5°C in the thermostat.

SOURCE AND PURITY OF MATERIALS:

The water was distilled twice. The NaOH was reagent grade. Nothing is said about the CuO.

ESTIMATED ERROR:

According to the authors the average standard deviation is about 0.06.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Gubeli, A. O.; Hebert, J.; Cote, P. A.; Taillon, R. *Helv. Chim. Acta* 1970, *53*, 186-97.

VARIABLES:

Concentration of NH_4OH at 25°C and constant ionic strength of 1.0 mol dm^{-3}.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in ammoniacal solutions at 25°C.

pH	pCu_{tot} [a]	pNH_3 tot [a]	pH	pCu_{tot} [a]	pNH_3 tot [a]
11.03	5.68	1.426	12.05	4.51	0.903
11.35	5.60	1.426	12.20	4.58	0.903
11.85	5.75	1.426	12.70	4.41	0.903
12.55	5.79	1.426	13.30	4.51	0.903
11.95	5.12	1.125			
12.25	5.00	1.125			
12.70	5.02	1.125			

[a] All concentrations are expressed as mol dm^{-3}.

A graph of the solubility of CuO as a function of pH shows that the solubility decreases from pH 6 to 7.5 and then is constant at about 10^{-6} mol dm^{-3} for the pH range 7.5 to 11.65. As the pH increases beyond 12 the solubility of CuO increases.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of CuO and solution were agitated steadily for several days, then allowed to settle for about a week. The copper content of the solution was determined colorimetrically (1) with 2,2'-biquinoline. The pH of the solution was determined with a glass electrode. Five series of solutions were used in which the total concentration of NH_3 was: 0.01, 0.02, 0.0375, 0.075 and 0.125 mol dm^{-3}. The pH of the solution was adjusted by adding $HClO_4$ or NaOH. All solutions were maintained at 25°C and brought to an ionic strength of 1.0 mol dm^{-3} by the addition of $NaClO_4$.

SOURCE AND PURITY OF MATERIALS:

The CuO was prepared by adding NaOH to a solution of copper perchlorate. The water was deoxygenated, deionized, and distilled twice. No information is given about the NH_4OH.

ESTIMATED ERROR:

This is given with each reported result.

REFERENCES:

1. Hoste, J.; Eeckhout, J.; Gillis, J. *Anal. Chim. Acta* 1953, 9, 263.

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Solov'eva, V.D.; Svirchevskaya, E.G.; Bobrova, V.V.: Eltsov, N.M. *Tr. Inst. Metal. Obogashch., Akad. Nauk Kaz. SSR* 1973, *49*, 37-44.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of CuO in solutions of sodium hydroxide.

t/°C	C_{NaOH}/mol dm^{-3}	$10^5 C_{Cu}$/mol dm^{-3}
105	7.5	750
105	10.0	781
105	14.75	4677
105	18.0	10000
200	2.5	125
200	5.0	812
200	7.5	2000
200	10.0	3375
200	12.5	6250
200	15.0	10325
200	18.3	12800
200	19.6	1850

Editor's note: The composition of the solid phases in equilibrium with the above solutions is not given.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The experiments were performed in steel autoclaves. The mixtures were probably brought to equilibrium isothermally. The solid phases were analyzed using X-ray diffraction and other physico-chemical methods. The liquid phases were analyzed chemically, but the procedures are not specified.

SOURCE AND PURITY OF MATERIALS:

The CuO was an analytically pure material and was further purified to remove Cu and Cu_2O. No other information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Solov'eva, V.D.; Bobrova, V.V.; Orlova, L.F.; Adeishvili, E.U. *Tr. Inst. Metal. Obogashch., Akad. Nauk Kaz. SSR* 1973, *49*, 45-8.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in NaOH solutions.

C_{NaOH}/mol dm^{-3}	10^5 C_{Cu}/mol dm^{-3} 20°C	105°C	200°C
2.0	98	210	350
4.0	201	423	960
5.6	405	641	1600
8.3	641	1280	3200
10.0	962	1920	3860
12.0	1920	3180	6400
14.5	2880	6400	9600
16.0	- - -	8000	11520
17.2	- - -	10880	13760
18.0	- - -	10240	11860
18.5	- - -	7340	10240

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Very little information is given about the experimental details. Apparently, the solutions were allowed to equilibrate isothermally. There is no information about temperature control, preparation of solutions, assurance that equilibrium had been reached, or methods used for analysis.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by mixing NaOH and $CuSO_4$ solutions. The precipitate was allowed to stand in contact with 5% NaOH for 1 hour in the absence of air, then filtered, washed, and dried in a desiccator. No other information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Selenium(IV) oxide; SeO_2; [7446-08-4]

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

ORIGINAL MEASUREMENTS:

Ojkova, T.; Gospodinov, G. Z. *Anorg. Allg. Chem.* 1982, *484*, 235-40.

VARIABLES:

Concentration of SeO_2 at 100°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of the $CuO-SeO_2-H_2O$ system at 100°C.

C_{CuO}/mass%	C_{SeO_2}/mass%	C_{CuO}/mol kg^{-1} [a]	C_{SeO_2}/mol kg^{-1} [a]	Solid phase
0.194	1.01	0.0247	0.092	$CuSeO_3 \cdot 2H_2O$
0.184	4.04	0.0242	0.380	"
0.170	8.25	0.0233	0.812	$CuSeO_3 \cdot H_2SeO_3$
0.166	8.68	0.0229	0.858	"
0.144	17.17	0.0219	1.87	"
0.108	30.74	0.0196	4.01	"
0.100	33.85	0.0190	4.62	"
0.086	39.87	0.0180	5.98	"
0.078	43.07	0.0172	6.83	"
0.066	47.78	0.0159	8.26	"
0.056	52.56	0.0149	10.0	"
0.042	58.71	0.0128	12.8	"
0.038	60.96	0.0122	14.1	"
0.024	67.93	0.0094	19.1	"

[a] The values are given as mol/kg H_2O and were calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cu(OH)_2$ was added to a solution of H_2SeO_3. The mixture was stirred for 24 hours, then placed in a sealed glass ampule and kept at 100°C for about 30 days. The solid and liquid phases were separated from each other by filtration. The copper content of the filtrate was determined colorimetrically with dithizone. The selenium content was measured iodometrically.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was freshly prepared but the method is not described. The H_2SeO_3 solutions were prepared by adding freshly sublimed SeO_2 to water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Potassium fluoride; KF; [7789-23-3]

(3) Hydrofluoric acid; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Jaeger, A. *Z. Anorg. Allg. Chem.* 1901, *27*, 22-40.

VARIABLES:

Concentration of HF at 25°C

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in aqueous HF at 25°C

C_{KF}/mol dm^{-3}	C_{HF}/mol dm^{-3}	C_{Cu}/mol dm^{-3}
0	0.12	0.0307
0	0.28	0.1164
0	0.57	0.2494
0	1.08	0.388
0	2.28	0.463
0.41	0.12	0.0356
0.41	0.28	0.06437
0.41	0.57	0.1442
0.41	1.11	0.2451
0.41	2.17	0.2517

The author suggests that the decrease in solubility of CuO in HF when KF is added may be due to the following reaction:

$$HF + KF = KHF_2.$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An equivalent amount of CuO was added to 48 ml of solvent. The mixture was shaken in a thermostat at 25°C. There is no indication about the length of time the mixtures were shaken. The copper content was determined by electrolytic deposition.

SOURCE AND PURITY OF MATERIALS:

The HF solutions were prepared by dilution of a redistilled chemically pure aqueous solution of HF. Nothing is said about the other materials that were used.

ESTIMATED ERROR:

No indication is given. The solubility values are listed as the "maximum values".

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Ammonium hydroxide; NH_4OH; [1336-21-6]
(3) Ammonium sulfate; $(NH_4)_2SO_4$; [7783-20-2]
(4) Sodium sulfate; Na_2SO_4; [7757-82-6]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Dawson, H. M. *J. Chem. Soc.* 1908, *95*, 370-81.

VARIABLES:

Composition of the solvent at 18°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in ammoniacal ammonium sulfate solutions at 18°C.[a]

C_{NH_3}/mol dm^{-3}	$C_{(NH_4)_2SO_4}$/mol dm^{-3} 0	0.01	0.025	0.05	0.1	0.2	0.4
0	- - -	- - - -	- - -	0.0004[b]	- - -	0.0157[b]	0.0180[b]
0.05	- - -	0.00129	0.00511	0.0130[b]	0.0215[b]	0.0325[b]	0.0579[b]
0.1	- - -	0.00326	0.0108	0.0233	0.0411[b]	- - - -	- - - -
0.2	0.00054	0.00649	0.0175	0.0384	0.0690	0.1027[b]	0.1397[b]
0.5	0.0033	0.0127	0.0284	0.0536	0.1013	0.1844	0.2805[b]
1.0	0.0109	0.0210	0.0386	0.0660	0.1185	0.2275	0.4135
2.0	0.0314	0.0462	0.0605	0.0886	0.1468	0.2591	0.4718
3.0	0.0548	0.0672	0.0847	0.1156	0.1740	0.2861	0.5044
4.0	0.0784	0.0922	0.1101	0.1397	0.2002	0.3188	0.5451
5.0	0.1041	0.1154	0.1320	0.1639	1.2239	0.3415	0.5615

[a] The numbers in the columns represent the concentration of copper as mol dm^{-3}.

[b] The author doubts that these values correspond to any definite equilibrium condition.

Solubility of $Cu(OH)_2$ in ammoniacal sodium sulfate solutions at 18°C.

C_{NH_3}/mol dm^{-3}	$C_{Na_2SO_4}$/mol dm^{-3}	C_{Cu}/mol dm^{-3}
1	0	0.0109
1	0.025	0.0134
1	0.1	0.0162
1	0.2	0.0192

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No information is given about the preparation of the saturated solutions or how the analysis for copper content was carried out.

SOURCE AND PURITY OF MATERIALS:

Crystalline $Cu(OH)_2$ was prepared by adding NH_4OH to aqueous $CuSO_4$, washing the precipitate, and drying it in a vacuum over H_2SO_4. The NH_4OH was prepared by distilling aqueous NH_4OH to which NaOH had been added and collecting the NH_3 vapor in conductivity water. The $(NH_4)_2SO_4$ was purified by repeated crystallization.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Ammonium hydroxide; NH_4OH; [1336-21-6]
(3) Barium hydroxide; $Ba(OH)_2$; [17194-00-2]
(4) Sodium hydroxide; NaOH [1310-73-2]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Dawson, H. M. *J. Chem. Soc.* 1908, *95*, 370-81.

VARIABLES:

Composition of the solvent at 18°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in ammoniacal $Ba(OH)_2$ and NaOH solutions at 18°C

C_{NH_3}/mol dm^{-3}	$C_{Ba(OH)_2}$/mol dm^{-3}	C_{NaOH}/mol dm^{-3}	C_{Cu}/mol dm^{-3}
1	0	0	0.0109
1	0.0025	0	0.00907
1	0.005	0	0.00801
1	0.01	0	0.00633
1	0.02	0	0.00526
2	0	0	0.0314
2	0.01	0	0.0277
4	0	0	0.0784
4	0.01	0	0.0747
1	0	0.01	0.00766
1	0	0.02	0.00655
1	0	0.03	0.00531
1	0	0.05	0.00456
1	0	0.10	0.00410

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No information is given but apparently equilibrium was approached isothermally, The method used to determine the copper content of the saturated solutions is not mentioned or described.

SOURCE AND PURITY OF MATERIALS:

Crystalline $Cu(OH)_2$ was prepared by adding NH_4OH to aqueous $CuSO_4$, washing the precipitate, and drying it over H_2SO_4 in a vacuum. The $Ba(OH)_2$ was purified by repeated crystallization. The NaOH was prepared by the action of sodium on water in a CO_2-free atmosphere. The NH_4OH was prepared by distilling aqueous NH_4OH to which NaOH had been added and collecting the NH_3 vapor in conductivity water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

(3) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Priklad. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH and of NaOH at 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Effect of NaOH on the solubility of $Cu(OH)_2$ in aqueous NH_3 at 18-20°C.

C_{NH_3}/g dm^{-3}	C_{NaOH}/g dm^{-3}	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [a]
50	0	3.73	0.059
50	5	2.53	0.040
50	10	2.20	0.035
50	20	2.05	0.032
100	0	6.79	0.107
100	5	5.79	0.091
100	10	4.66	0.073
100	20	4.66	0.073
200	0	9.85	0.155
200	5	7.79	0.123
200	10	6.26	0.099
200	20	6.39	0.101

[a] Calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of solid $Cu(OH)_2$ and solvent were shaken, then allowed to stand for 18 hours. After this period the mixtures were shaken again, allowed to stand to let the precipitate settle, and then filtered. An iodometric titration was used to determine the copper content of the filtrate.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and then dried over $CaCl_2$ in a desiccator. No information is given about any of the other materials.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Acetone; C_3H_6O; [67-64-1]

(3) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of acetone at 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Effect of acetone on the solubility of $Cu(OH)_2$ in aqueous NH_3 at 18-20°C.

$C_{acetone}$/g dm^{-3}	C_{Cu}/g dm^{-3}	$C_{acetone}$/mol dm^{-3} [a]	C_{Cu}/mol dm^{-3} [a]
0	9.73	0	0.153
3.9	9.45	0.067	0.149
7.8	9.32	0.134	0.147
15.6	8.92	0.269	0.140

[a] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cu(OH)_2$ was mixed with a solution containing the acetone and 200 g dm^{-3} of NH_3. The mixture was shaken, allowed to stand for 18 hours, then shaken again and filtered. The filtrate was analyzed for copper content by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and then dried over $CaCl_2$ in a desiccator. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Methanol; CH_4O; [67-56-1]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of methanol at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 [a] containing CH_3OH at 18-20°C.

C_{CH_4O}/g dm^{-3}	C_{Cu}/g dm^{-3}	C_{CH_4O}/mol dm^{-3} [b]	C_{Cu}/mol dm^{-3} [b]
0	9.85	0	0.155
7.9	8.65	0.247	0.136
39.5	8.65	1.23	0.136
79.0	8.00	2.47	0.126

[a] The concentration of NH_3 in all solutions was 200 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid $Cu(OH)_2$ and an ammoniacal solution containing 200 g NH_3 dm^{-3} and methanol were shaken, allowed to stand for 18 hours, and then shaken again. After the precipitate had settled out the mixture was filtered and the copper content of the filtrate was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried over $CaCl_2$ in a desiccator. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Ammonium hydroxide; NH_4OH; [1336-21-6]
(3) Ethanol; C_2H_6O; [64-17-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of ethanol at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions [a] containing C_2H_5OH at 18-20°C.

$C_{C_2H_6O}$/g dm^{-3}	C_{Cu}/g dm^{-3}	$C_{C_2H_6O}$/mol dm^{-3} [b]	C_{Cu}/mol dm^{-3} [b]
0	9.85	0	0.155
7.8	9.00	0.169	0.142
39.0	8.15	0.846	0.128
62.4	7.27	1.35	0.114
78.0	7.00	1.69	0.110

[a] The concentration of NH_3 in each solution was 200 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A mixture of solid $Cu(OH)_2$ and an ammoniacal solution containing 200 g NH_3 dm^{-3} and the alcohol was shaken, allowed to stand for 18 hours, then shaken again. After the precipitate had settled out the mixture was filtered and the copper content of the filtrate was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried over $CaCl_2$ in a desiccator. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) 1-Propanol; C_3H_8O; [71-23-8]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of 1-propanol at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions [a] containing 1-propanol at 18-20°C.

$C_{C_3H_8O}$/g dm^{-3}	C_{Cu}/g dm^{-3}	$C_{C_3H_8O}$/mol dm^{-3} [b]	C_{Cu}/mol dm^{-3} [b]
0	9.85	0	0.155
8.0	9.32	0.133	0.147
40.0	8.40	0.666	0.132
80.0	7.20	1.33	0.113

[a] The concentration of NH_3 in each of these solutions was 200 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid $Cu(OH)_2$ and an ammoniacal solution containing 200 g NH_3 dm^{-3} and the alcohol were mixed and shaken, then allowed to stand for 18 hours. After this standing the mixture was shaken again and filtered. The copper content of the filtrate was determined by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried over $CaCl_2$ in a desiccator. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Glucose; $C_6H_{12}O_6$; [50-99-7]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of glucose and of ammonium hydroxide.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Effect of glucose on the solubility of $Cu(OH)_2$ in aqueous NH_3 solutions.

C_{NH_3}/g dm^{-3}	Period of standing, in hours	$C_{glucose}$/g dm^{-3}	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [a]
91.0	3	0	8.00	0.126
91.0	3	10	16.10	0.253
91.0	24	0	8.00	0.126
91.0	24	10	13.10	0.206
91.0	72	0	8.00	0.126
91.0	72	10	12.85	0.202
12.0	24	0	11.35	0.179
12.0	24	10	16.30	0.257

[a] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of solid $Cu(OH)_2$ and ammoniacal solutions were shaken, allowed to stand for some time, then shaken again and filtered. The copper content of the filtrate was determined iodometrically. The temperature is not stated, but it appears from the article that the work was done at room temperature, about 19°C.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding excess NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried in a desiccator. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Sucrose; $C_{12}H_{22}O_{11}$; [57-50-1]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Priklad. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of sucrose and of ammonium hydroxide.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Effect of sucrose on the solubility of $Cu(OH)_2$ in aqueous NH_3 solutions.

C_{NH_3}/g dm^{-3}	Period of standing, in hours.	$C_{sucrose}$/g dm^{-3}	C_{Cu}/g dm^{-3}	C_{Cu}/mol dm^{-3} [a]
91	3	0	8.01	0.126
91	3	10	10.30	0.162
137	3	0	7.94	0.125
137	3	10	10.20	0.161

[a] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of solid $Cu(OH)_2$ and ammoniacal solution were shaken, allowed to stand for some time, then shaken again and filtered. The copper content of the filtrate was determined iodometrically. The temperature is not stated but it presumably was 18-20°C.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding excess NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried in a desiccator. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Urea; CH_4N_2O; [57-13-6]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH and of urea at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions [a] containing urea at a temperature of 18-20°C.

	C_{Cu}/g dm^{-3}		C_{Cu}/mol dm^{-3} [b]	
C_{urea}/g dm^{-3}	A	B	A	B
0	3.75	7.87	0.059	0.124
3.0	3.75	7.90	0.059	0.124

[a] The concentrations of NH_3 are; for columns A, 50 g dm^{-3}; for columns B, 100 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

30 g dm^{-3} of $Cu(OH)_2$ was added to the ammonia + urea solution. The mixture was shaken, allowed to stand for 18 hours, and then was shaken again. After sedimentation, the mixture was filtered, and the copper content of the filtrate was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

An excess of NaOH was added to an ammoniacal solution of $CuSO_4$. The precipitated $Cu(OH)_2$ was washed with cold water and dried in a desiccator. No other information is given.

ESTIMATED ERROR:

No indication is given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Ammonium carbonate; $(NH_4)_2CO_3$; [506-87-6]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH and of $(NH_4)_2CO_3$ at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions containing $(NH_4)_2CO_3$ at 18-20°C.[a]

C_{NH_3}/g dm^{-3}	C_{Cu}/g dm^{-3} A	B	C	D	C_{Cu}/mol dm^{-3} [b] A	B	C	D
50	3.86	8.0	12.80	20.20	0.061	0.126	0.201	0.318
100	7.65	11.25	13.90	25.30	0.120	0.177	0.219	0.398
132	11.65	- - -	22.70	- - -	0.183	- - -	0.357	- - -
182	9.85	- - -	20.40	- - -	0.155	- - -	0.321	- - -
200	9.65	12.25	17.44	24.95	0.152	0.193	0.274	0.393

[a] The concentrations of $(NH_4)_2CO_3$ are: columns A, none; columns B, 5 g dm^{-3}; columns C, 10 g dm^{-3}; columns D, 20 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of $Cu(OH)_2$ and solution were shaken, allowed to stand for 18 hours, then shaken again and filtered. The filtrate was analyzed iodometrically to determine its copper content.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried over $CaCl_2$ in a desiccator. No further information is given about the materials that were used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Ammonium sulfate; $(NH_4)_2SO_4$; [7783-20-2]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH and of $(NH_4)_2SO_4$ at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions containing $(NH_4)_2SO_4$ at 18-20°C. [a]

C_{NH_3}/g dm^{-3}	C_{Cu}/g dm^{-3} A	B	C	D	C_{Cu}/mol dm^{-3} [b] A	B	C	D
50	3.25	5.75	8.75	11.40	0.051	0.090	0.138	0.179
100	7.62	10.06	13.90	18.40	0.120	0.158	0.219	0.290
137	7.94	- - -	13.50	- - -	0.125	- - -	0.212	- - -
182	9.50	- - -	18.40	- - -	0.150	- - -	0.290	- - -

[a] The concentrations of $(NH_4)_2SO_4$ are: columns A, none; columns B, 5 g dm^{-3}; columns C, 10 g dm^{-3}; columns D, 20 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of $Cu(OH)_2$ and solution were shaken, allowed to stand for 18 hours, then shaken again and filtered. The filtrate was analyzed iodometrically to determine its copper content.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried over $CaCl_2$ in a desiccator.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Ammonium hydroxide; NH_4OH; [1336-21-6]
(3) Ammonium thiocyanate; NH_4SCN; [1762-95-4]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Priklad. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH and of NH_4SCN at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions containing NH_4SCN at 18-20°C. [a]

C_{NH_3}/g dm^{-3}	C_{Cu}/g dm^{-3} A	B	C	D	C_{Cu}/mol dm^{-3} [b] A	B	C	D
50	3.19	5.65	7.75	12.15	0.050	0.089	0.122	0.191
100	7.44	9.38	11.50	16.75	0.117	0.148	0.181	0.264
132	11.75	- - -	16.15	- - -	0.185	- - -	0.254	- - -
182	9.85	- - -	16.65	- - -	0.155	- - -	0.262	- - -
200	9.65	11.05	13.70	18.10	0.152	0.174	0.216	0.285

[a] The concentrations of NH_4SCN are: columns A, none; columns B, 5 g dm^{-3}; columns C, 10 g dm^{-3}; columns D, 20 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of $Cu(OH)_2$ and solution were shaken, allowed to stand for 18 hours, then shaken again and filtered. The filtrate was analyzed iodometrically to determine its copper content.

SOURCE AND PURITY OF MATERIALS:

The $Cu(OH)_2$ was prepared by adding an excess of NaOH to an ammoniacal solution of $CuSO_4$. The precipitate was washed with cold water and dried over $CaCl_2$ in a dessicator. No other information about the materials is given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Prikład. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of NH_4OH and of pyridine at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions [a] containing pyridine at a temperature of 18-20°C.

$C_{pyridine}$/g dm^{-3}	C_{Cu}/g dm^{-3} A	C_{Cu}/g dm^{-3} B	C_{Cu}/mol dm^{-3} [b] A	C_{Cu}/mol dm^{-3} [b] B
0	3.75	7.87	0.059	0.124
10	3.62	7.38	0.057	0.116
25	3.37	7.12	0.053	0.112
50	2.95	6.50	0.046	0.102

[a] The concentrations of NH_3 are; for columns A, 50 g dm^{-3}; and for columns B, 100 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

30 g dm^{-3} of $Cu(OH)_2$ was added to the solution of ammonium hydroxide and pyridine. The mixture was shaken, allowed to stand for 18 hours, and then shaken again. After sedimentation, the mixture was filtered, and the copper content of the filtrate was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

An excess of NaOH was added to an ammoniacal solution of $CuSO_4$. The precipitated $Cu(OH)_2$ was washed with cold water and dried in a desiccator. No further information is given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

(3) Aminobenzene (*aniline*); C_6H_7N; [62-53-3]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I. *Zhur. Priklad. Khim.* 1948, *21*, 235-44.

VARIABLES:

Concentration of aminobenzene at a temperature of 18-20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cu(OH)_2$ in aqueous NH_3 solutions [a] containing aminobenzene at a temperature of 18-20°C.

$C_{C_6H_7N}$/g dm^{-3}	C_{Cu}/g dm^{-3}	$C_{C_6H_7N}$/mol dm^{-3} [b]	C_{Cu}/mol dm^{-3} [b]
0	9.73	0	0.153
5.1	9.65	0.055	0.152
16.2	9.65	0.174	0.152
20.4	9.12	0.219	0.144

[a] The concentration of NH_3 in each solution was 200 g dm^{-3}.

[b] These values were calculated by the editor.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

30 g dm^{-3} of $Cu(OH)_2$ was added to the ammonium hydroxide solution containing the aminobenzene. The mixture was shaken, allowed to stand for 18 hours, and then shaken again. After sedimentation, the mixture was filtered, and the copper content of the filtrate was determined iodometrically.

SOURCE AND PURITY OF MATERIALS:

An excess of NaOH was added to an ammoniacal solution of $CuSO_4$. The precipitated $Cu(OH)_2$ was washed with cold water and then dried in a desiccator. No further information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) hydroxide; $Cu(OH)_2$; [20427-59-2]
(2) Lithium chloride; LiCl; [7447-41-8]
(3) Lithium hydroxide; LiOH; [1310-65-2]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Spivakovskii, V. B.; Makovskaya, G. V. *Zh. Neorg. Khim.* 1968, *13*, 1555-61; *Russ. J. Inorg. Chem. (Engl. transl.)* 1968, *13*, 815-9.

VARIABLES:

Composition of the solution used to precipitate the $Cu(OH)_2$, presumably at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

All the solubility data are presented only in the form of small graphs.

When quantities of LiOH and $CuCl_2$ solutions had been added in amounts equivalent to $Cu(OH)_2$, the copper concentration and the pH of the solution were measured. The activity coefficient of the Cu^{2+} ions was calculated using the Debye-Huckel equation. Such calculations gave a vlaue of 1.3×10^{-20} for the thermodynamic solubility product constant.

From the solubility of $Cu(OH)_2$ in alkaline solutions and the value of K_{so} the authors calculate, by successive approximations, the following instability constants.

Complex	K	Reaction
$CuOH^+$	1×10^{-6}	$CuOH^+ = Cu^{2+} + OH^-$
$Cu(OH)_2$	6.6×10^{-8}	$Cu(OH)_2 = CuOH^+ + OH^-$
$Cu(OH)_3^-$	5.3×10^{-2}	$Cu(OH)_3^- = Cu(OH)_2 + OH^-$
$Cu(OH)_4^{2-}$	7.2×10^{-1}	$Cu(OH)_4^{2-} = Cu(OH)_3^- + OH^-$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Aqueous solutions of $CuCl_2$ were treated with a solution containing LiOH and LiCl. Apparently the copper content of the solution was determined as increasing amounts of the precipitating solution were added, but the analytical method is not mentioned or described. The pH of the solution was also measured. The composition of the precipitate was determined from the amount of Cu^{2+} ion that had been removed from the solution and the amount of precipitating solution that had been added.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Sodium chloride; NaCl; [7647-14-5]
(3) Potassium chloride; KCl; [7447-40-7]
(4) Carbon dioxide; CO_2; [124-38-9]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Shlyapnikov, D. S.; Shtern, E. K. *Zh. Neorg. Khim.* 1977, *22*, 1100-6; *Russ. J. Inorg. Chem. (Engl. transl.)* 1977, *22*, 604-8.

VARIABLES:

Concentration of chlorides, pressure of CO_2, and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of CuO in solutions of chlorides.

Salt	C_{salt}/mol dm^{-3}	20°C, pCO_2 = 50 atm C_{Cu}/g dm^{-3}	200°C, pCO_2 = 90 atm C_{Cu}/g dm^{-3}
none	0	0.038	0.202
NaCl	1	0.2060	0.5310
"	2	0.2950	0.7400
"	3	0.3900	0.9950
"	4	0.4800	1.2000
KCl	1	0.2650	0.6500
"	2	0.4180	0.9750
"	3	0.6271	1.3400
"	4	0.8362	1.7200

X-ray and chemical analyses showed that at 200°C and pCO_2 = 100 atm, some of the CuO had been changed to $Cu_4Cl_2(OH)_6$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The CuO and an excess of chloride solution were placed in an autoclave and mechanically shaken for 24 hours. The mixture was then filtered through a corundum filter built into the autoclave. The copper content of the filtrate was determined by the thiosulfate method.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The chlorides were recrystallized.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]

(2) Copper(II) perchlorate; $Cu(ClO_4)_2$; [13770-18-8]

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Nasanen, R.; Tamminen, V. *J. Am. Chem. Soc.* 1949, *71*, 1994-8.

VARIABLES:

Ionic strength of the solvent at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility product of CuO at 25°C.[a]

$(\text{ionic strength})^{1/2}$	$10^2 C_{Cu}$	$10^2 C_{NaOH}$	C_{NaClO_4}	pH	pK_s^o
0.097	0.694	0.199	----	5.55	19.68
0.091	0.688	0.394	----	5.65	19.69
0.085	0.683	0.587	----	5.87	19.73
0.156	1.928	0.907	----	5.46	19.62
0.151	1.900	1.161	----	5.53	19.61
0.147	1.880	1.327	----	5.58	19.64
0.145	1.872	1.398	----	5.61	19.63
0.138	1.838	1.712	----	5.89	19.66
0.137	1.831	1.760	----	6.02	19.63
0.135	1.824	1.822	----	6.78	19.66
0.247	1.263	0.362	0.0440	5.55	19.60
0.242	1.243	0.713	0.0433	5.63	19.67

[a] All concentrations are in mol dm^{-3}.

The mean value of pK_s^o is 19.65 giving 2.2×10^{-20} mol^3 dm^{-9} for K_s^o. This was calculated from the relationship:

$$C_{OH^-} = (S_{CuO}/S_{hydroxysalt})^2 \, [ClO_4^-]$$ S is the solubility product constant.

which was derived by solving simultaneously the equations for the solubility product constant of CuO and of the cupric hydroxyperchlorate.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of $Cu(ClO_4)_2$, NaOH solution, and H_2O were prepared, kept at 25 ± 0.1°C and occasionally stirred. The pH of the solutions was measured until it became constant. The pH was measured with a glass electrode. In these solutions a cupric hydroxyperchlorate and CuO were equilibrium solid phases and from the K_s^o of the basic perchlorate (which was determined separately), the pH of the solution, and the concentration of the ClO_4^- ion, the K_s^o of CuO was calculated. This calculation was based on the assumption that the Cu^{2+} ion concentration was the same for all equilibria in the system.

SOURCE AND PURITY OF MATERIALS:

All materials were of purified or reagent grade quality. The $Cu(ClO_4)_2$ was prepared from CuO and $HClO_4$.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Copper(II) oxide; CuO; [1317-38-0]
(2) Bromine; Br_2; [7726-95-6]
(3) Acetonitrile; C_2H_3N; [75-05-8]
(4) Methyl acetate; $C_3H_6O_2$; [79-20-9]

ORIGINAL MEASUREMENTS:

Busheina, I. S.; Headridge, J. B. *Analyst* 1981, *106*, 221-6.

VARIABLES:

Method of determining the solubility at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CuO in organic solvent-bromine mixtures at 25°C.

	acetonitrile-bromine		methyl acetate-bromine	
	refluxing	no refluxing	refluxing	no refluxing
C_{Cu}/g per 100 ml	0.23	0.11	0.21	0.02
C_{Cu}/mol dm^{-3} [a]	0.036	0.017	0.033	0.003

[a] The mol dm^{-3} values were calculated by the compiler.

The purpose of this study was to determine the feasibility of using organic solvent-bromine mixtures for removing inclusions from metals.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvents consisted of 10 vol of organic material plus one vol of Br_2. Two methods were used: (a) Without refluxing. 300 mg of CuO was added to 30 ml of solvent and after the reaction had subsided, another 300 mg portion of CuO was added. This was continued until all noticeable reaction stopped. The mixture was then shaken mechanically for 15 min and placed in a thermostat at 25°C overnight. It was filtered through a Whatman Glass microfiber paper, Type GF/F. A sample of the filtrate was evaporated to dryness, the residue dissolved in acid and analyzed by means of atomic absorption spectrophotometry. (b) With refluxing. If no reaction was observed when the CuO was added to the solvent, the mixture was heated under reflux for 30 min and then allowed to cool (1).

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The solvents were subjected to an additional purification procedure.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Busheina, I. S.; Headridge, J. B. *Analyst* 1980, *105*, 600.

COMPONENTS:	EVALUATOR:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U. S. A. June 1984

CRITICAL EVALUATION:

So far as the unipositive oxidation state of silver is concerned, there is no stable solid hydroxide. The only oxide is Ag_2O. Rordam (1) made an investigation of the Ag_2O/Ag electrode prior to using it as a tool for measuring the acidity of substituted benzoic acid. He came to the conclusion that there were two modifications of Ag_2O because he found two different e.m.f. values for the electrode in solutions of alkalies. The different values were assumed to be related to the method of preparation: electrolytically formed Ag_2O having a value about 30 mV larger than the value obtained when precipitated Ag_2O was used. Later (2) it was shown that this difference in e.m.f. could be explained by a partial reduction of the material as well as by assuming two different modifications of Ag_2O. In retrospect, this work was done at a time when the Ag_2O/Ag electrode was not very well understood and was considered to be unreliable and irreproducible. Later work (5) established procedures for preparing stable and reproducible Ag_2O/Ag electrodes. But the possibility of two forms of Ag_2O has again been suggested (3). The two forms are supposedly a black, crystalline and a brown, amorphous (active) form. The suggestion is made that in making solubility measurements, at least ten days should be allowed for equilibration. This length of time is necessary to allow for conversion of the "active" form to the stable crystalline form.

In addition to the above considerations, the possibility of the presence of some colloidal Ag_2O must also be taken into account when making and interpreting solubility measurements (4).

Solubility in water

This system has been the subject of many investigations. The solubility has been determined over a wide range of temperatures and several experimental approaches have been used. The results have also been expressed in different ways. Some have expressed the solubility as the concentration of Ag_2O, others as the concentration of AgOH, and still others as the concentration of metallic silver.

Three experimental methods have been used: (a) measurement of the e.m.f. of appropriate cells; (b) measurement of the electrical conductance of a saturated solution and the use of this value with accepted values for individual ionic conductances; and (c) a method in which the silver content of the saturated solution is measured by analysis. Of these methods, the analytical method is expected to give the most reliable results. The other two methods are sensitive to the Ag^+ ion concentration in solution and these methods are justified only if it is known that all the dissolved silver is in the form of Ag^+ ions, or that suitable corrections can be made for other silver-containing solute species. The nature of the dissolved silver-containing species will be discussed later in this Critical Evaluation. The e.m.f. method generally depends on the reliability of the Ag_2O/Ag electrode and, until Hamer and Craig (5) described a method for preparing reproducible Ag_2O/Ag electrodes, this electrode was known to be erratic in its behavior.

Another factor to be considered in evaluating the solubility data is the length of time allowed for equilibration. In most of the work that has been reported the time allowed for equilibration was a matter of hours, usually about 5 or 6.

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CRITICAL EVALUATION:

Only one report shows an equilibration time of a matter of two weeks or so (6). In that work the analytical method was used to determine the solubility values. Only one temperature, 298 K, was used. The solubility of Ag_2O in water is given as 2.22×10^{-4} mol Ag kg^{-1}.

In one other report several days were allowed for equilibration and a solubility value of 1.39×10^{-4} mol AgOH dm^{-3} was given at 298 K (7). The conductance method was used to obtain this value and that may be the reason it is smaller than the value reported by Johnston, et al. (6). The conductance method, as noted above, may be sensitive to the presence of only some of the dissolved Ag_2O.

Remy and Kuhlmann (8) also used the conductance method and obtained the value 1.1×10^{-4} mol Ag_2O dm^{-3} (or 2.2×10^{-4} mol Ag dm^{-3}) for the solubility of Ag_2O in water at about 293 K. They allowed less than two hours for equilibration and also introduced corrections for temperature and for the presence of CO_2.

Laue (9) measured the solubility using several experimental methods but allowed only an hour or so for equilibration. He obtained larger values with the analytical method than with the conductance method but then adjusted these values downward to correct for the presence of CO_2.

Other values obtained at 298 K by the analytical method agree fairly well with the results of Johnston, et al. (6) even though only a few hours were allowed for equilibration. These other reported values are: 2.16×10^{-4} mol AgOH dm^{-3} (10); and 2.26×10^{-4} mol Ag dm^{-3} (11).

Rebiere (12) reported larger values but he prepared the Ag_2O by different methods and the difference between the largest and smallest values was about half the mean value. Therefore, those results are considered to be unreliable.

In one paper (13) the solubility determinations were made over a temperature range of 303-353 K. All the experimental methods were used. The largest values were obtained by the analytical method. The results are shown on Figure 1. Extrapolation of the values to 298 K gives a lower value than those reported above. This may reflect the relatively short time allowed for equilibration.

The recommended value for the solubility of Ag_2O in water at 298 K is 2.2×10^{-4} mol Ag kg^{-1} or 2.2×10^{-4} mol Ag dm^{-3}.

Solubility in aqueous solutions of alkalies.

The measurement of the solubility of Ag_2O in aqueous alkalies is complicated by the fact that the Ag_2O apparently undergoes a reduction to metallic silver. This was first observed by Laue (9) and later studied by others (14). The results show that the decomposition is dependent on the temperature, concentration of alkali, the presence of foreign materials, and photo effects. These facts make it difficult to know when, or whether, equilibrium is attained.

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CRITICAL EVALUATION:

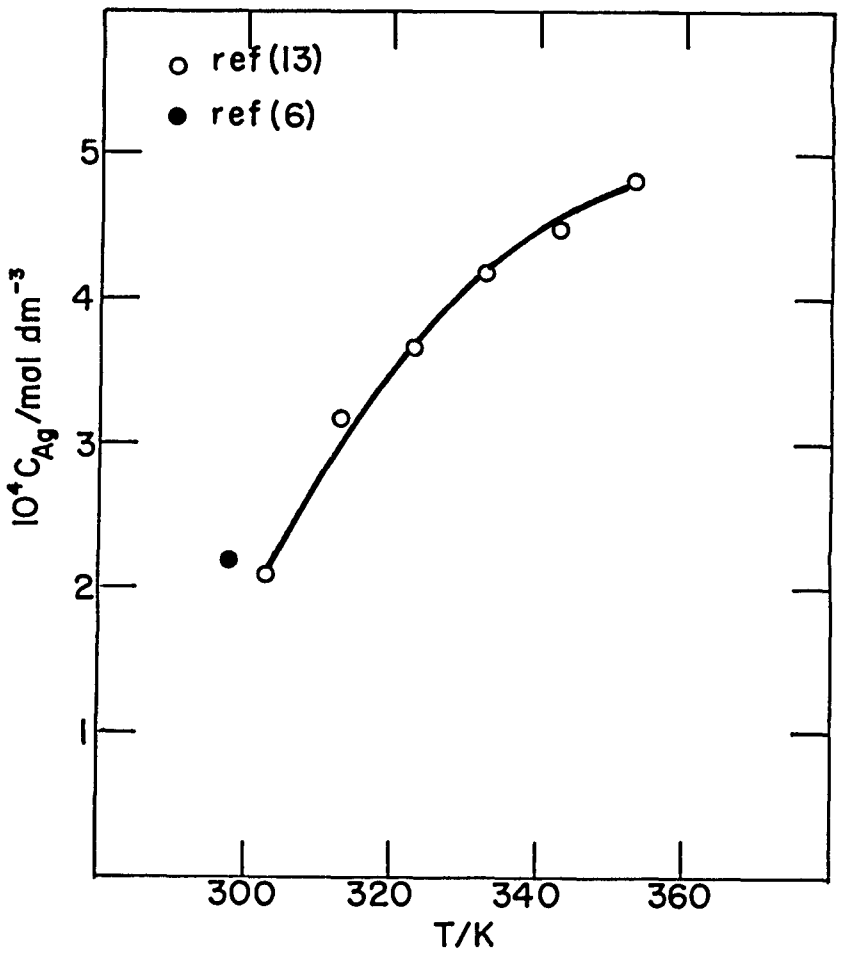

Figure 1. Solubility of Ag_2O in water.

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CRITICAL EVALUATION:

Aqueous NaOH. There are three reports dealing with this system. Laue (9) attempted to meet the complications caused by the reduction of the Ag_2O by limiting the time the mixtures were allowed to stand before measurements were made. For this reason he limited his study to NaOH solutions less concentrated than 5 mol dm^{-3}. With more concentrated NaOH solutions the filtration process required too much time. In another report on this system (3) the complication due to decomposition of the Ag_2O was obviated by allowing equilibration to take place in an oxygen atmosphere. The third report (6) makes no mention of this complication.

The solubility values for Ag_2O in NaOH concentrations up to 7 mol dm^{-3} show a fair amount of scatter. The agreement between the values of two investigations (6, 9) are within experimental uncertainty in NaOH concentrations less than 1 mol dm^{-3}. Differences become more pronounced with increasing NaOH concentrations, Figure 2. The scatter in the results is likely due to the instability of the dissolved Ag_2O. In the more dilute NaOH solutions the uncertainties are smaller and there is a definite minimum in the solubility curve, Figure 3. This minimum was also observed by Laue (9). The minimum was in about a 0.01 mol dm^{-3} NaOH solution and the solubility was about 9.3×10^{-6} mol Ag dm^{-3}. The values reported above were obtained in solutions whose total ionic strength was not controlled. In a recent investigation (3) the ionic strength was controlled. Only dilute solutions of NaOH were used and the temperature range was 298-363 K. It appears that the work was carried out with careful attention to experimental details. Yet the results do not add any clarity to the values on Figure 3. Consequently, the solubility of Ag_2O in aqueous NaOH solutions must be considered as not being definitively determined. This is due to the experimental difficulties associated with the establishment of solubility equilibria in the system.

Aqueous KOH. Relatively few data have been published for this system. The most extensive work (6) was carried out at 298 K in KOH concentrations up to 5 mol dm^{-3}. The solubility values are practically the same as those reported for aqueous NaOH by the same authors. The few numerical data reported by others (15, 16) agree with those of Johnston, et al., (6). In one paper (15) the data are presented in graphical form for the solubility of Ag_2O in KOH concentrations up to 13 mol dm^{-3}. There is a maximum in the solubility curve at a KOH concentration of about 6 mol dm^{-3}.

The solubility of Ag_2O in a KOH concentration of 1 mol dm^{-3} was measured at 278 and 300 K (16). In that investigation the solubility was found to go through a maximum about an hour after adding the solid Ag_2O to a KOH solution that was stirred at a constant rate. It was also observed that solutions of Ag_2O in aqueous KOH decreased in dissolved silver content when allowed to stand out of contact with excess solid Ag_2O. During this standing period a small precipitate of black metallic silver was formed. The maximum in the solubility as a function of time has been observed by others (3). The decrease was considered to be due to the conversion of "active" Ag_2O to the crystalline Ag_2O. At 298 K about 10 days were required to complete the process. The time needed to complete the process was less at higher temperatures. Whitby (17) observed the maximum while studying the solubility of Ag_2O in water. (No new solubility data are given in the article.) He detected the maximum after about 5 days, and then the solubility of Ag_2O decreased over the next two weeks.

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CRITICAL EVALUATION:

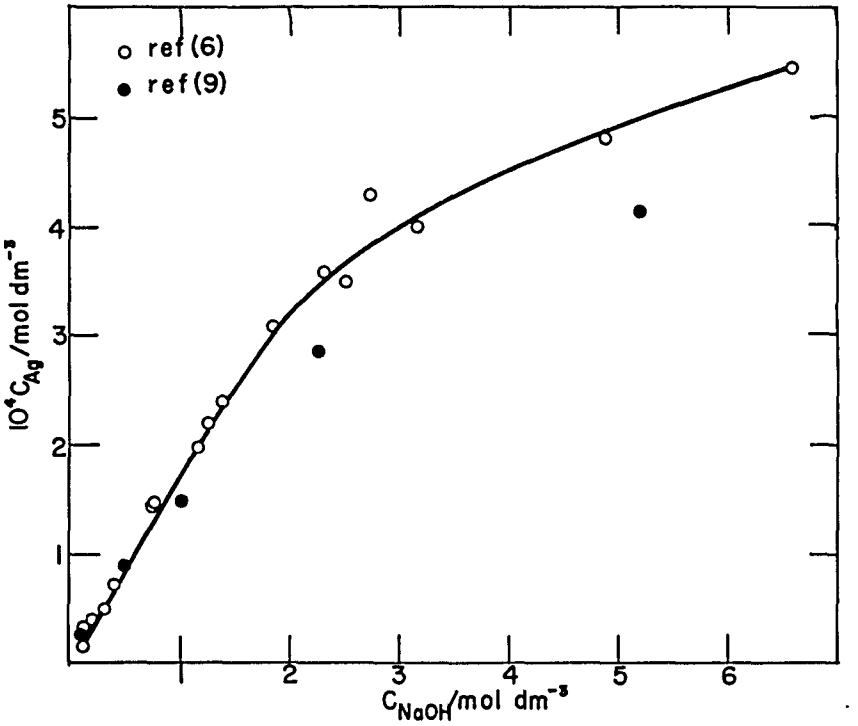

Figure 2. Solubility of Ag_2O in NaOH solutions at 298 K.

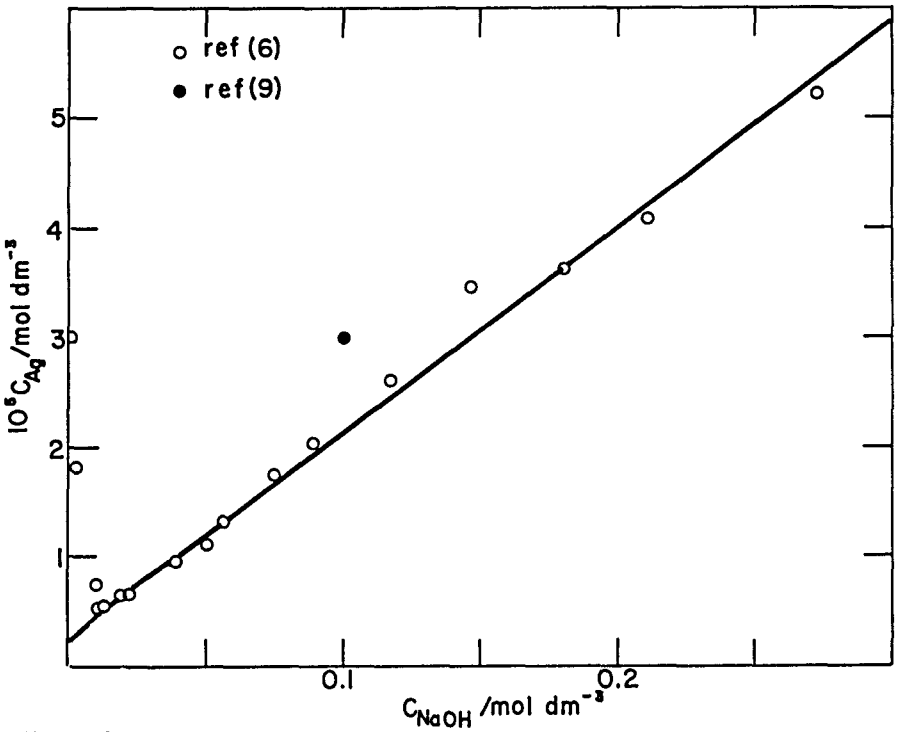

Figure 3. Solubility of Ag_2O in dilute NaOH solutions at 298 K. The solid line is equation (8).

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CRITICAL EVALUATION:

In another investigation, the solubility of Ag_2O in KOH concentrations up to 10 mol dm^{-3} was measured at 298, 323 and 351 K (18). The data are presented only in the form of 2 small graphs. The solubility increased with increasing temperatures. At 298 K the data appear to disagree with those reported above (6, 9). In the more concentrated KOH solutions the data show significant experimental uncertainties.

Values for the solubility of Ag_2O in aqueous KOH at elevated temperatures have been calculated from thermodynamic values (19). The calculations show that at temperatures from 298-573 K the solubility goes through a minimum at about pH=12. No data sheet was prepared for this article because the data were not obtained by solubility measurements.

Aqueous $Ba(OH)_2$. There is only one article that discusses this system (6). The data at 298 K are said to be the same, within experimental uncertainties, as the solubility of Ag_2O in aqueous NaOH and KOH reported by these same authors.

In summary, the solubility of Ag_2O appears to be the same in solutions of each of the alkalies reported above. The experimental uncertainties associated with these values are greater than those ordinarily encountered in making solubility measurements. The uncertainties are the result of the instability of Ag_2O in these environments. Therefore, the solubility values reported and discussed above can only be considered as tentative. It is possible that true equilibrium values cannot be obtained for the solubility of Ag_2O in aqueous solutions of alkalies.

However, the solubility data have been used to obtain an estimate of the acidic characteristics of Ag_2O. The solubility of Ag_2O in aqueous solutions can be expressed in terms of the solubility product reaction:

$$1/2\ Ag_2O(s) + 1/2\ H_2O = Ag^+ + OH^-, \qquad (1)$$

for which

$$K_1 = K^o_{so} = (a_{Ag^+}) \cdot (a_{OH^-})/(a_{H_2O})^{1/2} \qquad (2)$$

Numerous attempts have been made to evaluate K_1. The most direct way is to measure the e.m.f. of an appropriate cell containing the Ag_2O/Ag electrode. However, this electrode proved unsatisfactory and not reproducible until the work of Hamer and Craig (5) who developed a method for preparing stable and reproducible Ag_2O/Ag electrodes. They did not derive a value for K_1 from their work, but a calculation using their results yields a value of 1.88×10^{-8} at 298 K. Others (20) also attempted to evaluate K_1 from e.m.f. measurements and obtained a value of 3.2×10^{-8}, presumably at 298 K, but the temperature is not specified. A variation of this method (21) involved the use of a silver electrode whose potential in a saturated solution of Ag_2O in aqueous NaOH vs a calomel electrode was compared with the potential of a similar silver electrode in a dilute solution of $AgNO_3$ vs the same calomel electrode. Corrections were made for degree of ionization. No corrections were made for junction potentials, and the reproducibility of the results was not very good. Therefore, of the values reported above, those deduced from the work of Hamer and Craig (5) are to be preferred.

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CRITICAL EVALUATION:

Another experimental approach measures the Cl^-/OH^- ratio in solutions that are saturated simultaneously with AgCl and Ag_2O. The value of this ratio together with an accepted value for the solubility product constant of AgCl can yield a value for K_1. One of the earliest attempts to use this method (10) gave a value of 1.90×10^{-8} at 298 K. This work was repeated later (22) and a value of 1.98×10^{-8} at 298 K. was obtained (this value was not included in the original article but was calculated by the Editor from the data presented in the article). The same experimental approach has been used more recently (3). The ratio Cl^-/OH^- at 298 K appears to have two values which the authors attribute to an "active" and a crystalline form of Ag_2O. The value the authors consider to be the more reliable leads to a value of 8.12×10^{-9} for K_1. The authors did not confirm that both Ag_2O and AgCl solid phases were present at the time measurements were made. Where both solid phases were apparently present, the experimentally measured values were not very reproducible but were nearer the values reported above. Kozlov, et al. (3) contend that most investigators, even though the results are consistent with each other, used a metastable form of Ag_2O. They also refer to the work of Laue (9) but fail to note that a black precipitate observed by Laue was finely divided metallic silver. Thus, the conclusions in the paper of Kozlov, et al. (3) are considered of doubtful validity.

A third experimental approach which has been used to evaluate K_1 involves the measurement of pH in a solution containing $AgNO_3$ and NaOH with, or without, the presence of other, indifferent, electrolytes. The relative concentrations are controlled within such limits that the hydrolysis of the Ag^+ ions can be neglected. This method allows the evaluation of K_{so} as a function of total ionic strength and leads to a value of 1.95×10^{-8} at 298 K (23) for K_1. Another attempt to use this method (24) leads to a value of 6.7×10^{-9} at 298 K. The value was obtained in solutions having a total ionic strength of 1 mol dm^{-3} and therefore should have been larger, not smaller, than the earlier value (23). Part of the reason for the discrepancy may lie in the fact that the concentrations of Ag^+ and NaOH were not controlled to limit the hydrolysis of the Ag^+ ions. Therefore the result had to be obtained by writing equations involving the possible presence of other species, such as $Ag(OH)_2^-$, and then solving these equations simultaneously. Furthermore, the pH values were in the range 10-14. They were measured with a glass electrode and no indication is given that a correction was made for the effect of the alkali on the glass of the electrode. Therefore, there is a legitimate question about the validity of the basic experimental values obtained in this work.

Another experimental approach uses values obtained by a potentiometric titration of $AgNO_3$ with an alkali such as NaOH. There are several reports based on this experimental method, but in only three was the work carried out at 298 K. Nasanen (25) arrived at a value of 2.57×10^{-8} for K_1, using this approach. Two comments should be made: (a) the Ag_2O/Ag electrode was used as an indicator electrode and at that time it was an unreliable one; (b) the assumption apparently was made that all the silver in solution was present as Ag^+ ions. In the light of these comments, the result reported here is not to be preferred to those mentioned above. Similar work was carried out later (26) in which NH_4OH was used as the titrant. This complicates the interpretation of the results because of the formation of $Ag\text{-}NH_3$ complex ions. The author interprets his results to give a value of 2.37×10^{-8}. There is no evidence as to what, if any, solid phase was present during the titration.

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CRITICAL EVALUATION:

Oka (27) also used the titration method and reported a value of 1.32×10^{-8} for K_1 at 298 K. This result is rejected because of lack of experimental details. Then too, the method of treating the experimental data is not described. Another value reported for K_1 at 298 K is 3.8×10^{-8} (28) but the authors admit that this is an approximate value.

Laue (9) used several methods to evaluate K_1 at 298 K. He concluded that, on the basis of his work, the value is 1.85×10^{-8}.

The recommended value for K_1 at 298 K is 1.9×10^{-8}. This value has been obtained in several different investigations using different experimental approaches. This is the same value recommended in an earlier review (29). Solubility product determinations reported since then (3, 24) have not been sufficiently persuasive to alter this judgment.

Solubility product values have also been reported for other temperatures. Two values at 293 K were obtained by using measurements made during a potentiometric titration. A value of 1.51×10^{-8} $mol^2\ dm^{-6}$ (2) is a concentration product and based on assumptions about the degree of ionization of $AgNO_3$ solutions. Another assumption was that all the silver in solution was present as Ag^+ ions. Later (30) a value of 1.4×10^{-8} $mol^2\ dm^{-6}$ was derived for K_{so} at 293 K. In this work the concentration of Ag^+ was calculated rather than measured experimentally. Furthermore, attempts by the Editor to recalculate the data given in this paper led to different conclusions than those reported by the authors. Therefore, though the two values reported for 293 K are in fair agreement with each other, they cannot be accepted as definitive.

The experimental approach described in the previous paragraph was also used at 289 K and gave a value of 1.15×10^{-8} for K_1 (31). This value is subject to the same reservations as those expressed in the preceding paragraph.

Other values that have been reported as concentration products, but are rejected for lack of information about experimental details or for failure to include numerical data are: 5.2×10^{-9} $mol^2\ dm^{-6}$ (32); 1.87×10^{-8} $mol^2\ dm^{-6}$ (33); 10^{-8} $mol^2\ dm^{-6}$ (34); and 5.63×10^{-8} $mol^2\ dm^{-6}$ (35).

The acidic character of Ag_2O may be represented by reactions (3) and (4).

$$1/2\ Ag_2O(s) + 1/2\ H_2O = AgOH(sln) \quad (3)$$

$$1/2\ Ag_2O(s) + 1/2\ H_2O + OH^- = Ag(OH)_2^- \quad (4)$$

which have the following equilibrium constants:

$$K_3^o = (a_{AgOH})/(a_{H_2O})^{0.5} \quad (5)$$

$$K_4^o = (a_{Ag(OH)_2^-})/(a_{OH^-}) \cdot (a_{H_2O})^{0.5} \quad (6)$$

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CRITICAL EVALUATION:

The value of K_3^o is generally considered to be the value of the minimum solubility. The minimum solubility, as determined by solubility measurements (6), is 5×10^{-6} mol dm^{-3} at 298 K. A value of 1.6×10^{-6} mol dm^{-3} was obtained by a curve-fitting approach and extrapolation to zero ionic strength (3). Laue (9) reported a value of about 9×10^{-6} mol dm^{-3}. A recalculation of the data in the literature prior to 1960 yields a value of 1.8×10^{-6} mol dm^{-3} at 298 K (29). Because of the small values involved and the experimental uncertainties, the recommended value for K_3^o at 298 K is 2×10^{-6}.

The value of K_4^o has been determined from solubility data (6) in very dilute NaOH solutions. The assumptions made were that the activity of water was unity, and that the activity coefficients of all univalent ions had the same value. On the basis of these assumptions, a value of 1.95×10^{-4} at 298 K was obtained. Others (36) derived a value of 1.5×10^{-4} at constant ionic strength of 3 mol dm^{-3}. In arriving at this value it was assumed that in NaOH solutions more concentrated than 0.1 mol dm^{-3}, $Ag(OH)_2^-$ is the main solute species. Furthermore, values of pH in the vicinity of 13 were measured with a glass electrode. A recalculation of the results using a curve-fitting technique (29) gave a value of 1.9×10^{-4} at 298 K. A more recent attempt to evaluate K_4^o on the basis of solubility measurements (3) yielded values about a tenth of those reported above. The reason for this may be that in the latter work (3) measurements were made with a rather ill-defined Ag_2O. No other work reports values for K_4^o. Therefore, 1.9×10^{-4} is tentatively accepted as the value for K_4^o at 298 K.

One way to check these values is to write an equation for the total solubility of Ag_2O in alkaline solutions.

$$C_{Ag} = C_{Ag^+} + C_{AgOH} + C_{Ag(OH)_2^-} \qquad (7)$$

Substituting recommended or tentative values, this becomes

$$C_{Ag} = 1.9 \times 10^{-8}/C_{OH^-} + 2 \times 10^{-6} + 1.9 \times 10^{-4} C_{OH^-} \qquad (8)$$

Concentration values (mol dm^{-3}) rather than activities are used in equation (8) in order to check this expression against the experimentally reported solubility results. Equation (8) fits the data reasonably well in NaOH concentrations less than 0.8 mol dm^{-3}, Figure 3. At larger concentrations of NaOH the substitution of concentration for activity becomes an increasing approximation.

Equation (8) assumes that in aqueous alkali solutions the silver-containing solute species are: Ag^+, AgOH, and $Ag(OH)_2^-$. There is a fairly good consensus on this matter. However, other solute species have been suggested. Pleskov and Kabanov (37) measured the e.m.f. of a Ag_2O/Ag electrode in KOH solutions as a function of the silver concentration and the OH^- ion concentration. The slopes of the e.m.f. vs concentration lines suggested the presence of a polynuclear solute species. All the data are presented only in graphical form. On the basis of the data collected in KOH concentrations of 3-15 mol dm^{-3} the authors concluded that the solute species is $Ag_3O(OH)_2^-$ or $Ag_3(OH)_4^-$. Attempts to repeat this work in KOH concentrations of 1 and 12 mol dm^{-3} (28) failed to substantiate the conclusions of Pleskov and Kabanov (37). Antikainen, et al. (28) believed the cause of the difference was in the silver

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CRITICAL EVALUATION:

electrodes that were used. The determination of distribution equilibria of silver(I) between an alkaline solution of $NaClO_4$ and a benzene solution of quinoline (36) led to the conclusion that the main silver-containing solute species in alkaline solutions is mononuclear, i.e., $Ag(OH)_2^-$.

In an attempt to reconcile the fact that the solubility of Ag_2O in water as determined by analysis gives a larger value than the results of conductance measurements, Johnston, et al., (6) suggested the possibility of Ag_2OH^+ as a solute species. A study of the hydrolysis of the Ag^+ ion (38) yielded no evidence for the presence of Ag_2OH^+. Biedermann and Hietanen (38) suggest that a better explanation of the difference is the presence of impurities, such as CO_2. In larger NaOH or KOH concentrations, e.g., 15 mol dm^{-3}, there may be some ions of the type $Ag(OH)_3^{2-}$. However, there is no experimental evidence for this and the solubility measurements at such large concentrations of alkali are too few and, perhaps, too uncertain, to verify the presence of such a solute species.

Solubility in aqueous solutions of acidic oxides

Arsenic oxides. One report (39) deals with arsenic(III) oxide and another (40) with arsenic(V) oxide. The first report (39) contains no solubility data. No analysis for silver was made of the solutions. The object of the work was to determine how much of the arsenic (III) oxide would be removed from solution by a fixed amount of Ag_2O.

The second report (40) presents solubility data only in the form of a phase diagram at 293 K. The main objective of the work was to ascertain which silver arsenates could be formed at this temperature.

Boron(III) oxide. The only solubility report on this system is that of Sadeghi (41). The solubility of Ag_2O was determined over the temperature range 273-373 K. The data for temperatures below 303 K are given only in graphical form because of the imprecision of the values obtained. Rather extensive numerical solubility data are listed for the higher temperatures. The objective of this work was to determine the existence of a variety of silver(I) borates. The data are classified as tentative. The work appears to have been done carefully but only meager experimental details are given.

Chromium(VI) oxide. There has been a fair amount of interest in determining the number of silver chromates that can be prepared. But only one paper (42) presents solubility data for this system, and these data were obtained only at 303 K. There is no reason to reject these results, but because they are the only values available they are classed as tentative values.

Iodine(VII) oxide. One study of this system at 273 K has been reported (43). Solubility data are given but no compilation sheet has been prepared for this article. The data are rejected because of lack of experimental details. The article refers to other work for some of these details but does not indicate where these references are located.

Phosphorus(V) oxide. One article (44) appears to present solubility data for this system but the work really is a study of the solubility of silver

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CRITICAL EVALUATION:

phosphates. The analysis for silver was expressed as mass % Ag_2O, but no solubility of Ag_2O was studied or measured.

Selenium(IV) oxide. A study of this system was a companion piece to a study of the solubility of CuO in aqueous SeO_2 (45). The solubility data in this article are the only ones reported for the Ag_2O-SeO_2-H_2O system and the solubilities were measured only at 373 K. The values reported on the compilation sheet for this article are regarded as tentative until more work is reported on this system.

Solubility in aqueous NH_3 and its derivatives

Aqueous ammonia. There is very little information available on the solubility of Ag_2O in this system. Olmer (46) measured solubilities in NH_3 concentrations up to 6 mol dm^{-3}. The determinations were made at room temperature, ~290 K. More concentrated solutions of NH_3 produced explosive mixtures. Later Randall and Halford (47) made solubility measurements in solutions of NH_3 at concentrations up to 1.5 mol kg^{-1} at 298 K. No valid comparison can be made between the two sets of data (46, 47). The reported solubilities are larger at the lower temperature. Both these sets of data must be regarded as tentative.

Nasanen (26) also studied this system at 298 K but obtained no solubility data. He found that in sufficiently dilute solutions having a molar ratio $[NH_3]/[Ag] = 2$ no precipitate was formed. He studied this homogeneous equilibrium and found evidence for the presence of $Ag(NH_3)^+$ and $Ag(NH_3)_2^+$.

Aqueous solutions of methylamine. Only Olmer (46) has reported solubility data for Ag_2O in this system. The work was carried out at about 290 K. The author expresses his doubts about the accuracy of the results and it is best to concur with his judgment.

Aqueous solutions of the ethanolamines. Alner and Smeeth (30) measured the solubility of Ag_2O at 293 K in solutions of each of the three ethanolamines. Just a few data are given for each system. The interest of the authors was to determine the stability constant of each of the complexes that were formed, but they assumed in their calculations that only one complex, in which the ratio of ethanolamine to Ag^+ is 2:1, is formed in each system. The solubility results must be regarded as tentative.

Solubility in aqueous salt solutions.

This type of solubility measurement is usually made in order to measure the effect of change in total ionic strength on the solubility value. Laue (9) used KNO_3 as the source of ions and found that the solubility of Ag_2O in water did increase significantly with increasing concentrations of KNO_3. There are too few data to check whether this change in solubility follows the Debye-Huckel limiting law.

A study of the effect of the addition of inert salts to alkaline solutions (6) led the authors to conclude that there was no appreciable influence on the solubility of Ag_2O in the solutions of alkalies.

COMPONENTS:	EVALUATOR:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U. S. A. June 1984

CRITICAL EVALUATION:

Solubility in aqueous solutions of alcohols.

Methanol. In the only report on this system (48) the work was carried out at 298 K. Only one concentration of methanol was used. The concentration was chosen to give a sufficiently large value of the dielectric constant so that the electrolytes could be considered to act as strong electrolytes. The objective was to determine the change of solubility of Ag_2O with changes in pH, and to note the effect of a lower dielectric constant (lower than that of water) on the stability of the complex ions that were formed. As in aqueous solutions, the solubility of Ag_2O passes through a minimum with increasing pH. However, the solubility of Ag_2O is less in the methanol solutions and the minimum on the pH curve is broader, indicating a larger range of stability for AgOH. The solubility data are classed as tentative. There is no other work with which they can be compared.

Ethanol. There is also only one paper reporting on this system (11) but in this work, carried out at 298 K, the concentration of ethanol was varied and not held constant. Increasing concentrations of ethanol result in a decreased solubility of Ag_2O. There is no reason to have doubts about the data, but they must be classified as tentative until more work on this system is reported.

Solubility under hydrothermal conditions.

Only a few reports present information about the solubility of Ag_2O under these conditions. The reports are not very complete. In no papers are any values of the pressure recorded. In one paper (49) the solubility of Ag_2O in water is measured but hardly any experimental details are given. Another paper (50) presents solubility data but does not indicate in what concentration units the solubility values are expressed. The solubilities were measured in aqueous solutions of K_2SO_4 and KNO_3. The reason given for this procedure is that the "direct determination of Ag_2O solubility in water at elevated temperatures is difficult due to the tendency to form colloidal solutions." The solubilities measured in these salt solutions were then converted to water solubilities by means of an extended Debye-Huckel equation. Because no concentration units are specified, the values have been rejected. The same authors also measured the solubility of Ag_2O at elevated temperatures in solutions of KNO_3, with and without the addition of NH_4OH (51). The purpose was to evaluate the formation constant of $Ag(NH_3)_2^+$ at these temperatures. The data show that the solubility of Ag_2O in such solutions increases with increasing NH_3 concentration, but decreases with increasing temperature.

There is a considerable difference in solubility values reported for Ag_2O in water (13, 49). Therefore, the values must be considered as doubtful. The solubility of Ag_2O in water reaches a maximum at about 430 K. This maximum in the solubility curve has attracted some attention. Even though the values in one paper (50) have been rejected because of the failure to specify concentration units, still the numbers calculated for water solubility do show a maximum at about 440 K. It should be noted, however, that the solubility measurements from which the water solubility values were calculated show a steady increase with increasing temperature in the range 323-453 K. An attempt has been made to relate this maximum in solubility to a certain

COMPONENTS:	EVALUATOR:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U. S. A. June 1984

CRITICAL EVALUATION:

dielectric constant of the solvent (52). Solubility measurements of Ag_2O in dioxane-water mixtures (the data are not given) show a maximum in a solvent that has a dielectric constant (relative permittivity) of 40-45. The dielectric constant of water at about 430 K is also said to have the same value (52). However, solubility studies in water-ethanol mixtures (11) show no maximum in a dielectric constant range of 20-78.

In view of the small amount of data available, the incompleteness of the reports, and the fact that none of the work has been duplicated by others, all the solubility measurements of Ag_2O under hydrothermal conditions are to be classified as doubtful.

Table I. Constants for the Ag_2O-H_2O system at 298 K.

Reaction	Value	Evaluation
$1/2\ Ag_2O(s) + 1/2\ H_2O = AgOH(sln)$	$K_3^o = 2 \times 10^{-6}$	r
$1/2\ Ag_2O(s) + 1/2\ H_2O = Ag^+ + OH^-$	$K_{so}^o = 1.9 \times 10^{-8}$	r
$1/2\ Ag_2O(s) + 1/2\ H_2O + OH^- = Ag(OH)_2^-$	$K_4^o = 1.9 \times 10^{-4}$	t
solubility of Ag_2O in water	2.2×10^{-4} mol Ag kg^{-1}	r

[a] r = recommended; t = tentative

COMPONENTS:	EVALUATOR:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U. S. A. June 1984

CRITICAL EVALUATION:

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COMPONENTS:	EVALUATOR:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U. S. A. June 1984

CRITICAL EVALUATION:

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COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Noyes, A. A.; Kohr, D. A. *J. Am. Chem. Soc.* 1902, *24*, 1141-8.

VARIABLES:

The solubility in water was measured at 25°C

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in water at 25°C.

Conc. of Ag expressed as g AgI/250 ml

undersaturation	supersaturation
0.0125	0.0127
0.0130	0.0120
0.0125	0.0133
0.0102 [a]	0.0112 [a]

[a] These values were omitted by the authors in calculating the mean.

The mean value chosen by the authors is 0.0127 g AgI/250 ml which corresponds to 2.16×10^{-4} mol dm^{-3} as AgOH.

Compiler's note: This same article appears in *Z. Physik. Chem.* 1903, *42*, 36-42.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Ag_2O-H_2O mixtures were rotated in a thermostat at 25°C for 4 or 5 hours, and then were allowed to settle for a short while. After this, the liquid phase was sucked out and passed through a filter. The silver content was determined gravimetrically as AgI. Equilibrium was approached from both undersaturation and supersaturation.

SOURCE AND PURITY OF MATERIALS:

The Ag_2O was prepared by adding a clear solution of $Ba(OH)_2$ to an aqueous solution of $AgNO_3$. The precipitate was washed with 4 liters of freshly boiled water. During the process the precipitate was kept out of contact with CO_2.

ESTIMATED ERROR:

About 5%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Bottger, W. Z. *Physik, Chem.* 1903, *46*, 521-619.

VARIABLES:

Temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Saturated solutions of Ag_2O in water.

t/°C	10^6sp.cond.[a]	$(l_{Ag^+} + l_{OH^-})$[b]	C_{AgOH}/mol dm^{-3}	K_s^o
19.94	29.27[c]	237.2	1.23×10^{-4}	1.52×10^{-8}
24.94	35.98	259.1	1.39×10^{-4}	1.93×10^{-8}

[a] No unit is given for this value but it appears to be $\Omega^{-1}cm^{-1}$.

[b] No unit is given for this value but it appears to be $\Omega^{-1}cm^2mol^{-1}$.

[c] This value is the average of two measurements.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturated solutions of Ag_2O in water were prepared by mixing the two components in a rotating conductance cell in a thermostat. The conductance of the solutions was measured after several days.

SOURCE AND PURITY OF MATERIALS:

All materials were of analytical reagent grade quality and were recrystallized several times before being used. The Ag_2O was prepared by adding a solution of $Ba(OH)_2$ to aqueous $AgNO_3$. The precipitate was washed several times with water. Conductivity water was used throughout.

ESTIMATED ERROR:

The uncertainty in the individual measurements was less than 1%. The calculated results have an uncertainty of about 5%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Rebiere, G. *Bull. Soc. Chim.* 1915, *17*, 309-12.

VARIABLES:

Method of preparing the Ag_2O and its solubility in water at 25°C and 50°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in water.

	25°C		50°C	
Oxide [a]	C_{Ag_2O}/mg dm^{-3}	C_{Ag_2O}/mol dm^{-3} [b]	C_{Ag_2O}/mg dm^{-3}	C_{Ag_2O}/mol dm^{-3} [b]
I	50.00	2.16×10^{-4}	69.1	2.98×10^{-4}
II	51.9	2.23×10^{-4}	71.9	3.10×10^{-4}
III	53.8	2.32×10^{-4}	82.5	3.56×10^{-4}
IV	68.6	2.96×10^{-4}	90.4	3.90×10^{-4}

[a] The numbers refer to the method of preparation described below under "SOURCE AND PURITY OF MATERIALS".

[b] All these numbers have been recalculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

One gram of Ag_2O was added to 500 ml of water and the mixture was mechanically agitated for 2 hours in a constant temperature bath. The mixture was then filtered and the silver content was determined by adding ammoniacal KCN to the solution, then adding KI and titrating with dilute $AgNO_3$ to a bluish opalescence (1).

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used as solvent. Ag_2O was prepared as follows, using pure materials: (I) adding NaOH to aqueous $AgNO_3$; (II) adding $Ba(OH)_2$ to aqueous $AgNO_3$; (III) action of concentrated NaOH on freshly precipitated AgCl; (IV) action of concentrated NaOH on freshly precipitated Ag_2CO_3. The Ag_2O formed was collected on a filter, washed, dried between papers, and dried in a vacuum over H_2SO_4.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Rebiere, G. *Bull. Soc. Chim.* 1915, *17*, 306.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Water; H_2O; [7732-18-5]	Remy, H.; Kuhlmann, A. *Z. Anal. Chem.* 1924, *65*, 161-81.
VARIABLES: Method of measuring the solubility of Ag_2O in water.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in water.

Method	C_{Ag_2O}/mg dm^{-3}	C_{Ag_2O}/mol dm^{-3}
Conductimetric titration	25.29	1.09×10^{-4}
Specific conductance	24.80	1.07×10^{-4}

The solubility determined by conductimetric titration probably has about a 10% uncertainty because of the uncertainty in determing the inflection points in the titration curves.

The solubility value determined from the specific conductance measurement has an unknown uncertainty from two sources: (a) the measurement was made at about 19.5°C and then corrected to 18°C before the solubility calculation was made; and (b) the authors introduce a correction for the presence of CO_2 in the conductivity water. The latter correction is subject to some dispute.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Warm Ag_2O was added to conductivity water and the mixture was shaken until equilibrium was established. This was determined as the time when the specific conductance of the solution became constant--after 1.5 hours. The mixture was then filtered and the filtrate was titrated conductimetrically with excess dilute H_2SO_4 and then back-titrated conductimetrically with dilute KOH. The solubility of Ag_2O was calculated as equivalent to the H_2SO_4 used in this titration. The solubility was also calculated from the specific conductance of the saturated solution, using literature values for the specific ionic conductances.	Ag_2O was prepared by dissolving recrystallized $AgNO_3$ in conductivity water, adding freshly distilled NH_4OH, washing the precipitate, redissolving it in HNO_3, precipitating once again with NH_4OH, carefully washing the precipitate and heating it gently in a platinum crucible. Conductivity water was used throughout.
	ESTIMATED ERROR: No details are given. The temperature varied from 19 to 21°C during the measurements.
	REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Mathur, R. P. P.; Dhar, N. R. *Z. Anorg. Allg. Chem.* 1931, *199*, 387-91.

VARIABLES:

Method of measuring the solubility, and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of Ag_2O in water from analysis.

τ/°C	$10^4 C_{Ag}$/mol dm^{-3} [a]	$10^4 C_{Ag}$/mol dm^{-3} [b]
30	2.22	2.1
40	3.14	3.18
50	3.75	3.67
60	4.16	4.19
70	4.51	4.5
80	4.82	4.83

[a] Determined by weighing the residue after the solution had been evaporated to dryness.

[b] Determined gravimetrically by precipitating the Ag as AgCl.

Table II. Solubility of Ag_2O in water from e.m.f. measurements.

τ/°C	e.m.f./V	$10^4 C_{Ag}$/mol dm^{-3}
30	0.1552	1.981
40	0.1440	3.04
50	0.1462	3.61
60	0.163	4.09
70	0.165	4.48
80	0.165	4.79

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Three methods were used. (1) Ag_2O and conductivity water were shaken vigorously and then allowed to settle for 20 hours. A sample of the solution was evaporated to dryness and weighed, or the Ag^+ in solution was precipitated as AgCl and then weighed. (2) The e.m.f. of the cell Ag, 0.1 M $AgNO_3$| M KNO_3|(Ag_2O + H_2O), Ag was measured and C_{Ag} was calculated using the Nernst equation. (3) The specific conductance of the saturated solution was measured and the solubility was calculated from this value and the available values for the individual ionic conductances.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used throughout. The Ag_2O was prepared by mixing dilute aqueous $AgNO_3$ with aqueous NaOH. The precipitate was washed free of alkali with conductivity water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O, [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Mathur, R. P. P.; Dhar, N. R. *Z. Anorg. Allg. Chem.* 1931, *199*, 387-91.

EXPERIMENTAL VALUES: con't

Table III. Solubility of Ag_2O in water from conductance.

τ/°C	10^6 sp. cond./Ω^{-1} of solution	correction[a]	corrected	$10^4 c_{Ag}$/mol dm^{-3}
20	28.16	0.58	27.58	1.2
25	36.13	0.43	35.70	1.5
30	48.87	0.43	48.40	1.8

[a] Correction for the solvent conductance.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Britton, H. T. S.; Robinson, R. A. *Trans. Faraday Soc.* 1932, *28*, 531-45.

VARIABLES:

Ionic strength of solution at 16°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility product of AgOH at 16°C.

equiv. of NaOH added	pH [a]	$10^8 K_s o$ [c]	pH [b]	$10^8 K_s o$ [c]
0.1	7.48	1.62	7.97	1.32
0.2	7.54	1.58	8.04	1.35
0.3	7.61	1.55	8.11	1.38
0.4	7.69	1.55	8.17	1.33
0.5	7.81	1.62	8.25	1.30
0.6	7.92	1.62	8.34	1.29
0.7	8.03	1.51	8.49	1.34
0.8	8.21	1.45	8.70	1.44
0.9	8.56	1.58	9.04	1.58
	average = 1.56		average = 1.37	

[a] Original concentration of $AgNO_3$ solution was 0.1 mol dm^{-3}.

[b] Original concentration of $AgNO_3$ solution was 0.025 mol dm^{-3}.

[c] $K_s o = (C_{Ag^+}) \cdot (a_{OH^-})$

Using silver ion activity coefficients of 0.732 in 0.1 mol dm^{-3} solution and 0.840 in 0.025 mol dm^{-3} solution (1), the thermodynamic solubility product constant for AgOH is calculated to be 1.15×10^{-8}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

100 ml of $AgNO_3$ solution was titrated with NaOH solution having a concentration of 0.2 mol dm^{-3}. The pH of the solution was measured with a glass electrode. The silver ion concentration was calculated from the original concentration of the $AgNO_3$ and the amount of NaOH that had been added. No other experimental details are given. The purpose of the work was to illustrate the use of the glass electrode.

SOURCE AND PURITY OF MATERIALS:

No details are given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Lewis, G. N.; Randall, M. *Thermodynamics*, McGraw-Hill, New York, 1923, p. 362.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B.
J. Am. Chem. Soc. 1933, 55, 2311-25.

VARIABLES:

The temperature was 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in pure water at 25°C.

	$10^4 C_{Ag^+}$/mol kg^{-1} from undersaturation	$10^4 C_{Ag^+}$/mol kg^{-1} from supersaturation
	2.21	2.18
	2.23	2.32
	2.19	2.16
	2.18	2.31
	2.15	2.28
	2.23	
average	= 2.20	= 2.25

The average of all determinations is 2.22 x 10^{-4} mol/kg H_2O.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of Ag_2O and conductivity water were agitated for 10 to 18 days in a thermostat and then allowed to sediment 5 to 7 days in another thermostat at 25°C. The clear solution was siphoned off under N_2 pressure and forced through a silver filter. The silver content was determined by a potentiometric titration with a dilute solution of KI. Equilibrium was approached from both undersaturation and supersaturation.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was prepared and stored in contact with CO_2-free air. The Ag_2O was prepared by adding, dropwise and simultaneously, dilute solutions of $AgNO_3$ and $Ba(OH)_2$, into hot conductivity water. The precipitate was washed 15 times with conductivity water. The entire process was carried out in a N_2 atmosphere.

ESTIMATED ERROR:

In most determinations it was well below 1% and did not exceed 2%.

REFERENCES:

COMPONENTS:

(1) Silver(I) hydroxide; AgOH; [12258-15-0]

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

ORIGINAL MEASUREMENTS:

Nasanen, R.; *Suomen Kemistilehti* 1943, *16B*, 1-3.

VARIABLES:

Ionic strength of the solution at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

No titration data are given in the article, but only the following calculated results.

Solubility Product of silver(I) hydroxide at 25°C.

$\sqrt{\mu}$ [a]	10^3P [b]	pK_so [c]
0.0354	0.756	7.569
0.0659	0.808	7.511
0.0659	0.800	7.520
0.302	0.972	7.351
0.505	1.075	7.253[d]
1.000	1.32	7.083
1.370	1.29	7.106

[a] μ is the ionic strength of the solution as mol dm^{-3}.

[b] P is the reciprocal of the maximum slope of the titration curve.

[c] pK_so is calculated from the relationship: $P = 4.606\ (K_so)^{\frac{1}{2}}$.

[d] Compiler's note: this should be 7.263.

From the above results and the use of the Debye-Huckel equation for activity coefficients, the author calculates the thermodynamic solubility product of AgOH to be 2.57×10^{-8}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Dilute aqueous $AgNO_3$ was titrated potentio metrically with aqueous KOH under a N_2 atmosphere in a thermostat at 25°C. The solution was stireed and varying amounts of KNO_3 were added to control the ionic strength of the solution. A Ag_2O/Ag electrode served as the indicator electrode. By means of equations developed earlier (1, 2), the maximum slope of the titration curve was calculated and related to the solubility product.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Nasanen, R. Z. *Physik. Chem.* 1941, *188A*, 272.
2. Nasanen, R. Z. *Physik. Chem.* 1942, *190A*, 183.

COMPONENTS:

(1) Silver (I) oxide; Ag_2O; [20667-12-3]

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

ORIGINAL MEASUREMENTS:

Gavrish, M. L. : Galinker, I. S. *Zh. Neorg. Khim.* 1970, *15*, 1979-81; *Russ. J. Inorg. Chem.* (*Engl. transl.*) 1970, *15*, 1017-9.

VARIABLES:

Temperature from 25 to 260°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in water at elevated temperatures.

t/°C	c_{Ag_2O}/g kg^{-1}	$10^4 c_{Ag_2O}$/mol kg^{-1} [a]
25	0.022	0.95
130	0.52	22.4
150	0.64	27.6
180	0.64	27.6
200	0.63	27.2
210	0.55	23.7
220	0.48	20.7
230	0.46	19.9
245	0.22	9.5
250	0.23	9.9
260	0.22	9.5

[a] The mol/kg H_2O values were calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Very little information is given. The Ag_2O and water were placed in an autoclave which is described rather completely. No indication is given as to how long the mixtures were in the autoclave or the method that was used to determine the silver content of the solutions.

SOURCE AND PURITY OF MATERIALS:

No details are given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Jellinek, K.; Gordon, H. *Z. Physik. Chem.* 1924, *112*, 207-49.

VARIABLES:

Temperatures at 20° and 40°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of silver hydroxide.

t/°C	e.m.f./mV [a]	C_{Ag^+}/mol dm^{-3} [b]	C_{OH^-}/mol dm^{-3} [c]	$C_{Ag^+} \cdot C_{OH^-}$ [b]
20	178.4	1.1×10^{-6}	7.3×10^{-3}	7.8×10^{-9}
20	105.6	6.0×10^{-8}	9.1×10^{-2}	5.4×10^{-9}
21	106.4	6.2×10^{-8}	9.4×10^{-2}	5.8×10^{-9}
21	107.2	6.4×10^{-8}	9.4×10^{-2}	6.0×10^{-9}
40	142	7.4×10^{-7}	2.0×10^{-2}	1.5×10^{-8}
40	143	7.7×10^{-7}	1.6×10^{-2}	1.2×10^{-8}
40	129	4.6×10^{-7}	3.6×10^{-2}	1.7×10^{-8}
40	120	3.3×10^{-7}	3.6×10^{-2}	1.2×10^{-8}
40	102.1	1.7×10^{-7}	8.9×10^{-2}	1.5×10^{-8}

[a] No corrections were made for junction potentials.

[b] These values were all recalculated by the compiler.

[c] The OH^- ion concentration was calculated by assuming that the NaOH was completely dissociated.

The method of calculating the Ag^+ ion concentration is as follows: The e.m.f. of a Ag/0.1 mol dm^{-3} solution of $AgNO_3$ (assumed to be 80% dissociated) vs the calomel electrode was considered to be 0.461 V at 20°C and 0.454 V at 40°C. A comparison of these values with those in the Table above showed that

$$0.461 \text{ (or } 0.454) - \text{e.m.f.} = 0.058 \text{ (or } 0.062) \log (0.08)/[Ag^+]$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag_2O was added to a measured amount of aqueous NaOH. The mixture was stirred under a N_2 atmosphere for a predetermined (but unspecified) time. A Ag electrode was then inserted in the solution and its e.m.f. vs a calomel electrode was measured. This e.m.f. was compared with that of a Ag electrode in a 0.1 mol dm^{-3} $AgNO_3$ solution which was assumed to be 80% dissociated.

SOURCE AND PURITY OF MATERIALS:

Care was taken to exclude CO_2 in all procedures and from all reagents. The Ag_2O was prepared by adding dilute aqueous NaOH to dilute aqueous $AgNO_3$. The precipitate was washed ten times with hot water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Olmer, L. J. *Bull. Soc. Chim.* 1924, 35, 333-9.

VARIABLES:

Concentration of NH_4OH at room temperature, ~17°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous NH_3 at room temperature.

C_{NH_3}/mol dm^{-3}	C_{Ag}/mol dm^{-3}	C_{NH_3}/mol dm^{-3}	C_{Ag}/mol dm^{-3}
0.294	0.088	2.353	0.710
0.588	0.181	2.941	0.848
0.882	0.258	3.521	0.986
1.176	0.355	4.049	1.092
1.471	0.456	4.056	1.191
1.765	0.526	5.001	1.304
2.059	0.585	5.469	1.363

The author attempted to carry out the solubility studies at larger concentrations of NH_3, but he encountered explosive mixtures and inaccurate analyses.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A large excess of Ag_2O was added to aqueous NH_4OH. The mixture was agitated for 2 hours and then allowed to settle for 24 hours. The mixture was decanted and the silver content of the liquid phase was determined gravimetrically as AgCl. The ammonia content of the solution was determined by weighing it as NH_4Cl. All determinations were carried out in duplicate.

SOURCE AND PURITY OF MATERIALS:

The Ag_2O was prepared by adding a slight excess of aqueous $Ba(OH)_2$ to a solution of $AgNO_3$. The precipitate was washed with boiling water and dried in a vacuum for several days in the absence of light. Nothing is said about the source or quality of the other components.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Methylamine; CH_5N; [74-89-5]

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

ORIGINAL MEASUREMENTS:

Olmer, L. J. *Bull. Soc. Chim.* 1924, 35, 333-9.

VARIABLES:

Concentration of methylamine at room temperature, ~17°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous methylamine.

C_{CH_5N}/mol dm^{-3}	C_{Ag}/mol dm^{-3}
0.440	0.104
1.412	0.340
2.095	0.504
3.279	0.731
3.556	0.759
5.716	0.954
8.230	0.885
9.333	0.658

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Damp Ag_2O was added to solutions of methylamine. The mixtures were shaken intermittently for 24 hours, then decanted. Silver content of the liquid phase was determined gravimetrically as AgCl. The concentration of methylamine was determined gravimetrically as the hydrochloride. All measurements were made in duplicate.

SOURCE AND PURITY OF MATERIALS:

The Ag_2O was prepared by adding a slight excess of aqueous $Ba(OH)_2$ to a solution of $AgNO_3$. The precipitate was washed with boiling water, and dried in a vacuum for several days. The methylamine was purified by treatment with benzaldehyde and HCl.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Ethanol; C_2H_6O; [64-17-5]

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

ORIGINAL MEASUREMENTS:

Klosky, S.; Woo, L. *J. Phys. Chem.* 1926, *30*, 1179-80.

VARIABLES:

Ratio of ethanol to water in the solvent at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in water-ethanol mixtures at 25°C.[a]

$C_{ethanol}$/mass %	C_{Ag_2O}/mg dm^{-3}	$10^5 C_{Ag_2O}$/mol dm^{-3} [b]
0	26.2	11.3
10.95	19.7	8.5
22.92	18.1	7.8
34.30	17.6	7.6
45.70	17.4	7.5
64.00	14.5	6.3
77.00	12.0	5.2
91.50	9.1	3.9

[a] Each value is the average of two determinations.

[b] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of Ag_2O and solvent were contained in bottles placed in a thermostat at 25°C. The mixtures were stirred for about 10 hours, allowed to settle for an hour, and then filtered. A small amount of solution having 0.1 mol KCl dm^{-3} was added to the filtrate and the resulting turbidity was compared with a set of standards to determine the silver content.

SOURCE AND PURITY OF MATERIALS:

The Ag_2O was prepared by treating an aqueous solution of $AgNO_3$ with aqueous NaOH, washing the precipitate by decantation until it was free of sodium ions. The precipitate was then dried over concentrated H_2SO_4 in a desiccator. The ethanol was a 95% mixture that was redistilled twice.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

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

ORIGINAL MEASUREMENTS:

Laue, E. Z. *Anorg. Allg. Chem.* 1927, *165*, 325-63.

VARIABLES:

Method of measuring the solubility, and the temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of Ag_2O in water.[a]

t/°C	10^6sp. cond./Ω^{-1}	$10^4 C_{Ag}$/mol dm^{-3}
18	26.09[b]	1.14
20	28.58	1.20
25	35.48[b]	1.39

[a] Determined from specific conductance measurements. The measured values were corrected according to a table published earlier (2).

[b] Average of two values.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Two methods were used to measure the solubility of Ag_2O. (1) Ag_2O was mixed with water and the mixtures were rotated. The liquid phase was removed and another sample of water was added. This process was repeated 3 times to remove the finely divided particles. The specific conductance of the sample was measured (1) and the solubility determined from this value and literature values for individual ionic conductances (2). (2) Ag_2O-water mixtures were rotated for one hour and then filtered through a glass frit. The Ag content was determined by electrolytic deposition after the solutions had been made ammoniacal.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used throughout. Ag_2O was prepared by precipitation from aqueous $AgNO_3$ with aqueous $Ba(OH)_2$. The precipitate was washed thoroughly and dried over $CaCl_2$. The KNO_3 was a reagent grade material which was recrystallized twice.

ESTIMATED ERROR:

Where several results are given the error appears to be less than 5%.

REFERENCES:

1. Bottger, W. Z. *Physik. Chem.* 1903, *46*, 521.
2. Laue, E. Z. *Anorg. Allg. Chem.* 1927, *165*, 305.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

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

ORIGINAL MEASUREMENTS:

Laue, E. *Z. Anorg. Allg. Chem.* 1927, *165*, 325-63.

EXPERIMENTAL VALUES cont'd:

Table II. Solubility of Ag_2O in water at 25°C.

In a series of determinations in which the dissolved silver content was determined by analysis, the following values were obtained (expressed as mg Ag/100 ml 1.69, 1.74, 1.72, 1.61, 1.52, 1.75, 1.79, 1.52, 1.53, 1.61, 1.64, 1.56, 1.56, 1.61. The average is 1.63 mg Ag/100 ml, or 1.51×10^{-4} mol Ag dm^{-3}. Using a correction for CO_2(2), the author adjusts this to 1.31×10^{-4} mol Ag dm^{-3}.

Table III. Solubility of Ag_2O in KNO_3 solutions at 25°C.[a]

C_{KNO_3}/mol dm^{-3}	C_{Ag}/mg $(100\ ml)^{-1}$	$10^4 C_{Ag}$/mol dm^{-3} experimental	corrected[b]
0.01	1.97	1.83	1.60
0.1	2.33	2.16	1.90
0.5	2.55	2.36	2.08
2.0	3.11	2.89	2.82

[a] The Ag content was determined analytically. Each value is the average of 4 to 7 determinations.

[b] Corrected for the presence of CO_2(2).

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Laue, E. Z. *Anorg. Allg. Chem.* 1927, *165*, 325-63.

VARIABLES:

Concentration of NaOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in NaOH solutions at 25°C.

C_{OH^-}/mol dm^{-3}	C_{Ag} [a]	C_{OH^-}/mol dm^{-3}	C_{Ag} [a]
0.0002	0.99	1.06	1.77
0.0002	0.87	1.06	1.81
		1.06	1.87
0.001	0.13	1.04	1.69
0.001	0.19	1.04	1.84
		1.02	1.60
0.01	0.09	1.02	1.60
0.01	0.11	1.01	1.64
		1.00	1.46
0.10	0.39	1.03	1.73
0.10	0.25	1.03	1.50
		1.04	1.64
0.506	0.95	1.02	1.59
0.506	1.00	1.02	1.73
		1.01	1.40
1.05	1.43	1.01	1.53
1.05	1.49	1.01	1.58
1.05	1.69	1.00	1.51

[a] The concentration of Ag is expressed as mg/100 ml.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures of Ag_2O and NaOH solution were rotated in a thermostat at 25°C for one hour, and then filtered through a glass frit. The Ag content of the filtrate was determined by electrolytic deposition after the filtrate had been made ammoniacal.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used. The NaOH solutions were prepared by dilution of a saturated NaOH solution. The Ag_2O was prepared by precipitation from aqueous $AgNO_3$ using aqueous $Ba(OH)_2$. The precipitate was washed thoroughly and dried over $CaCl_2$ in a desiccator.

ESTIMATED ERROR:

No details are given, but the uncertainties appear to be greater than 10%.

REFERENCES:

1. Laue, E. Z. *Anorg. Allg. Chem.* 1927, *165*, 305.

COMPONENTS:

(1) Silver(I) oxide, Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Laue, E. *Z. Anorg. Allg. Chem.* 1927, *165*, 325-63.

EXPERIMENTAL VALUES: (con't)

Solubility of Ag_2O in NaOH solutions at 25°C

C_{OH^-}/mol dm^{-3}	C_{Ag} [a]	C_{OH^-}/mol dm^{-3}	C_{Ag} [a]
2.28	3.10	5.27	4.16
2.28	2.96	5.00	4.51
2.28	3.01	5.07	4.46
2.22	3.12	5.17	4.14
2.22	3.24	5.34	5.07
		5.34	5.10

[a] The concentration of Ag is expressed as mg/100 ml.

Because of the scatter in the above results, the author presents the following summarizing Table.

C_{OH^-}/mol dm^{-3}	$10^4 C_{Ag}$/mol dm^{-3}	$10^4 C_{Ag}$/mol kg^{-1}
0.10	0.30	0.30
0.506	0.91	0.91
1.03	1.50	1.50
2.26	2.86	2.86
5.20	4.23	4.31

The solubility values in the 0.0002 mol dm^{-3} solutions of NaOH were used by the author to arrive at another value for the solubility of Ag_2O in water. Applying corrections he has discussed earlier (1) he arrives at a value of 1.39 x 10^{-4}mol dm^{-3} for the solubility of Ag (from Ag_2O) in water at 25°C.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Randall, M.; Halford, J. O. *J. Am. Chem. Soc.* 1930, *52*, 178-91.

VARIABLES:

Concentration of ammonium hydroxide at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous NH_4OH at 25°C.

C_{NH_4OH}/mol kg^{-1}	C_{Ag^+}/mol kg^{-1}	C_{NH_4OH}/mol kg^{-1}	C_{Ag^+}/mol kg^{-1}
0.05302	0.01155	0.3200	0.07535
0.05532	0.01282	0.3540	0.07787
0.05821	0.01338	0.6519	0.1525
0.06173	0.01406	0.6767	0.1582
0.1479	0.03499	0.6950	0.1623
0.1575	0.03606	0.8673	0.2033
0.2456	0.05787	0.9518	0.2225
0.3155	0.07352	1.2304	0.2888

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Ag_2O and NH_4OH solutions were mixed and rotated in a thermostat at 25°C for at least 24 hours and then allowed to settle for a few hours. Samples of solution were placed in an excess of HCl and back-titrated with NaOH to determine the NH_4OH content. The silver content was determined by the Volhard method.

SOURCE AND PURITY OF MATERIALS:

The NH_4OH solutions were prepared by dilution of a U.S.P. concentrated NH_4OH solution. The Ag_2O was prepared by adding aqueous $AgNO_3$ to an excess of aqueous $Ba(OH)_2$. The precipitate was washed and heated to boiling in distilled water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B.
J. Am. Chem. Soc. 1933, 55, 2311-25.

VARIABLES:

Concentration of NaOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous NaOH at 25°C.

C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U [a]	$10^5 C_{Ag}$/mol dm^{-3} S [b]	C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U [a]	$10^5 C_{Ag}$/mol dm^{-3} S [b]
0.0012	- - -	3.29	0.2112	4.01	4.19
0.0013	2.94	- - -	0.2726	5.23	- - -
0.0023	1.83	- - -	0.3920	7.38	- - -
0.0101	0.76	- - -	0.3990	7.31	- - -
0.0113	0.50	0.58	0.7485	15.0	14.4
0.0124	- - -	0.55	0.7755	14.9	15.7
0.0196	0.62	0.69	1.174	19.3	20.6
0.0223	0.67	0.67	1.276	23.2	21.9
0.0394	0.93	1.01	1.385	24.2	23.1
0.0507	1.01	1.22	1.856	30.7	31.8
0.0566	1.25	1.39	2.330	35.3	38.8
0.0754	1.72	1.80	2.514	34.9	35.0
0.0889	1.83	2.24	2.757	43.6	43.3
0.1174	- - -	2.62	3.219	39.8	41.2
0.1463	3.44	3.50	4.894	47.5	48.3
0.1807	3.62	- - -	6.600	54.0	54.6

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag_2O and NaOH solution were mixed and shaken for 10-18 days in a thermostat and then allowed to sediment for 5-7 days in another thermostat at 25°C. The clear solution was siphoned off under N_2 pressure and forced through a filter (silver, or unglazed porcelain, or porous Jena glass). Silver content was determined by a potentiometric titration with KI. Total alkali was determined by titration with a standard acid. Equilibrium was approached from both undersaturation and supersaturation.

SOURCE AND PURITY OF MATERIALS:

The NaOH solutions were prepared by the reaction of sodium amalgam with conductivity water. Ag_2O was prepared by adding, dropwise and simultaneously, dilute solutions of $AgNO_3$ and of $Ba(OH)_2$ to very hot conductivity water. The precipitate was washed 15 times with conductivity water. The entire process was carried out under a N_2 atmosphere. Conductivity water was used throughout.

ESTIMATED ERROR:

In the majority of the determinations it was well below 1%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, 55, 2311-25.

VARIABLES:

Concentration of KOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous KOH at 25°C.

C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U[a]	S[b]	C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U[a]	S[b]
0.0005	10.3	- - -	0.0600	1.51	1.40
0.0008	- - -	4.39	0.0827	1.76	1.78
0.0012	- - -	3.08	0.1225	2.50	2.63
0.0029	1.42	- - -	0.1712	3.48	3.62
0.0093	0.65	- - -	0.4116	7.96	7.96
0.0095	0.63	0.66	0.6708	11.68	12.32
0.0098	0.53	- - -	1.628	25.3	30.0
0.0138	0.58	0.64	2.063	30.8	32.8
0.0205	0.60	0.67	3.006	38.7	- - -
0.0254	0.72	0.76	3.605	41.3	43.8
0.0313	0.90	0.87	5.007	- - -	47.0
0.0457	1.03	1.12	5.238	50.9	47.0

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag_2O was added to the solvent and the mixture was shaken for 10-18 days, and then allowed to sediment for 5-7 days in another thermostat at 25°C. The clear solution was siphoned off under N_2 pressure and forced through a porous silver filter. Total alkali concentration was determined by titration with standard acid. The silver content was determined by a potentiometric titration with dilute aqueous KI. Equilibrium was approached from undersaturation and from supersaturation.

SOURCE AND PURITY OF MATERIALS:

The KOH solutions were prepared by the reaction of potassium amalgam with water. Ag_2O was prepared by adding, dropwise and simultaneously, aqueous $AgNO_3$ and aqueous $Ba(OH)_2$ to hot water. The precipitate was washed 15 times with water. The entire process was carried out under a N_2 atmosphere. All the water was conductivity water.

ESTIMATED ERROR:

Less than 1%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Barium hydroxide; $Ba(OH)_2$; [17194-00-2]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B.
J. Am. Chem. Soc. 1933, 55, 2311-25.

VARIABLES:

Concentration of $Ba(OH)_2$ at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous $Ba(OH)_2$ at 25°C.

C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$ mol dm^{-3} U[a]	$10^5 C_{Ag}$ mol dm^{-3} S[b]	C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U[a]	$10^5 C_{Ag}$/mol dm^{-3} S[b]
0.0004	17.8	- - -	0.0204	0.67	0.61
0.0007	- - -	7.37	0.0342	0.85	0.87
0.0016	2.43	3.27	0.0413	1.12	1.17
0.0027	1.28	1.24	0.0537	1.36	1.32
0.0076	0.61	- - -	0.0663	1.52	1.51
0.0153	0.65	0.73	0.0939	- - -	2.04
0.0178	0.69	- - -	0.1318	2.81	2.86
0.0191	0.54	0.86	0.1630	3.39	3.66
0.0208	0.69	0.69	0.2946	5.86	6.01

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid Ag_2O was agitated, in contact with $Ba(OH)_2$ solutions, in a shaking device for 10 to 18 days. The mixtures were allowed to sediment for 5-7 days in another thermostat at 25°C. The clear solution was siphoned off and forced through a porous silver filter under N_2 pressure. Equilibrium was approached from undersaturation and from supersaturation. Total alkalinity was determined by titration with standard acid. Silver content was determined by a potentiometric titration with a dilute KI solution.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used throughout. $Ba(OH)_2$ was reagent grade material and was recrystallized 5 times. Ag_2O was prepared by adding aqueous $AgNO_3$ and aqueous $Ba(OH)_2$ to hot conductivity water. The precipitate was washed 15 times with water. All these operations were carred out under a N_2 atmosphere.

ESTIMATED ERROR:

Less than 1 %.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

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

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B.
J. Am. Chem. Soc. 1933, 55, 2311-25.

VARIABLES:

Concentration of KNO_3 and alkalinity of the solution at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in alkaline KNO_3 solutions at 25°C.

C_{KNO_3}/mol dm^{-3}	C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$ /mol dm^{-3} U [a]	S [b]
0.0120	0.0382	0.98	1.09
0.0302	0.0338	0.98	0.84
0.0524	0.0410	1.22	1.00
0.0690	0.0471	1.33	1.47
0.0855	0.0413	1.20	1.10
0.104	0.0387	1.08	1.15
0.254	0.0638	1.64	1.79
0.300	0.0358	1.01	0.98
0.415	0.0376	0.93	1.06
0.641	0.0641	1.55	1.58
1.02	0.0367	1.04	1.03
1.34	0.0648	1.32	1.36
1.43	0.0589	1.58	1.69
1.85	0.0461	1.16	1.06
2.07	0.0644	1.45	1.39
2.46	0.0578	1.72	1.72
3.01	0.0469	1.10	1.14
3.15	0.0567	1.31	1.31
3.46	0.0451	1.16	1.23
3.71	0.0518	1.19	1.22
3.88	0.0521	1.22	1.34

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag_2O and solvent were mixed in a shaking device and shaken 10-18 days in a thermostat. After settling for 5-7 days in another thermostat at 25°C, the clear liquid was siphoned off and forced through a filter of unglazed porcelain or of porous Jena glass. All this was done under a N_2 pressure. Total alkalinity was determined by titration with a standard acid. The silver content was determined by a potentiometric titration with KI. No information is given about the substance that was used to make the solutions alkaline.

SOURCE AND PURITY OF MATERIALS:

Conductivity water was used throughout. The KNO_3 was a reagent grade material and was recrystallized twice. Ag_2O was produced by adding $AgNO_3$ and $Ba(OH)_2$ to very hot water and then washing the precipitate 15 times with water. All this was done in a N_2 atmosphere.

ESTIMATED ERROR:

Less than 1%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Potassium sulfate; K_2SO_4; [7778-80-5]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B.
J. Am. Chem. Soc. 1933, *55*, 2311-25.

VARIABLES:

Alkalinity of solution and concentration of K_2SO_4 at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in alkaline K_2SO_4 solutions at 25°C.

$C_{K_2SO_4}$/equiv dm^{-3}	C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U[a]	S[b]
0.0019	0.0492	1.16	1.10
0.0049	0.0406	1.05	1.03
0.0090	0.0407	1.13	1.23
0.0351	0.0434	1.17	1.30
0.0553	0.0414	1.05	1.10
0.0795	0.0392	1.18	1.04
0.1010	0.0554	1.23	1.47
0.1178	0.0392	1.07	1.07

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag_2O and solvent were mixed in a shaking device and shaken 10 to 18 days in a thermostat. After sedimenting for 5 to 7 days in another thermostat at 25°C, the clear liquid was siphoned off under N_2 pressure and forced through a filter of unglazed porcelain or of porous Jena glass. Total alkalinity was determined by titration with standard acid. Silver content was determined by potentiometric titration with dilute aqueous KI. Nothing is stated about what substance was used to make the K_2SO_4 solutions alkaline.

SOURCE AND PURITY OF MATERIALS:

The K_2SO_4 was a reagent grade material that was recrystallized twice from conductivity water. Ag_2O was produced by adding dilute aqueous $AgNO_3$ and dilute aqueous $Ba(OH)_2$ simultaneously to hot water and washing the precipitate 15 times. All this was done under a N_2 atmosphere. Conductivity water was used throughout.

ESTIMATED ERROR:

Less than 1%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Barium nitrate; $Ba(NO_3)_2$; [10022-31-8]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Cuta, F.; Garrett, A. B.
J. Am. Chem. Soc. 1933, 55, 2311-25.

VARIABLES:

Concentration of barium nitrate at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in alkaline $Ba(NO_3)_2$ solutions at 25°C.

$C_{Ba(NO_3)_2}$/equiv dm^{-3}	C_{OH^-}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3} U [a]	S [b]
0.0011	0.0342	0.85	0.93
0.0016	0.0309	0.78	0.91
0.0033	0.0328	0.85	1.01
0.0051	0.0278	0.94	0.91
0.0087	0.0354	0.98	1.08
0.0254	0.0358	1.01	1.03
0.0607	0.0325	0.90	0.96
0.0851	0.0422	1.07	1.13
0.1749	0.0451	1.14	1.19
0.2871	0.0440	1.23	1.24

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Ag_2O and solvent were shaken together in a mixing device in a thermostat for 10-18 days. After settling for 5-7 days in another thermostat at 25°C, the clear liquid was siphoned off and forced through a filter of unglazed porcelain or porous Jena glass. This was all done under a pressure of N_2. Total alkalinity was determined by titration with a standard acid. The silver content was measured by a potentiometric titration with KI. Equilibrium was approached both from undersaturation and from supersaturation. There is no information as to how the solutions were made alkaline.

SOURCE AND PURITY OF MATERIALS:

Ag_2O was prepared by dropping dilute aqueous $AgNO_3$ and dilute aqueous $Ba(OH)_2$ simultaneously into hot water. Under a N_2 atmosphere the precipitate was washed 15 times. Conductivity water was used throughout. The $Ba(NO_3)_2$ was reagent grade material and was recrystallized twice from water.

ESTIMATED ERROR:

Well below 1%.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Chromium(VI) oxide; [1333-82-0]

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

ORIGINAL MEASUREMENTS:

Campbell, A. N.; Lemaire, H. P. *Can. J. Research* 1947, 25B, 243-54.

VARIABLES:

Concentration of CrO_3 at 30°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous CrO_3 at 30°C.

C_{Ag_2O}/mass%	C_{CrO_3}/mass%	$10^3 C_{Ag_2O}$/mol kg^{-1} [a]	C_{CrO_3}/mol kg^{-1} [a]	Solid phase [b]
0.09	0.21	3.90	0.021	A + B
0.08	0.21	3.46	0.021	"
0.11	0.19	4.76	0.019	"
0.10	0.18	4.33	0.018	"
0.07	0.34	3.03	0.034	B
0.08	2.55	3.55	0.262	"
0.1	4.07	4.50	0.425	"
0.1	7.11	4.65	0.766	"
0.1	8.11	4.70	0.884	"
0.1	15.4	5.11	1.82	"
0.1	24.0	5.69	3.16	"
0.1	35.1	6.66	5.42	"
0.1	46.9	8.16	8.89	"
0.1	53.5	9.30	11.5	"
0.1	58.5	10.4	14.1	"
0.1	61.9	11.4	16.3	C + D
0.1	61.9	11.4	16.3	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = Ag_2CrO_4; B = solid solution; C = $Ag_2Cr_2O_7$; D = CrO_3.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Increasing quantities of CrO_3 were added to 10 g of moist Ag_2O suspended in 100 ml of water. The mixtures were stirred constantly in a constant temperature bath and the conductance of the solutions was measured daily to ensure attainment of equilibrium. The mixtures were then filtered. The silver content was determined by the Volhard method. The chromate ion concentration was measured by adding excess $FeSO_4$ and back-titrating with $KMnO_4$.

SOURCE AND PURITY OF MATERIALS:

Ag_2O was prepared by the addition of a dilute solution of NaOH to aqueous $AgNO_3$. The precipitate was washed several times with hot and cold water and placed in a desiccator. The CrO_3 was a commercial product with a purity of 99.87%. Twice-distilled water was used.

ESTIMATED ERROR:

Nothing is stated except that the temperature was controlled to within 0.03°C.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) 2-Aminoethanol (*ethanolamine*); C_2H_7NO; [141-43-5]

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

ORIGINAL MEASUREMENTS:

Alner, D. J.; Smeeth, A. G. *J. Chem. Soc.* 1958, 4207-10.

VARIABLES:

Concentration of 2-Aminoethanol at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous MEA[a] at 20°C.

$10^2 C_{MEA}$/equiv dm^{-3}	$10^2 C_{Ag_2O}$/equiv dm^{-3}	pH
5.1	1.1	11.98
10.2	2.25	12.31
15.3	3.45	12.48
20.4	4.67	12.55
22.5	5.86	12.61

[a] MEA is the 2-Aminoethanol

The authors use the above information to evaluate the stability constant of the $Ag(MEA)_2^+$ complex. This calculation is based on the following assumptions: (a) $[Ag(MEA)_2^+] = [OH^-]$; (b) the excess MEA is unionized and therefore has an activity coefficient of unity; (c) only one Ag-MEA complex is formed to any significant extent; (d) the activity of the Ag^+ ion can be calculated from the K_s^o for AgOH, i.e., 1.413×10^{-8} at 20°C. With these assumptions, the value of the stability constant is expressed as $\log \beta_2 = 6.91$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Moist Ag_2O was added to solutions of 2-Aminoethanol of known concentration, and shaken mechanically (for an unspecified time) in black bottles at 20°C until equilibrium was reached. The pH of the solution was determined with a glass electrode. The silver content of the solution was determined by the Volhard titration method.

SOURCE AND PURITY OF MATERIALS:

The Ag_2O was prepared by adding the stoichiometric amount of NaOH to a dilute solution of $AgNO_3$. The precipitate was washed with hot water until free of electrolytes, and then filtered. The 2-Aminoethanol was purified by distilling it under reduced pressure.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) 2,2'-iminodiethanol (*diethanolamine*); $C_4H_{11}NO_2$; [111-42-2]

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

ORIGINAL MEASUREMENTS:

Alner, D. J.; Smeeth, A. G. *J. Chem. Soc.* 1958, 4207-10.

VARIABLES:

Concentration of the 2,2'-iminodiethanol at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous DEA [a] at 20°C.

$10^2 C_{DEA}$/equiv dm^{-3}	$10^3 C_{Ag_2O}$/equiv dm^{-3}	pH
5.0	4.2	11.72
10.0	8.6	11.98
15.0	13.2	12.12
20.0	17.8	12.23
25.0	22.4	12.31

[a] DEA is the 2,2'-iminodiethanol.

The authors used the above data to report the stability constant of $Ag(DEA)_2^+$. The result was reported as log β_2 = 5.80. This was based on the following assumptions: (a) only one complex is formed, i.e., $Ag(DEA)_2^+$; (b) the activity of the complex is equal to the activity of the OH^- ion; (c) the excess DEA is unionized and therefore has an activity coefficient of unity; (d) K_{so}^o for AgOH is 1.413 x 10^{-8} at 20°C; (e) the activity coefficients of univalent ions was calculated from the relationship:

$$-\log f = 0.505 \sqrt{I}/(1 + \sqrt{I})$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess moist Ag_2O was added to solutions of 2,2'-iminodiethanol of known concentration, and the mixture was shaken mechanically in black bottles at 20°C until equilibrium was reached. The pH of the solutions was measured with a glass electrode. The silver content of the clear filtrate was determined by the Volhard method.

SOURCE AND PURITY OF MATERIALS:

The 2,2'-iminodiethanol was purified by distillation under reduced pressure. The Ag_2O was prepared by adding a stoichiometric amount of NaOH to a dilute solution of $AgNO_3$. The precipitate was washed with hot water until free of electrolytes, and then filtered.

ESTIMATED ERROR:

No indication is given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) 2,2',2"-Nitrilotriethanol (*triethanolamine*); $C_6H_{15}NO_3$; [120-71-6] (3) Water; H_2O; [7732-18-5]	Alner, D. J.; Smeeth, A. G. *J. Chem. Soc.* 1958, 4207-10.
VARIABLES:	**PREPARED BY:**
Concentration of 2,2',2"-nitrilotriethanol at 20°C.	T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous TEA[a] at 20°C.

$10^2 C_{TEA}$/equiv dm^{-3}	$10^3 C_{Ag_2O}$/equiv dm^{-3}	pH
10.1	1.6	11.35
15.2	2.4	11.53
20.2	3.2	11.64
25.3	4.0	11.73

[a] TEA is the 2,2',2"-nitrilotriethanol.

The authors used these data to evaluate the stability constant of $Ag(TEA)_2^+$. The result was reported as $\log\beta_2 = 4.23$. This result is based on the following assumptions:

1- only one complex is formed, i.e., $Ag(TEA)_2^+$;

2- the activity of this complex is equal to the activity of OH^- ion in the solution;

3- the excess TEA is unionized and therefore has an activity coefficient = 1;

4- K_s^o for AgOH = 1.413×10^{-8} at 20°C;

5- the activity coefficients of the univalent ions was calculated from the relationship: $-\log f = 0.505\sqrt{I}/(1 + \sqrt{I})$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Excess moist Ag_2O was added to solutions of the 2,2',2"-nitrilotriethanol and the mixtures were shaken mechanically in black bottles at 20°C until equilibrium was attained. The pH of the solutions was measured with a glass electrode. The silver content of the clear filtrate was determined by a Volhard titration.	Ag_2O was prepared by adding a stoichiometric amount of NaOH to a dilute solution of $AgNO_3$. The precipitate was washed with hot water until it was free of electrolytes, and then filtered. The 2,2',2"-nitrilotriethanol was purified by distillation under a reduced pressure. The resulting material had a purity of 99.7%.
	ESTIMATED ERROR:
	No details are given.
	REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Nasanen, R.; Merilainen, P. *Suomen Kemistilehti* 1960, *33B*, 197-9.

VARIABLES:

Ionic strength of the solution at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility product of Ag_2O at 25°C. Mean ionic strength is 0.00865 mol dm^{-3}.

$10^3 C_{Ag}$/mol dm^{-3} [a]	$10^3 C_{OH^-}$/mol dm^{-3} [a]	pH	log K
8.77	3.51	8.609	6.297
8.70	4.35	8.683	6.288
8.62	5.17	8.785	6.290
8.55	5.98	8.910	6.287
8.47	6.78	9.086	6.281

Table II. Solubility product of Ag_2O at 25°C. Mean ionic strength is 0.0182 mol dm^{-3}.

$10^3 C_{Ag}$/mol dm^{-3} [a]	$10^3 C_{OH^-}$/mol dm^{-3} [a]	pH	log K
18.9	5.66	8.186	6.307
18.5	7.41	8.265	6.311
18.2	9.09	8.343	6.302
17.9	10.71	8.451	6.305
17.5	12.28	8.576	6.297

[a] These are the total concentrations of $AgNO_3$ and NaOH that were added.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Varying amounts of a solution of NaOH were added to a constant amount of $AgNO_3$, but in all cases the molar ratio of NaOH:$AgNO_3$ was less than one. Sometimes KNO_3 or $NaClO_4$ were added to modify the ionic strength of the solution. The sample bottles were filled in a N_2 atmosphere. After a standing period of several days, the pH of the solution was measured with a glass electrode. The concentration of the Ag^+ ion was calculated as the difference between the total concentrations of $AgNO_3$ and NaOH. $K = C_{Ag^+}/C_{H^+}$ was calculated for the following reaction: $1/2Ag_2O(s) + H^+ = Ag^+ + 1/2H_2O$.

SOURCE AND PURITY OF MATERIALS:

Nothing is stated about this.

ESTIMATED ERROR:

The log K values are considered accurate to within 0.01 logarithmic unit.

REFERENCES:

1. Nasanen, R.; Merilainen, P. *Suomen Kemistilehti* 1960, *33B*, 149.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water, H_2O; [7732-18-5]	Nasanen, R., Merilainen, P. *Suomen Kemistilehti* 1960, 33B, 197-9.

EXPERIMENTAL VALUES, contd:

Table III. Solubility product of Ag_2O in KNO_3 solutions at 25°C.

I/mol dm^{-3}	log K	pK_w [a]	pK_s^o
0.0087	6.29	13.91	7.62
0.0182	6.30	13.88	7.58
0.262	6.36	13.73	7.37
1.010	6.55	13.73	7.18
2.000	6.73	13.88	7.15

Table IV. Solubility product of Ag_2O in $NaClO_4$ solutions at 25°C.

I/mol dm^{-3}	pK_w [a]	pK_s^o
0.260	13.73	7.37
1.000	13.77	7.29
3.000	14.17	7.45

[a] These values were taken from earlier work by these authors (1).

The authors derive the following equation from their data:

$$\log K = 6.29 + 0.28I - 0.031I^2.$$

From this equation and from the fact that $K_s^o = K \cdot K_w$ they arrive at $pK_s^o = 7.71$ (I = 0, 25°C).

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Dirkse, T. P.; Vander Lugt, L. A.; Schnyders, H. *J. Inorg. Nucl. Chem.* 1963, *25*, 859-65.

VARIABLES:

Temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in 1 mol KOH dm^{-3}

$10^4 C_{Ag_2O}$/mol dm^{-3}

t/°C	after 1 hour	after 1 week
5	1.19	0.9
27	2.17	1.7

The decrease in solubility with time is explained in terms of a reaction of Ag_2O with the aqueous KOH resulting in the formation of a soluble intermediate, $Ag(OH)_2^-$.

In another series of tests the solubility of Ag_2O in 1 mol KOH dm^{-3} at 22°C was measured over a period of 10 weeks. These results are presented only in graphical form. They show that the solubility decreases when the solutions are exposed to daylight. When the solutions are kept in the dark, the solubility of Ag_2O remains constant if excess solid oxide is present but decreases with time if no excess solid oxide is present. The reactions responsible for this are considered to be:

$$Ag_2O + 2OH^- + H_2O = 2Ag(OH)_2^-$$

$$2Ag(OH)_2^- = 2Ag = 1/2\ O_2 + H_2O + 2OH^-.$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally with continuous stirring of the mixtures. Before analysis, the mixtures were filtered through a fine pore Pyrex glass frit. Silver content was determined by a potentiometric titration with KI (1).

SOURCE AND PURITY OF MATERIALS:

Ag_2O was a commercially available product. The KOH was carbonate-free. Distilled water was used as solvent.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, *55*, 2311.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Boron(III) oxide; B_2O_3; [1303-86-2]

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

ORIGINAL MEASUREMENTS:

Sadeghi, N. *Ann. Chim.* 1967, 2, 123-31.

VARIABLES:

Concentration of B_2O_3 in the temperature range 0 to 100°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Composition of the Ag_2O-B_2O_3-H_2O system at 30°C.

C_{Ag_2O}/mass %	$C_{B_2O_3}$/mass %	C_{Ag_2O}/mol kg^{-1} [a]	$C_{B_2O_3}$/mol kg^{-1} [a]	Solid phase [b]
0	3.50	0	0.521	A
0.10	3.64	0.0045	0.543	"
0.32	3.77	0.0144	0.565	"
0.55	4.00	0.025	0.602	"
0.81	4.40	0.037	0.667	A + B
0.80	4.33	0.036	0.656	B
0.70	3.70	0.032	0.556	"
0.56	2.80	0.025	0.416	"
0.50	2.40	0.022	0.355	"
0.46	2.22	0.020	0.328	"
0.41	1.80	0.018	0.264	"
0.30	1.0	0.013	0.146	"
0.17	0.30	0.0074	0.043	B + C
0.10	0.15	0.0043	0.022	C
0.0027	0	0.00012	0	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = H_3BO_3; B = $Ag_2O \cdot 2B_2O_3 \cdot 2H_2O$; C = Ag_2O.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The method is described only as a classical method. Borax was used to provide the B_2O_3 in the solutions. The silver content was determined by the Volhard method. The boric acid content was determined by titration with NaOH. The composition of the solid phases was determined by the Schreinemakers wet-residue method and by x-ray diffraction.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The Ag_2O was prepared by adding a solution of $Ba(OH)_2$ to a solution of $AgNO_3$.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O: [20667-12-3]	Sadeghi, N. *Ann, Chim.* 1967, *2*, 123-31
(2) Boron(III) oxide; B_2O_3; [1303-86-2]	
(3) Water; H_2O; [7732-18-5]	

EXPERIMENTAL VALUES, contd:

Table II. Composition of the Ag_2O-B_2O_3-H_2O system at 56°C.

C_{Ag_2O}/mass %	$C_{B_2O_3}$/mass %	C_{Ag_2O}/mol kg^{-1} [a]	$C_{B_2O_3}$/mol kg^{-1} [a]	Solid phase [b]
0	6.65	0	1.023	A
0.2	6.78	0.009	1.047	"
0.4	6.83	0.02	1.057	"
0.63	6.95	0.029	1.080	"
0.67	7.05	0.031	1.097	"
0.90	7.15	0.042	1.117	"
1.00	7.30	0.0471	1.143	"
1.12	7.40	0.0528	1.162	"
1.20	7.50	0.0567	1.180	"
1.40	7.75	0.0665	1.225	"
1.50	7.80	0.0714	1.235	A + D
1.57	7.90	0.0748	1.253	A[c]
1.70	8.20	0.0814	1.307	A[c] + B[c]
1.70	7.90	0.0811	1.255	B[c]
1.60	7.70	0.0761	1.219	"
1.55	7.40	0.0735	1.167	"
1.50	7.30	0.0710	1.150	"
1.45	7.60	0.0688	1.200	D
1.43	7.40	0.0677	1.166	"
1.40	7.14	0.0661	1.121	"
1.40	6.85	0.0658	1.072	D + B
1.32	6.60	0.0619	1.030	B
1.2	6.1	0.056	0.95	"
1.15	5.75	0.0533	0.887	"
1.08	5.45	0.0499	0.838	"
0.96	4.50	0.044	0.684	"
0.88	4.50	0.040	0.683	"
0.84	4.30	0.038	0.651	"
0.82	4.10	0.037	0.619	"
0.75	3.80	0.034	0.572	"
0.72	3.50	0.032	0.525	"
0.63	3.10	0.028	0.463	"
0.57	2.60	0.025	0.386	"
0.50	2.10	0.022	0.310	"
0.46	1.90	0.020	0.280	"
0.43	1.60	0.019	0.235	"
0.37	1.35	0.016	0.197	"
0.34	1.05	0.015	0.153	"
0.30	0.90	0.013	0.131	"
0.27	0.60	0.012	0.087	"
0.25	0.50	0.011	0.072	B + C
0.20	0.42	0.0087	0.061	C
0.15	0.22	0.0065	0.032	"
0.0047	0	0.00020	0	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = H_3BO_3; B = $Ag_2O \cdot 2B_2O_3 \cdot 2H_2O$; C = Ag_2O; D = $2Ag_2O \cdot 5B_2O_3 \cdot 5H_2O$.

[c] These solid phases are metastable.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3]	Sadeghi, N. *Ann. Chim.* 1967, 2, 123-31
(2) Boron(III) oxide; B_2O_3; [1303-86-2]	
(3) Water; H_2O; [7732-18-5]	

EXPERIMENTAL VALUES, contd:

Table III. Composition of the Ag_2O-B_2O_3-H_2O system at 78°C.

C_{Ag_2O}/mass %	$C_{B_2O_3}$/mass %	C_{Ag_2O}/mol kg^{-1} [a]	$C_{B_2O_3}$/mol kg^{-1} [a]	Solid phase [b]
0	10.80	0	1.739	A
1.20	11.70	0.0595	1.929	"
2.55	13.20	0.131	2.250	A + D
2.95	13.55	0.152	2.331	A[c]
3.50	14.50	0.184	2.540	A[c] + B[c]
2.50	10.80	0.124	1.789	B[c]
2.50	12.95	0.128	2.200	D
1.70	9.25	0.0824	1.492	"
1.25	5.60	0.0579	0.864	B + D
0.70	2.85	0.031	0.424	B
0.43	1.20	0.019	0.175	B + C
0.20	0.55	0.0087	0.080	C
0.019	0	0.00082	0	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = H_3BO_3; B = $Ag_2O \cdot 2B_2O_3 \cdot 2H_2O$; C = Ag_2O; D = $2Ag_2O \cdot 5B_2O_3 \cdot 5H_2O$.

[c] These solid phases are metastable.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3]	Sadeghi, N. *Ann. Chim.* 1967, 2, 123-31
(2) Boron(III) oxide; B_2O_3; [1303-86-2]	
(3) Water; H_2O; [7732-18-5]	

EXPERIMENTAL VALUES, contd:

Table IV. Composition of the Ag_2O-B_2O_3-H_2O system at 100°C.

C_{Ag_2O}/mass %	$C_{B_2O_3}$/mass %	C_{Ag_2O}/mol kg^{-1} [a]	$C_{B_2O_3}$/mol kg^{-1} [a]	Solid phase [b]
0	16.10	0	2.756	A
0.8	16.60	0.04	2.887	"
1.80	17.10	0.096	3.029	"
2.00	17.60	0.107	3.144	"
2.25	18.00	0.122	3.242	"
3.35	19.80	0.188	3.701	"
3.70	20.40	0.210	3.861	"
3.90	20.80	0.223	3.968	"
4.40	21.60	0.257	4.193	"
4.50	21.80	0.263	4.249	"
4.90	22.20	0.290	4.374	A + D
4.60	21.40	0.268	4.154	D
4.50	21.20	0.261	4.098	"
4.40	20.80	0.254	3.994	"
4.40	20.60	0.253	3.945	"
4.20	20.00	0.239	3.790	"
4.00	19.50	0.226	3.661	"
3.90	19.00	0.218	3.540	"
3.60	17.90	0.198	3.275	"
3.30	16.80	0.178	3.020	"
3.15	16.40	0.169	2.928	"
3.00	15.60	0.159	2.753	"
2.95	15.25	0.156	2.678	"
2.65	13.95	0.137	2.403	"
2.50	13.30	0.128	2.269	"
2.30	12.00	0.116	2.011	"
2.05	11.16	0.102	1.847	"
1.92	10.50	0.095	1.722	"
1.95	10.05	0.096	1.640	"
1.60	8.30	0.077	1.323	"
1.30	6.60	0.061	1.029	"
1.20	6.00	0.058	0.929	"
1.10	5.40	0.051	0.830	"
0.88	4.00	0.040	0.604	"
0.90	3.70	0.041	0.557	B + D
0.80	3.30	0.036	0.494	B
0.70	2.80	0.031	0.417	"
0.66	2.80	0.030	0.417	"
0.55	2.13	0.024	0.314	"
0.57	1.80	0.025	0.265	B + C
0.50	1.60	0.022	0.235	C
0.40	1.40	0.018	0.205	"
0.37	1.20	0.016	0.175	"
0.25	0.90	0.011	0.131	"
0.17	0.60	0.0074	0.087	"
0.044	0	0.0019	0	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = H_3BO_3; B = $Ag_2O \cdot 2B_2O_3 \cdot 2H_2O$; C = Ag_2O; D = $2Ag_2O \cdot 5B_2O_3 \cdot 5H_2O$.

Isotherms for the Ag_2O-B_2O_3-H_2O system were also determined at 0 and 18°C. The results at these temperatures are given only in graphical form. The data at 0°C are considered to be rather imprecise because of the small values involved.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Selenium(IV) oxide; SeO_2; [7446-08-4]

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

ORIGINAL MEASUREMENTS:

Ojkova, T.; Gospodinov, G. *Z. Anorg. Allg. Chem.* 1982, *484*, 235-40.

VARIABLES:

Concentration of SeO_2 at 100°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility isotherm of the Ag_2O-SeO_2-H_2O system at 100°C. [a]

C_{Ag_2O}/mass %	C_{SeO_2}/mass %	C_{Ag_2O}/mol kg^{-1} [b]	C_{SeO_2}/mol kg^{-1} [b]	Solid phase
0.14	0.77	0.0061	0.070	Ag_2SeO_3
0.16	2.69	0.0071	0.250	"
0.18	6.13	0.0083	0.590	"
0.19	14.42	0.0096	1.52	"
0.20	19.63	0.011	2.21	"
0.23	29.91	0.014	3.86	"
0.25	34.00	0.016	4.66	"
0.26	39.29	0.019	5.86	"
0.27	48.97	0.023	8.69	"
0.43	52.10	0.039	9.89	"
0.40	56.82	0.040	11.97	"
0.66	62.93	0.078	15.58	"
0.68	63.07	0.081	15.68	"
2.2	69.87	0.34	22.6	- - -

[a] These data were not given in the paper but were kindly supplied in a personal communication from Dr. G. G. Gospodinov.

[b] The mol/kg H_2O values were calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

One gram of Ag_2O was added to 50 ml of a solution of SeO_2 in H_2O. The mixture was stirred for 24 hours. The glass ampule was then sealed and kept in a thermostat at 100°C for 30 days. The solid and liquid phases were separated from each other by filtration. Silver content was determined by titration with NH_4CNS. The selenium content was determined by iodometric titration.

SOURCE AND PURITY OF MATERIALS:

The SeO_2 was freshly prepared and purified by sublimation. No information is given about the source of Ag_2O or the water.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Kozlov, K.; Kuznetsov, V. N.; Khodakovskii, I. L. *Geokhimiya* 1983, 215-27; *Geochem. Int.* (*Engl. transl.*) 1983, 137-49.

VARIABLES:

Concentration of sodium hydroxide, total ionic strength, and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Table I. Equilibrium values for the reaction:[a]

$$AgCl(s) + OH^- = 1/2\ Ag_2O(s) + 1/2\ H_2O + Cl^-$$

t/°C	C_{Cl^-}/mol kg^{-1}	I/mol kg^{-1}	Solid phase	C_{Cl^-}/C_{OH^-}
25	0.007	0.20	Ag_2O + AgCl	0.0222
25	0.007	0.20	Ag_2O + AgCl	0.00888 [b]
25	0.007	0.20	Ag_2O + AgCl	0.00821 [b]
25	0.007	0.30	AgCl	0.0218
25	0.007	1.0	AgCl	0.0214
60	0.01	0.30	Ag_2O	0.0366 [b]
60	0.01	0.30	AgCl	0.0360 [b]
60	0.01	0.70	AgCl	0.0362 [b]
60	0.01	1.00	AgCl	0.0341 [b]
60	0.01	0.30	AgCl	0.0763

[a] The solid phase was allowed to equilibrate isothermally with a 0.200 mol kg^{-1} solution of NaOH.

[b] The Ag_2O present is said to be an active form rather than the crystalline form.

K_{so} for AgOH was calculated from log K_{so} = -9.75 + log C_{Cl^-}/C_{OH^-}, where -9.75 is log K_{so} for AgCl.

The authors report a value of log K^o_{so} = -8.08 ± 0.02 at 25°C, but this appears to be a concentration product rather than a thermodynamic value.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Two methods were used. In one method, solid Ag_2O and/or AgCl was added to a 0.200 mol kg^{-1} solution of NaOH and allowed to equilibrate. Then the concentration ratio of Cl^-/OH^- was measured and used with the solubility product value for AgCl to obtain the solubility product value for Ag_2O. In the second method, mixtures of solid Ag_2O and aqueous NaOH solutions were allowed to equilibrate isothermally in an O_2 atmosphere. This was done to prevent the decomposition of the Ag_2O. A jet of O_2 was used to stir the mixtures occasionally. The analyses were made by potentiometric titration: with HCl to determine OH^- ion; with $AgNO_3$ to determine Cl^- ion; and with KI to determine Ag^+ ion. The silver content was also determined by atomic absorption spectrometry. Total ionic strength was attained by the addition of $NaClO_4$.

SOURCE AND PURITY OF MATERIALS:

Chemically pure materials were used and were recrystallized several times. Ag_2O was prepared by a method described earlier (1). The water was double-distilled and was boiled to remove CO_2.

ESTIMATED ERROR:

The temperature was controlled to within 0.05°C. The analytical uncertainties were less than 6%.

REFERENCES:

1. Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, 55, 2311.

COMPONENTS:
(1) Silver(I) oxide; Ag_2O; [20667-12-3]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Kozlov, K.; Kuznetsov, V. N.; Khodakovskii, I. L. *Geokhimiya* 1983, 215-27; *Geochem. Int.* (*Engl. transl.*) 1983, 137-49.

EXPERIMENTAL VALUES, contd:

Table II. Solubility of Ag_2O in NaOH solutions.

T/K	I/mol kg^{-1}	C_{NaOH}/mol kg^{-1}	$10^6 C_{Ag^+}$/mol kg^{-1}
298.15	2.65	0.00835	2.16
"	"	0.0209	2.55
"	"	0.0342	4.35
"	"	0.0523	6.65
"	"	0.0838	8.40
"	"	0.0839	8.36
"	"	0.115	10.3
"	"	0.370	27.6
333.15	"	0.00809	2.60
"	"	0.0202	3.53
"	"	0.0523	4.03
"	"	0.115	13.6
"	"	0.206	19.7
"	"	0.370	23.7
298.15	1.14	0.00719	2.30
"	"	0.00719	2.13
"	"	0.0116	2.27
"	"	0.0180	2.48
"	"	0.177	9.67
"	"	0.177	9.49
333.15	"	0.0119	2.86
"	"	0.0180	3.19
"	"	0.0310	4.35
"	"	0.0452	4.60
"	"	0.177	14.2
"	"	0.233	17.5
363.15	"	0.00700	6.57
"	"	0.00719	5.78
"	"	0.0452	7.97
"	"	0.177	27.3
298.15	0.53	0.0168	2.54
"	"	0.0422	2.57
"	"	0.106	4.44
"	"	0.166	8.27
333.15	"	0.329	21.7
"	"	0.00672	6.16
"	"	0.0422	11.0
"	"	0.166	29.6
"	"	0.329	66.0
"	"	0.00672	12.5
363.15	"	0.0422	19.3
"	"	0.106	39.1
"	"	0.166	82.9
"	"	0.329	121

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kozlov, K.; Kuznetsov, V. N.; Khodakovskii, I. L. *Geokhimiya* 1983, 215-27; *Geochem. Int.* (*Engl. transl.*) 1983, 137-49.

EXPERIMENTAL VALUES, contd:

Table III. Calculated constants [a]

t/°C	I/mol kg^{-1}	-log K_{s1} [b]	-log K_{s2} [c]
25	0.53	5.80	4.37
25	1.14	5.75	4.36
25	2.65	5.77	4.16
60	0.53	5.44	3.82
60	1.14	5.78	4.13
60	2.65	5.82	4.13
90	0.53	5.20	3.46
90	1.14	5.55	3.85
25	0	5.79 ± 0.10	4.37 ± 0.05
60	0	5.46 ± 0.15	3.86 ± 0.10
90	0	5.38 ± 0.15	3.66 ± 0.15

[a] The constants were calculated from the results in Table II. An equation was written for the total concentration of Ag in terms of Ag^+, AgOH and $Ag(OH)_2^-$. This equation was solved by successive approximations to minimize the sum of the squares of the differences in experimental and calculated values. The values at zero ionic strength were calculated on the assumption that the constants have a linear dependence on ionic strength.

[b] For the equation: $1/2\ Ag_2O(s) + 1/2\ H_2O = AgOH\ (aq)$

[c] For the reaction: $1/2\ Ag_2O(s) + 1/2\ H_2O + OH^- = Ag(OH)_2^-(aq)$

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Silver nitrate; $AgNO_3$; [7761-88-8]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Britton, H. T. S. *J. Chem. Soc.* 1925, *127*, 2956-70.

VARIABLES:

Concentration of NaOH at 20°C

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility product constant of AgOH at 20°C.[a]

v/ml[b]	e.m.f./V	$10^7 C_{Ag^+}$/mol dm^{-3}	$10^4 C_{OH^-}$/mol dm^{-3}	$10^8(C_{Ag^+} \cdot C_{OH^-})$
27.62	0.263	24.0	59.4	1.43
30.0	0.269	18.9	76.9	1.45
35.0	0.279	12.7	111	1.41
40.1	0.285	9.98	143	1.43
50.1	0.293	7.46	200	1.49
60.0	0.300	5.51	250	1.38
71.1	0.303	4.89	289[c]	1.46
80.0	0.303	4.89	333	1.63
90.0	0.3045	4.60	368	1.70[d]
100.0	0.306	4.35	400	1.74

a Measurements were made only after all colloidal material had disappeared.

b Volume of 0.1 mol NaOH dm^{-3} solution added to 100 ml of 0.2 mol $AgNO_3$ dm^{-3}.

c Compiler's note; this should be 299.

d Compiler's note; this should be 1.69.

The average value of K_{so} in the above table is 1.51×10^{-8} mol^2 dm^{-6}. This is a concentration product. The assumption that the degree of ionization of the $AgNO_3$ in the reference electrode was 81.4% is significantly larger than the activity coefficient of 0.75 calculated from the extended Debye-Huckel equation (1). Recalculating the above values using this activity coefficient gives an average K_{so} of 1.42×10^{-8} mol^2 dm^{-6}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A solution of $AgNO_3$ containing 0.02 mol dm^{-3} was titrated with a NaOH solution containing 0.1 mol dm^{-3}. During the titration the e.m.f. was measured between a silver electrode immersed in this solution and a silver electrode immersed in a solution containing 0.1 mol $AgNO_3$dm^{-3}. A saturated solution of KNO_3 served as a bridge between these 2 electrode systems. The concentration of silver ion was calculated from the equation: $E_{cell} = -0.063-0.058 \log [Ag^+]$. The OH- ion concentration was assumed to be equal to the concentration of the excess alkali that had been added.

SOURCE AND PURITY OF MATERIALS:

No details are given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

1. Kielland, J. *J. Am. Chem. Soc.* 1937, *59*, 1675.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

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

ORIGINAL MEASUREMENTS:

Antikainen, P. J.; Dyrssen, D. *Acta Chem. Scand.* 1960, *14*, 86-94.

VARIABLES:

Concentration of NaOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in NaOH solutions at 25°C. [a]

$\log C_{OH^-}$/mol dm^{-3}	$\log C_{Ag}$/mol dm^{-3}	$\log C_{Ag}/C_{OH^-}$ [b]
-1.42	-5.08	(-3.66)
-1.04	-4.76	(-3.72)
-0.883	-4.65	-3.77
-0.827	-4.60	-3.77
-0.578	-4.50	-3.92
-0.461	-4.30	-3.84
-0.248	-4.06	-3.81

[a] The solutions all had a Na^+ ion concentration of 3 mol dm^{-3}.

[b] The authors assume, on the basis of distribution experiments, that the only solute species are: Ag^+, AgOH and $Ag(OH)_2^-$. With the further assumption that at OH^- ion concentrations greater than 0.1 mol dm^{-3} the main solute species is $Ag(OH)_2^-$, the authors arrive at a value of $\log K_s2 = -3.82 \pm 0.06$ for the following reaction:

$$\tfrac{1}{2}Ag_2O(s) + \tfrac{1}{2}H_2O + OH^- = Ag(OH)_2^-.$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The Ag_2O and solvent were mixed and slowly tilted at least 2 days. The Na^+ concentration in the solvent was maintained at 3 mol dm^{-3} by the addition of NaOH and $NaClO_4$. After equilibration the phases were separated by centrifuging. Silver analysis was done by means of radioactive ^{110m}Ag. The hydroxide ion concentration was determined with the use of a glass electrode.

SOURCE AND PURITY OF MATERIALS:

The $NaClO_4$ was prepared by the reaction of Na_2CO_3 with $HClO_4$. It was recrystallized twice. Distilled water was used. Nothing is said about the source or purity of the Ag_2O. The NaOH was a reagent grade material.

ESTIMATED ERROR:

No information is given except as the results are reported.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]

(2) Potassium hydroxide; KOH; [1310-58-3]

(3) Zinc oxide; ZnO; [1314-13-2]

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

ORIGINAL MEASUREMENTS:

Amlie, R. F.; Ruetschi, P. *J. Electrochem. Soc.* 1961, *108*, 813-9.

VARIABLES:

Solvent composition at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of Ag_2O in aqueous KOH at room temperature.

C_{KOH}/mol dm^{-3}	C_{ZnO}/mol dm^{-3}	C_{Ag}/mol dm^{-3}
7.0	1.9	4.05×10^{-4}
7.0	0	4.8×10^{-4}
5.04	1.52	4.3×10^{-4}
5.04	0	4.7×10^{-4}

Solubility data for other concentrations are presented graphically. They show that the solubility of Ag_2O in aqueous KOH reaches a maximum value for C_{Ag} of about 4.5×10^{-4} mol dm^{-3} in 6 mol KOH dm^{-3} and then decreases to about 3.5×10^{-4} mol dm^{-3} in 13 mol KOH dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were shaken mechanically for 3 to 4 weeks. After being allowed to stand for 1 or 2 hours, the mixtures were filtered through a Pyrex fritted glass filter. Silver content was determined by a potentiometric titration with KI (1).

SOURCE AND PURITY OF MATERIALS:

All materials were of a purified, commercially available grade.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, *55*, 2311.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Perchloric acid; $HClO_4$; [7601-90-3]
(4) Water, H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Gubeli, A. O.; Ste-Marie, J. *Can. J. Chem.* 1967, *45*, 827-32.

VARIABLES:

pH of the solutions at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of AgOH as a function of pH at 25°C.

pH	pAg	pH	pAg
10.28	4.36	11.90	4.89
10.60	4.63	11.96	4.89
10.78	4.80	11.98	4.97
11.04	4.93	12.20	4.79
11.36	4.95	12.66	4.59
11.42	5.01	13.24	4.23
11.60	5.01	13.32	4.14
11.76	4.93	13.44	4.03

Using $K_ps = [Ag^+] \cdot [OH^-]$ and $\phi_x = [Ag(OH)_x^{1-x}]/[Ag^+] \cdot [OH^-]^x$

the authors arrive at an expression for total concentration of silver.

$$[Ag_{tot}] = \frac{K_ps}{[OH^-]} (1 + \phi_1[OH^-] + \phi_2[OH^-]^2)$$

Writing this equation for 3 experimental points the authors write 3 equations which, when solved simultaneously, give the following values:

$pK_ps = 8.17 \pm 0.01$; $p\phi_1 = -3.02 \pm 0.01$; $p\phi_2 = -4.69 \pm 0.02$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

It is not precisely clear how the solutions were prepared. It appears that NaOH was added to solutions of $AgClO_4$ to precipitate Ag_2O and then the pH of the solution was adjusted by adding $HClO_4$ or NaOH. The mixtures were stirred continuously for 5 to 6 days in a constant temperature bath at 25°C and then allowed to settle. The silver content was determined by counting the radioactivity of ^{110}Ag. The pH of the solution was measured with a glass electrode. CO_2 and O_2 were excluded from the mixtures. The total ionic strength of each solution was 1 mol dm^{-3}.

SOURCE AND PURITY OF MATERIALS:

Nothing is stated except that pure water was used.

ESTIMATED ERROR:

This is given for each value that is reported.

REFERENCES:

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]
(2) Potassium nitrate; KNO_3 [7757-79-1]
(3) Ammonium hydroxide; NH_4OH; [1336-21-6]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kozlowska-Kolodziej, B.; Bartecki, A.
Rocz. Chem. 1973, *47*, 1841-8.

VARIABLES:

Temperature of 343 to 403 K and concentration of NH_4OH.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of Ag_2O in 1 mol KNO_3 dm^{-3}

T/K	$10^4 C_{Ag^+}$/mol dm^{-3}
343	8.1
353	9.7
363	11.3
373	12.7
383	14.5
393	16.1
403	18.1

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of solid Ag_2O and aqueous NH_3 solutions containing 1 mol KNO_3 dm^{-3} were placed in an autoclave supplied with a mechanical stirrer. The mixtures were stirred until the silver content of the liquid phase became constant (this required about 6 hours). The temperature was controlled to within 0.1 K. The pressure was read on a manometer but the values are not given. The pH of the solutions was read, but these values are not supplied in the article. Silver concentration was determined by a potentiometric titration. No further details are given.

SOURCE AND PURITY OF MATERIALS:

The water was redistilled and was CO_2-free. Ag_2O was synthesized according to directions of others (1). No other information is given.

ESTIMATED ERROR:

Probably less than 1%.

REFERENCES:

1. Brauer, J. *Handbuch der Praparativen Anorganischen Chemie, Bd. II*, Stuttgart, 1960.

COMPONENTS:

(1) Silver(I) oxide; Ag_2O; [20667-12-3]
(2) Potassium nitrate; KNO_3; [7757-79-1]
(3) Ammonium hydroxide; NH_4OH; [1336-21-6]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kozlowska-Kolodziej, B.; Bartecki, A. *Rocz. Chem.* 1973, *47*, 1841-8.

EXPERIMENTAL VALUES, contd:

Table II. Solubility of Ag_2O in aqueous NH_3 containing 1 mol KNO_3 dm^{-3}.

T/K	C_{NH_3}/mol dm^{-3}	C_{Ag^+}/mol dm^{-3}	log K [a]
343	0.0380	0.00979	1.39
"	0.0256	0.00690	1.38
"	0.0202	0.00571	1.33
"	0.0128	0.00423	1.34
353	0.0376	0.00932	1.59
"	0.0252	0.00658	1.58
"	0.0199	0.00548	1.54
"	0.0124	0.00378	1.54
363	0.0371	0.00886	1.78
"	0.0245	0.00626	1.79
"	0.0196	0.00523	1.78
"	0.0122	0.00365	1.82
373	0.0364	0.00835	1.99
"	0.0240	0.00591	2.01
"	0.0193	0.00494	2.02
"	0.0120	0.00350	2.05
383	0.0235	0.00544	2.29
"	0.0190	0.00472	2.32
"	0.0118	0.00344	2.39
393	0.0228	0.00521	2.55
"	0.0187	0.00452	2.58
"	0.0114	0.00341	2.55
403	0.0224	0.00496	2.83
"	0.0179	0.00343	2.80
"	0.0109	0.00335	2.82

[a] These values are for the reaction:

$$Ag_2O(s) + 4NH_3 + H_2O = 2Ag(NH_3)_2^+ + 2OH^-.$$

In deriving these values the following assumptions were made:

1- $[Ag(NH_3)_2^+] = [OH^-] = C_{Ag^+}$ in Table II.

2- $[NH_3] = [NH_3]^\circ - 2\,[Ag(NH_3)_2^+]$ where $[NH_3]^\circ$ is C_{NH_3} of Table II.

The following equation was developed for the above data:

$$\log K = 1977.2 - 760.2 \log T - 64313/T + 0.3973\,T.$$

COMPONENTS:	EVALUATOR:
(1) Silver(II) oxide; AgO, [1301-96-8] (2) Water; H_2O, [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. April 1984

CRITICAL EVALUATION:

As a member of the transition series of metals, silver has oxidation states greater than +1. However, the only oxide in which silver has a higher oxidation state is AgO. Silver has no solid hydroxide for any of its oxidation states.

Although AgO has been known for a long time and is easy to prepare, the nature of the oxidation state of silver in AgO has been the source of some disagreement. At one time AgO was considered to be a peroxide of unipositive silver, and its formula was written as Ag_2O_2. However, Barbieri (1) showed that this was not a tenable assumption because, when acidified, AgO did not produce hydrogen peroxide.

Later, AgO was considered to be a compound of bipositive silver (2). However, further evidence cast some doubt on this assumption. For example, a study of the magnetic properties of AgO showed it to be diamagnetic (3), whereas bipositive silver should be paramagnetic, having at least one unpaired electron.

When more refined x-ray techniques became available and when neutron diffraction techniques had been developed, a further study of AgO indicated that there were two different Ag-O distances in the AgO crystal (4,5). McMillan (6) suggested that this, as well as the diamagnetism of the compound, could be accounted for by assuming that the silver in AgO was present as an equimolar mixture of Ag^+ and Ag^{3+}.

A photoelectron spectroscopy (ESCA) study of AgO (7) yielded only one peak for silver. This peak was a broad one and could have been the net effect of two peaks: one for Ag^+, and one for Ag^{3+}. No resolution of this broad peak was attempted.

Although AgO is formally called silver(II) oxide, the evidence to date indicates that it more likely is silver(I,III) oxide. Some of the apparently conflicting data reported for AgO may be accounted for by this lack of precise understanding of the oxidation state of silver in AgO.

The main interest in the study of AgO has been associated with its presence on the silver electrode in silver-alkaline batteries. The only solubility data reported for AgO are a result of this interest. And because silver-alkaline batteries use aqueous KOH as the electrolyte, all the solubility data reported for AgO are for its solubility in aqueous KOH. There is, however, very little numerical solubility data.

A study of the solubility of AgO in aqueous KOH solutions (8) showed that the concentration of dissolved silver is a function of time and passes through a maximum. Evidence was collected to show that the AgO in aqueous KOH solutions undergoes a decomposition to Ag_2O and to metallic silver. There is no consensus on the mechanism or the rates of these reactions.

A few numerical solubility data are given for room temperature (9). Most of the numerical solubility data are reported for 298 K (10). So far as comparisons can be made, these solubility values are the same as those for Ag_2O (11). This observation was also made in another report (12) although no numerical solubility data are included in that report.

The fact that the solubilities of Ag_2O and AgO in aqueous KOH appear to be the same, has elicited several explanations. A polarographic study of aqueous KOH solutions saturated with Ag_2O and AgO separately (9) showed that essentially the same polarogram was obtained for each of the two oxides. The conclusion drawn from the results is that the same solute species is formed regardless of whether Ag_2O or AgO is used to saturate the aqueous KOH. The common solute species is the one corresponding to unipositive silver, i.e., $Ag(OH)_2^-$ in the more concentrated KOH solutions. The validity of this explanation will depend on further study of the kinetics of the reduction of AgO to Ag_2O in aqueous KOH solutions.

Fleischer (13) has suggested an explanation based on the equilibrium restrictions required by the phase rule. His argument is that AgO always contains Ag_2O and, hence, two solid phases are present. According to the phase rule this dictates that the concentration of the solution phase is invariant, i.e., the solubility value should be the same whether the aqueous KOH is saturated with Ag_2O or with AgO.

The mechanism of the dissolution of AgO was investigated by McMillan (14). He could observe no paramagnetic species in solutions of AgO in aqueous KOH. He concluded that the mechanism of dissolution of AgO is different in acid media than in alkaline media. In the former, AgO dissolves as some form of Ag^{2+} while in alkaline media McMillan suggested that the solute species would be AgOH, $Ag(OH)_2^-$ and $Ag(OH)_4^-$.

COMPONENTS:	EVALUATOR:
(1) Silver(II) oxide; AgO; [1301-96-8] (2) Water, H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. April 1984

CRITICAL EVALUATION:

In conclusion, there are too few solubility data for AgO to recommend any values. Furthermore, the data that have been reported are to be received with reservations because of uncertainties about the attainment of equilibrium, the nature of the oxidation state of silver in AgO, and the kinetic and mechanistic factors associated with the dissolution process. A further possible complication is that while AgO can be prepared by different methods, there is evidence that these different preparations are not necessarily the same. There are differences, e.g., in the X-ray diffraction patterns of the various products (10, 15).

REFERENCES

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2. Klemm, W. *Z. Anorg. Allg. Chem.* 1931, *201*, 32.
3. Neiding, A. B.; Kazarnovski, I. A. *Doklady Akad. Nauk SSSR* 1951, *78*, 713.
4. Scatturin, V.; Bellon, P.; Zanetti, R. *Ricerca Sci.* 1957, *27*, 2163.
5. Scatturin, V.; Bellon, P.; Salkind, A. *Ricerca Sci.* 1960, *30*, 1034.
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7. Hammond, J. S.; Gaarenstroom, S. W.; Winograd. N. *Anal. Chem.* 1975, *47*, 2193.
8. Dirkse, T. P.; Vander Lugt, L. A.; Schnyders, H. *J. Inorg. Nucl. Chem.* 1963, *25*, 859.
9. Amlie, R. F.; Ruetschi, P. *J. Electrochem. Soc.* 1961, *108*, 813.
10. Dirkse, T. P.; Wiers, B. *J. Electrochem. Soc.* 1959, *106*, 284.
11. Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, *55*, 2311.
12. Kovba, L. D.; Balashova, N. A. *Zhur. Neorg. Khim.* 1959, *4*, 225; *Russ. J. Inorg. Chem.* (*Engl. transl.*) 1959, *4*, 94.
13. Fleischer, A. *J. Electrochem. Soc.* 1968, *115*, 816.
14. McMillan, J. A. *Nature* 1962, *195*, 594.
15. Schwab, G. M.; Hartmann, G. *Z. Anorg. Allg. Chem.* 1955, *281*, 183.

COMPONENTS:

(1) Silver(II) oxide; AgO; [1301-96-8]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Dirkse, T. P.; Wiers, B. *J. Electrochem. Soc.* 1959, *106*, 284-7.

VARIABLES:

Concentration of KOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of AgO in aqueous KOH at 25°C.[a]

C_{KOH}/mol dm^{-3}	$10^5 C_{Ag}$/mol dm^{-3}
0.0372	1.11
0.0743	1.25
0.149	2.4
0.186	3.5
0.297	5.3
0.309	7.4
0.372	7.7
0.557	9.5
0.591	13.1
0.743	12.9
1.49	31
2.93	49
4.78	61

[a] The article presents the solubility data only in the form of a graph. That graph was based on the above numerical data.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally at 25°C with constant stirring for at least 2 days. The mixtures were filtered through a Pyrex glass frit. The silver content was determined by a potentiometric titration with dilute aqueous KI (1) after the solutions had first been treated with HNO_3 to reduce any Ag^{2+} to Ag^+ (2). The KOH solutions were prepared by quantitative dilution of a stock solution to which some $Ba(OH)_2$ had been added to remove carbonate ions.

SOURCE AND PURITY OF MATERIALS:

The AgO was a commercially available product which was analyzed and found to be about 99% AgO. The KOH was a reagent grade material. The water was first deionized and then distilled.

ESTIMATED ERROR:

Less than 5%.

REFERENCES:

1. Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, *55*, 2311.

2. Jursa, F.; Jelinek, J. *Z. Anorg. Allg. Chem.* 1925, *148*, 130.

COMPONENTS:

(1) Silver(II) oxide; AgO; [1301-96-8]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Dirkse, T. P.; Vander Lugt, L. A.; Schnyders, H. *J. Inorg. Nucl. Chem.* 1963, *25*, 859-65.

VARIABLES:

Temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of AgO in 1 mol KOH dm^{-3}

t/°C	$10^4 c_{Ag}$/mol dm^{-3} after 1 hour	after 1 week
5	1.3	0.88
27	2.48	1.72

The decrease of solubility with time is expleained in terms of the following reactions:

$$AgO + OH^- + H_2O = Ag(OH)_3^-$$

$$2Ag(OH)_3^- = 2Ag(OH)_2^- + H_2O + 1/2\ O_2$$

$$2Ag(OH)_2^- = Ag_2O(s) + H_2O + 2OH^-$$

In another series of tests the solubility of AgO in 1 mol KOH dm^{-3} at 22°C was measured over a period of 10 weeks. The data are presented only in graphical form and show that the solubility of AgO is constant if excess solid AgO is present in contact with the solution, but that it gradually decreases when no excess solid AgO is present. This is explained as due to the following reaction:

$$2Ag(OH)_2^- = 2Ag + 1/2\ O_2 + H_2O + 2OH^-.$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were allowed to equilibrate isothermally with constant stirring. After filtration, the silver content of the filtrate was determined by a potentiometric titration with KI (1).

SOURCE AND PURITY OF MATERIALS:

The AgO was a commercially available product. The KOH was carbonate-free. Distilled water was the solvent.

ESTIMATED ERROR:

No details are given.

REFERENCES:

Johnston, H. L.; Cuta, F.; Garrett, A. B. *J. Am. Chem. Soc.* 1933, *55*, 2311.

COMPONENTS:	EVALUATOR:
(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. April 1984

CRITICAL EVALUATION:

Although gold has several oxidation states, the only oxide or hydroxide for which solubility data are reported is $Au(OH)_3$. There are only three papers reporting solubility data for this hydroxide. Two of these report data for 298 K, one in HNO_3 solutions (1), and the other in NaOH solutions (2). The third paper (3) reports solubility values in sulfuric acid solutions in the temperature range 291-303 K. A few solubility data for $Au(OH)_3$ in a dilute HNO_3 solution (4) are rejected because the average uncertainty in the values is about 2/3 of the value reported. Because no two papers report data for the same system all these data can only be classified as tentative.

One of these reports (2) gives solubility data for $Au(OH)_3$ in water at 298 K. The value is 3.1×10^{-6} mol kg^{-1}. The average uncertainty in the values reported to give this average is about 10%.

The solubility of $Au(OH)_3$ in aqueous NaOH passes through a maximum in a NaOH concentration of about 0.45 mol kg^{-1}, followed by a minimum in a NaOH concentration of about 1 mol kg^{-1}, Figure 1. The peak in solubility was a result of a change in the solid phase. This change in the solid phase was determined by chemical analysis as well as by microscopic examination. The originally brownish hydroxide changed to a needle-like green solid at the solubility peak. The composition of this new solid phase corresponded to Na_2HAuO_3. The solubility values up to NaOH concentrations of 0.5 mol kg^{-1} can be explained by the following equilibria:

$$Au(OH)_3 + OH^- = H_2AuO_3^- + H_2O \quad (1)$$

$$Au(OH)_3 + 2OH^- = HAuO_3^{2-} + 2H_2O \quad (2)$$

with equilibrium constant values of

$$K_1^\circ = (a_{H_2AuO_3^-}) \cdot (a_{H_2O^-})/(a_{OH^-}) = 5.25 \times 10^{-4} \quad (3)$$

$$K_2^\circ = (a_{HAuO_3^{2-}}) \cdot (a_{H_2O})^2/(a_{OH^-})^2 = 23.0 \times 10^{-4}. \quad (4)$$

To account for the decrease in solubility in NaOH concentrations of 0.5 to 1 mol kg^{-1} it is necessary to assume an additional equilibrium, perhaps equation (5).

$$Na_2HAuO_3 = 2Na^+ + HAuO_3^{2-} \quad (5)$$

For NaOH concentrations larger than 1 mol kg^{-1} other equilibria are involved, perhaps resulting in the formation of AuO_3^{3-}.

Figure 2 combines data for acid and alkaline solutions (1, 2) at 298 K. The point of minimum solubility is difficult to determine. Johnston and Leland (2) suggest that this minimum is on the acid side of neutral, i.e., the water solubility does not represent the minimum solubility. From this it follows that a saturated solution of $Au(OH)_3$ in water contains $Au(OH)_3$(sln) plus another species, perhaps $H_2AuO_3^-$.

The solubility data reported for acid solutions do not agree well with each other, Figure 3. The solubilities are plotted as a function of the hydrogen ion concentration. The difference may be a result of the analytical method used in each case. Of the three papers reporting solubility data, the analytical method for determining the gold content was different for each investigation.

It is difficult to make a further evaluation because of the sparsity of data and the very small values of solubility.

REFERENCES

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2. Johnston, H. L.; Leland, H. L. *J. Am. Chem. Soc.* 1938, *60*, 1439.
3. Jirsa, F.; Jelinek, H. *Z. Elektrochem.* 1924, *30*, 286.
4. Jirsa, F.; Jelinek, H. *Z. Elektrochem.* 1924, *30*, 534.

COMPONENTS:	EVALUATOR:
(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. April 1984

CRITICAL EVALUATION:

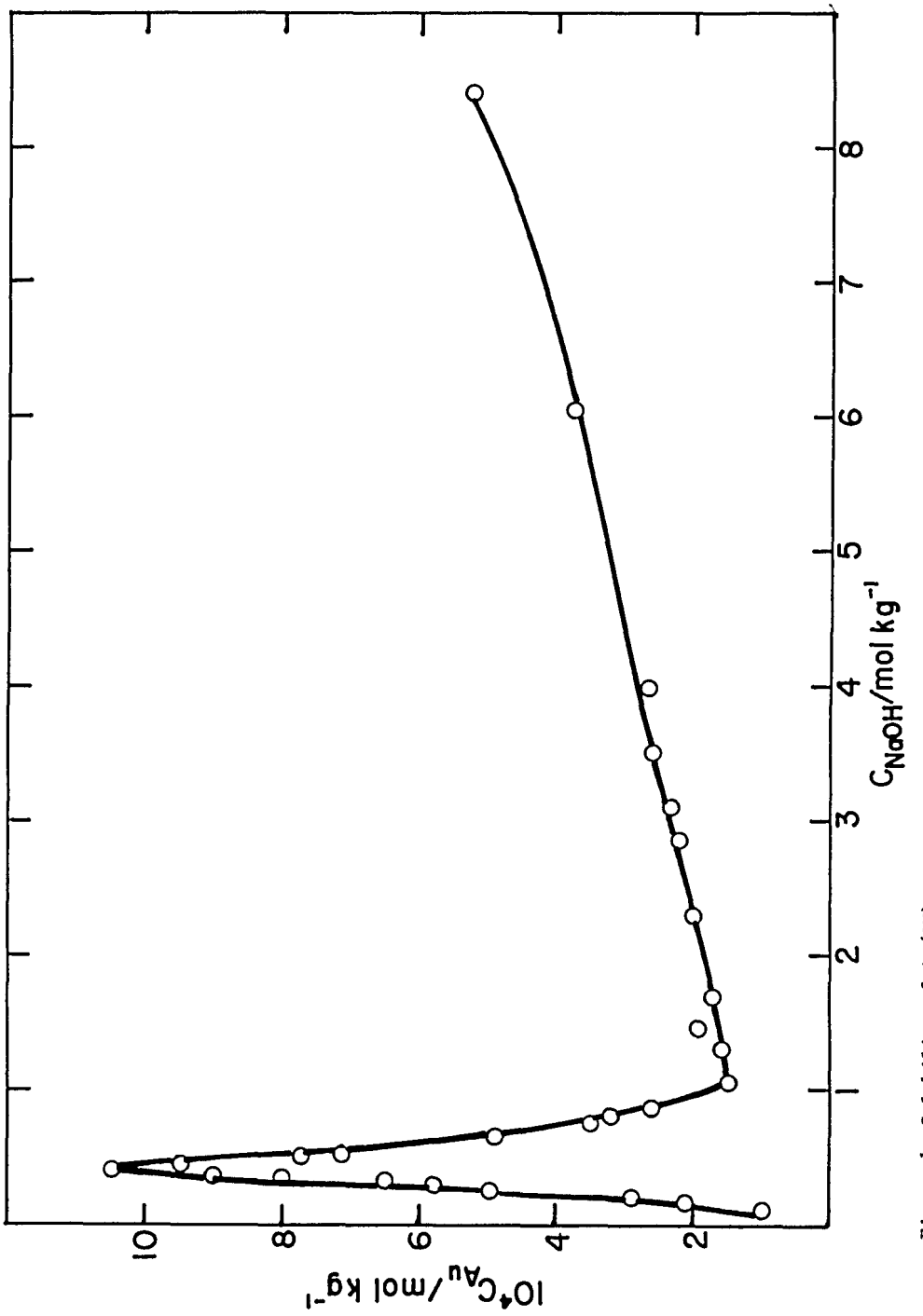

Figure 1. Solubility of $Au(OH)_3$ in aqueous NaOH at 298 K, ref. (2).

COMPONENTS:	EVALUATOR:
(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. April 1984

CRITICAL EVALUATION:

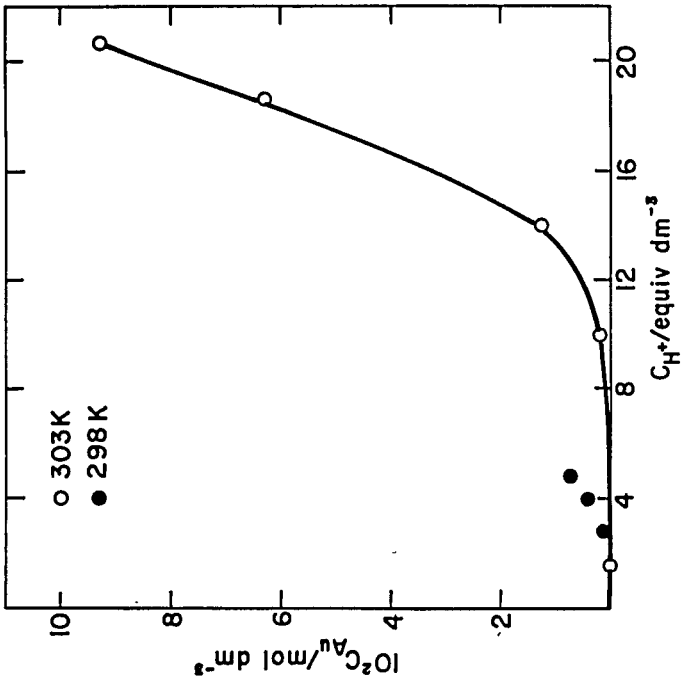

Figure 3. Solubility of $Au(OH)_3$ in nitric acid at 298 K (1) and in H_2SO_4 at 303 K (3).

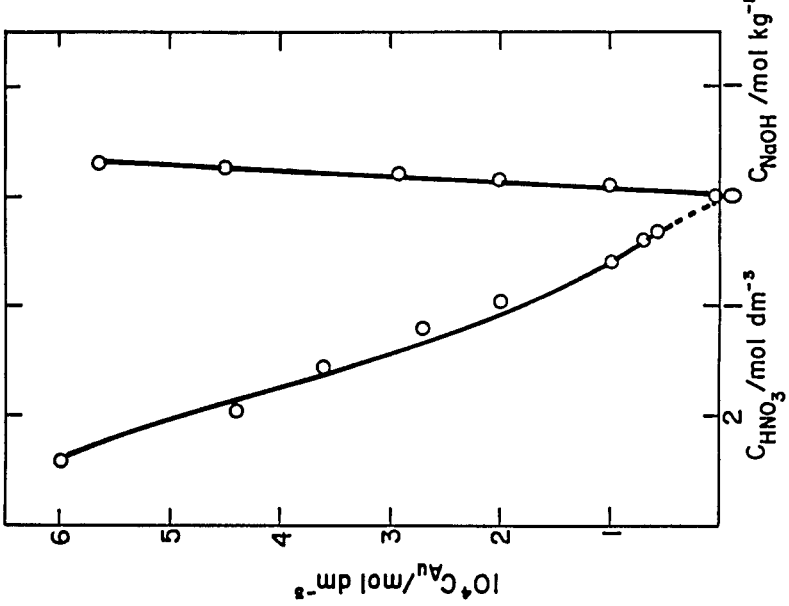

Figure 2. Solubility of $Au(OH)_3$ at 298 K in HNO_3 solutions (1) and in NaOH solutions (2).

COMPONENTS:

(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2]

(2) Sulfuric acid; H_2SO_4; [7664-93-9]

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

ORIGINAL MEASUREMENTS:

Jirsa, F.; Jelinek, H. Z. *Elektrochem.* 1924, *30*, 286-9.

VARIABLES:

The concentration of sulfuric acid and the temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Au(OH)_3$ in aqueous H_2SO_4.

Duration of shaking/hours	$C_{H_2SO_4}$/equiv dm^{-3}	C_{Au}/mol dm^{-3}	t/°C
24	20.7	0.0928	29.7
48	20.7	0.0936	"
160	20.7	0.0920	"
18	14.0	0.0128	"
48	10.1	0.0026	"
144	10.1	0.0021	"
210	18.71	0.0629	19.0
408	18.58	0.0627	"
600	18.74	0.0632	"
744	18.60	0.0624	"
912	18.79	0.0632	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid $Au(OH)_3$ was dissolved in hot concentrated H_2SO_4. Water and acid were added to this solution to precipitate $Au(OH)_3$ by hydrolytic action. The mixture was shaken for some time in sealed tubes, and then filtered. The acid content of the filtrate was determined by titration. The gold content was determined gravimetrically by reducing the dissolved gold with formaldehyde. The mixture was heated for some time after the addition of the formaldehyde.

SOURCE AND PURITY OF MATERIALS:

The $Au(OH)_3$ was prepared by treating a gold electrode anodically in a dilute H_2SO_4 solution. The $Au(OH)_3$ precipitated at the electrode. No information is given about any of the other materials that were used.

ESTIMATED ERROR:

No details are given but duplicate results agree to within 5%.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2]	Jirsa, F.; Jelinek, H. *Z. Elektrochem.* 1924, *30*, 286-9.
(2) Sulfuric acid; H_2SO_4; [7664-93-9]	
(3) Water; H_2O; [7732-18-5]	

EXPERIMENTAL VALUES contd:

Solubility of $Au(OH)_3$ in aqueous H_2SO_4 at 18.0°C.

Duration of shaking/hours	$C_{H_2SO_4}$/equiv dm^{-3}	C_{Au}/mol dm^{-3}
24	1.57	0.00013
24	1.59	0.00011
48	1.46	0.000081
144	1.01	0.000039
150	1.01	0.000043
192	1.01	0.000039
410	1.01	0.000042
280	0.89	0.000032
432	0.89	0.000039
624	0.89	0.000035
768	0.89	0.000036
144	0.54	0.000031
552	0.53	0.000015
600	0.53	0.000015
624	0.53	0.000018

Compiler's comment: This article is the same as the following:

Jirsa, F.; Jelinek, J. *Chem. Listy* 1924, *18*, 1-4.

COMPONENTS:

(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Johnston, H. L.; Leland, H. L. *J. Am. Chem. Soc.* 1938, *60*, 1439-45.

VARIABLES:

Concentration of sodium hydroxide at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Au(OH)_3$ in H_2O at 25°C.

C_{Au}/mol kg^{-1}	
U [a]	S [b]
0.034×10^{-4}	0.032×10^{-4}
0.028×10^{-4}	0.037×10^{-4}
0.026×10^{-4}	0.030×10^{-4}

average = 0.031×10^{-4}

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid $Au(OH)_3$ and solvent were mixed and shaken in a constant temperature bath at 25 ± 0.01°C for at least 3 weeks, then allowed to sediment for 2-10 days. Clear solution was removed by decantation and passed through a sintered Jena glass filter. Other mixtures were shaken for 4 days at 40°C and then transferred to the 25°C bath and treated as above. Alkali content was determined by titration with H_2SO_4. Gold content was determined by potentiometric titration with $FeSO_4$ in an atmosphere of N_2.

SOURCE AND PURITY OF MATERIALS:

$Au(OH)_3$ was produced by a method described by others (1) and washed thoroughly. The NaOH solutions were prepared from pure amalgams. Conductivity water was used throughout. All other materials were of reagent grade quality.

ESTIMATED ERROR:

No estimate is given.

REFERENCES:

1. Roseveare, W. E.; Buehrer, T. F. *J. Am. Chem. Soc.* 1927, *49*, 1989.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2]	Johnston, H. L.; Leland, H. L. *J. Am. Chem. Soc.* 1938, *60*, 1439-45.
(2) Sodium hydroxide; NaOH; [1310-73-2]	
(3) Water; H_2O; [7732-18-5]	

EXPERIMENTAL VALUES contd:

Solubility of $Au(OH)_3$ in aqueous NaOH at 25°C.

C_{NaOH}/mol kg^{-1}	$10^4 C_{Au}$/mol kg^{-1} U [a]	S [b]
0.0683	- - -	0.73
0.0752	0.89	0.85
0.0939	0.97	1.00
0.0968	- - -	1.51
0.1005	1.01	1.00
0.1100	1.13	1.09
0.1507	2.01	2.00
0.1678	- - -	2.13
0.1696	2.33	2.31
0.1998	2.91	- - -
0.2364	- - -	4.44
0.2595	4.49	4.50
0.2997	5.49	5.79
0.3254	- - -	6.53
0.3547	7.99	7.98
0.3778	9.05	9.02
0.3900	- - -	9.73
0.4138	- - -	10.54
0.4215	- - -	9.79
0.4402	9.44	- - -
0.4941	7.70	7.77
0.519	- - -	7.14
0.522	7.33	7.20
0.543	7.60	6.34
0.660	- - -	4.90
0.667	4.62	4.69
0.748	3.46	3.53
0.790	3.23	3.17
0.840	2.61	2.63
1.048	1.47	1.44
1.049	1.50	1.48
1.299	1.60	- - -
1.445	- - -	1.94
1.682	1.69	1.70
2.293	2.01	2.01
2.845	2.22	2.20
3.095	2.39	2.32
3.541	2.61	2.62
3.983	2.68	2.63
6.05	3.76	3.84
8.37	5.32	5.23

[a] Equilibrium was approached from undersaturation.

[b] Equilibrium was approached from supersaturation.

COMPONENTS:

(1) Gold(III) hydroxide; $Au(OH)_3$; [1303-52-2]

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

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

ORIGINAL MEASUREMENTS:

Bezzubenko, A. A.; Peshchevitskii, B. I. *Izvest. Sibir. Otdel. Akad. Nauk SSSR* 1961, 62-7.

VARIABLES:

Concentration of nitric acid at 25 ± 0.05°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Au(OH)_3$ in aqueous HNO_3 at 25°C.

C_{HNO_3}/mol dm^{-3}	$10^3 C_{Au}$/mol dm^{-3}
10.1	380
7.64	79
6.05	23
4.84	7.4
4.03	4.1
2.84	1.2
2.42	0.57
2.42	0.63
1.94	0.44
1.55	0.36
1.21	0.27
0.96	0.20
0.60	0.10
0.41	0.070
0.32	0.057

One determination at 40°C showed that the solubility in a HNO_3 concentration of 1.35 mol dm^{-3} is 2.5 x 10^{-4} mol Au dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid $Au(OH)_3$ was treated with concentrated HNO_3 and heated strongly. The resulting solution was treated with known volumes of water to precipitate $Au(OH)_3$. The mixtures were then placed in a constant temperature bath at 25°C for an unspecified time. After this the mixture was filtered through a glass filter. The acid content of the filtrate was determined by titration with borax or with NaOH. The gold content of the filtrate was determined colorimetrically after forming Au-bromide complexes.

SOURCE AND PURITY OF MATERIALS:

$Au(OH)_3$ was formed by treating $KAuCl_4$ with Na_2CO_3 at an elevated temperature and then washing the product with H_2SO_4 and with dilute HNO_3. All materials were of a chemically pure grade.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

So far as the stable oxides and hydroxides are concerned, zinc exists only in the dipositive form. ZnO is a stable material but there are also indications that metastable forms of ZnO exist, depending on the method of preparation. The rate of solubility, and to some extent the solubility itself, of ZnO in an alkali solution was found to be dependent on the previous history of the ZnO (1). There is also mention of seven solid phases of ZnO (2). A rather extensive review of the literature showed that the values of many physical characteristics of ZnO depend on the method of preparation or the previous history of the material (3), and, consequently, there is much discrepancy in the values reported in the literature. The so-called "active zinc oxides" had lower densities and higher catalytic activities than the "stable zinc oxides," yet all had the same X-ray diffraction pattern. A study of the effect of particle size on the solubility showed that the solubility product of ZnO as determined by solubility measurements in 1 mol NaOH dm^{-3} did increase as the particle size decreased and as the surface area of the ZnO increased (4).

Zinc hydroxide, on the other hand, is a substance whose purity and stability have often been called into question. Zinc hydroxide is frequently prepared by adding an alkali to a solution of a zinc salt. Hantzsch (5) noted that the use of $ZnSO_4$ did not give a pure $Zn(OH)_2$. Feitknecht (6) observed that the addition of NaOH to a solution of a zinc salt produced a basic salt rather than $Zn(OH)_2$. This was confirmed later (7) when it was shown that the addition of alkalies to a solution of $Zn(NO_3)_2$ did not produce a pure $Zn(OH)_2$ but, rather, a product contaminated with the anions of the zinc salt.

Zinc hydroxide has also been considered to be unstable (8, 9). Thermodynamic calculations are said to show that $Zn(OH)_2$ is unstable with respect to ZnO (8). It has also been observed that $Zn(OH)_2$ undergoes a change on standing, especially in the presence of alkalies (10). This change is a decrease in solubility and is often ascribed to a loss of water. The rate of this change may be affected by the previous history of the preparation.

The instability of $Zn(OH)_2$ has also been observed in other work (11). In order to determine the free energy of formation of ZnO, the e.m.f. of the following cell was measured. The e.m.f. was constant after 48 hours and then

$$H_2(g)|\text{dil. } Ba(OH)_2|ZnO(s) + Zn$$

remained constant for some time. However, when $Zn(OH)_2$ was substituted for ZnO in the above cell, the e.m.f. showed a continual drift. The conclusion of this work was that $Zn(OH)_2$ is metastable with respect to ZnO at 298 K but that the free energy driving force is small.

Pure $Zn(OH)_2$ appears to have been produced by a method described by Dietrich and Johnston (12). The calculated amount of NH_4OH is added to a solution of $ZnCl_2$ or $ZnSO_4$. The precipitate that is formed is separated by filtration and washed thoroughly. The washed precipitate is then dissolved in the requisite amount of concentrated NH_4OH and the NH_3 is gradually removed from solution by absorption from the vapor phase by concentrated H_2SO_4. After about a week crystals of $Zn(OH)_2$ begin to precipitate. The $Zn(OH)_2$ so produced is stable when kept under water at 338 K. At higher temperatures the crystals begin to decompose.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

In view of all these questions about the character of $Zn(OH)_2$ it is not surprising that there have been references to different kinds of $Zn(OH)_2$. Klein (13) maintained that there are three kinds of $Zn(OH)_2$ varying in solubility and in stability. His article contains no useful solubility data. Experimental details are meager, no temperature is specified, and there is no certainty that equilibrium was attained in any of the measurements given. Feitknecht, as a result of extensive and intensive work with metal hydroxides (2) has identified six forms of $Zn(OH)_2$: amorphous-, α-, β-, γ-, δ- and ε-$Zn(OH)_2$. The conditions for the preparation of these are described and the X-ray diffraction patterns of each is also given. These various forms of $Zn(OH)_2$ vary in stability, with ε-$Zn(OH)_2$ being the most stable. The reactions used to prepare these forms of $Zn(OH)_2$ are: (a) the addition of an alkali to an aqueous solution of a zinc salt; and (b) the dilution of a solution of a zincate. By varying the concentration of reagents, the rate of mixing and stirring, the extent of dilution, etc., one or the other varieties of $Zn(OH)_2$ are precipitated. Although X-ray diffraction patterns are given, no chemical analyses are presented. Therefore, there is no certainty that the products were $Zn(OH)_2$ rather than basic salts or contaminated forms of $Zn(OH)_2$. Incidentally, no reference is made to the work of Dietrich and Johnston (12) which was published five years earlier and in which a procedure is described for producing a stable form of $Zn(OH)_2$. Further information about these various types of $Zn(OH)_2$ was published later (14, 15).

Thus, in evaluating solibility data for $Zn(OH)_2$ the most reliable, truly equilibrium, values are to be expected only when some time was allowed for equilibrium to be established. Results obtained from working with freshly precipitated $Zn(OH)_2$ are suspect and this includes much of the work which was used to calculate solubility product values.

There is one other consideration in evaluating the solubility data and that has to do with whether, in the experimental work, colloidal mixtures were present rather than, or in addition to, true solutions. The claim has been made that solutions of $Zn(OH)_2$ in aqueous KOH are partly in colloidal form (16). Others have maintained that the extent of peptization of $Zn(OH)_2$ in aqueous NaOH solutions depends on the amount of excess solid phase, but the solutions become optically clear at higher concentrations of NaOH (17). Most investigators of the solubility of ZnO or $Zn(OH)_2$ have been aware of these claims and have made certain that the solutions were optically clear, although it is possible that, even then, some colloidal material may have been present.

In addition to the solubility of ZnO and $Zn(OH)_2$ as reported on the accompanying data sheets, there is also literature data on so-called supersaturated zincate solutions. Such solutions have been prepared by dissolving ZnO in hot solutions of alkali. They have been prepared more commonly by treating a zinc electrode anodically in solutions of alkalies. However, such solutions have no definite quasi-equilibrium values but appear to be more accurately described as solutions in a steady-state condition. The amount of dissolved zinc species can be varied by controlling the conditions used to prepare the solutions. Furthermore, such solutions, when once prepared, undergo a gradual decrease in concentration of dissolved zinc species until the dissolved zinc content is the same as that for solutions in equilibrium with ZnO (18). This process is completed in about a year at room temperature. Because of the lack of equilibrium values for, and the

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

instability of the supersaturated zincate solutions, data for such systems have not been compiled and will not be evaluated.

Solubility in water

Zinc oxide. Five papers report a value for the solubility of ZnO in water. In one of these (19) electrical conductance was used as the experimental approach. Two methods were used: (a) a conductimetric titration; and (b) the measurement of specific conductance which was used together with available literature values for individual ionic conductances. The average of these determinations was 3.67×10^{-5} mol dm^{-3} at 293 K. Busch (20) used a potentiometric titration to establish the solubility. He found a value of $(1.92 \pm 0.15) \times 10^{-5}$ mol dm^{-3} at 302 K. Both these values can only be considered tentative or approximate in view of the small differences involved in one case (19) and the shallowness of the titration curve in the other (20).

A value of 7.75×10^{-5} mol dm^{-3} was reported as a result of a direct determination of the solubility of ZnO in water (21). The temperature was not specified but it was probably 288 to 293 K. A much smaller value was reported in a more recent work (22). The value is 5.22×10^{-6} mol dm^{-3}. However, this result is not very reliable because the pH of the water that was used varied from 5.8 to 9.2, the temperature was not carefully controlled, and the average deviation of the individual results from the mean is about 30%. A maximum value of 3×10^{-4} mol dm^{-3} at 298 K has also been reported. It was obtained by extrapolation of solubility data in NaOH solutions to zero concentration of NaOH (23). No great confidence was placed in the extrapolation procedure, and values of the order of 10^{-5} mol dm^{-3} are more likely to be the true values.

Zinc hydroxide. Five papers report a value for the solubility of $Zn(OH)_2$ in water and in four of these the temperature was maintained at 298 K. One value given is 7.8×10^{-4} mol dm^{-3} (24). This value was not obtained by a solubility measurement but was obtained along with a study of the extent of hydrolysis of sodium zincate. A set of equations was derived on the assumption that one of the values for a hydrolysis product was the solubility of $Zn(OH)_2$ in water. Even then, in only one instance was a positive value calculated for this term. Consequently, this value is considered doubtful. Furthermore, the $Zn(OH)_2$ was formed by adding NaOH to aqueous $ZnSO_4$, and, in view of the discussion above, this casts doubt on the purity of the $Zn(OH)_2$ that was used in this work.

The use of an extrapolation method (12) gave a value of 2×10^{-5} mol kg^{-1}. This is considered to be a maximum value. A direct determination of the solubility of $Zn(OH)_2$ in water (25) gave a value of $(100 \pm 0.1) \times 10^{-5}$ mol kg^{-1}. Herz (26) reports a value of $(1.4$ to $2.6) \times 10^{-5}$ mol dm^{-3}. However, this value was obtained from calculations of equilibrium quotients for the $Zn(OH)_2$-NH_4^+-H_2O system.

In a work dealing with the solubility of $Zn(OH)_2$ in aqueous H_2O_2 solutions, values for the solubility of $Zn(OH)_2$ in water were determined to be 7.7×10^{-5} mol kg^{-1}, 2.2×10^{-4} mol kg^{-1} and 1.27×10^{-4} mol kg^{-1} at 273, 293 and 303 K, respectively(27). There is some question about the composition and purity of the $Zn(OH)_2$ used in this work.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Because of these divergent values, about all that can be said about the solubility of $Zn(OH)_2$ in water at 298 K is that it is of the order of 10^{-5} mol dm^{-3}.

Solubility in aqueous solutions of varying pH.

Much of the earlier work dealing with the solubility of ZnO or $Zn(OH)_2$ was motivated by the desire to determine the extent to which these substances showed acidic and basic characteristics. In this section we will be concerned with solubilities in aqueous solutions of alkalies and acids and the information this gives about the acidic and basic character of ZnO and $Zn(OH)_2$. ZnO is recognized as the more stable of these two substances.

Solubility of ZnO in aqueous NaOH. There are several papers that deal with the solubility of ZnO in aqueous NaOH solutions. Some preliminary work was done by Huttig and Steiner (1). (This work was done with aqueous KOH rather than with aqueous NaOH.) They studied the effect of various factors on the rate of solubility of ZnO in aqueous KOH solutions. One of the concerns was the effect of the amount of the solid phase on the rate of solubility. There were at that time numerous statements in the literature that the solubility of $Zn(OH)_2$ in aqueous alkali solutions did depend on the amount of solid phase present. But Huttig and Steiner found this to be an unimportant factor in the solubility of ZnO. In their work they arbitrarily assumed the equilibrium solubility to be the solubility after 90 minutes of stirring at a constant rate. Using this definition they found that the temperature to which $ZnCO_3$ has been heated to produce the ZnO did have a bearing on the solubility value. The solubility decreased as the decomposition temperature increased to a value of 773 K. Above this temperature there was no dependence of solubility on the decomposition temperature of the $ZnCO_3$. As expected, they also found that the solubility increased with decreasing particle size. In view of this work it is obvious that in evaluating the solubility data of ZnO in aqueous alkalies it is important to know the previous history of the ZnO. Furthermore, a sufficient time should be allowed for equilibration in order to minimize the effect of particle size.

Goudriaan (28) determined the phase diagram of the Na_2O-ZnO-H_2O system at 303 K. He observed that ZnO, $Na_2ZnO_2 \cdot 4H_2O$ and $NaOH \cdot H_2O$ were the solid phases, Figure 1. A later work (29) repeated that part of the system for which ZnO is the solid phase and was in very good agreement with the earlier work (28). A still later investigation (30) at 298 K gave solubility values slightly larger than those reported earlier for 303 K (28). They also found $NaZn(OH)_3$ to be the solid zincate phase rather than a form of $Na_2Zn(OH)_4$ as reported by Goudriaan (28).

Deshpande and Kabadi (31) measured the solubility of ZnO in aqueous NaOH over a temperature range of 308-348 K. The results do not show a correlation of solubility with temperature. It appears that the solubility of ZnO in aqueous NaOH is not temperature-dependent, but there is too much scatter in the data to verify this statement. Furthermore, there is a question about the accuracy of the concentration of NaOH in these data. This value was determined by back-titrating with NH_4OH after excess acid had been added. The solutions apparently still contained zinc which could react with the NH_4OH and thus give smaller values for the NaOH concentration. This suspicion is borne out by the

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

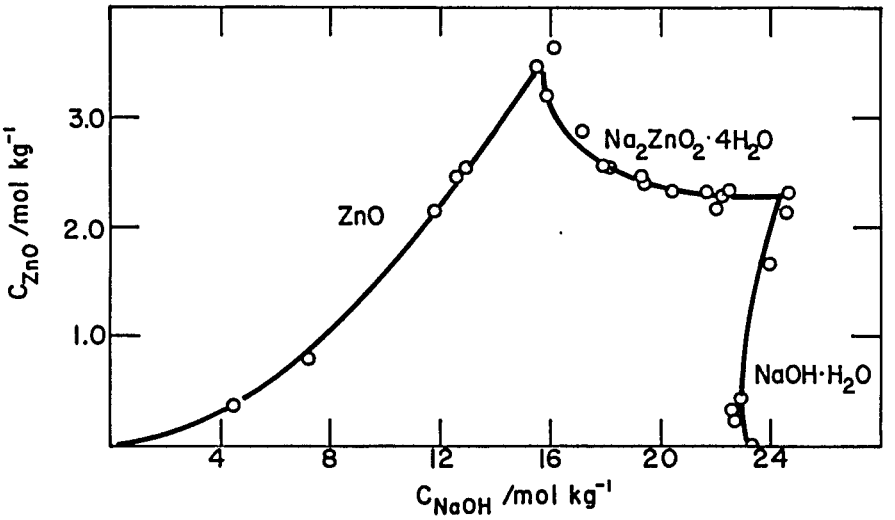

Figure 1. The Na_2O-ZnO-H_2O system at 303 K, ref. (28).

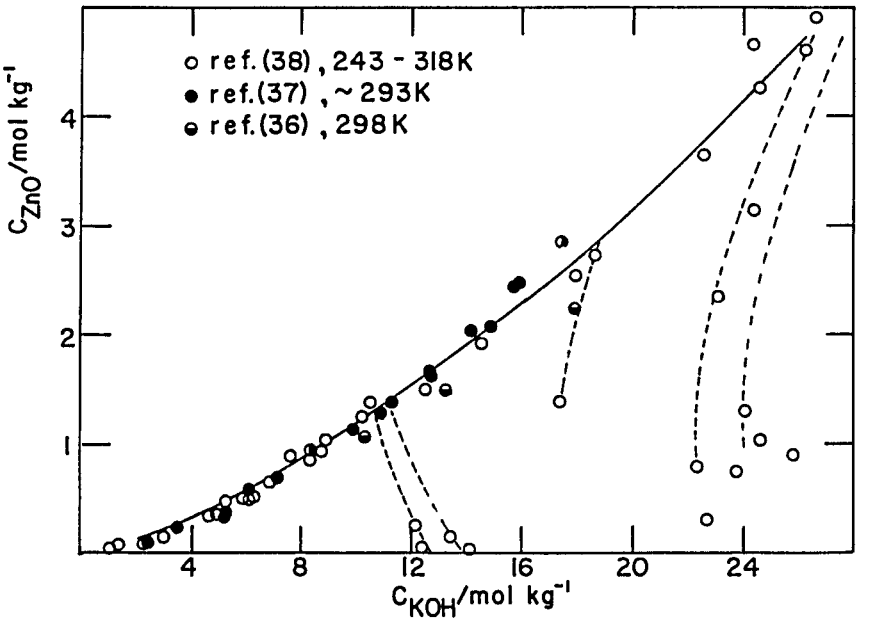

Figure 2. Solubility of ZnO in KOH solutions. The solid line is equation (5) and ZnO is the solid phase. Along the dashed lines the solid phase is a hydrate of KOH.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

fact that the results agree fairly well with those of Goudriaan (28) at the lower concentrations of dissolved zinc but deviate increasingly as the concentration of dissolved ZnO increases.

A few solubility values were obtained by extrapolation of rate of dissolution data in concentrations of NaOH 1-4 mol dm^{-3} (32). The solubility values are smaller than those reported by others (29) for the same temperature.

Urazov, et al., determined solubility values in this system at 298 and 348 K (33). Their results agree well with those of Goudriaan (28) up to NaOH concentrations of 12 mol kg^{-1}. However, they report $Zn(OH)_2$ rather than ZnO to be the equilibrium solid phase for these solutions. This difference cannot be resolved because of lack of information about experimental details and the method of analysis in the one paper (33). In larger concentrations of NaOH other solid phases appear and the analytical results become less reproducible. The solubility of ZnO in aqueous NaOH is significantly larger at 348 than at 298 K (33).

A review of the data for the solubility of ZnO in aqueous NaOH solutions indicates that there are significant differences in the values reported. The disagreement does not appear to be due primarily to differences in temperature. A possible reason for the discrepancy is that in the reports we have been discussing, relatively large concentrations of NaOH were used, probably because of a common interest of the investigators to determine whether sodium zincates could be prepared and, if so, under what conditions. In some investigations there apparently was more interest in determining the composition of the solid phases than that of the solutions. While occasional statements are made about temperature control, no details are given about the control of the analytical or other procedures. In view of the work reported by Huttig and Steiner (1), more reliance can be placed on work in which the ZnO has been heated to at least 770 K. This, apparently was done in the work of some (28, 29, 32) but not in others (30), and it is a fact that the results of the former agree fairly well with each other while the results of the latter are larger--as would be expected from a ZnO that had not been heated to such a high temperature (1). Therefore, the solubility results of the former (28, 29, 32) are considered to be the most reliable and acceptable for the solubility of ZnO in NaOH solutions of concentrations up to 16 mol dm^{-3}.

But the above data are not suitable for determining the acidic constants of ZnO because the NaOH concentrations were too large to use theoretical relationships. Some data obtained in more dilute NaOH solutions have been used to evaluate such constants (23). No other solubility data have been reported for such dilute NaOH solutions. The treatment of the data followed the procedure described by others (34). Extrapolation of a plot of solubility data of ZnO vs NaOH concentration gave a value of about 3×10^{-4} mol dm^{-3}. This should be the value for the solubility of ZnO, or $Zn(OH)_2$, in water, but it is only an approximate value because extrapolation was made from a line of changing slope. This value is about 10 times the value reported by others and discussed earlier. However, it is not to be preferred because similar work in KOH solutions gave a value of approximately zero for this concentration of ZnO or $Zn(OH)_2$ in water.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

The acidic character of ZnO can be represented by equations (1) and (2).

$$ZnO(s) + OH^- + H_2O = Zn(OH)_3^- \quad (1)$$

$$ZnO(s) + 2OH^- + H_2O = Zn(OH)_4^{2-} \quad (2)$$

The corresponding equilibrium constants are:

$$K_1° = a_{Zn(OH)_3^-}/a_{OH^-} \quad (3)$$

$$K_2° = a_{Zn(OH)_4^{2-}}/(a_{OH^-})^2 \quad (4)$$

The treatment of these results in dilute NaOH solutions (23) gives $K_1° = 6 \times 10^{-4}$ and $K_2° = 6 \times 10^{-3}$. Values for these same constants based on other experimental work will be given and discussed later.

Solubility of ZnO in aqueous KOH solutions. The solubility of ZnO in aqueous KOH solutions is characterized by being temperature-independent over a wide range of temperatures. The solubility of ZnO in 36.3 mass % KOH is constant over the range 211 to 299 K (35). The temperature independence may extend up to 418 K, but not enough data have been reported to warrant a categorical statement to this effect (36). There is good agreement in the solubility values reported in the temperature range 243 to 318 K, Figure 2. The data for that Figure are taken from 3 different sources (36, 37, 38). Equation (5) was developed to describe the line drawn through those data points on Figure 2 for which ZnO is the solid phase. The equation has a standard deviation of C_{ZnO}

$$C_{ZnO} = -0.145 + 0.0941(C_{KOH}) + 0.0036(C_{KOH})^2 \quad (5)$$

about the regression line of s = 0.1355. It is a strictly empirical equation with concentration values expressed as mol/kg H_2O. In these concentrated KOH solutions such an equation can hardly be derived, or interpreted, on the basis of theoretical considerations.

Some of the data that have been reported (35, 39, 40) express the concentrations in terms of mol dm^{-3}. A few of the data agree well with equation (5), e.g., (35). Other reports (39) give larger solubility values than those shown on Figure 2. But no information is given as to how these data were obtained so they can be rejected. In other work (40) the analytical method has already been evaluated above in connection with ref. (31). There is no solubility-temperature pattern in these data and at the higher concentrations of ZnO the values of the KOH concentration are too low as would be expected from the analytical method that was used. These values, therefore, are considered doubtful, and the recommended values are those expressed by equation (5) for at least the temperature range 243 to 318 K.

The solubility of ZnO in more dilute solutions of KOH has been reported in two papers (1, 23). The results agree very well with each other. In one paper (23) the data have been used to evaluate $K_1°$ and $K_2°$. The values for these constants are reported to be 6×10^{-4} and $(100 \pm 2) \times 10^{-4}$, respectively, at 298 K.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Solubility of $Zn(OH)_2$ in aqueous NaOH solutions. Although there are several papers giving solubility values for $Zn(OH)_2$ in aqueous NaOH, most of these values may be considered questionable in view of the discussion given above in the introduction to this Critical Evaluation, i.e., there are questions about the stability of the $Zn(OH)_2$ that was used, and with respect to the time allowed for equilibration. Because of the effect of particle size of the $Zn(OH)_2$ on its nature and stability, at least a few weeks should have been allowed for the equilibration process.

The effect of the nature of the solid $Zn(OH)_2$ on its solubility in aqueous NaOH is brought out in a few of the papers. In Goudriaan's work (28) the solid $Zn(OH)_2$ had changed to ZnO when standing in contact with NaOH solutions of concentrations 1.53 and 12.6 mol kg^{-1} for two to three weeks. Later (29) somewhat similar work showed that in NaOH solutions of concentrations up to 7.15 mol dm^{-3} the solid $Zn(OH)_2$ did not change during a two-week period, while in concentrations of 9.87 mol dm^{-3} the $Zn(OH)_2$ did change physically during this same two-week period. This change is called aging. It is sensitive to a variety of experimental conditions, it manifests itself by a decrease in solubility, and is generally considered to be due to a loss of water from the solid $Zn(OH)_2$. These changes were also noted and recorded by others (31, 41). Deshpande and Kabadi (31) prepared the solid $Zn(OH)_2$ by two different methods. The solubility of the one type was lower than that of the other type at all temperatures, and the difference in solubility appeared to increase with increasing NaOH concentrations. The solubility values are subject to the same reservations expressed above with respect to the solubility of ZnO reported by these same authors. Nevertheless, the differences observed between the two types of $Zn(OH)_2$ may be real. The transition of $Zn(OH)_2$ to ZnO while standing in contact with aqueous NaOH is said to take place more rapidly as the concentration of NaOH is increased but often the time required for the transition is of the order of 150 days (30).

In the light of the observations just recorded it is not surprising that the various results reported for the solubility of $Zn(OH)_2$ in aqueous NaOH solutions show considerable variation, Figure 3. Some of these results (42, 43) are questionable because the solid $Zn(OH)_2$ probably was not pure or stable. No temperature is reported either although it appears that the results were obtained at room temperature. The results reported for a temperature of 293 K (30, 44) are in fair agreement with each other. Only one set of results is reported for a temperature of 298 K (12). These results appear to be quite reliable although only one day was allowed for equilibration. However, we can only consider these results to be tentative until other solubility work is reported at this temperature.

In more dilute NaOH solutions there is additional work reported at 298 K (24) and these few data agree well with the other work reported for this temperature (12). Some careful work in rather dilute NaOH solutions (25) also appears to corroborate these data but there is only one NaOH concentration that is common to the concentration ranges used by these two groups of investigators. The latter work (25) appears to be a reasonable extension of the former work (12), but, in view of the fact that there are no other data to corroborate any of these values they are at present to be considered as tentative.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

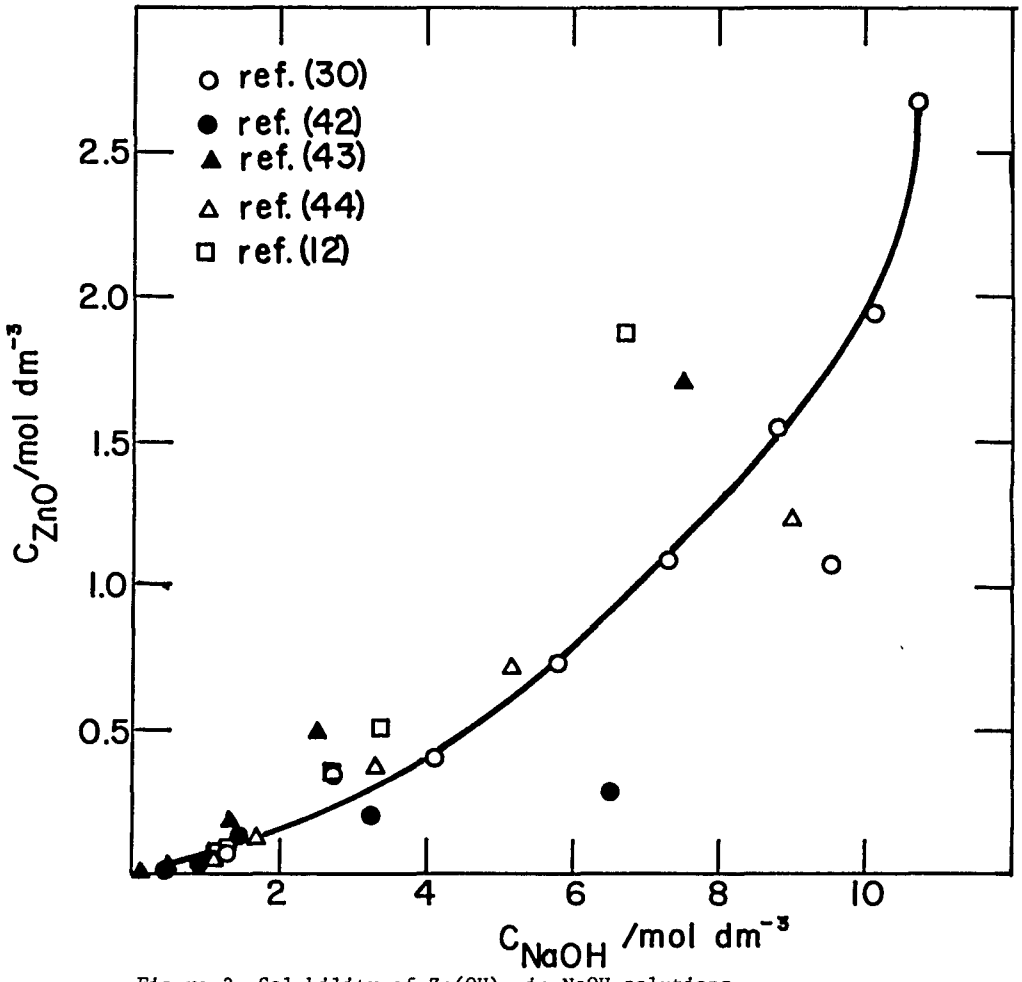

Figure 3. Solubility of $Zn(OH)_2$ in NaOH solutions.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Only two papers present solubility data at different temperatures and, here again, the results are at variance with each other. In work covering the temperature range 293-373 K (30) there appears to be very little temperature effect, Figure 4. The main differences at 293 and 313 K are at NaOH concentrations greater than 13 mol dm-3 where $Zn(OH)_2$ or ZnO is no longer the equilibrium solid phase, but some type of zincate begins to precipitate instead. At 373 K the solid phase has become ZnO so that these results are really solubility data for ZnO rather than for $Zn(OH)_2$. On the other hand, there are data that appear to show a temperature dependent solubility in the range 273-313 K (12), Figure 5.

The solubility of $Zn(OH)_2$ in solutions of varying pH was studied at 285.5 to 348 K (45). Solutions in the alkaline range were produced by the addition of NaOH. The solubility of $Zn(OH)_2$ was reported as a function of pH. The pH was measured with a glass electrode, and there is no indication that any correction was made for this in the alkaline region. Therefore, there is a question about the absolute values in the higher pH region. However, even so, the results do show a slight temperature dependence for the solubility of $Zn(OH)_2$ in the pH range 9 to 12.

The variances and discrepancies just discussed with respect to the solubility of $Zn(OH)_2$ in aqueous NaOH likely have their origin in the non-uniformity of the materials designated as $Zn(OH)_2$. Because of this, all the solubility data for this system can, at best, be considered as tentative.

Solubility of $Zn(OH)_2$ in aqueous KOH solutions. Only four papers give data on this system (37, 40, 43, 46) and, again, there are discrepancies in the values reported. Reservations about the work in one paper (40) have already been discussed earlier in this Critical Evaluation. The $Zn(OH)_2$ was prepared by two different methods and, while the absolute values are subject to question, the results showed that the one preparation (b) had a smaller solubility at all temperatures. The solubility was studied in the temperature range 308 to 348 K but no temperature-dependence is apparent. A summary of the results reported by the others is given on Figure 6. There are differences in the results and this again is related to the uncertainties with respect to the solid $Zn(OH)_2$ that was used. As in the case of the $Zn(OH)_2$-NaOH-H_2O system, the results that have been reported can only be considered tentative, perhaps even doubtful.

Solubility in dilute solutions of mineral acids. There are no reports on the solubility of ZnO in such solutions and only two reports on the solubility of $Zn(OH)_2$ (25, 45). Both of these reports deal with the solubility in dilute HCl solutions. The one paper (25) presents the data only in graphical form. The other paper (45) presents the data as pH vs $C_{Zn(OH)_2}$ at temperatures ranging from 285.5 to 348 K. This latter report appears to present somewhat larger solubility values in the vicinity of pH = 8. Both papers show that the solubility of $Zn(OH)_2$ has a minimum value above pH = 8. It appears to be located more precisely at pH = 9 to 10 and the solubility at the minimum increases with increasing temperature.

Acidic and basic characteristics of ZnO and $Zn(OH)_2$. The dissolution of $Zn(OH)_2$ and ZnO in aqueous solutions may proceed by one or more of the following reactions. Reactions (1) and (2) correspond to (10) and (11), respectively.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

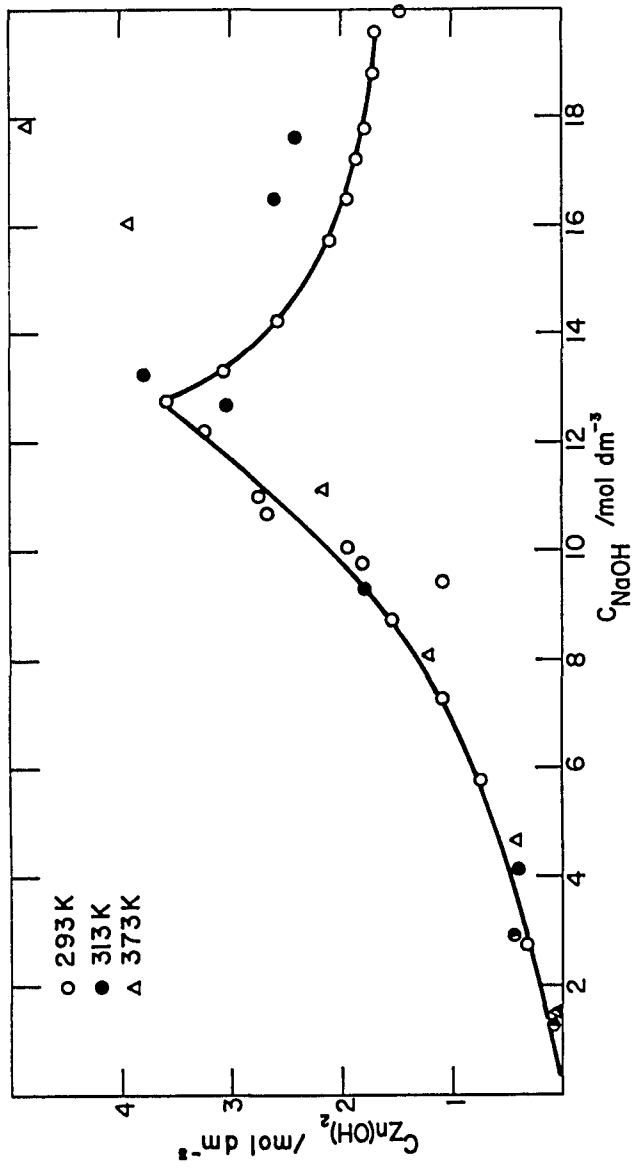

Figure 4. Solubility of $Zn(OH)_2$ in aqueous NaOH (30).

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

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

EVALUATOR:

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June 1984

CRITICAL EVALUATION:

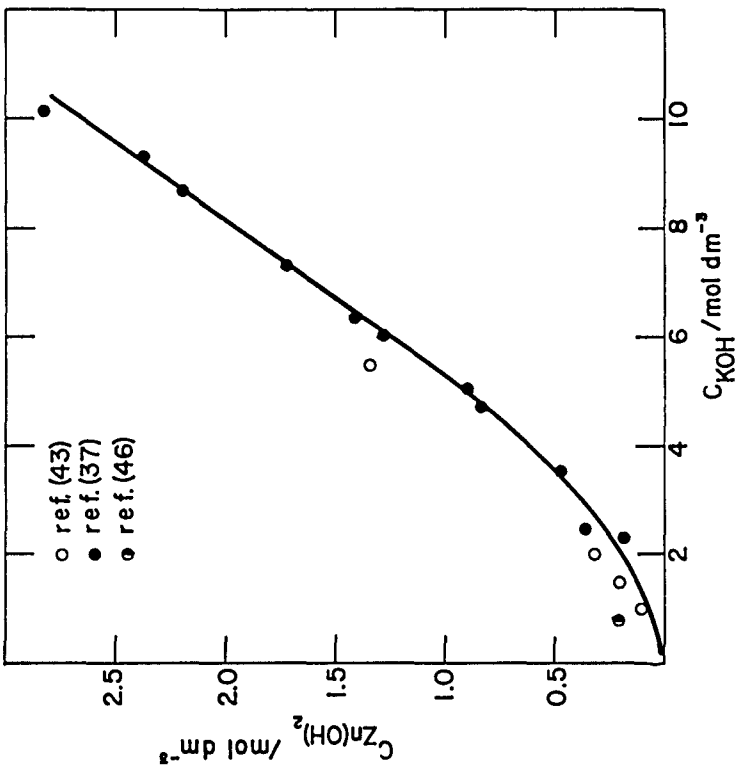

Figure 6. Solubility of $Zn(OH)_2$ in KOH solutions.

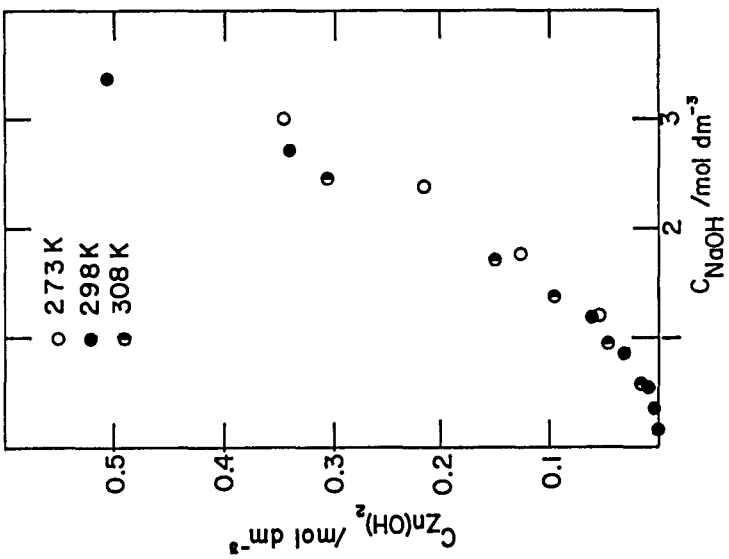

Figure 5. Solubility of $Zn(OH)_2$ in NaOH solutions (12).

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

$$Zn(OH)_2(s) + 2\ H^+ = Zn^{2+} + 2\ H_2O \quad (6)$$

or $$ZnO(s) + 2\ H^+ = Zn^{2+} + H_2O \quad (6a)$$

$$Zn(OH)_2(s) + H^+ = ZnOH^+ + H_2O \quad (7)$$

or $$ZnO(s) + H^+ = ZnOH^+ \quad (7a)$$

$$Zn(OH)_2(s) = Zn(OH)_2(sln) \quad (8)$$

or $$ZnO(s) + H_2O = Zn(OH)_2(sln) \quad (8a)$$

$$Zn(OH)_2(s) = Zn^{2+} + 2\ OH^- \quad (9)$$

or $$ZnO(s) + H_2O = Zn^{2+} + 2\ OH^- \quad (9a)$$

$$Zn(OH)_2(s) + OH^- = Zn(OH)_3^- \quad (10)$$

$$Zn(OH)_2(s) + 2\ OH^- = Zn(OH)_4^{2-} \quad (11)$$

Reaction (8) or (8a) is considered to be the reaction at the point of minimum solubility. The value of the minimum solubility is most easily determined by extrapolation of solubility curves in the very dilute acid and alkaline regions. Such extrapolation gives a value of 4×10^{-6} mol kg^{-1} (25) and 2.6×10^{-6} mol kg^{-1} (45) at 298 K. Because of the small values involved and the fact that the procedure admittedly "concentrates most of the uncertainties (in the value of K_8)" (45), the value of K_8 is tentatively given as 3×10^{-6} mol kg^{-1} at 298 K. Although this is strictly speaking an equilibrium quotient it should be very close to the true equilibrium constant K_8^o or K_{8a}^o.

$$K_8^o = a_{Zn(OH)_2} \quad (12)$$

In acid solutions reactions (6), (6a), (7) and (7a) should be the main ones for the dissolution process. Equations (13)-(16) represent the equilibrium constant expressions for these processes.

$$K_6^o = (a_{Zn^{2+}})\cdot(a_{H_2O})^2/(a_{H^+})^2 \quad (13)$$

$$K_{6a}^o = (a_{Zn^{2+}})\cdot(a_{H_2O})/(a_{H^+})^2 \quad (14)$$

$$K_7^o = (a_{ZnOH^+})\cdot(a_{H_2O})/(a_{H^+}) \quad (15)$$

$$K_{7a}^o = (a_{ZnOH^+})/(a_{H^+}) \quad (16)$$

There is only one paper that attempts to evaluate K_6^o (25). The assumption here is that equation (6) adequately describes the solubility behavior of $Zn(OH)_2$ in dilute HCl solutions. Using solubility data and the Debye-Huckel

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(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

limiting law, K_6^o is calculated to be 7×10^{10} at 298 K. However, this value is based on the further assumption that $a_{H_2O} = 1$. Because there is no corroborating work, this value is to be considered a tentative one. With the assumptions made by the authors (25) the value of K_6^o and of K_{6a}^o should be the same. In view of the assumption made about the activity of the water, these values must, however, be considered as approximate values.

There is also only one paper (45) that allows K_7^o to be evaluated. The method used is to write an equation for the total solubility of $Zn(OH)_2$ in aqueous solutions in terms of the various zinc-containing species listed in equations (6)-(11). On the basis of reasonable assumptions about the relative concentrations of these solute species in different pH ranges, the equation for total solubility is simplified by neglecting certain terms, and the solubility data are then used to solve the equation and evaluate various constants. Using one of the derived values together with the ion product constant of water, the value of K_7^o is calculated to be 2.54×10^3 at 298 K. This is a tentative and approximate value because the assumptions are made that concentrations can be substituted for activities in the dilute solutions that were used. Furthermore, the activity of water is assumed to be unity.

No direct evaluation of K_{7a} is reported.

Many attempts have been made to evaluate the equilibrium constant for reaction (9), i.e., the solubility product constant. It has frequently been determined by titrating a solution of a zinc salt with aqueous NaOH or KOH and measuring the pH of the solution when a precipitate begins to form. The resulting equilibrium constant is then expressed as

$$K_9 = K_{so} = (C_{Zn^{2+}}) \cdot (a_{OH^-})^2 \qquad (17)$$

so that it is a hybrid between a concentration product and a true thermodynamic equilibrium constant. There are several reservations about the legitimacy of this procedure. First, it assumes that the dissolved $Zn(OH)_2$ is completely dissociated in solution and that all the zinc is present as Zn^{2+} ions. Second, the precipitate formed is usually not $Zn(OH)_2$ but is a basic salt (47). Third, measurements are made with a freshly precipitated substance and, therefore, probably do not deal with a true equilibrium condition. In fact, it has been observed (48) that the pH of such solutions decreases on standing and the precipitate also undergoes a change with time. This is especially true with respect to $Zn(OH)_2$ because of the variety of forms reported and the instability of most of these. Therefore, it is not surprising that there is a wide variety of values reported for K_9 or K_{so}. The values obtained by the above method are (all in $mol^3\ dm^{-9}$ at 298 K): 7.3×10^{-17} (49); 3.4×10^{-16} (50); 1×10^{-17} (47) which was recalculated by others (6) to be 1.6×10^{-17}; and 2.6×10^{-16} (51). One paper (48) gives values of 3.9×10^{-16} to 6.0×10^{-17} depending on the form of $Zn(OH)_2$ and the total ionic strength of the solution. An attempt was made by others (58) to repeat the work of Kolthoff and Kameda (47). The attempt was unsuccessful because of inability to reproduce the pH values. The suggestion was made that the $ZnSO_4$ used by Kolthoff and Kameda may have been contaminated with basic zinc sulfate.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Another method commonly used to evaluate K_9 or K_{so} is to measure the pH of a solution in equilibrium with solid $Zn(OH)_2$ and then determine the zinc content of the solution by chemical analysis. The values obtained are substituted in equation (17) and have the units $mol^3\ dm^{-9}$. This method also is subject to the criticism that the assumption is made that all the zinc in solution is present as Zn^{2+} ions. The values obtained by this method (all at 298 K unless otherwise indicated) are: 1.69×10^{-21} (52); 5.25×10^{-17} in 0.2 mol $KNO_3\ dm^{-3}$ (53); 1.7 to 3.9×10^{-16} at 296 K (54); 2.0×10^{-15} to 2.24×10^{-16} in 0.2 mol $KNO_3\ dm^{-3}$ (55); 2.24×10^{-16} in 0.2 mol $KNO_3\ dm^{-3}$ (56); and 1.74×10^{-17} (57).

Both the above described experimental methods assume that $Zn(OH)_2$ is a strong base and completely dissociated in solution. There is experimental evidence (47) that $Zn(OH)_2$ is a strong base with respect to the first step in its ionization but that the second step, equation (18), is rather weak. Thus, all the values reported above are questionable. The objection to these methods

$$ZnOH^+ = Zn^{2+} + OH^- \qquad (18)$$

has been met to some extent in the work of Reichle, et al. (45). In their treatment of the solubility data they arrived at a value of 1.74×10^{-17} for K_9 or K_{so} at 298 K. However, other work which appears to be equally valid (25) leads to a value of 7×10^{-18} for K_9 at 298 K. These two values have been derived from solubility data. However, there is a difference. The latter value was, in effect, derived from solubility data in dilute HCl solutions while the former were derived from solubility data in dilute NaOH solutions. There was more scatter in the data for the HCl solutions and, thus, the value 1.74×10^{-17} mol dm^{-3} suggested by Reichle, et al., (45) is to be preferred.

A third method that has been used to evaluate K_9 derives this value from the e.m.f. measurement of a suitably chosen cell (12). The values so derived are thermodynamic values. The only reported value derived from this method is 3×10^{-17} and it is tentatively accepted as the K_{so}^{o} value for $Zn(OH)_2$ at 298 K. It is classed as tentative only because there is no report of other work similar to it.

Other values reported for K_9 or K_{so}, but rejected for lack of experimental details are 10^{-13} to 10^{-17} (59); 10^{-14} (60); 1.69×10^{-21} (52). Also rejected are: (1) a value of 6.3×10^{-21} at 293 K was determined by Tyndallometry (61) and is rejected because it obviously was a measurement made with a freshly precipitated product; (2) a value of 1.29×10^{-17} (62) is rejected because it was based on a pH measurement obtained when aqueous $ZnCl_2$ was titrated with NaOH. The pH values were not reproducible and the value of K_9 decreased markedly with decreasing zinc content; (3) a value of 10^{-18} was based on data obtained by measuring the pH and $C_{Zn^{2+}}$ at the moment of precipitation when aqueous $Zn(NO_3)_2$ was titrated with NaOH (65). However, recalculating this value from the experimental data presented in the paper gave a value of 10^{-19}.

Because of the uncertainty as to the composition and stability of the zinc hydroxide used in all these investigations, attention should also be given to solubility product measurements made by using a stable or inactive form of ZnO.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

The reaction is given in equation (9a). All the reported results are in the form given by equation (17) and these are subject to the same reservations expressed above. A value of 10^{-17} mol^3 dm^{-9} at 298 K was obtained by an extrapolation of rate of dissolution data (60). There are no solubility data presented in this article. Another value, determined by extrapolation of data from the solubility of ZnO in aqueous $ZnSO_4$ solutions, is 1.97×10^{-17} mol^3 dm^{-9} at 291 K (63). Feitknecht and Haberli (48) report a value of 2.75×10^{-18} mol^3 dm^{-9} at 298 K but in their work the concentration of Zn^{2+} was sometimes determined by analysis, and at other times by a calculation assuming certain reactions to have occurred. Other values are 2.5 to 3.8×10^{-17} mol^3 dm^{-9} at 296 K (54) and 9.77×10^{-17} mol^3 dm^{-9} at 298 K in 0.2 mol KNO_3 dm^{-3} (55). In a research which studied the solubility of ZnO at 298 K as a function of molar surface area and particle size a maximum value of 10^{-16} was given for K_{so} (4).

No data are reported for a thermodynamic solubility product constant based on equation (9a). However, a treatment of values obtained from equation (17) by the method of Davies (64) gives $pK^o_{so} = 16.82 \pm 0.04$, or $K^o_{so} = 1.5 \times 10^{-17}$ (4). Therefore, all that can be given is a concentration product, and at 298 K the best value appears to be $K_{so} = 9.8 \times 10^{-17}$ mol^3 dm^{-9} in a solution having a total ionic strength of 0.2 mol dm^{-3}. At zero ionic strength the value will be smaller. Tentatively, a value of 1.5×10^{-17} is suggested for K^o_{9a} at 298 K.

The identity of the solute species in solutions of $Zn(OH)_2$ or ZnO in aqueous alkalies has been to some extent a matter of dispute. Some have claimed that $Zn(OH)_3^-$ or $HZnO_2^-$ is the main solute species in aqueous NaOH solutions (9, 66) while, more recently, $Zn(OH)_4^{2-}$ or ZnO_2^{2-} is considered to be also a prominent solute species in these solutions. Some (66) based their contention that $Zn(OH)_3^-$ is the main solute species on data obtained by titrating aqueous solutions of zinc salts with a dilute NaOH solution. Others (9), present no experimental data on which to base this conclusion.

Two papers present data for K^o_{10} and K^o_{11} at 298 K (25, 45).

$$K^o_{10} = a_{Zn(OH)_3^-}/a_{OH^-} \quad (19)$$

$$K^o_{11} = a_{Zn(OH)_4^{2-}}/(a_{OH^-})^2 \quad (20)$$

The values for K^o_{10} are: 1.32×10^{-3} (45) and 1.20×10^{-3} (25). The recommended value at 298 K is 1.3×10^{-3}. The values for K^o_{11} are: 2.20×10^{-2} (25) and 6.47×10^{-2} (45). There is one reservation about this latter value. It was derived from data in the pH region of about 13 and this pH was measured with a glass electrode. No mention is made of a correction to this value for the effect of NaOH on the glass. Consequently, there is some uncertainty about the higher pH values. A tentative value of $K^o_{11} = 4 \times 10^{-2}$ is suggested.

The fact that the values of K^o_{10} and K^o_{11} are within a factor of 10 has been suggested (25) as the reason why pH titrations may have failed to give evidence of both $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ in solutions of alkalies (66).

Only one report (23) deals with reactions (1) and (2), which may be considered as as reactions (10a) and (11a), respectively. Values for K^o_1 and

COMPONENTS:	EVALUATOR:
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(2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]	
(3) Water; H_2O; [7732-18-5]	

CRITICAL EVALUATION:

K_2^o have been reported earlier in this Critical Evaluation. The tentative values at 298 K are: $K_1^o = 6 \times 10^{-4}$ and $K_2^o = 10^{-2}$.

Values for formation constants have also been derived from solubility data. These values are listed in Table I. They are submitted as thermodynamic constants. The agreement is fairly good for the formation constants of $ZnOH^+$ and $Zn(OH)_2$, but the discrepancy is significant for $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$. A

Table I. Formation constants for $Zn(OH)_x^{2-x}$ ions at 298 K.

	ref (45)	ref (57)
$Zn^{2+} + OH^- = ZnOH^+$	1.46×10^6	2×10^6
$Zn^{2+} + 2OH^- = Zn(OH)_2(sln)$	1.51×10^{11}	1.5×10^{11}
$Zn^{2+} + 3OH^- = Zn(OH)_3^-$	7.59×10^{13}	2×10^{14}
$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$	3.72×10^{15}	5×10^{17}

reason for this lies in the solubility data. The data of Gubeli and Ste-Marie (57) were obtained from solutions of constant ionic strength at 1 mol dm^{-3} while the ionic strength was not controlled in the other work (45). As a result, the solubility values are larger in the one work (57) and this difference increases at the higher pH values, Figure 7. The formation constant for $ZnOH^+$ was also reported to be 2.3×10^4 based on a study of the hydrolysis of zinc ions (47). This work was later criticized by others (58) who could not reproduce the pH values that were reported. Dietrich and Johnston (12) determined the formation constant of $Zn(OH)_4^{2-}$ from solubility data and derived a value of 2.8×10^{15} from solutions in which the total ionic strength was not controlled. This is in reasonable agreement with the value in Table I that was obtained under comparable circumstances (45). The values reported in Table I are to be considered as tentative.

Table II. Values for equilibrium constants at 298 K.

Reaction	Value	evaluation[a]
$ZnO(s) + H_2O + OH^- = Zn(OH)_3^-$	$K_1^o = 6 \times 10^{-4}$	t
$ZnO(s) + 2OH^- + H_2O = Zn(OH)_4^{2-}$	$K_2^o = 10^{-2}$	t
$Zn(OH)_2(s) + 2H^+ = Zn^{2+} + 2H_2O$	$K_6^o = 7 \times 10^{10}$	t
$Zn(OH)_2(s) + H^+ = ZnOH^+ + H_2O$	$K_7^o = 2.54 \times 10^3$	t
$Zn(OH)_2(s) = Zn(OH)_2(sln)$	$K_8^o = 3 \times 10^{-6}$ mol kg^{-1}	t
$Zn(OH)_2(s) = Zn^{2+} + 2OH^-$	$K_9^o = 3 \times 10^{-17}$	t
$ZnO(s) + H_2O = Zn^{2+} + 2OH^-$	$K_{9a}^o = 1.5 \times 10^{-17}$	t
	$K_{9a} = 9.8 \times 10^{-17}$ mol^3 dm^{-9}	t
$Zn(OH)_2(s) + OH^- = Zn(OH)_3^-$	$K_{10}^o = 1.3 \times 10^{-3}$	r
$Zn(OH)_2(s) + 2OH^- = Zn(OH)_4^{2-}$	$K_{11}^o = 4 \times 10^{-2}$	t

[a] t = tentative; r = recommended.

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CRITICAL EVALUATION:

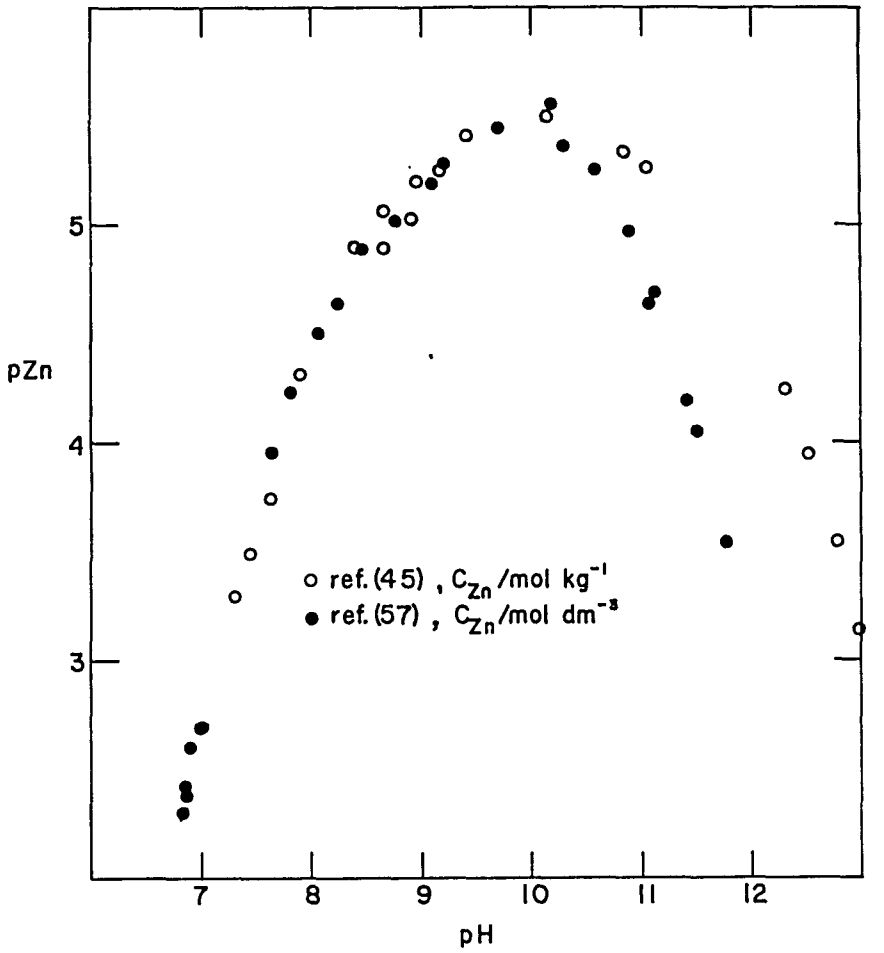

Figure 7. Solubility of ZnO as a function of pH at 298 K. Open circles, total ionic strength was not controlled; closed circles, total ionic strength kept at 0.1 mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Solubility in aqueous solutions of acidic oxides.

Solubility measurements of ZnO or $Zn(OH)_2$ in aqueous solutions of acidic oxides appear, in most instances, to be incidental to the main purpose of the investigation. The purpose usually was to determine which zinc salts could be formed. Emphasis was placed on the structure of these salts and the conditions under which they could be formed. Therefore, in several papers, the solubility data are presented only in a graphical form. The studies in this area are rather scattered and in only a few instances was a given system studied by more than one investigator. Consequently, it is sometimes impossible to make comparisons and the resulting solubility data must, perforce, be regarded as tentative.

Solutions of arsenic(V) oxide. This system has been the subject of two separate studies. In one report (67) the data are presented only in the form of a phase diagram with no temperature specified, but presumably in the vicinity of 303 K. The solid phases reported are: $ZnHAsO_4 \cdot H_2O$ and $Zn(H_2AsO_4)_2$. In the other study (68) the temperature was held at 293 K. The solubility curve of ZnO in aqueous As_2O_5 appears to be very similar in both papers although more than 5 solid zinc arsenates were identified in the second paper (68). No further comparison of the work in these two papers is possible because one paper (67) contains no numerical solubility data.

Solutions of boron(III) oxide. The $ZnO-B_2O_3-H_2O$ system has been discussed by Bondareva and co-workers in several papers, e.g., (69), but the emphasis is on identifying and determining the crystal structure of the zinc borates that can be formed. The borates have generally been formed under hydrothermal conditions. Most of the tabular data deals with values determined by X-ray diffraction, but none of it has to do with solubility data. The Figures given in these papers are mainly drawings of the crystalline structure of the borates. Only occasionally is there a phase diagram. Therefore, no data sheets have been prepared from any of these papers.

Solutions of chromium(VI) oxide. Three papers present solubility data for the $ZnO-CrO_3-H_2O$ system. Two of these (70, 71) present data for 298 K while the other (72) reports data at 308 K. The interest in each of these papers is on the types of zinc chromates that are formed and, in one paper (71), their use as corrosion inhibitors. The data in these papers are quite consistent with each other, Figure 8, even though the concentrations are expressed in different units. The concentration range of CrO_3 was extensive in one paper (71) but rather limited in the others (70, 72). While the solubility data are in agreement there is hardly any agreement as to the composition of the solid phases in equilibrium with these solutions. The solubility of ZnO appears to be influenced but little by the temperature, Figure 9. Equation (21) was derived empirically to fit the data presented in these papers. The

$$C_{ZnO} = 0.0073 + 0.517 \cdot C_{CrO_3} - 0.0001 \cdot (C_{CrO_3})^2 \qquad (21)$$

concentrations are expressed as mol/kg H_2O. Equation (21) is recommended to express the solubility of ZnO in this system.

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CRITICAL EVALUATION:

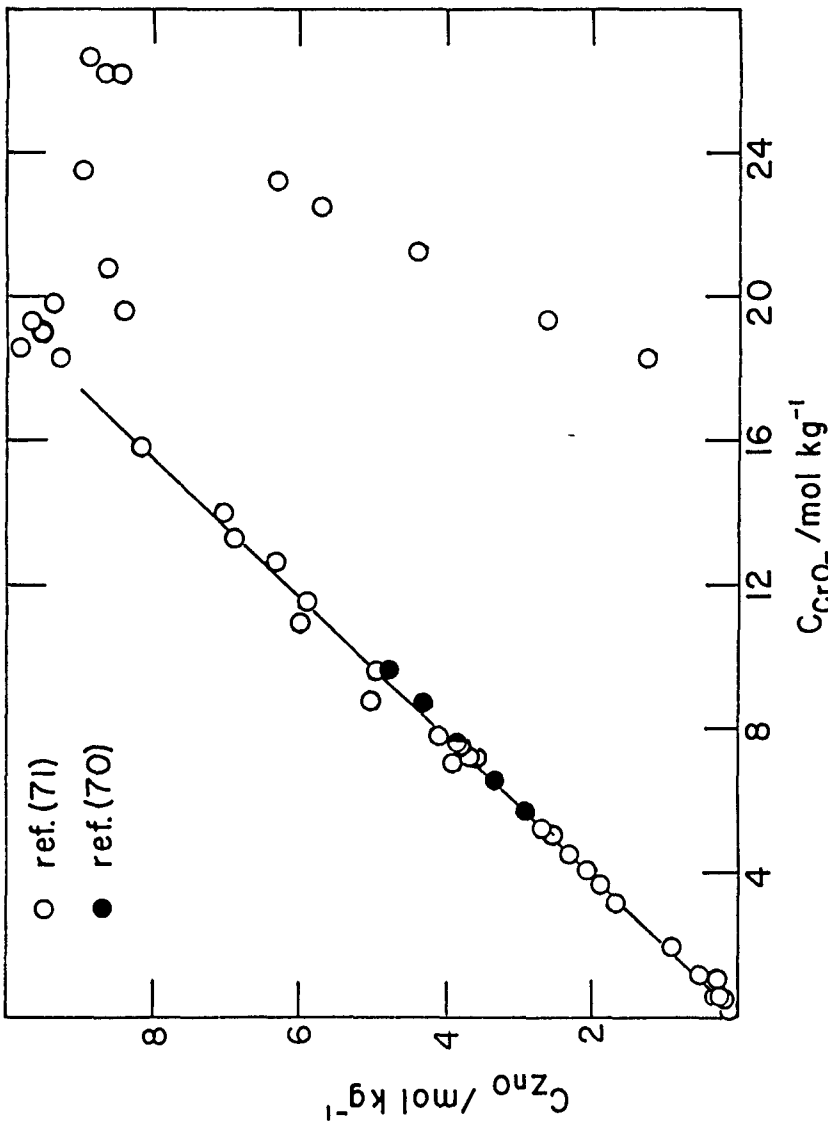

Figure 8. Solubility of ZnO in aqueous CrO_3 at 298 K. The solid line is equation (2]). For ref. (70) the concentration units are mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

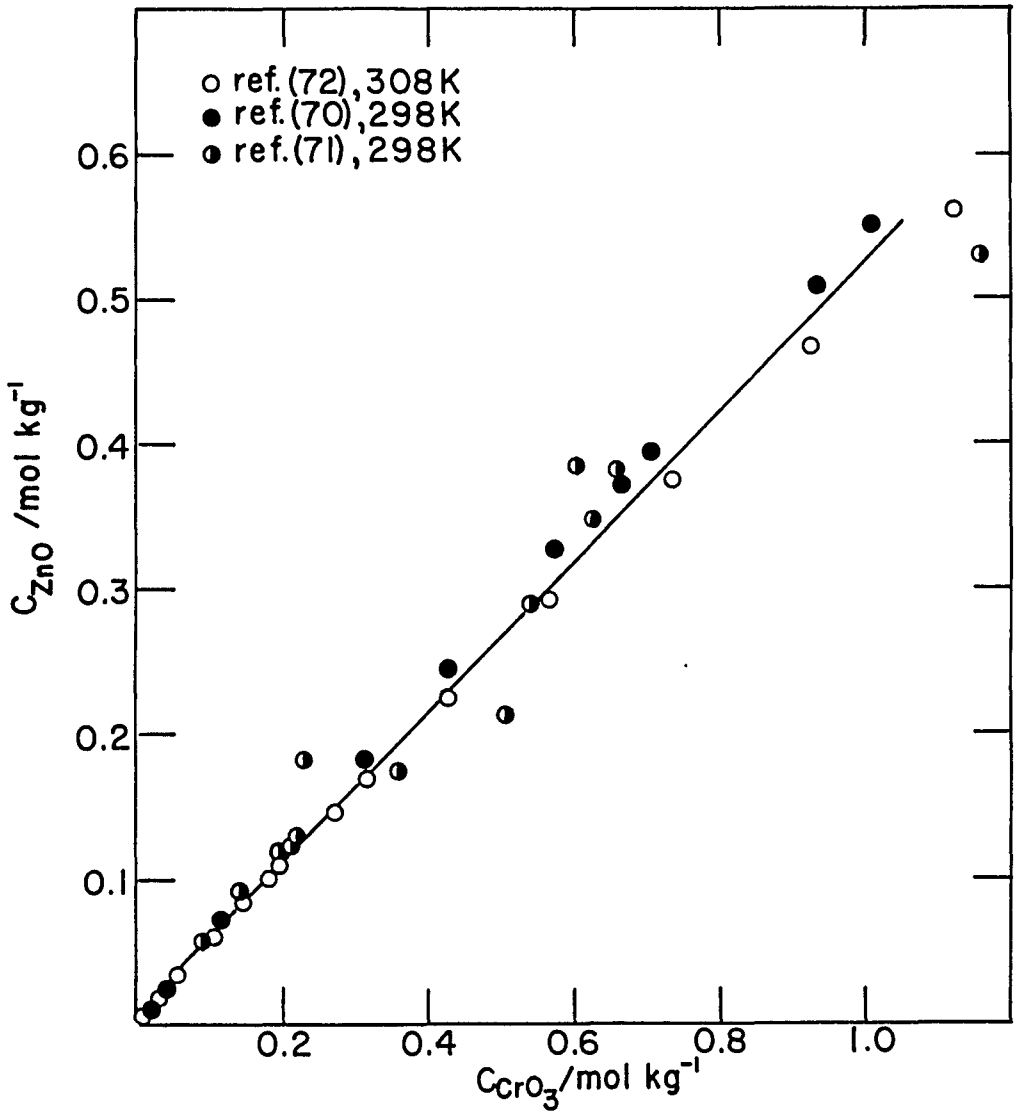

Figure 9. Solubility of ZnO in aqueous CrO_3. The solid line is equation (21). For refs. (70) and (72) the concentration units are mol dm^{-3}.

COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

Solutions of phosphorus(V) oxide. Three papers report solubility data for this system. One (73) presents data for 298 and 310 K. Solubilities were measured only in P_2O_5 concentrations up to 55 mass%. The interest of the authors was to identify the zinc phosphates that precipitated from these solutions. A later paper (74) presented the solubility data for this system at 273, 298 and 333 K, and extended the solubility determinations to systems containing up to 65 mass% P_2O_5. As a result, an additional solid phase, $Zn(H_2PO_4)_2 \cdot 2H_3PO_4$ was observed at the higher concentrations of P_2O_5. No numerical solubility data are given in the paper but the results at 298 K appear to duplicate those of Eberley, et al. (73), except in the region of 35-45 mass% P_2O_5. More recently, another paper (75) has appeared with solubility data for this system at 298 K. The solubility was determined up to P_2O_5 concentrations of 65 mass%. Most of the data for the phase diagram were obtained by measuring the solubilities of the corresponding zinc phosphates rather than that of ZnO or $Zn(OH)_2$. Interestingly, experimental data are missing in the range of 35-45 mass% P_2O_5. This is the range in which there is disagreement between the other two papers (73, 74). All three papers agree on the solid phases present at 298 K with the exception of the phase, $ZnHPO_4 \cdot H_2O$ which Eberley, et al. (73) find at 310 K but not at 298 K. Only one paper (73) contains numerical solubility data at 298 K. The other papers appear to agree with these data, but they cannot be considered to be corroborative because either the numerical data are not given (74) or were not obtained by measuring the solubility of ZnO or $Zn(OH)_2$. Consequently, the data presented by Eberley, et al. (73) are to be considered tentative at this time.

Solutions of sulfur dioxide. One study of this system (76) was carried out in conjunction with a study of the feasibility of using the system for leaching zinc from its ores. The study was made at 288 and 298 K. The graphical presentation of the data show that the solubility of ZnO increases with increasing concentration of SO_2, but at 298 K a solubility maximum is reached. The solid phase is said to be $ZnSO_3 \cdot 2.5H_2O$. No data sheet was prepared for this article because of the absence of numerical solubility data and because very few experimental details were given in the article.

This system was also studied at 293 K (77). The solubility of ZnO appears to increase linearly with the concentration of SO_2. The solid phase, in all but 2 instances, was $ZnSO_3 \cdot 2.5H_2O$, in agreement with the earlier work (76), but there was no evidence for a solubility maximum within the experimental limits of the work. The two articles (76, 77) express the solubilities differently, so no comparison can be made. The data of Jager (77) are considered as tentative values. At present there is no reason for rejecting them or for considering them to be doubtful.

Solutions of sulfur trioxide. There is only one paper (78) that deals with the $ZnO-SO_3-H_2O$ system. The data were collected as a supplement to a rather thorough study of the $ZnSO_4-H_2SO_4-H_2O$ system. The data were collected at 298 K. Up to SO_3 molalities of about 3 mol kg^{-1} the ZnO and SO_3 appear to be dissolved in a 1:1 ratio, leading to the formation of $ZnSO_4$. However, the solid phase that precipitates from these solutions is a basic zinc sulfate, $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$. At larger molalities of SO_3 the 1:1 relationship breaks down and a hydrated zinc sulfate begins to precipitate from the solutions. The data in this paper appear to be reliable but they cannot be accepted as definitive until further work on this system is reported.

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CRITICAL EVALUATION:

Solubility in aqueous solutions of NH_3 and its derivatives.

Zinc oxide. The solubility of ZnO in aqueous NH_3 has been reported in three papers. Euler (79) presents only two data at 294 K, but no experimental details are supplied. Kononov, et al. (80) report measurements at 298 K but the data are given only in graphical form. The interest in that paper appears to be the effect of dissolved $(NH_4)_2SO_4$ on the solubility of ZnO in aqueous NH_3. The effect is to decrease the solubility of ZnO (probably by precipitation) only after the molar ratio of $(NH_4)_2SO_4$ to ZnO exceeds one. The third paper (81) also uses aqueous NH_3 with dissolved $(NH_4)_2SO_4$ as the solvent. The investigation was motivated by an interest in the leaching of zinc from its ores. Only three numerical data--none for the solubility of ZnO in aqueous NH_3 alone--are given and no comparison is possible with the work reported in the other papers.

Zinc hydroxide. There are three papers that report the solubility of $Zn(OH)_2$ in aqueous NH_3, two at 298 K (12, 82) and one at 293 K (44). The understanding or interpretation of this system is complicated by the fact that both the OH^- ion and the NH_3 serve as ligands to the zinc ions in solution. Something of this complexity is illustrated by the pH vs pZn data for a few solutions of $Zn(OH)_2$ in aqueous NH_3 (82). In the most dilute NH_4OH solution used, 0.005 mol dm^{-3}, the solubility of $Zn(OH)_2$ passes through a minimum at about pH = 9.3. In more concentrated NH_4OH, 0.02 mol dm^{-3}, the data are more erratic and the solubility minimum is at pH = 8.5. In the most concentrated NH_4OH solutions that were used, 0.04 mol dm^{-3}, the solubility of $Zn(OH)_2$ shows a maximum at pH = 9.5 and then decreases to a minimum at pH = 10.5, after which the solubility again increases.

Where the solubility of $Zn(OH)_2$ is expressed in terms of the concentration of NH_4OH (12, 44), the results are fairly consistent. The solubility of $Zn(OH)_2$ increases with increasing NH_4OH concentration and, at 298 K, reaches a maximum in a solution having a NH_4OH concentration of about 8 mol dm^{-3}. The solubility decreases with increasing temperature. The data of Dietrich and Johnston (12) appear to be the best for this system but are considered tentative until additional work is reported.

In addition to the data in the above papers, some early solubility data at 294 K were reported (79) but these are rejected because of lack of experimental details and uncertainty as to the composition of the $Zn(OH)_2$ that was used.

Some of the interest in the $Zn(OH)_2$-NH_3-H_2O system has been motivated by a desire to determine the nature of the zinc-containing solute species, but there is no general agreement in this area, probably because of different experimental conditions. A study of the change of pH of aqueous NH_3 as it becomes saturated with either $Zn(OH)_2$ or ZnO (8) indicated to the authors that the solute species at 298 K in such solutions ranging in concentration from 1-12 mol dm^{-3} were: $Zn(OH)_2(NH_3)_2$, $Zn(OH)(NH_3)_3^+$, $Zn(OH)_3(NH_3)^-$ and $Zn(OH)_2(NH_3)$. No solubility values are given in the paper. Others (82) found evidence from the solubility data for $Zn(OH)_2$, $Zn(OH)_3(NH_3)^-$ and $Zn(NH_3)_4^{2+}$. The formation constants of these substances at 298 K as reported (82) cannot be confirmed by other work. De Wijs (49) measured the partial pressure of NH_3 in equilibrium with the ZnO-NH_3-H_2O system but reported no solubility measurements. On the basis of her

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results she reports the value of the formation constant of $Zn(NH_3)_4^{2+}$ at 298 K to be 1.02×10^9 mol^4 dm^{-12}. She also reported evidence for the presence of $Zn(NH_3)_2^{2+}$ with a formation constant value of 7.1×10^4 mol^2 dm^{-6}.

Derivatives of NH_3. The solubility of $Zn(OH)_2$ in aqueous solutions of NH_4Cl, NH_4NO_3 and $(NH_4)_2SO_4$ has been reported (26). However, no temperature is specified although the measurements appear to have been made at room temperature. Corrections were made for the degree of ionization of the zinc salts but there is no indication what these corrections were nor how they were made. Furthermore, no details of the analytical methods are given. Consequently, these solubility values are classified as doubtful.

There is one report (83) on the solubility of ZnO in aqueous solutions of 2,2',2''-nitrilotriethanol (triethanolamine). However, the paper contains values for only 3 experimental data points. There are no other data with which this work can be compared. Therefore, these values must be considered tentative, at best.

In another paper (84), the solubility of ZnO in aqueous glycine is reported. Because no other similar results have been reported these results, too, must be considered to be tentative.

Solubility in aqueous salt solutions.

Aqueous $ZnCl_2$. The earliest information dealing with the solubilities in this system was contained in a report to a meeting of the American Wood-Preservers' Association (85). Solutions of $ZnCl_2$ of concentrations suitable for timber injection would deposit a white sludge. The suggestion was made that the sludge may have been a basic zinc chloride and therefore the solubility of ZnO in aqueous $ZnCl_2$ solutions was investigated at 293, 313, 333 and 353 K. However, there is no indication as to the experimental procedure by which these results were obtained and the data, as presented, are difficult to interpret. The only clue to the concentration of $ZnCl_2$ is the specific gravity of the system, but there is no indication of the temperature at which the specific gravity was measured nor whether it was measured before or after the ZnO had dissolved in the solutions. Therefore, these data are not included in the data sheets. Qualitatively, the solubility of ZnO increases with increasing concentration of $ZnCl_2$ and with increasing temperature.

The other papers dealing with this system have as their main interest the identification of the solid phases associated with this system (86, 87, 88). Only one paper presents solubility data (86). In this paper the data are presented in the form of a smoothed square phase diagram, but the concentration units are not specified. If the data are plotted as C_{ZnO} vs C_{ZnCl_2} (both expressed as mol/kg H_2O) the data appear to have a great deal of scatter in them. Therefore, these data are not to be considered as realiable.

In another paper (87) the system was studied at 303 K. However, it is stated that the solubility of ZnO in the aqueous $ZnCl_2$ solutions was less than the experimental uncertainty and, therefore, these solubility determinations were not made.

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CRITICAL EVALUATION:

More recently, this system has again been investigated (88) in an effort to identify any solid zinc oxychlorides associated with the system, but no solubility data are presented in the paper.

Aqueous $MgCl_2$. There is only one report on this system (89). Solubility data for $Zn(OH)_2$ are given at 293, 313, 333 and 353 K for a limited range of $MgCl_2$ concentrations. The $Zn(OH)_2$ becomes more soluble as the concentration of $MgCl_2$ increases. The solubility also increases with increasing temperature. However, the values as given cannot be accepted as reliable because the solid phase was not shown to be $Zn(OH)_2$. It was prepared by mixing equivalent amounts of $ZnCl_2$ and NaOH. As pointed out earlier in this Critical Evaluation, such a procedure does not necessarily produce $Zn(OH)_2$ as a product of the reaction.

Solubility in aqueous hydrogen peroxide.

A study of this system was part of a larger program dealing with the formation of metal peroxides. The first paper (27) gives solubility data for the liquid phase while the second paper (90) is a study of the solid phases associated with the saturated solutions. It is difficult to evaluate the solubility data because there is no other work similar to it with which the data can be compared. It should be noted that the water solubility of $Zn(OH)_2$ at 293 and 303 K is reported to be of the order of 10^{-4} mol kg^{-1} which is about ten times the value suggested earlier in this Evaluation. The increased solubility may be due to the solid $Zn(OH)_2$ that was used. It was prepared by the addition of NH_4OH to an aqueous solution of $Zn(NO_3)_2$. No indication is given whether the $Zn(OH)_2$ was used immediately after preparation or whether it had first been allowed to age. Freshly precipitated $Zn(OH)_2$, as noted earlier in this Evaluation, will have a larger solubility. Because of this uncertainty, the solubility data given for this system must be considered doubtful at the present time.

Solubility in Sea Water

Only one paper reports work on this subject (21) and in this paper only the solubility of ZnO is measured in Baltic Sea water. No temperature is specified but it presumably was 288 or 291 K. The solubility values are sensitive to pH, as they are in water. There is no other work with which the values reported here can be compared. Much of the article discusses the analytical problems and the use of proper analytical procedures. Therefore, the values reported in this paper are accepted as tentative values.

Solubility under hydrothermal conditions

Although there are many papers that discuss the dissolution of ZnO under hydrothermal conditions, only two present numerical solubility data (91, 92). The authors of the other papers used hydrothermal conditions to prepare zinc germanates (93) or zinc borates (69, 94-97), but these papers all stress only the identification and characterization of the solid phases that are produced. They contain no solubility data.

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CRITICAL EVALUATION:

One paper (91) deals with the effect of CO_2 under pressure on the solubility of ZnO in aqueous NaCl. Only a few solubility values are given--not enough to establish the effect of the variables on the solubility of ZnO. The data apparently are preliminary values obtained in a larger program of research. Because of this, these data are to be considered tentative.

Two papers (92, 98) discuss the solubility of ZnO in solutions of alkalies. Numerical data are presented for very dilute solutions of NaOH at 373, 423 and 473 K (92). At each of these temperatures there is a solubility minimum in very dilute (10^{-2} to 10^{-4} mol dm^{-3}) solutions of NaOH. There is a good deal of uncertainty in most of the values. Because of this, and the fact that these are the only numerical results available, the data presented in this paper are considered tentative, but not very reliable. The other paper (98) discusses the solubility of ZnO in much more concentrated solutions of NaOH and KOH (6-9 mol kg^{-1}) and at temperatures upward from 473 K. Therefore, the data should be complementary to those of Khodakovskii and Yelkin (92), but only two numerical data are given. The graphs that are included in the paper show that the solubility of ZnO in the NaOH and KOH solutions increases linearly from 473-673 K. The slope of this line appears to be independent of the prevailing pressure.

Solubility in miscellaneous systems.

Only one value is reported for the solubility of ZnO in aqueous Na_2S solutions (99). Very little information is given about the experimental details. Furthermore, no other similar data have been reported. Therefore, this one value is classed as tentative, at best.

Some work has been reported on the solubility of ZnO in aqueous sodium tartrate solutions (100). No solubility data are given. The interest of the author, apparently, was in determining the nature of the zinc compound that is formed in this system. Others (101) have also studied the solubility of ZnO in tartrate solutions. The data for the solubility of ZnO in aqueous sodium potassium tartrate is presented only in the form of two small graphs. The authors state that the solubility of ZnO in such solutions decreases as the temperature is increased from 298 to 353 K. This temperature effect is also reported to be true for the solubility of ZnO in potassium oxalate solutions. In both these solutions, the solubility of ZnO varies linearly with the concentration of the tartrate or oxalate. The linear relationship also is reported for the solubility of ZnO in aqueous sodium citrate solutions but here the solubility is independent of the temperature in the range 298-353 K.

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COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

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COMPONENTS:	EVALUATOR:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. June 1984

CRITICAL EVALUATION:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Water; H_2O; [7732-18-5]	Remy, H.; Kuhlmann, A. *Z. Anal. Chem.* 1924, *65*, 161-81.
VARIABLES:	PREPARED BY:
Method of measuring the solubility of ZnO in water.	T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in water at 20°C.

method	mol ZnO dm^{-3}	mg ZnO dm^{-3}
conductimetric titration	3.58×10^{-5}	2.92
specific conductance	3.76×10^{-5}	3.06

The solubility values calculated from specific conductance measurements assumed that the dissolved ZnO was present in solution as a completely dissociated hydroxide.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Hot ZnO was added to water and the mixture was shaken. Solubility was calculated from 2 types of measurements: (a) the specific conductance was measured and used with literature values for individual ionic conductances; (b) the solution was titrated conductimetrically with H_2SO_4. The main concern in this work was to note and correct for the contribution of dissolved CO_2.	ZnO was produced by heating the precipitate that was formed when freshly distilled NH_4OH was added to an aqueous solution of pure $Zn(NO_3)_2$. Conductivity water was used.
	ESTIMATED ERROR:
	The temperature was not controlled but varied from 19 to 21°C. In the titrations, the results had a reproducibility within 1% of the average value.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Water; H_2O; [7732-18-5]	Busch, W. *Z. Anorg. Allgem. Chem.* 1927, *161*, 161-79.
VARIABLES:	**PREPARED BY:**
All work was done at 29.0°C.	T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in water at 29.0°C.

ml of solution used	130
ml H_2SO_4 added	20
factor of H_2SO_4	1.019×10^{-3} [a]
factor of KOH	1.151×10^{-3} [a]
ml of KOH needed for back titration	13.36
dissolved ZnO	1.92×10^{-5} mol dm^{-3}

[a] These obviously are concentration values but no units are given.

The purpose of this work was to determine the suitability of the potentiometric titration method for determining the solubility of slightly soluble materials. According to the author, the results are affected by the previous treatment of the solute (therefore the ZnO was heated to 850°C before being used), and by the presence of small amounts of colloidal material (therefore ultrafiltration was used before electrometric measurements were made). The solubility of ZnO was calculated from the amount of H_2SO_4 required to dissolve the ZnO.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
ZnO, after being heated to 850°C, was placed in conductivity water and shaken for 6-7 hours in a thermostat at 29.0°C. The mixture was then filtered, using an ultrafilter. A sample of the filtrate was added to excess H_2SO_4 and the excess acid was determined by a potentiometric titration with KOH. Care was taken to exclude CO_2.	Freshly distilled NH_4OH was added to an aqueous solution of pure $Zn(NO_3)_2$ to precipitate $Zn(OH)_2$. The $Zn(OH)_2$ was washed thoroughly and then heated at 850°C to produce ZnO. Conductivity water was used.
	ESTIMATED ERROR:
	The final solubility values have an uncertainty of 1×10^{-6} mol dm^{-3}. The author attributes this to the titration procedure.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Water; H_2O; [7732-18-5]	Hagisawa, H. *Bull. Inst. Phys. Chem. Research (Tokyo)* 1939, *18*, 368-81.
VARIABLES:	PREPARED BY:
Composition of the solvent.	H. Akaiwa

EXPERIMENTAL VALUES:

Solubility product of $Zn(OH)_2$ at 298 K[a]

cm^3 of NaOH added	pH	10^4 mol Zn(II) dm^{-3}	$K_so \times 10^{16}$
1	7.890	4.68	2.8
2	7.926	4.42	3.1
3	7.942	4.15	3.2
4	7.965	3.89	3.3
5	7.992	3.62	3.5
6	8.009	3.67	3.5
7	8.031	3.11	3.6
8	8.053	2.86	3.7
9	8.077	2.61	3.7
10	8.098	2.36	3.7

average $K_so = [Zn^{2+}]\ a^2_{OH-} = (3.4 \pm 0.29) \times 10^{-16}$ [b]

[a] 200 cm^3 of 0.0004955 mol dm^{-3} $ZnSO_4$ solution was titrated with 0.00991 mol dm^{-3} NaOH solution.

[b] the standard deviation was calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
An aqueous $ZnSO_4$ solution was titrated with a dilute NaOH solution. The pH of the solution was measured in a cell using a glass electrode and a saturated calomel electrode. The zinc content apparently was determined by calculating the difference between the original zinc content and the amount used up by precipitation.	$ZnSO_4$ was dissolved in water at 343 K and recrystallized by cooling and adding alcohol. During the recrystallization process CO_2 was bubbled through the solution to avoid hydration of Zn(II). The CO_2 was removed from the solid by drying.
	ESTIMATED ERROR:
	The final results have a standard deviation of 0.29.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Baltic Sea water (3) Water; H_2O; [7732-18-5]	Ragg, M. *Farbe u. Lack* 1950, *56*, 435-41
VARIABLES: Composition of solvent.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO at pH = 8.0

in distilled water		in Baltic Sea water	
mg dm^{-3}	mol dm^{-3} [a]	mg dm^{-3}	mol dm^{-3} [a]
6.3	7.7×10^{-5}	2.5	3.1×10^{-5}

[a] calculated by compiler

During the first 3 hours of agitation the pH of the distilled water changed from 6.1 to 8.0. This was considered to be due to the transformation of ZnO to $Zn(OH)_2$. During this same time interval the pH of the Baltic Sea water changed from 8.1 to 8.0. This was considered to be caused by the removal of $Ca(HCO_3)_2$ as $CaCO_3$.

The temperature is not specified but from the context in the article it appears to be either 15 or 18°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
0.5 g of ZnO were added to 100 ml of solvent. The mixture was agitated until the pH = 8. The mixture was then filtered and the filtrate was analyzed for zinc content. The analytical method is not described, but indications are that the zinc content was determined by a colorimetric method using dithizone.	Distilled water and filtered Baltic Sea Water were used as solvents. The ZnO was of a purified grade.
	ESTIMATED ERROR: No data are given as to the reproducibility of the procedures or the results.
	REFERENCES:

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Collat, J. W. *Anal. Chem.* 1958, *30*, 1726-9.

VARIABLES:
Method of measuring pH.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility products of $Zn(OH)_2$

From current-voltage experiments.

$C_{Zn^{2+}}$/mmol dm^{-3}	t/°C.	C_{KNO_3}/mol dm^{-3}	Solid phase[a]	pOH	pK_s^o
10.5	22	0.27	A	6.55	15.08
10.0	24	0.27	B	6.60	15.20

From zero-current potential measurements.

$C_{Zn^{2+}}$/mol dm^{-3}	t/°C.	C_{KNO_3}/mol dm^{-3}	Solid phase[a]	pH	K_s^o
0.00085	24	0.195	A	7.83	3.9×10^{-16}
0.0100	24	0.168	A	7.26	3.3×10^{-16}
0.0666	24	0	A	6.72	1.8×10^{-16}
0.0100	24	0.170	C	7.19	2.4×10^{-16}
0.0235	25	0.0294	C	6.98	2.2×10^{-16}
0.0118	25	0.0648	C	7.08	1.7×10^{-16}
0.0094	24	0.0718	D	6.71	2.5×10^{-17}
0.0235	24	0.0295	D	6.60	3.8×10^{-17}

[a] A = amorphous $Zn(OH)_2$; B = aged (β_1) $Zn(OH)_2$; C = ε-$Zn(OH)_2$; D = ZnO.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The dropping mercury electrode was used to measure the pH in a solution of a quinone. The solution was buffered by the presence of Zn^{2+} ions. The buffer reaction consisted of the formation of the insoluble hydroxide. An amount of HNO_3 calculated to give the desired concentration of Zn^{2+} ions was added to $Zn(OH)_2$ or ZnO. The pH of the buffered solution was measured by making the usual current-voltage measurements, and also by measuring the potential at zero current.

SOURCE AND PURITY OF MATERIALS:
The quinhydrone was purified by recrystallization from hot water. Other materials used were of the purest grade available. Amorphous $Zn(OH)_2$ was prepared by adding NaOH to a solution of a zinc salt. ε-$Zn(OH)_2$ was prepared as described by others (1).

ESTIMATED ERROR:
No details are given.

REFERENCES:
1. Dietrich, H. G.; Johnston, J. *J. Am. Chem. Soc.* 1927, *49*, 1419.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

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

ORIGINAL MEASUREMENTS:

Jenkins, S. H.; Keight, D. G.; Humphreys, R. E. *Air Water Pollution* 1964, *8*, 537-56

VARIABLES:

Different samples of CO_2-free distilled water at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in distilled water

		Bottle 1		Bottle 2		Bottle 3	
pH of H_2O	temp, °C	pH of soln	C_{Zn}, ppm	pH of soln	C_{Zn}, ppm	pH of soln	C_{Zn}, ppm
8.58	20.0	7.78	0.48	7.66	0.56	7.60	0.56
8.75	18.2	7.92	0.40	7.95	0.64	7.10	0.64
8.90	17.0	7.56	0.33	7.80	0.22	8.24	0.24
9.20	18.4			8.80	0.29	8.92	0.30
8.20	22.0			8.12	0.28	8.46	0.22
8.40	20.0			7.75	0.36	8.04	0.31
8.31	20.0			7.68	0.68	7.98	0.39
8.05	17.0			6.70	0.41	7.20	0.34
7.00	16.5			7.02	0.60	7.50	0.49
8.30	17.5			7.00	0.67	7.28	0.53
5.80	19.0			6.71	0.46	6.90	0.32
5.85	19.5			7.22	0.48	7.40	0.28

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

ZnO was washed several times with distilled water to remove soluble impurities. The washed oxide was placed in different bottles filled with distilled water. The bottles were shaken intermittently for 3 days and then allowed to stand for 3 days to allow the suspended material to settle. Samples were removed, filtered through HA millipore filters and analyzed for zinc content colorimetrically using the dithizone method. After the first extraction the procedure was repeated many times.

SOURCE AND PURITY OF MATERIALS:

The distilled water was CO_2-free. The ZnO was a commercially available grade.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Schindler, P.; Althaus, H.; Feitknecht, W. *Helv. Chim. Acta* 1964, *47*, 982-91.

VARIABLES:
Type of zinc hydroxide.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility products of zinc hydroxide at 25.0°C.

Solid phase	log $*K_so$ [a]	log K_so [a]	log $*K_so$ [b]	log K_so [b]
amorph. $Zn(OH)_2$	12.70 ± 0.02	-14.70 ± 0.03	12.48 ± 0.03	-15.52 ± 0.03
β_1-$Zn(OH)_2$	11.98	-15.42	11.76	-16.24
β_2-$Zn(OH)_2$	12.02	-15.38	11.80	-16.20
γ-$Zn(OH)_2$	11.96	-15.44	11.74	-16.26
δ-$Zn(OH)_2$	12.07	-15.33	11.85	-16.15
ε-$Zn(OH)_2$	11.75	-15.65	11.53	-16.47
active ZnO [c]	11.56	-15.84	11.34	-16.66
inactive ZnO [d]	11.39	-16.01	11.17	-16.83

[a] These values were determined experimentally in solutions containing 0.2 mol KNO_3 dm^{-3} or 0.2 mol $NaClO_4$ dm^{-3}.

[b] These values were calculated for infinite dilution from the free energy of formation and E° for the zinc electrode.

[c] Active ZnO was formed by adding an equivalent amount of NaOH to a solution of $Zn(ClO_4)_2$ and allowing the precipitate to stand for several days at room temperature.

[d] Inactive ZnO was formed by heating the ZnO at 900°C.

Note: $K_so = C_{Zn^{2+}} (a_{OH^-})^2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Solutions were equilibrated at 25°C with the selected solid phase. The solid phases were: amorphous $Zn(OH)_2$; β_1-$Zn(OH)_2$; β_2-$Zn(OH)_2$; γ-$Zn(OH)_2$; δ-$Zn(OH)_2$; ε-$Zn(OH)_2$; active and inactive ZnO. The hydrogen ion concentration in these solutions was measured by an e.m.f. measurement. The zinc content was determined by a compleximetric titration. From these results the value of $*K_so = [Zn^{2+}]/[H^+]^2$ was determined. The relationship log K_so = log $*K_so$ + 2log K_w allows the solubility products to be calculated. Log K_w = -13.70 ± 0.2 at 25°C. in 0.2 mol KNO_3 dm^{-3}.

SOURCE AND PURITY OF MATERIALS:
All materials were of reagent grade quality.

ESTIMATED ERROR:
The authors state that the uncertainty in the results was generally less than 0.1%.

REFERENCES:

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Rubenbauer, J. Z. *Anorg. Allg. Chem.* 1902, *30*, 331-7.

VARIABLES:
Concentration of Sodium hydroxide.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in aqueous NaOH.

g Na/20 ccm	C_{NaOH}/mol dm^{-3} [a]	g Zn/20 ccm	C_{ZnO}/mol dm^{-3} [a]
0.1012	0.220	0.0040	0.00306
0.1978	0.430	0.0150	0.0115
0.4278	0.930	0.0442	0.0338
0.6670	1.451	0.1771	0.135
0.9660	2.101	0.9630 [b]	0.736
1.4951	3.252	0.2481	0.190
2.9901	6.503	0.3700	0.283

[a] Calculated by the compiler.

[b] This result appears to be an error.

The author says that shaking the mixture for 10 hours gave the same zinc content as obtained after shaking for only 5 hours.

The author further notes that in the most concentrated NaOH solution the $Zn(OH)_2$ dissolved very rapidly but then almost immediately precipitated out of solution. This transient zinc content was about 10 times the value at equilibrium.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures of moist $Zn(OH)_2$ and aqueous NaOH were shaken vigorously for about 5 hours. A small sample was filtered, and the filtrate was analyzed for zinc content by precipitating the zinc as $ZnCO_3$, heating it, and weighing the ZnO. No temperature is stated in the article but it appears that the solubility values were determined at room temperature.

SOURCE AND PURITY OF MATERIALS:

$Zn(OH)_2$ was prepared by adding NaOH to aqueous $ZnSO_4$. The precipitate was washed and then dried on a clay plate. The NaOH was prepared from metallic Na and was carbonate-free.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water; H_2O; [7732-18-5]	Wood, J. K. *J. Chem. Soc.* 1910, *97*, 878-90
VARIABLES:	PREPARED BY:
Concentration of NaOH at 25°C.	T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in aqueous NaOH at 25°C.

mol Zn(II) dm^{-3}	mol Na(I) dm^{-3}
0.00311	0.2636
0.0057	0.3871
0.0129	0.5414
0.0425	0.9280

From the first two data points in the above Table the author calculates the solubility of $Zn(OH)_2$ in water at 25°C to be 0.00078 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Equilibrium was reached isothermally and was determined by repeated analyses. The analytical procedures are not mentioned or described.	The $Zn(OH)_2$ was prepared by precipitation from $ZnSO_4$ with NaOH. The precipitate was washed thoroughly before being used. The source or purity of the other materials is not mentioned.
	ESTIMATED ERROR:
	No details are given.
	REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Chromium(VI) oxide; CrO_3; [1333-82-0]

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

ORIGINAL MEASUREMENTS:

Groger, M. *Z. Anorg. Chem.* 1911, *70*, 135-44.

VARIABLES:

Concentration of CrO_3 at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous CrO_3 at 25°C.

C_{CrO_3}/mol dm^{-3}	C_{ZnO}/mol dm^{-3}	C_{CrO_3}/mol dm^{-3}	C_{ZnO}/mol dm^{-3}
0.00010	0.00016	0.933	0.510
0.00010	0.00016	1.01	0.552
0.00010	0.00016	1.51	0.812
0.00604	0.00503	1.92	1.03
0.0214	0.0142	1.92	1.03
0.0419	0.0275	2.85	1.51
0.114	0.0717	3.92	2.06
0.115	0.0723	4.50	2.34
0.222	0.131	4.61	2.41
0.314	0.183	4.63	2.42
0.431	0.247	4.75	2.48
0.575	0.328	5.74	2.94
0.665	0.372	6.60	3.37
0.667	0.373	7.69	3.90
0.706	0.394	8.79	4.35
		9.70	4.78

Five individual zinc chromates were identified by the author: $4ZnO \cdot CrO_3 \cdot 3H_2O$; $3ZnO \cdot CrO_3 \cdot 2H_2O$; $4ZnO \cdot 2CrO_3 \cdot 3H_2O$; $3ZnO \cdot 2CrO_3 \cdot H_2O$; $ZnO \cdot CrO_3 \cdot H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A slurry of ZnO and chromic acid was prepared and placed in a flask. The mixture was shaken in a thermostat at 25°C for 3 days The solid and liquid phases were separated from each other by filtration. The chromium content was determined by iodometric titration. The ZnO content was determined indirectly. A measured amount of solution was placed in a crucible together with a weighed amount of ZnO and evaporated on a water bath. The precipitate was dried, weighed, and analyzed for Cr_2O_3. This value, together with the known amount of Cr in the solution, was used to calculate the ZnO content of the solution.

SOURCE AND PURITY OF MATERIALS:

No details are given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Phosphorus(V) oxide; P_2O_5; [1314-56-3]

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

ORIGINAL MEASUREMENTS:

Eberly, N. E.; Gross, C. V.; Crowell, W. S. *J. Am. Chem. Soc.* 1920, *42*, 1433-9.

VARIABLES:

Concentration of P_2O_5 and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in phosphoric acid solutions at 25°C.

mass % P_2O_5	mass % ZnO	mass % P_2O_5	mass % ZnO
5.08	2.38	28.70	13.48
9.76	4.65	30.09	14.16
12.42	6.13	32.55	15.40
13.52	6.56	33.79	15.82
14.00	6.74	37.15	17.30
14.15	6.92	37.76	17.65
14.37	6.97	39.61	18.04
14.83	7.34	42.05	16.14
15.98	7.71	44.53	13.20
17.15	8.26	48.70	9.58
18.33	8.73	52.25	7.64
22.75	10.74	55.97	7.23
26.48	12.47		

In no instance was ZnO the solid phase. All solid phases were types of zinc phosphate: $Zn_3(PO_4)_2 \cdot 4H_2O$; $ZnHPO_4 \cdot 3H_2O$; $Zn(H_2PO_4)_2 \cdot 2H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Slightly supersaturated solutions were made up and allowed to form a precipitate on standing (with occasional agitation) in a constant temperature bath. Analyses were repeated at 2 week intervals until constant results were obtained. Phosphoric acid was determined gravimetrically as magnesium pyrophosphate. ZnO content was determined by titration with $K_4Fe(CN)_6$. The composition of the solid was determined by the Schreinemakers' wet-residue method.

SOURCE AND PURITY OF MATERIALS:

U. S. P. grade materials were used.

ESTIMATED ERROR:

The temperature was controlled to within 0.1°C at 25°C and to within 0.25°C at 37°C. No other details are given.

REFERENCES:

COMPONENTS	ORIGINAL MEASUREMENTS
(1) Zinc oxide; ZnO; [1314-13-2] (2) Phosphorus(V) oxide; P_2O_5; [1314-56-3] (3) Water; H_2O; [7732-18-5]	Eberly, N. E.; Gross, C. V.; Crowell, W. S. *J. Am. Chem. Soc.* 1920, *42*, 1433-9.

EXPERIMENTAL VALUES, contd. - - - -

Solubility of ZnO in phosphoric acid solutions at 37°C.

mass % P_2O_5	mass % ZnO	mass % P_2O_5	mass % ZnO
4.87	2.08	37.80	15.78
9.46	4.12	39.93	16.12
13.60	6.27	42.42	15.81
18.13	8.78	42.65	16.82
19.48	9.66	44.89	17.83
20.32	10.16	46.11	18.05
21.96	10.88	46.41	14.74
26.75	13.26	48.99	12.55
29.65	14.77	51.35	11.26
33.39	17.06	51.92	11.12
34.58	17.92	54.32	10.82
36.13	16.00		

In no instance was ZnO the solid phase. The only solid phase identified was $ZnHPO_4 \cdot H_2O$.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Goudriaan, F. *Proc. Acad. Sci. Amsterdam* 1919, *22*, 179-89; *Rec. trav. Chim.* 1920, *39*, 505-14.

VARIABLES:

Concentration of NaOH at 30.0°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous NaOH at 30.0°C.

mass % Na_2O	mass % ZnO	mass % H_2O	Solid phase
11.8	2.6	85.6	ZnO
17.4	5.0	77.6	"
24.6	12.6	62.8	"
24.9	12.9	62.2	"
23.7	11.3	65.0	"
27.3	16.0	56.7	"
27.8	16.5	55.7	ZnO + $Na_2O \cdot ZnO \cdot 4H_2O$
28.0	14.9	57.1	$Na_2O \cdot ZnO \cdot 4H_2O$
33.5	10.9	55.6	"
36.7	9.5	53.8	"
31.8	11.7	56.5	"
30.1	13.2	56.7	"
33.2	11.2	55.6	"
31.5	11.8	56.7	"
36.9	10.1	53.0	"
34.7	10.4	54.9	"
36.1	10.2	53.7	"
36.8	9.9	53.3	"
39.2	9.7	51.1	$Na_2O \cdot ZnO \cdot 4H_2O$ + $Na_2O \cdot 3H_2O$
39.4	9.0	51.6	$Na_2O \cdot 3H_2O$
39.6	7.2	53.2	"
40.7	2.0	57.3	"
40.5	1.6	57.9	"
40.9	1.1	58.0	"
41.9	0.0	58.1	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally. No mention is made of any of the analytical procedures that were used. The composition of the solid phase was determined by the Schreinemakers' wet-residue method.

SOURCE AND PURITY OF MATERIALS:

The NaOH was prepared from metallic sodium. The ZnO was prepared by heating $ZnCO_3$ or by heating the precipitate formed when the calculated quantity of NH_4OH was added to a solution of $Zn(NO_3)_2$. Distilled water was boiled before use.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Goudriaan, F. *Proc. Acad. Sci. Amsterdam* 1919, *22*, 179-89; *Rec. trav. Chim.* 1920, *39*, 505-14.

VARIABLES:

Concentration of NaOH at 30.0°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of $Zn(OH)_2$ in aqueous NaOH at 30.0°C.

No.	mass % Na_2O	mass % ZnO	mass % H_2O	Solid phase
26	24.6	12.5	62.9	ZnO
27	19.9	15.2	64.9	$Zn(OH)_2$
28[a]	4.6	1.0	96.4	"
29	4.5	0.4	95.1	ZnO
30	13.7	7.2	79.1	$Zn(OH)_2$
31	10.1	4.7	85.2	"

[a] These mass % values do not add up to 100.

The author maintains that $Zn(OH)_2$ is metastable with respect to ZnO and the results in the above Table are intended to support this claim. $Zn(OH)_2$ was the solid phase added to each of the solutions in the above Table. In Nos. 27, 28, 30 and 31 only 24 hours elapsed before analysis and in each case the solid phase is still $Zn(OH)_2$. In No. 26 at least 2 weeks elapsed before the analysis was made, and in No. 29 3 weeks elapsed before the filtrate was removed and analyzed. During this period of standing the solid phase changed to ZnO.

Where $Zn(OH)_2$ is the solid phase, the solubility values of Zn(II) in solution are much larger than for solutions made by dissolving ZnO in aqueous NaOH. When ZnO is the solid phase (Nos. 26, 29) the solubility values are the same as for solutions in which ZnO is dissolved in aqueous NaOH.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally. No mention is made of any of the analytical procedures. The composition of the solid phase was determined by the Schreinemakers' wet-residue method.

SOURCE AND PURITY OF MATERIALS:

NaOH was prepared from metallic sodium. Distilled water was boiled before being used. The $Zn(OH)_2$ was prepared by dropwise addition of a solution of $ZnSO_4$ to a KOH solution until a turbidity persisted. On standing, this solution gave a heavy, sandy precipitate of $Zn(OH)_2$.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Dietrich, H. G.; Johnston, J. *J. Am. Chem. Soc.* 1927, *49*, 1419-31.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in NaOH solutions.

mol NaOH dm^{-3}	$1000R^a$	mol NaOH dm^{-3}	$1000R^a$
temp., 25°C.		temp., 0°C.	
0.1554	7.513	0.5652	22.29
0.3416	16.50	1.204	47.02
0.5430	25.39	1.781	68.94
0.8641	40.17	2.398	89.37
1.167	55.21	3.003	114.2
1.395	65.52		
2.700	125.3	temp. 35°C.	
3.364	150.4		
6.69	279.7	0.5679	29.60
		0.9618	49.32
		1.383	68.84
		1.710	86.54
		2.456	122.9

[a] R = number of moles of $Zn(OH)_2$ per mole of alkali.

Extrapolation of the values in the above Table gives the solubility of $Zn(OH)_2$ in water at 25°C as 2×10^{-5} mol/kg H_2O.

By measuring the e.m.f. of the cell: $Zn|Zn(OH)_2|NaOH\ (aq)|HgO|Hg$, the authors obtained a value of 3.3×10^{-17} for K_s^o at 25°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached from undersaturation and from supersaturation. The mixture was rotated in a thermostat for 24 hours, by which time equilibrium (as determined by analysis) had been reached. A portion of the filtrate was added to excess HCl and back-titrated with NaOH. The zinc content was determined by electrometric titration with $K_4Fe(CN)_6$ (1).

SOURCE AND PURITY OF MATERIALS:

$Zn(OH)_2$ was prepared by adding the calculated quantity of NH_4OH to a solution of a zinc salt, separating and washing the precipitate, dissolving the precipitate in excess NH_4OH, and then allowing the NH_3 to evaporate. The NaOH was carbonate-free. Distilled water was used throughout.

ESTIMATED ERROR:

The average deviation was below 0.5%.

REFERENCES:

1. Willard, H. H.; Fenwick, F. *J. Am. Chem. Soc.* 1922, *44*, 2504, 2516.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Dietrich, H. G.; Johnston, J.
J. Am. Chem. Soc. 1927, *49*, 1419-31.

VARIABLES:

Concentration of ammonium hydroxide and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in NH_4OH solutions.

mol NH_4OH dm^{-3}	$1000R^a$	mol NH_4OH dm^{-3}	$1000R^a$
temp., 25°C		temp. 0°C.	
0.1569	4.916	0.5099	20.07
0.2402	7.584	1.152	32.78
0.5527	15.32	1.517	40.73
0.6468	17.64	1.739	43.14
1.088	26.11	2.455	52.13
1.265	29.44	3.344	62.32
1.697	34.06		
2.416	42.85	temp., 35°C	
3.753	51.55		
5.086	55.90	0.4781	12.55
		0.5049	13.11
		1.035	22.58
		1.753	31.18
		2.432	37.68

[a] R = number of moles of $Zn(OH)_2$ per mole of alkali.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached from undersaturation and from supersaturation. The mixtures were rotated in a thermostat for 24 hours, by which time equilibrium (as determined by analysis) had been reached. A portion of the filtrate was added to excess HCl and back-titrated with NaOH. The zinc content was determined by electrometric titration using $K_4Fe(CN)_6$ (1).

SOURCE AND PURITY OF MATERIALS:

$Zn(OH)_2$ was prepared by adding the calculated quantity of NH_4OH to a solution of a zinc salt, separating and washing the precipitate, dissolving the precipitate in excess NH_4OH, and then allowing the NH_3 to evaporate. Chemically pure NH_4OH was distilled. Distilled water was used as solvent.

ESTIMATED ERROR:

The average deviation was below 0.5%.

REFERENCES:

1. Willard, H. H.; Fenwick, F.; *J. Am. Chem. Soc.* 1922, *44*, 2504, 2516.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water; H_2O; [7732-18-5]	Müller, E.; Müller, J.; Fauvel, A. Z. Elektrochem. 1927, 33, 134-44.
VARIABLES:	PREPARED BY:
Concentration of NaOH at 30°C.	T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in NaOH solutions at 30°C.

mol NaOH dm^{-3}	mol $Zn(OH)_2$ dm^{-3} [a]
2.11	0.073
4.05	0.333
6.09	0.702
8.27	1.152[b]
8.27	1.190[b]
9.81	1.470[c]
9.81	1.522[c]
12.12	2.310
14.50	3.027
16.04	3.647

[a] These values were determined after 60 days of shaking.

[b,c] In the second set of results in each of these pairs, a larger amount (almost double) of solid phase was added to the original NaOH solutions.

The authors stress that the NaOH concentrations include that which has reacted with the ZnO. The values are not necessarily the equilibrium concentrations of NaOH.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Equilibrium was reached isothermally with agitation. Zinc content was determined by potentiometric titration with $K_4Fe(CN)_6$. Total alkali content was determined by titration with HCl.	The NaOH was carbonate-free. ZnO was produced by heating the precipitate formed when NaOH was added to a solution of pure $Zn(NO_3)_2$. The water was boiled before use.
	ESTIMATED ERROR:
	The precision of the zinc titration was 0.6%. No other details are given.
	REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Müller, E.; Müller, J. Fauvel, A.
Z. Elektrochem. 1927, *33*, 134-44.

VARIABLES:

Concentration of sodium hydroxide at 30°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in NaOH solutions at 30°C.

mol NaOH dm^{-3}	mol $Zn(OH)_2$ dm^{-3} [a]	nature of solid phase
3.97	0.595	crystalline
7.15	2.271	crystalline
9.87	1.883[b]	amorphous

[a] These values were determined after the solutions had been shaken for two weeks.

[b] In this experiment the $Zn(OH)_2$ content after 1 day was 4.363 mol dm^{-3} and the precipitate was still crystalline.

The authors also made several solubility measurements with amorphous $Zn(OH)_2$ (formed by adding NaOH slowly to a solution of $Zn(NO_3)_2$ and avoiding an excess of NaOH). However, during these determinations the solid phase changed. The authors refer to this as ageing and consider the process to be, among other things, a loss of water. This ageing is affected by various experimental conditions and decreases the solubility of the solid material.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally with agitation. Zinc content was determined by potentiometric titration with $K_4Fe(CN)_6$. Total alkali content was determined by titration with HCl.

SOURCE AND PURITY OF MATERIALS:

The NaOH was carbonate-free. Crystalline $Zn(OH)_2$ was prepared by adding an excess of amorphous $Zn(OH)_2$ to 15 mol NaOH dm^{-3}, shaking the mixture, filtering it, and diluting the filtrate with water. The diluted solution then gave a precipitate of crystalline $Zn(OH)_2$. The water was boiled before being used.

ESTIMATED ERROR:

The precision of the zinc titration was 0.6%. No other details are given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Fricke, R.; Humme, H.; *Z. Anorg. Allgem. Chem.* 1928, *172*, 234-42.

VARIABLES:

Concentration of sodium hydroxide at 30.0°C

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of $Zn(OH)_2$ in NaOH solutions at 30.0°C.

grams of $Zn(OH)_2$ used	ml of NaOH solution used	duration of shaking	mass % NaOH	mass % ZnO	% H_2O in solid phase	nature of solid phase
2	20	23 hrs	7.20	1.44	- - -	crystalline
2	20	8 days	7.02	1.415	- - -	"
4	20	23 hrs	13.4	5.16	- - -	"
4	20	8 days	13.2	5.15	- - -	"
5	20	2.5 hrs	17.65	9.77	- - -	"
5	20	23 hrs	17.85	9.63	- - -	"
5	20	8 days	17.75	9.85	18.22	"
6	15	2.5 hrs	20.85	14.82	- - -	"
6	15	23 hrs	21.0	14.77	- - -	"
6	15	8 days	22.05	8.66	1.1	amorphous
7	15	2.5 hrs	22.95	19.42	- - -	crystalline
7	15	23 hrs	23.0	18.82	- - -	
7	15	8 days	24.65	12.81	1.0	amorphous
8	15	2.5 hrs	24.55	24.87	- - -	crystalline
8	15	23 hrs	25.75	21.86	- - -	amorphous
8	15	8 days	28.25	13.77	1.4	"
9	15	2.5 hrs	30.2	24.68	- - -	"
9	15	23 hrs	30.95	23.17	- - -	"
9	15	8 days	31.75	21.59	2.15	"

The authors present qualitative evidence which shows that the solubility of $Zn(OH)_2$ in NaOH solutions does not depend on the amount of excess solid phase.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally. The NaOH solutions were made by dilution of a concentrated carbonate-free solution. Distilled water was used and was boiled before use. Zinc content was determined by precipitating $ZnCO_3$, heating it, and weighing as ZnO. Alkali content was determined by titrating a diluted solution with HCl. The precipitates were analyzed for H_2O content by measuring the weight loss during heating.

SOURCE AND PURITY OF MATERIALS:

Crystalline $Zn(OH)_2$ was prepared by the method described earlier (1). Presumably this involved adding the requisite amount of NH_4OH to a solution of $Zn(NO_3)_2$ or $ZnCl_2$, washing the precipitate, dissolving it in aqueous NaOH and slowly diluting the resulting solution. The $Zn(OH)_2$ that then precipitates is granular.

ESTIMATED ERROR:

No details are given as to the reproducibility of the solubility values.

REFERENCES:

1. Fricke, R.; Ahrndts, T. *Z. Anorg. Allgem. Chem.* 1924, *134*, 344.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc chloride; $ZnCl_2$; [7646-85-7]

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

ORIGINAL MEASUREMENTS:

Holland, H. C. *J. Chem. Soc.* 1930, 643-8.

VARIABLES:

Concentration of $ZnCl_2$ and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of ZnO in $ZnCl_2$ solutions[a].

x	y	solid phase[b]	x	y	solid phase[b]
		temp., 25°C			
0.001	0.001	E	0.155	0.165	F
0.009	0.009	"	0.162	0.169	"
0.033	0.034	"	0.165	0.173	"
0.034	0.035	"	0.163	0.172	G
0.049	0.050	"	0.172	0.177	"
0.075	0.078	"	0.184	0.193	"
0.094	0.097	"	0.191	0.196	"
0.113	0.119	"	0.195	0.198	"
0.134	0.142	"	0.202	0.209	"
0.146	0.155	E + F	0.245	0.252	"
0.151	0.163	F	0.264	0.269	"
		temp., 50°C.			
0.009	0.009	E	0.159	0.167	G
0.091	0.095	"	0.160	0.168	"
0.143	0.153	"	0.165	0.171	"
0.144	0.153	F	0.200	0.205	"
0.154	0.161	"			

[a] The values are mass% values based on the equation $\underset{a}{1/2H_2O} + \underset{b}{1/2ZnCl_2} = \underset{c}{HCl} + \underset{d}{1/2ZnO}$ where $x = (b + c)/(a + b + c + d)$ and $y = (b + d)/(a + b + c + d)$.

[b] E = $ZnCl_2 \cdot 5ZnO \cdot 8H_2O$; F = $ZnCl_2 \cdot ZnO \cdot 2H_2O$; G = $ZnCl_2 \cdot ZnO \cdot H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally by mixing ZnO, $ZnCl_2$ (or HCl) and H_2O and shaking the mixture for several days in a thermostat. Chloride was determined by the Volhard method. Zinc was determined by titration with $K_4Fe(CN)_6$. The composition of the solid phase was determined by the Schreinemakers' wet-residue method.

SOURCE AND PURITY OF MATERIALS:

All reagents were of a high standard of purity.

ESTIMATED ERROR:

The temperature was controlled to within 0.1°C at 25°C and to within 0.05°C at 50°C. All apparatus was standardized. No other details are given.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Huttig, G. F.; Steiner, B. *Z. Anorg. Allg. Chem.* 1931, *199*, 149-64.

VARIABLES:

Physical characteristics of zinc oxide.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Effect of the thermal history on the solubility of ZnO in 0.2822 mol KOH/dm^{-3} at 20°C.

T/°C.[a]	mol ZnO[b]	$C_{ZnO}/10^{-3}$ mol dm^{-3} 10 min.	20 min.	30 min.	90 min.
300	0.005	2.31	2.35	2.40	2.49
300	0.01	2.37	2.49	2.51	2.55
300	0.02	2.64	2.64	2.62	2.58
400	0.005	1.29	1.51	1.63	1.78
400	0.01	1.38	1.54	1.66	1.81
400	0.02	1.56	1.58	1.64	1.76
500	0.005	1.06	1.33	1.45	1.51
500	0.01	1.05	1.30	1.43	1.55
500	0.02	1.08	1.29	1.42	1.56
800	0.01	0.83	1.27	1.34	1.45
1000	0.005	0.80	1.09	1.29	1.47
1000	0.01	0.79	1.13	1.30	1.49
1000	0.02	0.78	1.16	1.34	1.46

[a] The ZnO was prepared by heating $ZnCO_3$ to the temperatures indicated in this column.

[b] Amount of solid ZnO used in the solubility determinations.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A weighed amount of ZnO was placed in a beaker, thermostatted at 20°C, and then 0.5 dm^3 of 0.2822 mol KOH dm^{-3} was added while the mixture was stirred at a constant rate of 650 rpm. Samples were removed after 10, 20, 30 and 90 minutes, filtered, and analyzed for zinc content. The analysis was done gravimetrically by weighing zinc as ZnP_2O_7. Provisions were made for excluding CO_2 during the experimental work.

SOURCE AND PURITY OF MATERIALS:

The KOH was carbonate-free. No other details are given.

ESTIMATED ERROR:

No details are given about the reproducibility of any of the procedures.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Potassium hydroxide; KOH, [1310-58-3] (3) Water; H_2O; [7732-18-5]	Huttig, G. F.; Steiner, B. Z. *Anorg. Allg. Chem.* 1931, *199*, 149-64.

EXPERIMENTAL VALUES: contd.

Table II. Effect of previous history on the solubility of ZnO in 0.2822 mol KOH/dm^{-3} at 20°C.

T/°C[a]	mol ZnO[b]	$C_{ZnO}/10^{-3}$mol dm^{-3} 10 min.	20 min.	30 min.	90 min.
400	0.005	1.47	1.88	2.08	2.15
400	0.01	1.56	1.98	2.18	2.21
400	0.02	1.93	2.30	2.30	2.37
1000	0.005	0.82	1.12	1.29	1.51
1000	0.01	0.82	1.16	1.31	1.43
1000	0.02	0.86	1.11	1.34	1.47

[a] The ZnO was prepared by heating zinc oxalate to the temperatures shown in this column.

[b] Amount of solid ZnO used in the solubility determinations.

Table III. Effect of particle size on the solubility of ZnO in 0.2822 mol KOH dm^{-3} at 20°C.

T/°C[a]	particle size of ZnO	$C_{ZnO}/10^{-3}$mol dm^{-3} 10 min.	20 min.	30 min.	90 min.
300	240-100μ	2.21	2.40	2.48	2.56
300	70-50μ	2.35	2.45	2.53	2.57
300	<50μ	2.40	2.46	2.50	2.58
1000	240-100μ	0.63	0.98	1.16	1.38
1000	70-50μ	0.80	1.14	1.34	1.48
1000	<50μ	0.83	1.11	1.29	1.53

[a] The ZnO was prepared by heating $ZnCO_3$ to the temperatures given in this column.

The authors state that the solubility value determined after 90 min is the equilibrium value. They state that the concentration does not change with longer times.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Scholder, R.; Hendrich, G. Z. *Anorg. Allgem. Chem.* 1939, *241*, 76-92.

VARIABLES:

Concentration of NaOH at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in NaOH solutions at 20°C.

mol NaOH dm^{-3}	mol ZnO dm^{-3}	Solid phase	Duration of shaking in days
1.34	0.047	ZnO	24
2.84	0.212	"	29
6.10	0.834	"	29
9.49	1.734	"	29
12.72	2.744	"	24
14.42	2.535	$NaZn(OH)_3$	24
17.45	1.795	"	24

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally. Alkali content was determined by dissolving the sample in H_2SO_4 and back-titrating with NaOH. The zinc content was determined gravimetrically as pyrophosphate.

SOURCE AND PURITY OF MATERIALS:

Pure, carbonate-free NaOH was used. The ZnO was formed by saturating boiling NaOH solution with ZnO, cooling, filtering, and adding crystalline $Zn(OH)_2$ to the filtrate. After 12 days the $Zn(OH)_2$ had been transformed to ZnO and this was filtered off and dried over H_2SO_4.

ESTIMATED ERROR:

No details are given except that the temperature was controlled to within 0.1°C.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Scholder, R.; Hendrich, G. Z. *Anorg. Allgem. Chem.* 1939, *241*, 76-92.

VARIABLES:

Concentration of sodium hydroxide and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of $Zn(OH)_2$ in NaOH solutions at 20°C.

mol NaOH dm^{-3}	mol ZnO dm^{-3}	Solid phase[a]	duration of shaking in days
1.32	0.079	A	69
2.76	0.344	"	69
4.15	0.407	B	161
5.81	0.735	"	192
7.29	1.095	"	190
8.76	1.555	"	154
8.78	3.443	A + B	1.7
9.45	1.088	B	185
9.80	1.822	"	185
10.11	1.940	"	185
10.67	2.680	C	57
11.04	2.751	B + C	73
12.24	3.240	B	126
12.80	3.606	B + C	126
13.34	3.071	D	44
14.25	2.576	"	57
15.76	2.115	"	82
16.52	1.944	"	204
17.18	1.863	"	19
17.82	1.778	"	46
18.77	1.716	"	38
19.58	1.685	"	38
20.00	1.475	E	42
20.14	1.425	E + F	32

[a] A = $Zn(OH)_2$; B = ZnO; C = $NaZn(OH)_3 \cdot 3H_2O$; D = $NaZn(OH)_3$; E = $Na_2Zn(OH)_4$; F = $NaOH \cdot H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally. Samples were added to H_2SO_4 and back-titrated with NaOH to determine alkali content. Zinc content was determined gravimetrically as the pyrophosphate. The same methods were used to analyze the solution and the solid phases.

SOURCE AND PURITY OF MATERIALS:

The NaOH was carbonate-free. Crystalline $Zn(OH)_2$ was prepared by dissolving ZnO in a hot NaOH solution, cooling this, diluting it tenfold with water and allowing it to stand 2 to 3 weeks. During this time the crystalline $Zn(OH)_2$ precipitated from the solution.

ESTIMATED ERROR:

The temperature was controlled to within 0.1°C., but no other details are given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Scholder, R.; Hendrich, G. Z. *Anorg. Allgem. Chem.* 1939, *241*, 76-92.

EXPERIMENTAL RESULTS, contd. -----

Solubility of $Zn(OH)_2$ in NaOH solutions.

mol NaOH dm^{-3}	mol ZnO dm^{-3}	Solid phase[a]	Duration of shaking in days
	temp., 40°C		
1.32	0.09	A + B	79
2.93	0.45	"	79
4.17	0.41	B	79
9.30	1.81	"	79
12.67	3.03	"	79
13.24	3.78	D	27
16.48	2.61	"	38
17.59	2.41	"	38
20.52	1.84	D + E	38
21.94	1.33	E + F	10
	temp., 100°C.		
1.48	0.04	B	14
4.64	0.42	"	8
8.05	1.19	"	7
11.15	2.16	"	6
15.98	3.91	"	6
17.84	4.79	"	4
18.67	5.16	"	4
18.75	5.49	B + D	5
20.84	5.35	D	11

[a] A = $Zn(OH)_2$; B = ZnO; D = $NaZn(OH)_3$; E = $Na_2Zn(OH)_4$; F = $NaOH \cdot H_2O$

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sulfur trioxide; SO_3; [7446-11-9]

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

ORIGINAL MEASUREMENTS:

Copeland, L. C.; Short, O. A. *J. Am. Chem. Soc.* 1940, *62*, 3285-91.

VARIABLES:

Concentration of SO_3 at 25.0°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Equilibrium concentrations in the $ZnO-SO_3-H_2O$ system at 25°C.

mass % SO_3	mol SO_3/kg H_2O[a]	mass% ZnO	mol ZnO/kg H_2O[a]	Solid phase[b]
1.9	0.25	1.8	0.23	A
4.4	0.60	4.4	0.59	"
8.0	1.19	8.1	1.19	"
10.7	1.70	10.7	1.67	"
13.6	2.33	13.6	2.30	"
14.5	2.55	14.5	2.51	"
17.6	3.39	17.6	3.34	"
18.3	3.61	18.3	3.55	A + B

[a] Calculated by the compiler.

[b] A = $3Zn(OH)_2 \cdot ZnSO_4 \cdot 4H_2O$; B = $ZnSO_4 \cdot 7H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of ZnO and $ZnSO_4$ solutions were boiled, filtered to remove undissolved ZnO, and cooled to 25°C. The filtrate was allowed to set for about 4 weeks with occasional shaking. Zinc content was determined by titration with $K_4Fe(CN)_6$. SO_3 content was determined gravimetrically by precipitation as $BaSO_4$.

SOURCE AND PURITY OF MATERIALS:

U. S. P. grade materials were used.

ESTIMATED ERROR:

The authors state that duplicate mixtures agreed to within 2 to 3%.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Potassium hydroxide; KOH; [1310-58-3] (3) Water; H_2O; [7732-18-5]	Iofa, Z. A.; Mirlina, S. Ya.; Moisiejeva, N. B. *Zhur. Prikład Khim.* 1949, *22*, 983-94.
VARIABLES: Temperature and KOH concentration.	PREPARED BY: T. Michalowski

EXPERIMENTAL VALUES:

The data are presented almost exclusively in graphical form. The maximum solubility at 0°C is 2.81 mol kg^{-1} of ZnO in 8.1 mol kg^{-1} of KOH. Up to this KOH concentration the solubility of ZnO increases with increasing KOH concentration and ZnO is the equilibrium solid phase. At a KOH concentration of 8.1 mol kg^{-1} the zinc begins to precipitate as a zincate and the solubility of ZnO in aqueous KOH then decreases rapidly with increasing KOH concentration.

At 30°C the solubility of ZnO also increases with increasing KOH concentration, but more rapidly than at 0°, so that in a KOH concentration of 7 mol kg^{-1} the ZnO solubility at 30°C is almost double that at 0°C.

The authors also describe the various forms of $Zn(OH)_2$--α,β,γ, and ε. The solubility decreases with increasing stability, with ε-$Zn(OH)_2$ being the most stable form.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Equilibrium was attained isothermally at 0, 15 and 30°C in a thermostat.	No information is given.
	ESTIMATED ERROR: No details are given.
	REFERENCES:

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]

(2) Zinc sulfate; $ZnSO_4$; [7733-02-0]

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

ORIGINAL MEASUREMENTS:
Akselrud, N. V.; Fialkov, Ya. A. *Ukrain. Khim. Zhur.* 1950, *16*, 283-95.

VARIABLES:
Concentration of $ZnSO_4$ at 18.0°C.

PREPARED BY:
T. Michalowski

EXPERIMENTAL VALUES:

Composition of equilibrium solutions at 18.0°C.

mol Zn(II) dm^{-3}	pH	$-\log K_s o$
0	----	16.705[a]
0.0154	6.71	16.6620
0.0482	6.51	16.5528
0.0823	6.43	16.4862
0.1520	6.31	16.4601
0.4580	6.04	16.5120
0.9275	5.82	16.6489
1.0257	5.78	16.6797
1.5273	5.60	16.8688
2.2340	5.38	17.1334

[a]This value was determined by extrapolation of the [Zn(II)] vs $-\log K_s o$ curve for the three most dilute solutions to [Zn(II)] = 0.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
ZnO was added to solutions of $ZnSO_4$ and the mixture was shaken in a thermostat at 18.0°C until equilibrium was reached. The pH of the solution was measured potentiometrically and the Zn content was determined polarographically or by titration with $K_4Fe(CN)_6$.

SOURCE AND PURITY OF MATERIALS:
Reagent grade materials were used. The $ZnSO_4$ was recrystallized twice from water.

ESTIMATED ERROR:
Not enough information is given to estimate this.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Arkhipov, M. I.; Pakshver, A. B.; Podbornova, N. I. *Zhur. Priklad. Khim.* 1950, *23*, 650-6; *J. Applied Chem. USSR (Engl. transl.)* 1950, *23*, 685-91.

VARIABLES:

Concentration of NaOH at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in NaOH solutions at 20°C.

g NaOH dm^{-3}	mol NaOH dm^{-3} [a]	g Zn dm^{-3}	mol $Zn(OH)_2 dm^{-3}$ [a]
68.4	1.71	8.0	0.12
132.0	3.30	24.7	0.38
202.0	5.05	45.5	0.70
360.0	9.00	80.4	1.23

[a] Calculated by compiler.

The following results were obtained by diluting saturated solutions of $Zn(OH)_2$ in aqueous NaOH with water until a precipitate began to settle out.

mol NaOH dm^{-3}	mol $Zn(OH)_2$ dm^{-3}
0.180	0.0052
0.355	0.0104
0.610	0.0217
1.120	0.0464

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The $Zn(OH)_2$ was introduced into an amount of solvent 14 times its weight. The mixture was allowed to stand 24 hours at 20°C. After filtration, the filtrate was analyzed for Zn content by determination with molybdenum blue (1). In another experiment, saturated solutions of $Zn(OH)_2$ in aqueous NaOH were diluted with water until a precipitate began to form. The mixture was then allowed to stand in the dark for 2 days at 20°C. It was then filtered and the filtrate was analyzed for zinc and NaOH content. The method for NaOH analysis is not described.

SOURCE AND PURITY OF MATERIALS:

The $Zn(OH)_2$ was prepared by a procedure described earlier (2). No information is given about the source of any other materials.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Razumeev, A. *Synthetic Fiber Handbook*, State Chem. Press, 1937.
2. Pakshver, A.; Arkhipov, M.; Geller, B. *J. Applied Chem. USSR* 1950, *23*, 2.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Ammonia; NH_3; [7664-41-7]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Arkhipov, M. I.; Pakshver, A. B.; Podbornova, N. I. *Zhur. Prikład. Khim.* 1950, *23*, 650-6; *J. Applied Chem. USSR (Engl. transl.)* 1950, *23*, 685-91.

VARIABLES:

Concentration of NH_3 at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in aqueous NH_3 solutions at 20°C.

g NH_3 dm^{-3}	mol NH_3 dm^{-3} [a]	g Zn dm^{-3}	mol $Zn(OH)_2$ dm^{-3} [a]
46.7	2.74	10.6	0.16
82.3	4.83	16.2	0.25
130.5	7.66	19.3	0.30
139.0	8.16	19.3	0.30
188.5	11.07	18.2	0.28
213.0	12.51	18.7	0.29

[a] Calculated by the compiler.

The following results were obtained by diluting saturated solutions of $Zn(OH)_2$ in aqueous NH_3 with water until a precipitate began to settle out.

mol NH_3 dm^{-3}	mol $Zn(OH)_2$ dm^{-3}
0.256	0.0124
0.186	0.0070
0.156	0.0040
0.100	0.0023

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The $Zn(OH)_2$ was introduced into an amount of solvent 14 times its weight. The mixture was allowed to stand 24 hours at 20°C. After filtration, the filtrate was analyzed for Zn content by determination with molybdenum blue (1). In another experiment, saturated solutions of $Zn(OH)_2$ in aqueous NH_3 were diluted with water until a precipitate began to form. The mixture was then filtered and the filtrate was analyzed for Zn and NH_3 content. The method of analysis for NH_3 is not described.

SOURCE AND PURITY OF MATERIALS:

The $Zn(OH)_2$ was prepared by a procedure described earlier (2). No information is given about the source or purity of any other materials.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Razumeev, A. *Synthetic Fiber Handbook*, State Chem. Press, 1937.
2. Pakshver, A.; Arkhipov, M.; Geller, B. *J. Applied Chem. USSR* 1950, *23*, 2.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1951, *20A*, 28-38.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of saturated solutions of ZnO in aqueous NaOH.

mass% ZnO	mol ZnO/kg H_2O[a]	mass% Na_2O	mol NaOH/kg H_2O[a]
temp., 35°C.			
0.192	0.024	3.03	1.04
0.4815	0.063	4.850	1.71
1.413	0.199	10.75	4.12
3.512	0.519	12.82	5.14
4.980	0.765	15.08	6.28
5.920	0.931	15.87	6.76
8.426	1.40	17.88	8.09
9.841	1.73	20.08	9.55
temp., 45°C.			
0.202	0.025	2.28	0.779
0.555	0.072	4.505	1.58
2.365	0.344	13.240	5.23
4.627	0.737	18.20	7.86
6.68	1.12	20.04	9.12
8.143	1.42	21.30	10.06
10.07	1.82	22.05	10.83
12.041	2.28	23.14	11.90

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally by adding ZnO to the NaOH solutions and mechanically shaking the mixtures for 3 hours in a thermostat. Zinc content was determined by titration with $K_4Fe(CN)_6$. Alkali content was determined by dissolving the sample in excess H_2SO_4 and back-titrating with NH_4OH.

SOURCE AND PURITY OF MATERIALS:

Reagent grade materials were used.

ESTIMATED ERROR:

No details are given except that the temperature was controlled to within 0.1°C.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1951, *20A*, 28-38.

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of ZnO in aqueous NaOH.

mass% ZnO	mol ZnO/kg H_2O[a]	mass% Na_2O	mol NaOH/kg H_2O[a]
	temp., 55°C.		
0.227	0.029	3.46	1.20
0.755	0.099	5.57	1.98
2.561	0.362	10.12	3.89
5.050	0.784	15.34	6.42
7.889	1.30	17.31	7.71
9.530	1.64	19.07	8.90
11.95	2.21	21.50	10.77
14.021	2.68	21.80	11.30
	temp., 65°C.		
0.1829	0.023	3.022	1.04
0.531	0.070	6.39	2.29
2.009	0.283	10.80	4.13
4.730	0.729	15.52	6.49
8.601	1.43	17.54	7.92
10.580	1.86	19.58	9.35
12.862	2.37	20.50	10.25
16.031	3.14	21.32	11.34
	temp., 75°C.		
0.1820	0.023	3.98	1.38
0.456	0.060	6.89	2.48
1.600	0.235	14.90	5.95
4.221	0.663	17.55	7.48
8.810	1.55	21.538	10.31
11.348	2.16	24.123	12.46
14.299	2.89	25.089	13.80
18.038	3.93	25.556	15.10

[a] Calculated by the compiler.

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:
Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1951, *20A*, 28-38.

VARIABLES:
Method of preparation of $Zn(OH)_2$, concentration of NaOH, and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of saturated solutions of crystalline $Zn(OH)_2$ (prep. "a") in aqueous NaOH.

mass% ZnO	mol ZnO/kg H_2O[a]	mass% Na_2O	mol NaOH/kg H_2O[a]
	temp. 35°C		
0.410	0.052	3.00	1.00
1.521	0.199	4.501	1.55
3.390	0.478	9.410	3.48
5.512	0.745	13.55	5.40
9.123	1.51	16.540	7.18
11.510	1.98	17.22	7.79
14.341	2.74	21.462	10.79
16.815	3.44	23.120	12.42
	temp. 45°C		
0.5620	0.071	2.74	0.914
1.780	0.233	4.390	1.51
5.002	0.748	12.801	5.02
7.988	1.30	16.23	6.95
12.33	2.18	18.04	8.36
15.510	2.91	19.120	9.44
18.39	3.64	19.64	10.22
22.110	4.88	22.215	12.87

[a]Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally by adding $Zn(OH)_2$ to the NaOH solutions and mechanically shaking the mixtures for 3 hours in a thermostat. Zinc content was determined by titration with $K_4Fe(CN)_6$. Alkali content was determined by dissolving the sample in excess H_2SO_4 and back-titrating with NH_4OH.

SOURCE AND PURITY OF MATERIALS:

Reagent grade materials were used. $Zn(OH)_2$ was prepared two ways: (a) adding the calculated amount of NH_4OH to aqueous $ZnSO_4$, filtering, washing the precipitate, redissolving it in excess NH_4OH, and allowing the NH_3 to evaporate; (b) dissolving ZnO in aqueous NaOH with heating, cooling, filtering, and diluting the filtrate with water.

ESTIMATED ERROR:
No indication is given of the precision of any of the procedures except that the temperature was controlled to within 0.1°C.

REFERENCES:

COMPONENTS	ORIGINAL MEASUREMENTS
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water; H_2O; [7732-18-5]	Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1951, *20A*, 28-38.

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of crystalline $Zn(OH)_2$ (prep. "a") in aqueous NaOH.

mass% ZnO	mol ZnO/kg H_2O[a]	mass% Na_2O	mol NaOH/kg H_2O[a]
	temp. 55°C		
0.709	0.091	3.64	1.23
1.94	0.125	5.34	1.86
5.825	0.360	10.930	4.24
8.77	1.40	14.03	5.86
13.44	2.32	15.30	6.93
16.92	3.14	16.89	8.23
19.83	3.94	18.34	9.57
23.00	4.95	19.90	11.24
	temp. 65°C		
0.545	0.069	2.817	0.940
1.423	0.190	6.44	2.25
4.903	0.724	11.90	4.61
8.580	1.37	14.54	6.09
13.385	2.29	14.68	6.58
16.958	3.20	18.03	8.95
20.21	4.07	18.80	9.94
23.61	5.11	19.65	11.17
	temp. 75°C		
0.445	0.057	2.90	0.968
1.298	0.174	7.10	2.50
3.939	0.599	15.29	6.11
7.804	1.29	17.70	7.66
14.134	2.58	18.63	8.94
17.018	3.34	20.30	10.45
21.256	4.53	21.056	11.77
24.38	5.58	21.90	13.15

[a]Calculated by the compiler

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Sodium hydroxide; NaOH [1310-73-2] (3) Water; H_2O; [7732-18-5]	Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1951, *20A*, 28-38.

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of $Zn(OH)_2$ (prep. "b") in aqueous NaOH.

mass% ZnO	mol ZnO/kg H_2O[a]	mass% Na_2O	mol NaOH/kg H_2O[a]
	temp., 35°C.		
0.398	0.052	5.132	1.75
1.002	0.134	7.090	2.49
2.960	0.417	9.838	3.64
4.836	0.717	12.34	4.81
7.693	1.24	11.110[b]	4.70
9.950	1.71	18.62	8.41
12.516	2.33	21.38	10.43
14.010	2.74	23.080	11.83
	temp., 45°C.		
0.5204	0.066	2.738	0.913
1.380	0.179	4.44	1.51
4.101	0.582	12.28	4.57
6.592	1.05	16.63	6.99
10.111	1.73	18.241	8.21
13.860	2.58	20.03	9.77
15.941	3.08	20.56	10.44
20.292	4.52	24.57	14.37
	temp., 55°C.		
0.603	0.077	3.35	1.13
1.510	0.199	5.46	1.89
4.391	0.640	11.38	4.36
7.45	1.18	14.95	6.21
11.423	1.92	15.59	6.89
15.235	2.80	18.02	8.71
18.490	3.60	18.50	9.47
21.950	4.61	19.591	10.81
	temp., 65°C.		
0.5310	0.068	2.93	0.979
0.9481	0.125	6.164	2.14
4.112	0.613	13.500	5.29
2.102[c]	0.340	17.00	7.23
12.530	2.22	18.136	8.44
16.660	3.21	19.60	9.92
19.511	4.03	20.99	11.38
22.800	4.69	21.43	11.57
	temp., 75°C.		
0.355	0.045	3.156	1.06
0.832	0.110	6.513	2.27
3.154	0.483	16.60	6.67
6.555	1.26	19.30	9.71
13.186	2.47	21.20	10.43
16.710	3.38	22.50	11.94
20.310	4.41	23.05	13.13
23.341	5.44	23.92	14.63

[a] Calculated by the compiler.

[b] This appears to be an error. From the context of the Table this value should be 16.110 giving a value of 6.82 mol NaOH/kg H_2O.

[c] This value appears to be an error. Presumably it should be 7.102 which gives a value of 1.15 mol ZnO/kg H_2O.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1952, *21A*, 14-21.

VARIABLES:

Concentration of KOH and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous KOH.

mass% ZnO	C_{ZnO}/mol kg^{-1} [a]	mass% K_2O	C_{KOH}/mol kg^{-1} [a]
	temp., 35°C.		
0.180	0.0234	5.314	1.19
0.512	0.0719	12.015	2.92
1.598	0.241	16.850	4.39
2.044	0.326	20.910	5.76
4.179	0.704	22.90	6.67
5.590	0.992	25.200	7.73
7.029	1.32	27.310	8.83
8.031	1.57	29.000	9.78
	temp., 45°C.		
0.206	0.0266	4.700	1.05
0.691	0.0912	6.220	1.42
2.049	0.316	18.360	4.90
3.501	0.586	23.070	6.67
5.521	0.992	26.130	8.12
7.390	1.42	28.530	9.45
9.25	1.90	31.060	11.05
10.844	2.33	31.940	11.85

[a] Data converted to mol/kg H_2O by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally by shaking the mixtures for 3 hours in a thermostat. Zinc content was determined by titration with $K_4Fe(CN)_6$. Alkali content was determined by dissolving the sample in excess H_2SO_4 and back-titrating with NH_4OH.

SOURCE AND PURITY OF MATERIALS:

The water was freshly redistilled. The ZnO and KOH were reagent grade. Care was taken to exclude CO_2.

ESTIMATED ERROR:

No details are given except that the temperature was controlled to within 0.1°C.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1952, *21A*, 14-21.

EXPERIMENTAL VALUES, contd.

Solubility of ZnO in aqueous KOH.

mass% ZnO	C_{ZnO}/mol kg^{-1} [a]	mass% K_2O	C_{KOH}/mol kg^{-1} [a]
	temp., 55°C.		
0.218	0.0285	5.700	1.29
0.748	0.102	9.430	2.23
2.559	0.391	17.130	4.53
4.70	0.771	20.37	5.70
6.97	1.23	23.56	7.20
8.530	1.65	27.800	9.27
9.89	1.97	28.300	9.72
12.042	2.54	29.680	10.81
	temp., 65°C.		
0.1757	0.0226	4.2730	0.949
0.5200	0.0709	9.4100	2.22
1.743	0.272	19.510	5.26
3.660	0.610	22.660	6.53
7.610	1.44	27.680	9.08
9.166	1.80	28.440	9.67
10.986	2.26	29.340	10.44
12.638	2.73	30.560	11.42
	temp., 75°C.		
0.1653	0.0213	4.3580	0.969
0.5010	0.0684	9.532	2.25
1.433	0.224	20.036	5.42
3.266	0.553	24.220	7.09
7.804	1.48	27.422	8.99
9.539	1.92	29.416	10.23
11.410	2.39	30.040	10.89
13.86	3.06	30.56	11.67

[a] Data converted to mol/kg H_2O by the compiler.

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1952, *21A*, 14-21.

VARIABLES:
Method of preparing $Zn(OH)_2$, concentration of KOH, and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ (prep. "a") in aqueous KOH.

mass% ZnO	C_{ZnO}/mol kg^{-1} [a]	mass% K_2O	C_{KOH}/mol kg^{-1} [a]
		temp., 35°C.	
0.3865	0.0513	7.0630	1.62
1.280	0.185	13.730	3.43
2.331	0.363	18.840	5.07
4.070	0.663	20.510	5.77
6.194	1.082	23.506	7.10
8.390	1.586	26.640	8.70
10.360	2.094	28.850	10.08
11.810	2.507	30.320	11.12
		temp., 45°C.	
0.547	0.0709	4.715	1.06
1.502	0.202	7.046	1.64
4.667	0.750	18.850	5.23
6.524	1.130	22.570	6.76
10.50	2.064	26.990	9.17
12.954	2.819	30.600	11.51
15.84	3.755	32.34	13.25
18.123	4.561	33.060	14.38

[a] Data converted to mol/kg H_2O by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Equilibrium was approached isothermally by shaking the mixtures for 3 hours in a thermostat. Zinc content was determined by titration with $K_4Fe(CN)_6$. Alkali content was determined by dissolving the sample in excess H_2SO_4 and back-titrating with NH_4OH.

SOURCE AND PURITY OF MATERIALS:
The water was freshly redistilled. All other materials were of reagent grade quality. The $Zn(OH)_2$ was prepared in 2 ways; (a) by adding the calculated amount of NH_4OH to aqueous $ZnSO_4$, filtering, washing the precipitate and redissolving it in excess NH_4OH, then allowing the NH_3 to evaporate; (b) dissolving ZnO in aqueous NaOH with heating, cooling, filtering, and diluting the filtrate with H_2O.

ESTIMATED ERROR:
No details are given except that the temperature was controlled to within 0.1°C.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Potassium hydroxide; KOH; [1310-58-3] (3) Water; H_2O; [7732-18-5]	Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1952, *21A*, 14-21.

EXPERIMENTAL VALUES, contd.

Solubility of $Zn(OH)_2$ (prep. "a") in aqueous KOH.

mass% ZnO	C_{ZnO}/mol kg^{-1} [a]	mass% K_2O	C_{KOH}/mol kg^{-1} [a]
		temp., 55°C.	
0.679	0.0891	5.700	1.29
1.755	0.242	9.090	2.16
4.88	0.758	16.03	4.30
7.509	1.251	18.780	5.41
11.138	2.054	22.230	7.08
13.980	2.796	24.590	8.50
16.815	3.653	26.640	10.00
19.500	4.650	28.980	11.94
		temp., 65°C.	
0.466	0.0600	4.050	0.90
1.028	0.141	9.230	2.18
3.980	0.618	16.890	4.53
6.923	1.210	22.800	6.89
11.301	2.200	25.590	8.61
14.331	3.056	28.050	10.34
17.66	4.030	28.50	11.24
20.39	4.986	29.37	12.41
		temp., 75°C.	
0.423	0.0548	4.800	1.08
1.003	0.138	9.457	2.24
2.992	0.453	15.930	4.17
6.730	1.123	19.670	5.67
11.634	2.318	26.720	9.20
14.480	3.070	27.570	10.10
18.512	4.277	28.320	11.31
21.248	5.261	29.131	12.46

[a] Data converted to mol/kg H_2O by the compiler.

COMPONENTS:	ORIGINAL MAESUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Potassium hydroxide, KOH; [1310-58-3] (3) Water; H_2O; [7732-18-5]	Deshpande, V. V.; Kabadi, M. B. *J. Univ. Bombay* 1952, *21A*, 14-21.

EXPERIMENTAL VALUES, contd.

Solubility of $Zn(OH)_2$ (prep. "b") in aqueous KOH.

mass% ZnO	C_{ZnO}/mol kg^{-1} [a]	mass% K_2O	C_{KOH}/mol kg^{-1} [a]
		temp., 35°C.	
0.326	0.0432	6.890	1.58
1.030	0.147	13.152	3.25
2.023	0.312	18.400	4.91
3.590	0.581	20.473	5.72
4.700	0.800	23.156	6.81
6.340	1.140	25.32	7.87
7.911	1.517	28.010	9.28
9.522	1.913	29.315	10.18
		temp., 45°C.	
0.5003	0.0647	4.460	1.00
1.270	0.170	7.145	1.66
3.624	0.569	18.070	4.90
4.994	0.843	22.190	6.47
7.915	1.473	26.090	8.39
9.832	1.960	28.540	9.83
12.710	2.766	30.840	11.60
41.891 [b]	9.69	32.000	12.79
		temp., 55°C.	
0.600	0.0790	6.140	1.40
1.476	0.204	9.460	2.26
4.290	0.661	15.950	4.25
6.831	1.167	21.250	6.27
9.533	1.780	24.690	7.97
11.803	2.346	26.380	9.06
13.934	2.978	28.590	10.56
17.99	4.245	29.95	12.21
		temp., 65°C.	
0.461	0.0586	2.929	0.64
0.777	0.106	9.116	2.15
3.39	0.533	18.41	5.00
5.990	1.044	23.550	7.10
9.662	1.887	27.430	9.26
12.012	2.483	28.560	10.20
13.991	3.058	29.810	11.26
18.733	4.540	30.580	12.81
		temp., 75°C.	
0.4061	0.0528	5.031	1.13
0.611	0.0833	9.234	2.17
2.532	0.386	16.890	4.45
5.616	0.962	22.670	6.71
9.780	1.917	27.531	9.32
12.430	2.607	29.000	10.51
15.132	3.361	29.560	11.35
19.019	4.604	30.230	12.65

[a] Data converted to mol/kg H_2O by the compiler.

[b] This appears to be a misprint. It possibly should be 14.891, giving a value of 3.444 mol ZnO/kg H_2O.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Sochevanov, V. G. *Zhur, Obshchei Khim.* 1952, *22*, 1073-85; *J. Gen. Chem. USSR (Engl. transl.)* 1952, *22*, 1119-1128.

VARIABLES:

Concentration of potassium hydroxide.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of saturated solutions of ZnO in aqueous KOH at 18-22°C.

K_2O, mol%	ZnO mol%	sp. gr.	mol KOH/kg H_2O[a]	mol ZnO/kg H_2O[a]	KOH, mol dm^{-3}[a]	ZnO, mol dm^{-3}[a]
2.05	0.182	1.119	2.32	0.10	2.33	0.10
3.98	0.59	1.224	4.63	0.34	4.55	0.34
5.15	1.01	1.292	6.10	0.60	5.90	0.58
8.73	2.09	1.472	10.88	1.30	9.89	1.18
9.97	2.60	- - -	12.67	1.65	- - -	- - -
11.43	3.20	1.589	14.88	2.08	12.60	1.76
12.11	3.79	1.653	15.85	2.50	13.51	2.11
1.0	0.0		1.12	- - -		
2.0	0.20		2.27	0.11		
3.0	0.42		3.45	0.24		
4.0	0.65		4.66	0.38		
5.0	0.90		5.90	0.53		
6.0	1.18		7.18	0.71		
7.0	1.50		8.50	0.91		
8.0	1.84		9.86	1.13		
9.0	2.22		11.26	1.39		
10.0	2.64		12.72	1.68		
11.0	3.18		14.24	2.06		
12.0	3.72		15.82	2.45		
13.0	4.30		17.47	2.89		

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally. Mixtures were kept at 18-24°C for more than 60 days with occasional shaking. Zinc content was determined by a volumetric acidometric method (1). Alkali content was determined by dissolving the sample in H_2SO_4 and back-titrating with aqueous KOH.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Hahn, F. L.; Hartlieb, E. *Z. Anal. Chem.* 1927, *71*, 225.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Sochevanov, V. G. *Zhur. Obshchei Khim*, 1952, *22*, 1073-85; *J. Gen. Chem. USSR (Engl. transl.)* 1952, *22*, 1119-28.

VARIABLES:

Concentration of potassium hydroxide.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of saturated solutions of $Zn(OH)_2$ in aqueous KOH at 18-22°C.

K_2O, mol%	mol KOH/kg H_2O[a]	ZnO, mol%	mol ZnO/kg H_2O[a]	sp. gr.	KOH, mol dm^{-3}[a]	ZnO, mol dm^{-3}[a]
2.14	2.43	0.37	0.21	1.132	2.43	0.21
4.28	5.05	1.53	0.90	1.276	4.91	0.88
5.27	6.34	2.36	1.42	1.351	6.06	1.36
7.44	9.31	3.79	2.37	1.490	8.50	2.17
1.0	1.12	0.0	- - -			
2.0	2.28	0.34	0.19			
3.0	3.47	0.83	0.48			
4.0	4.70	1.44	0.85			
5.0	5.98	2.12	1.27			
6.0	7.31	2.82	1.72			
7.0	8.70	3.56	2.21			
8.0	10.15	4.44	2.82			

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally by keeping the mixtures at 18-24°C for more than 60 days. The mixtures were shaken occasionally. Alkali content was determined by adding an excess of H_2SO_4 and back-titrating with aqueous KOH.[4] Zinc content was determined by a volumetric acidometric method (1).

SOURCE AND PURITY OF MATERIALS:

Reagent grade materials were used. The $Zn(OH)_2$ was prepared by saturating hot aqueous KOH with ZnO, filtering, and diluting the filtrate with 15-20 times its volume of water. This solution precipitated crystalline $Zn(OH)_2$ over a period of 2 weeks.

ESTIMATED ERROR:

No details are given but the deviation in duplicate results are less than 1%.

REFERENCES:

1. Hahn, F. L.; Hartlieb, E. *Z. Anal. Chem.* 1927, *71*, 225.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water; H_2O; [7732-18-5]	Dirkse, T. P.; Postmus, C.; Vandenbosch, R. *J. Am. Chem. Soc.* 1954, *76*, 6022-4.
VARIABLES:	PREPARED BY:
Concentration of NaOH at 25.0°C.	T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous NaOH at 25.0°C.[a]

Concn. of NaOH		
mol dm^{-3}	mol kg^{-1}	$10^4 c_{ZnO}$/mol dm^{-3}
0.578	0.581	87.5
0.520	0.521	75.4
0.462	0.462	55.7
0.405	0.404	48.6
0.347	0.345	31.1
0.289	0.287	29.7
0.231	0.229	13.4
0.173	0.171	7.5
0.116	0.114	3.8
0.058	0.057	5.9

[a] In the original article the data are presented only in graphical form. Those graphs are based on these data.

Extrapolation of the above data to infinite dilution gives a value of about 3×10^{-4} mol dm^{-3}. This is considered to the solubility of $Zn(OH)_2$ in water at this temperature.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The mixtures of solid ZnO and aqueous NaOH were kept for a month in a constant temperature bath and shaken frequently. Analysis for zinc was done amperometrically (1).	Reagent grade materials were used. Special precautions were taken to exclude CO_2.
	ESTIMATED ERROR:
	About 3%.
	REFERENCES:

1. Nimer, E. C.; Hamm, R. E.; Lee, G. C. *Anal. Chem.* 1950, *22*, 790.

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Dirkse, T. P.; Postmus, C., Vandenbosch, R. *J. Am. Chem. Soc.* 1954, *76*, 6022-4.

VARIABLES:
Concentration of KOH at 25.0°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous KOH at 25.0°C.[a]

conc. of KOH mol dm^{-3}	mol kg^{-1}	$10^4 C_{ZnO}$/mol dm^{-3}
0.674	0.680	89.9
0.607	0.609	73.2
0.539	0.540	59.5
0.472	0.470	45.7
0.404	0.402	32.7
0.337	0.333	23.0
0.270	0.265	15.8
0.202	0.199	8.4
0.135	0.132	3.7
0.067	0.066	1.5

[a] The data are presented only in graphical form in the article. Those graphs are based on these numerical data.

In the article the data are treated according to a method suggested earlier (2). This treatment gives thermodynamic values for the equilibrium constants of the following reactions.

$$ZnO(s) + OH^- + H_2O = Zn(OH)_3^- \qquad K = 6 \times 10^{-4}$$

$$ZnO(s) + 2OH^- + H_2O = Zn(OH)_4^{2-} \qquad K = (100 \pm 2) \times 10^{-4}$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The mixtures of solid ZnO and aqueous KOH were kept for a month in a constant temperature bath. They were shaken rather frequently. Analysis for zinc was done amperometrically (1).

SOURCE AND PURITY OF MATERIALS:
Reagent grade materials were used.

ESTIMATED ERROR:
About 3%.

REFERENCES:
1. Nimer, E. C.; Hamm, R. E.; Lee, G. C. *Anal. Chem.* 1950, *22*, 790.
2. McDowell, L. A.; Johnston, H. L. *J. Am. Chem. Soc.* 1936, *58*, 2009.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Fulton, J. W.; Swinehart, D. F. *J. Am. Chem. Soc.* 1954, *76*, 864-7.

VARIABLES:

Concentration of NaOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility[a] of $Zn(OH)_2$ in aqueous NaOH at 25°C.

C_{NaOH}/mol kg^{-1}	$10^6 C_{ZnO}$/mol kg^{-1}	C_{NaOH}/mol kg^{-1}	$10^6 C_{ZnO}$/mol kg^{-1}
0.000413	5.83	0.0311	75.7
0.000858	6.07	0.0386	107
0.00182	5.49	0.0497	151
0.00452	9.05	0.0669	247
0.00721	13.7	0.102	509
0.00986	19.5	0.190	1610
0.0186	36.6		

[a] Each value is the average of a pair of samples, one approaching equilibrium from supersaturation and one from undersaturation.

The solubility of $Zn(OH)_2$ in water at 25°C was 1.0(±0.1) x 10^{-5} mol/kg H_2O.

Some solubility measurements were also made in dilute HCl solutions but no numerical values are reported. The data are reported only graphically as a pH vs concentration of zinc plot.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures were equilibrated in nitrogen-filled flasks for 10 days. Equilibrium was approached from undersaturation and from supersaturation. The mixtures were allowed to sediment for up to two weeks before samples were taken for analysis. Zinc content was determined either colorimetrically using dithizone or by titration with $K_4Fe(CN)_6$. The temperature during equilibration was controlled at 25 ± 0.05°C.

SOURCE AND PURITY OF MATERIALS:

$Zn(OH)_2$ was prepared by adding NH_4OH to aqueous $ZnSO_4$, washing the precipitate with H_2O and NH_4OH over a week or two. The washed precipitate was dissolved in concentrated NH_4OH and the NH_3 was removed by air diffusion into H_2SO_4. The water used was conductivity water. All other materials were of reagent grade quality.

ESTIMATED ERROR:

Less than 1%.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]
(2) Chromium(VI) oxide; CrO_3; [1333-82-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Hayek, E.; Hatzl, H.; Schmid, H. *Monatsh.* 1954, *85*, 92-7.

VARIABLES:

Concentration of CrO_3 at 35°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous CrO_3 at 35°C.

C_{CrO_3}/mol dm^{-3}	C_{ZnO}/mol dm^{-3}	Solid phase
0.0004	0.0003	ZnO + $Zn(OH)_2$
0.0004	0.0003	- - - - - -
0.0080	0.0059	$ZnCrO_4 \cdot 2.5Zn(OH)_2$
0.0296	0.019	"
0.0563	0.035	"
0.105	0.062	"
0.117	0.069	"
0.148	0.085	"
0.181	0.103	"
0.196	0.110	"
0.271	0.148	"
0.316	0.170	$ZnCrO_4 \cdot Zn(OH)_2$
0.427	0.225	"
0.566	0.293	"
0.735	0.375	"
0.925	0.467	"
1.120	0.562	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

2.34 g of ZnO was added to 100 ml of the CrO_3-H_2O solution. The mixture was shaken vigorously for 30 min and then slowly in a thermostat at 35°C for 8 to 12 weeks. The electrical conductivity of the solution was measured to determine when equilibrium had been established. The liquid and solid phases were then separated from each other by filtration. Analysis was done iodometrically or by the method of van der Meulen (1).

SOURCE AND PURITY OF MATERIALS:

All materials were of analytical reagent grade quality. The ZnO was heated strongly before it was used.

ESTIMATED ERROR:

No information is given.

REFERENCES:

1. Meulen, J. H. van der *Chem. Weekbl.* 1940, 37, 436.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium chloride; NaCl; [7647-14-5]

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Urazov, G. G.; Lipshits, B. M.; Lovchikov, V. S. *Tsvetnye Metal.* 1956, *29*, 37-42.

VARIABLES:

Concentration of NaOH at 25° and at 75°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility in the system Na_2O-H_2O-ZnO at 25.0°C.

C_{Na_2O}/mass%	C_{ZnO}/mass%	C_{H_2O}/mass%	C_{NaOH}/mol kg^{-1} [a]	C_{ZnO}/mol kg^{-1} [a]	Solid phase [b]
1.40	0.16	98.44	0.459	0.020	A
3.89	1.12	94.99	1.32	0.145	"
5.47	1.58	92.95	1.90	0.209	"
7.56	2.03	90.41	2.70	0.276	"
8.83	1.51	89.66	3.18	0.207	"
11.06	2.03	86.91	4.11	0.287	B
14.10	3.75	82.15	5.54	0.561	"
16.73	4.90	78.37	6.89	0.768	"
19.29	7.21	73.50	8.47	1.21	"
21.47	8.38	70.15	9.87	1.47	"
23.80	10.03	66.17	11.6	1.86	"
24.76	17.04	58.20	13.7	3.60	C
26.90	15.32	57.78	15.0	3.26	"
27.58	15.03	57.39	15.5	3.22	"
29.54	11.53	58.93	16.2	2.40	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: A = $Zn(OH)_2$; B = ZnO; C = $Na[Zn(OH)_3]\cdot H_2O$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally in a water bath whose temperature was controlled to within 0.1°C. The mixtures of ZnO and solution were agitated in the constant temperature bath until zinc analyses of the solution reached a constant value. The method of analysis is not described. It appears that the composition of the solid phase was determined by the method of wet-residues. Solubility measurements at the boiling point were made in a steel cylinder immersed in the heating medium (either liquid paraffin or a molten lead-tin alloy). Water and NaOH were introduced into the cylinder, the mixture was brought to a boil, and the ZnO was then added with agitation.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No details are given.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium chloride; NaCl; [7647-14-5]

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Urazov, G. G.; Lipshits, B. M.; Lovchikov, V. S. *Tsvetnye Metal.* 1956, 29, 37-42.

EXPERIMENTAL RESULTS, contd:

Table II. Solubility in the system Na_2O-H_2O-ZnO at 75.0°C.

C_{Na_2O}/mass%	C_{ZnO}/mass%	C_{H_2O}/mass%	C_{NaOH}/mol kg^{-1} [a]	C_{ZnO}/mol kg^{-1} [a]	Solid phase [b]
1.34	0.15	98.51	0.439	0.019	B
1.90	0.31	97.79	0.627	0.039	"
2.63	0.68	96.69	0.877	0.086	"
3.79	1.48	94.73	1.29	0.192	"
4.88	2.55	92.57	1.70	0.338	"
6.25	3.48	90.27	2.23	0.474	"
7.77	5.06	87.17	2.88	0.713	"
9.77	6.72	83.51	3.77	0.989	"
11.59	8.56	79.85	4.68	1.32	"
12.60	9.72	77.68	5.23	1.54	"
14.34	11.44	74.22	6.23	1.89	"
15.58	12.36	72.26[c]	6.97	2.11	"
18.17	14.74	67.09	8.74	2.70	"
20.78	17.33	61.89	10.8	3.44	"
23.53	20.05	56.42	13.5	4.37	"
23.88	20.36	55.76	13.8	4.49	"
25.07	22.84	52.09	15.5	5.39	C
27.44	20.53	52.03	17.0	4.85	"
28.98	19.73	51.29	18.2	4.73	"
29.60	19.41	50.99	18.7	4.68	"
34.38	17.64	47.98	23.1	4.52	"
35.12	16.20	48.68	23.3	4.09	D
38.61	12.32	49.07	25.4	3.08	"
39.98	11.29	48.73	26.5	2.85	"
42.22	9.54	48.24	28.2	2.43	"
42.74	9.26	52.00[d]	28.7	2.37	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: B = ZnO; C = $NaZn(OH)_3$; D = $Na_2Zn(OH)_4$.

[c] This appears to be an error. It probably should be 72.06.

[d] This appears to be an error. It probably should be 48.00.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium chloride; NaCl; [7647-14-5]

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS

Urazov, G. G.; Lipshits, B. M. Lovchikov, V. S. *Tsvetnye Metal.* 1956, *29*, 37-42.

EXPERIMENTAL VALUES, contd:

Table III. Solubility in the system Na_2O-H_2O-ZnO at the boiling point of the solution.

t/°C	C_{Na_2O}/mass%	C_{ZnO}/mass%	C_{H_2O}/mass%	C_{NaOH}/mol kg^{-1} [a]	C_{ZnO}/mol kg^{-1} [a]	Solid phase [b]
121.0	14.5	4.8	80.7	5.80	0.73	B
133.5	24.8	15.0	60.2	13.3	3.06	"
145.0	28.6	19.2	52.2	17.7	4.52	"
155.0	31.0	25.8	43.2	23.1	7.34	"
- - -	33.25	29.9	36.85	29.1	9.97	"
- - -	43.4	30.0	26.60	52.6	13.9	"
269.0	45.7	27.9	26.40	55.8	13.0	E
315.0	52.31	23.5	24.19	69.8	11.9	"
- - -	63.2	16.4	20.40	99.9	9.88	"
- - -	68.43	7.9	23.67	93.3	4.10	"

[a] The mol/kg H_2O values were calculated by the compiler.

[b] The solid phases are: B = ZnO; E = $4[2ZnO \cdot Na_2O] \cdot 3H_2O$.

Table IV. Influence of NaCl on the solubility of ZnO in aqueous NaOH at 25.0°C.[a]

C_{NaOH}/mass%	C_{NaCl}/mass%	C_{Zn}/mass%
10.7	0	1.39
12.6	0	1.9
11.6	15.7	0.95
18.4	0	3.93
18.4	10.7	3.2
23.2	0	5.5
23.2	8.34	4.5
31.5	0	8.0
31.5	2.56	7.86

[a] The solutions apparently were saturated with respect to NaCl.

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Zinc oxide; ZnO; [1314-13-2] (2) Sodium chloride; NaCl; [7647-14-5] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	Urazov, G. G.; Lipshits, B. M. Lovchikov, V. S. *Tsvetnye Metal.* 1956, *29*, 37-42.

EXPERIMENTAL VALUES, contd:

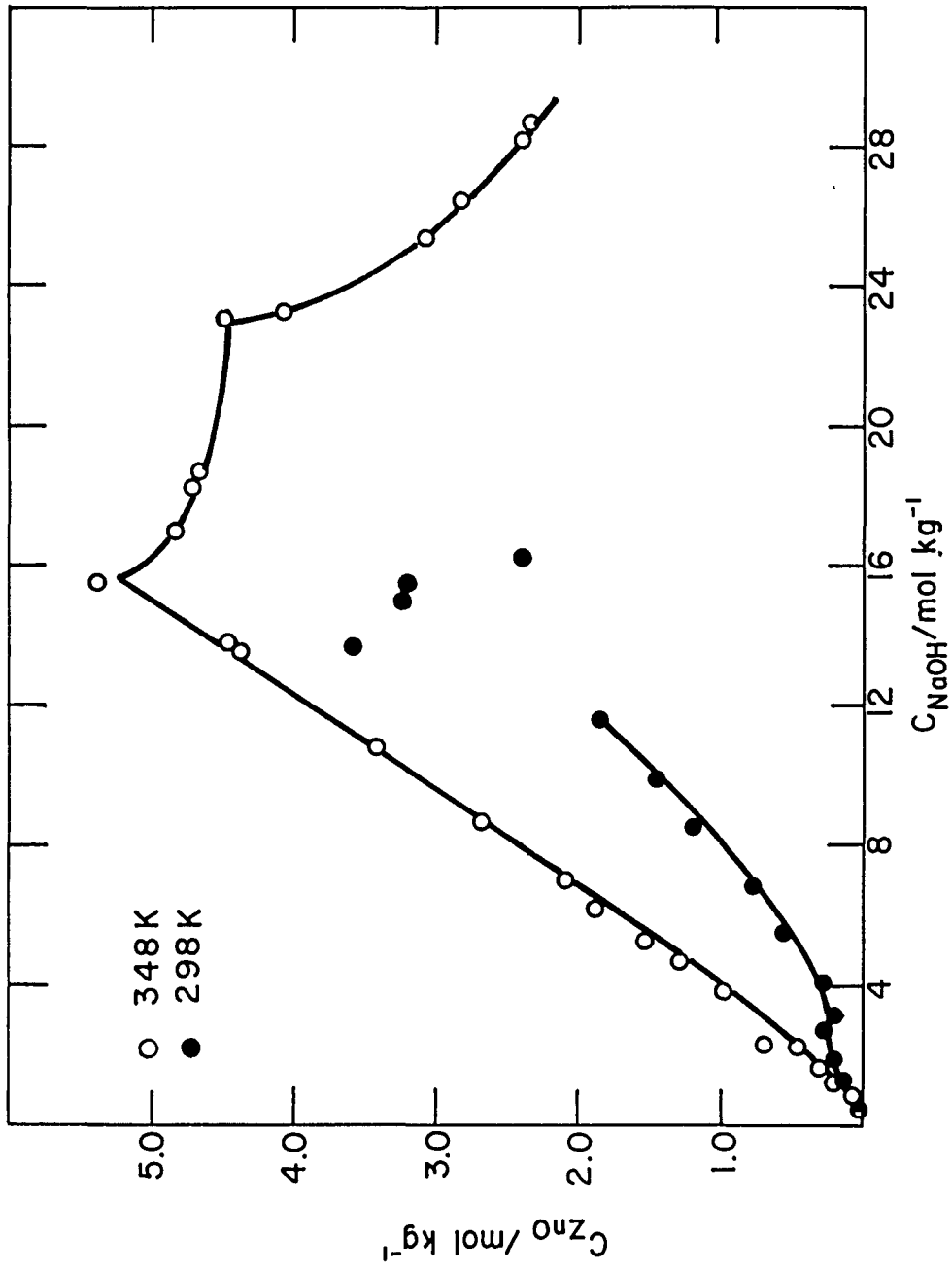

Figure 1. Solubility in the $ZnO-Na_2O-H_2O$ system.

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]
(2) Chromium(VI) oxide; CrO_3; [1333-82-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Woodward, A. E.; Allen, E. R.; Anderson, R. H. *J. Phys. Chem.* 1956, *60*, 939-43.

VARIABLES:
Concentration of chromium(VI) oxide at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:
Composition of equilibrium solutions of the $ZnO-CrO_3-H_2O$ system at 25°C.

mass% ZnO	mass% CrO_3	mass% ZnO	mass% CrO_3	mass% ZnO	mass% CrO_3
0.04	0.08	14.8	35.8	18.6	55.0
0.21	0.34	14.6	35.7	17.9	57.6
0.47	0.90	15.0	36.6	16.3	60.6
0.74	1.37	15.4	36.7	16.5	60.7
0.95	1.89	15.8	37.0	16.4	60.5
1.36	3.40	15.4	36.5	16.0	60.8
1.62	4.75	16.4	39.0	13.4	60.5
2.88	5.54	17.1	40.7	12.5	60.6
2.45	5.20	18.9	42.4	10.3	61.0
2.60	5.72	18.3	43.8	6.9	61.4
2.85	6.01	18.6	45.4	3.6	62.3
3.73	10.0	19.4	46.0		
6.00	15.5	19.4	47.0	<0.01	0.004
9.45	22.0	20.5	48.7	<0.01	0.006
10.1	24.1	21.1	51.0	<0.01	0.005
10.8	26.0	21.1	51.7	<0.01	0.002
11.5	27.7	21.1	52.0	<0.01	0.003
12.2	29.5	21.0	52.0	0.288	0.555
12.6	30.1	21.9	50.8	0.979	2.047
14.1	33.6	20.4	52.9	1.442	2.198
15.7	35.1	18.8	53.8	2.191	5.003

The solid phases identified were: $2ZnO \cdot CrO_3 \cdot H_2O$; $1.5ZnO \cdot CrO_3 \cdot 3H_2O$; $ZnO \cdot CrO_3 \cdot 2H_2O$; $ZnO \cdot 2CrO_3 \cdot 2H_2O$; CrO_3.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Equilibrium was reached isothermally by slowly rotating the mixtures in a constant temperature bath. Equilibrium was determined by analysis of samples every 3 to 4 days. Chromium content was determined iodometrically (1). Zinc content was determined volumetrically with $KBrO_3$ and $Na_2S_2O_3$ (2).

SOURCE AND PURITY OF MATERIALS:
Distilled water was used as solvent. All materials were of reagent grade quality.

ESTIMATED ERROR:
Duplicate results agreed to within 0.5%.

REFERENCES:
1. Brizzolara, A. A.; Denslow, R. R.; Rumbel, S. W. *Ind. Eng. Chem.* 1937, *29*, 656.
2. Kolthoff, I. M.; Sandell, E. B.; *Textbook of Quantitative Inorganic Analysis*, 3rd Ed., The Macmillan Co., New York, 1952, 607.

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sulfur dioxide; SO_2; [7446-09-5]

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

ORIGINAL MEASUREMENTS:
Jager, L. *Chem. Przmysł.* 1957, 7, 544-5.

VARIABLES:
Concentration of SO_2.

PREPARED BY:
T. Michalowski

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous SO_2 at 20.0°C

mass % ZnO	C_{ZnO}/mol kg^{-1} [a]	mass % SO_2	C_{SO_2}/mol kg^{-1} [a]	Solid phase [b]
7.78	1.22	14.10	2.82	A
6.50	0.97	11.05	2.09	"
5.51	0.79	9.14	1.67	"
4.12	0.57	6.62	1.16	"
3.24	0.43	5.18	0.88	"
0.50	0.062	0.63	0.10	"
0.45	0.056	0.58	0.091	"
0.39	0.048	0.49	0.077	"
0.10	0.012	0.10	0.016	
0.090	0.011	0.086	0.013	B
0.039	0.005	0.024	0.004	"

[a] Calculated by the compiler.

[b] Solid phases are: A = $ZnSO_3 \cdot 5/2H_2O$; B = $2ZnSO_3 \cdot 3ZnO \cdot 3H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
A 10% suspension of ZnO in water was placed in a flask, and nitrogen was passed over it for 1/2 hour to remove oxygen. The suspension was treated with SO_2, the flask was closed and placed in a thermostat at 20.0°C. Equilibrium was reached in 10-14 days. SO_2 content was determined iodometrically and zinc content was measured by titration with EDTA.

SOURCE AND PURITY OF MATERIALS:
No information is given.

ESTIMATED ERROR:
No information is given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Hydrogen peroxide; H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S. Z.; Ladeinova, L. V.; *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1957, 3-17; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. transl.)* 1957, 1-15.

VARIABLES:

Concentration of H_2O_2 and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Composition of saturated solutions of the $Zn(OH)_2$-H_2O_2-H_2O system at 30°C.

$C_{H_2O_2}$/wt %	$10^3 C_{ZnO}$/wt %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^4 C_{ZnO}$/mol kg^{-1} [a]	Solid phase [b]
- - -	1.03	- - -	1.27	A
1.92	6.08	0.58	7.62	A + B
6.27	4.28	1.97	5.61	B
8.45	8.13	2.71	10.9	"
11.83	10.68	3.95	14.9	"
13.43	12.10	4.56	17.3	"
15.68	24.30	5.47	35.4	B + C
19.89	12.18	7.30	18.7	C
26.09	9.42	10.38	15.7	"
34.60	4.68	15.56	8.80	"
40.74	8.90	20.22	18.5	"
42.18	8.93	21.46	19.0	D
43.00	5.70	22.19	12.3	"
44.18	4.10	23.28	9.02	"
55.27	1.15	36.34	3.16	"
55.77	4.25	37.09	11.8	"
57.16	14.25	39.25	40.9	"
58.33	22.58	41.19	66.6	D + E
62.25	5.57	48.51	18.1	E
67.51	2.43	61.11	9.19	"
78.61	0.78	108.1	4.48	"
82.52	1.98	138.8	13.9	E + F
85.31	0.77	170.8	6.44	F
86.98	0.75	196.5	7.08	"
88.45	0.53	225.2	5.64	"
93.23	0.78	405.0	14.2	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally by stirring the mixtures for 1.5 to 2 hours. Active oxygen was determined by titration with $KMnO_4$. Zinc content was measured colorimetrically with dithizone.

SOURCE AND PURITY OF MATERIALS:

The hydrogen peroxide was vacuum distilled. The $Zn(OH)_2$ was prepared by adding NH_4OH to a solution of $Zn(NO_3)_2$.

ESTIMATED ERROR:

The temperature was controlled to within 0.5°C but no other details are given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide, $Zn(OH)_2$; [20427-58-1]

(2) Hydrogen peroxide, H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S. Z.; Ladeinova, L. V. *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1957, 3-17, *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. transl.)* 1957, 1-15.

EXPERIMENTAL VALUES. contd.

Composition of saturated solutions of the $Zn(OH)_2$-H_2O_2-H_2O system.

$C_{H_2O_2}$/wt %	$10^3 C_{ZnO}$/wt %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^4 C_{ZnO}$/mol kg^{-1} [a]	Solid phase [b]
		temp., 20°C.		
----	1.80	----	2.21	A
0.45	0.52	0.13	0.64	"
1.67	3.13	0.50	3.91	"
3.48	9.30	1.06	11.8	A + B
4.72	4.18	1.46	5.39	B
7.62	2.19	2.43	2.91	"
9.23	1.87	2.99	2.53	"
12.94	1.72	4.37	2.43	"
18.19	17.86	6.54	26.8	"
21.43	16.23	8.02	25.4	D
26.04	2.14	10.36	3.55	"
28.20	1.62	11.55	2.77	"
38.30	1.13	18.26	2.25	"
43.86	2.53	22.98	5.54	"
46.54	10.94	25.61	25.1	D + E
50.66	4.29	30.20	10.7	E
54.00	2.37	34.53	6.33	"
57.50	12.90	39.80	37.3	"
57.98	27.78	40.61	81.3	E + F
60.29	5.42	44.67	16.8	F
72.35	4.23	76.96	18.8	"
83.07	4.44	144.3	32.2	"
86.15	8.31	183.1	73.8	F + G
88.68	3.84	230.4	41.7	G

[a] Data converted to mol/kg H_2O by the compiler.

[b] A = $Zn(OH)_2$; B = $ZnO_2 \cdot 2H_2O$; C = $ZnO_2 \cdot 1.5H_2O$; D = $ZnO_2 \cdot H_2O$; E = $ZnO_2 \cdot 0.5H_2O$; F = ZnO_2; G = $ZnO_2 \cdot H_2O_2$.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Hydrogen peroxide; H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S. Z.; Ladeinova, L. V. *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1957, 3-17; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. transl.)* 1957, 1-15.

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of the $Zn(OH)_2$-H_2O_2-H_2O system.

$C_{H_2O_2}$/wt %	$10^3 C_{ZnO}$/wt %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^4 C_{ZnO}$/mol kg^{-1} [a]	Solid phase [b]
		temp., 0°C		
----	0.63	----	0.77	A
0.07	0.74	0.02	0.91	A + B
3.50	0.44	1.07	0.56	B
6.25	0.39	1.96	0.51	"
9.08	1.43	2.94	1.93	"
10.36	3.42	3.40	4.69	"
13.96	3.66	4.77	5.23	"
15.09	9.01	5.23	13.0	B + D
19.42	5.77	7.09	8.80	D
23.83	1.11	9.20	1.79	"
27.16	2.36	10.97	3.98	"
28.34	5.23	11.63	8.97	D + E
32.10	1.65	13.90	2.99	E
34.74	1.29	15.66	2.43	"
40.24	4.29	19.80	8.82	"
40.93	5.00	20.38	10.4	E + F
43.65	1.98	22.78	4.32	F
43.81	0.63	22.93	1.38	"
50.77	1.06	30.33	2.65	"
54.83	0.86	35.70	2.34	"
63.77	1.29	51.77	4.37	"
73.82	2.01	82.93	9.43	"
74.38	19.72	85.45	94.6	F + G
79.83	7.76	116.5	47.3	G
90.15	1.05	269.2	13.1	"

[a] Data converted to mol/kg H_2O by the compiler.

[b] A = $Zn(OH)_2$; B = $ZnO_2 \cdot 2H_2O$; D = $ZnO_2 \cdot H_2O$; E = $ZnO_2 \cdot 0.5H_2O$; F = ZnO_2; G = $ZnO_2 \cdot H_2O_2$.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Hydrogen peroxide, H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S. Z.; Ladeinova, L. V. *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1957, 3-17; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. transl.)* 1957, 1-15.

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of the $Zn(OH)_2$-H_2O_2-H_2O system.

$C_{H_2O_2}$/wt %	$10^3 C_{ZnO}$/wt %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^4 C_{ZnO}$/mol kg^{-1} [a]	Solid phase [b]
		temp., -10°C.		
13.80	3.89	4.71	5.54	D
19.04	3.30	6.92	5.01	"
20.43	4.37	7.55	6.75	D + E
21.54	3.22	8.07	5.04	E
22.43	2.75	8.50	4.36	"
28.30	2.16	11.61	3.70	"
35.21	3.84	15.98	7.28	"
35.48	4.80	16.17	9.14	"
36.37	5.30	16.81	10.2	"
38.69	6.61	18.56	13.2	E + H
40.67	4.10	20.16	8.49	H
41.62	2.60	20.97	5.47	"
45.22	2.10	24.28	4.71	"
50.74	1.49	30.30	3.72	"
51.62	1.23	31.38	3.12	"
52.43	1.12	32.42	2.89	"
58.51	0.91	41.48	2.69	"
61.38	1.87	46.75	5.95	"
61.89	1.86	47.76	6.00	"
61.93	2.05	47.85	6.62	"
62.32	8.03	48.66	26.2	H + F
64.41	1.40	53.23	4.83	F
66.68	0.62	58.86	2.29	"
70.83	1.84	71.42	7.75	"
72.65	2.30	78.13	10.3	F + G
72.90	1.55	79.12	7.03	G
75.52	1.12	90.73	5.62	"
80.48	1.41	121.3	8.87	"
85.32	1.20	170.9	10.0	"
89.18	0.77	242.4	8.74	"

[a] Data converted to mol/kg H_2O by the compiler.

[b] D = $ZnO_2 \cdot H_2O$; E = $ZnO_2 \cdot 0.5H_2O$; F = ZnO_2; G = $ZnO_2 \cdot H_2O_2$; H = $ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Hydrogen peroxide; H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Makarov, S. Z.; Ladeinova, L. V.; *Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk* 1957, 3-17; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. transl.)* 1957, 1-15

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of the $Zn(OH)_2$-H_2O_2-H_2O system.

$C_{H_2O_2}$/wt %	$10^3 C_{ZnO}$/wt %	$C_{H_2O_2}$/mol kg^{-1} [a]	$10^4 C_{ZnO}$/mol kg^{-1} [a]	Solid phase [b]
		temp., -20°C		
30.09	3.37	12.66	5.92	E
36.87	4.32	17.18	8.41	"
38.96	4.99	18.77	10.0	"
40.23	27.80	19.81	57.2	E + H
41.51	4.03	20.87	8.46	H
41.74	3.29	21.07	6.94	"
47.52	1.33	26.63	3.11	"
48.03	7.44	27.19	17.6	H + F
48.78	2.79	28.01	6.69	F
54.02	2.02	34.55	5.40	"
56.76	2.13	38.61	6.05	"
63.43	1.50	51.01	5.04	"
63.47	1.36	51.10	4.57	"
64.47	1.65	53.37	5.71	"
66.63	1.20	58.73	4.42	"
69.86	4.07	68.17	1.51	"
70.78	7.82	71.27	32.9	F + G
71.63	2.98	74.26	12.9	G
71.71	1.88	74.55	8.16	"
73.31	0.84	80.79	3.87	"
76.25	1.48	94.43	7.66	"
77.55	2.53	101.6	13.8	G + I
79.23	0.52	112.2	3.08	I
81.66	1.62	131.0	10.9	"

[a] Data converted to mol/kg H_2O by the compiler.

[b] E = $ZnO_2 \cdot 0.5H_2O$; F = ZnO_2; G = $ZnO_2 \cdot H_2O_2$; H = $ZnO_2 \cdot 0.5H_2O_2 \cdot H_2O$; I = $ZnO_2 \cdot 2H_2O_2$.

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Dirkse, T. P. *J. Electrochem. Soc.* 1959, *106*, 154.

VARIABLES:
Concentration of KOH and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of saturated solutions of ZnO in aqueous KOH.

mass% K	mol KOH/kg H_2O[a]	mass% Zn	mol ZnO/kg H_2O[a]
	temp., 44.6°C.		
10.05	3.03	0.80	0.15
17.62	6.28	2.30	0.49
22.1	17.83	4.33	1.05
31.8	18.03	7.48	2.54
34.4	22.6	9.29	3.65
34.7	24.4	11.05	4.66
38.6	22.7	0.81	0.28
38.8	23.8	2.03	0.74
38.3	24.1	3.49	1.31
39.1	24.7	2.78	1.05
40.1	25.9	2.29	0.88
	temp., 3°C.		
7.90	2.30	0.55	0.09
14.01	4.61	1.74	0.34
20.01	7.69	3.82	0.88
21.29	8.44	3.97	0.94
26.9	12.6	5.36	1.50
32.2	18.7	7.89	2.74
32.6	17.4	4.31	1.38

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Equilibrium was approached from both undersaturation and supersaturation. The mixtures were allowed to stand with occasional shaking for several months. The mixtures were contained in Pyrex flasks and in polyethylene vessels. Zinc content was determined by titration with $K_4Fe(CN)_6$ and spectrophotometrically with dithizone (1). Potassium content was determined colorimetrically with dipicrylamine (2, 3).

SOURCE AND PURITY OF MATERIALS:
C. P. ZnO was added to carbonate-free KOH. Distilled water was used as solvent.

ESTIMATED ERROR:
Less than 1%.

REFERENCES:
1. Cowling, H.; Miller, E. J. *Ind. Eng. Chem., Anal. Ed.* 1941, *13*, 145.
2. Amdur, E. *Ind. Eng. Chem., Anal. Ed.* 1940, *12*, 731.
3. Faber, R.; Dirkse, T. P. *Anal. Chem.* 1953, *25*, 808.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Dirkse, T. P. *J. Electrochem. Soc.* 1959, *106*, 154.

EXPERIMENTAL VALUES, contd.

Composition of saturated solutions of ZnO in aqueous KOH.

mass% K	mol KOH/kg H_2O[a]	mass% Zn	mol ZnO/kg H_2O[a]
	temp., -20°C.		
17.4	6.19	2.38	0.50
18.8	6.94	2.96	0.65
15.4	5.25	2.38	0.48
17.3	6.11	2.28	0.48
21.4	8.48	3.80	0.90
24.3	10.63	5.28	1.38
28.0	12.22	0.95	0.25
28.6	12.45	0.25	0.05
	temp., -30°C.		
17.1	6.03	2.43	0.51
19.4	7.24	3.04	0.68
17.4	6.19	2.46	0.52
21.9	8.77	3.85	0.92
24	10.3	4.89	1.26
29.9	13.55	0.52	0.14
30.8	14.22	0.32	0.09
	temp., 25°C.		
3.66	0.99	0.28	0.05
4.93	1.36	0.48	0.08
8.18	2.39	0.55	0.10
15.0	5.03	1.83	0.37
21.3	8.40	3.61	0.85
21.9	8.75	3.71	0.89
28.9	14.62	6.34	1.92
30.9	17.47	8.41	2.85
35.3	24.58	10.20	4.25
36.0	26.71	11.05	4.91
36.1	26.31	10.53	4.59
36.3	24.37	7.91	3.16
36.4	23.09	6.02	2.29
37.7	22.37	2.28	0.80

[a] Calculated by the compiler.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Landsberg, R.; Furtig, H.; Muller, L. *Wissen. Z. Techn. Hochscule fur Chemie Leuna-Merseburg* 1959/60, *2*, 453-8.

VARIABLES:

Concentration of sodium hydroxide at 20 ± 0.2°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

The rate of dissolution (mol cm^{-2} s^{-1}) was measured in NaOH solutions containing varying amounts of dissolved ZnO. For a given NaOH concentration there was a linear relationship between the rate of dissolution and the concentration of ZnO. Extrapolation of this line to zero rate of dissolution gives the concentration of ZnO at saturation. The results obtained at 20°C are:

C_{NaOH}/mol dm^{-3}	C_{ZnO}/mol dm^{-3}
1	0.01
2	0.045
3	0.102
4	0.188

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Small compressed discs of ZnO were prepared, heated for 5 hours at 1000°C, attached to a rod which was rotated at 2055 rpm in a NaOH solution containing dissolved ZnO. The rate of dissolution of the ZnO in the disc was measured by taking samples of the solution at specified times and analyzing them for zinc content. Analysis was done polarimetrically in an ammoniacal solution (1).

SOURCE AND PURITY OF MATERIALS:

No information is given except about the ZnO.

ESTIMATED ERROR:

No information is given.

REFERENCES:

1. Eucken, Z. B. A.; Suhrmann, R. *Phys.-Chem. Praktikumsaufgaben* 1952, Leipzig.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

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

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

ORIGINAL MEASUREMENTS:

Schindler, P.; Althaus, H.; Schurch, A.; Feitknecht, W. *Chimia* 1962, *16*, 42-4.

VARIABLES:

pH of the solvent at 25.0°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in solutions of varying pH at 25.0°C.

$10^3 C_{H^+}$/mol dm^{-3} in solution before reaction with $Zn(OH)_2$	pH of solution after saturation	$10^3 C_{Zn^{2+}}$/mol dm^{-3}	log $*K_s o$[a]	$Zn(OH)_2$ prep.
10.00	7.018	5.02	11.74	a
6.67	7.114	3.31	11.75	b
5.00	7.187	2.39	11.75	b
4.00	7.228	1.94	11.75	b
3.33	7.255	1.65	11.73	b
2.00	7.391	0.97	11.77	b
1.00	7.549	0.48	11.78	a
0.40	7.697	0.23	11.75	b
0.10	8.049	0.04	11.73	a

[a] $*K_s o = (C_{Zn^{2+}}) \cdot (C_{H^+})^{-2}$ for the reaction $\varepsilon Zn(OH)_2\ (s) + 2H^+ = Zn^{2+} + 2H_2O$

The average log $*K_s o$ = 11.75 ± 0.03 at 25°C in 0.2 mol KNO_3 dm^{-3}.

Using log K_w = -13.70 ± 0.02 at 25°C in 0.2 mol KNO_3 dm^{-3} the value of log $K_s o$ is calculated to be -15.65 ± 0.05 at 25°C in 0.2 mol KNO_3 dm^{-3}.

Using approximations for activity coefficients (3) the value of log $K_s o$ at 25°C and zero ionic strength is calculated to be -16.5 ± 0.1.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvent was forced through the solid in a closed container. This was done 10 to 20 times and the pH of the solvent was determined by measuring the e.m.f. across a glass electrode and a Ag/AgCl electrode immersed in the solvent. After the pH became constant a sample of the solution was removed and analyzed for zinc content by a compleximetric titration. The pH of the solvent was adjusted by the addition of HNO_3. The ionic strength in all solutions was 0.2 mol KNO_3 dm^{-3}.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The ε-$Zn(OH)_2$ was prepared in 2 ways; (a) by the method of Dietrich and Johnston (1); and (b) by the method described by Feitknecht (2).

ESTIMATED ERROR:

The authors give no details but the uncertainty in the final results appears to be less than 5%.

REFERENCES:

1. Dietrich, H. G.; Johnston, J. *J. Am. Chem. Soc.* 1927, *49*, 1419.
2. Feitknecht, W. *Helv. Chim. Acta* 1930, *13*, 314.
3. Guggenheim, E. A. *Phil. Mag.* 1935, *19*, 588.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Potassium hydroxide; KOH; [1310-58-3] (3) Water; H_2O; [7732-18-5]	Laudise, R. A.; Kolb, E. D. *Am. Mineral.* 1963, *48*, 642.
VARIABLES:	PREPARED BY:
Temperature.	F. Izumi

EXPERIMENTAL VALUES:

Solubilities of ZnO in 6.47 mol kg^{-1} KOH were measured at 55 MPa. They were 4.62% at 360°C and 3.57% at 200°C. These values were calculated as (weight of ZnO dissolved) x 100/(weight of H_2O + weight of KOH).

This paper also presents graphical data on solubilities of ZnO in aqueous solutions of KOH and NaOH.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Solubilities were determined by means of weight loss determinations carried out on crystalline ZnO contained in welded platinum capsules filled with the basic solutions. The capsules were heated in Tuttle-type pressure vessels, and the pressure was established by pumping water into these vessels.	All materials were of reagent grade purity. The crystalline ZnO was obtained by selection from spontaneously nucleated crystals formed in hydrothermal growth runs.
	ESTIMATED ERROR: Temperature: within ± 3°C. Pressure: within ± 3 MPa. Solubility: within ± 0.09% for 360°C and within ± 0.16% for 200°C.
	REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

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

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

ORIGINAL MEASUREMENTS:

Pinto, L.; Egger, K.; Schindler, P. *Helv. Chim. Acta* 1963, *46*, 425-7.

VARIABLES:

pH of the solvent at 25°C in 0.2 mol KNO_3 dm^{-3}.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of saturated solutions of ε-$Zn(OH)_2$ in aqueous solutions of varying pH.[a]

$-\log (C_{H^+}/\text{mol dm}^{-3})$	$-\log (C_{Zn^{2+}}/\text{mol dm}^{-3})$	$\log {}^*K_s o$[b]
7.93_9	4.14_0	11.74
7.93^5	4.15_3	11.72
7.88_7	4.06_2	11.71
7.77_7	3.81_9	11.74
7.60_7	3.50_4	11.71
7.46_7	3.22_3	11.71
7.36_3	3.02_9	11.70
7.28_5	2.84_2	11.73
7.22_2	2.73_4	11.71

[a] This work is a repeat of earlier work (2) except that a more sensitive method is used for the analysis of zinc.

[b] ${}^*K_s o = (C_{Zn^{2+}}) \cdot (C_{H^+})^{-2}$

The average value of $\log {}^*K_s o = 11.72 \pm 0.02$ at 25°C in 2 mol KNO_3 dm^{-3}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solvent, containing HNO_3 and KNO_3, was passed through samples of solid ε-$Zn(OH)_2$ in a closed tube and the pH of the solvent was determined by measuring the e.m.f. between a glass electrode and a Ag/AgCl electrode inserted in the solvent. This process was repeated until the pH of the solvent became constant. Then a sample of the solution was removed and analyzed for zinc content. Zinc analysis was done by means of a ^{65}Zn radioactive tracer. All solutions had an ionic strength of 0.2 mol KNO_3 dm^{-3}. The work was carried out only at 25°C.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The ε-$Zn(OH)_2$ was prepared by the method described by others (1).

ESTIMATED ERROR:

The uncertainty in the values appears to be less than 5%.

REFERENCES:

1. Dietrich, H. G.; Johnston, J. *J. Am. Chem. Soc.* 1927, *49*, 1419.
2. Schindler, P.; Althaus, H.; Schurch, A.; Feitknecht, W. *Chimia* 1962, *16*, 42.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

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

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

ORIGINAL MEASUREMENTS:

Schindler, P.; Althaus, H.; Hofer, F.; Minder, W. *Helv. Chim. Acta* 1965, *48*, 1204-15.

VARIABLES:

Particle size and molar surface area of the ZnO.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility constants of ZnO at 25°C.[a]

S/m^2 [b]	$\log {}^*K_s o$ [c]
1290	11.56 ± 0.02
1490	11.54 ± 0.02
1960	11.55 ± 0.02
540	11.47 ± 0.02
870	11.45 ± 0.02
280	11.42 ± 0.02
40	11.39 ± 0.02

[a] Each result is the average of 6 to 8 determinations. All results are for a solution containing 0.2 mol $NaClO_4$ dm^{-3}.

[b] S is the molar surface area.

[c] ${}^*K_s o = K_s o/(K_w)^2$

The above data can be represented by the following equation with a 90% confidence level.

$$\log {}^*K_s o = (11.40 \pm 0.04) + (9.0 \pm 3.5) \times 10^{-5}\ S.$$

Using $K_w = -13.70 \pm 0.02$, the following values are calculated:

$\log K_s o = -16.00 \pm 0.04$ and $\log K_s^\circ o = -16.82 \pm 0.04$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The ZnO was placed in a column and the solvent (water containing 0.2 mol $NaClO_4$ dm^{-3}) was forced through the column 10 to 20 times until the pH of the solution became constant. A sample of the solution was removed and analyzed for zinc content by a compleximetric titration. The pH was determined by measuring the e.m.f. across a glass electrode and a AgCl/Ag electrode placed in the solution. All measurements were made at 25.0 ± 0.5°C. The method of Davies (1) was used to obtain the thermodynamic solubility product constant.

SOURCE AND PURITY OF MATERIALS:

The ZnO was prepared (a) by thermal decomposition of zinc oxalate, (b) by dehydrating ε-$Zn(OH)_2$ at 80°C for 60 hours in a vacuum over soda lime, and (c) by adding, with intense stirring, equivalent quantities of aqueous NaOH and aqueous $Zn(ClO_4)_2$ and allowing the precipitate to stand for 1 week in contact with the solution.

ESTIMATED ERROR:

This is indicated for each result that is reported.

REFERENCES:

1. Davies, C. W. *Ion Association*, Butterworths, London 1960, p. 41.

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-14-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:
Baker, C. T.; Trachtenberg, I. *J. Electrochem Soc.* 1967, *114*, 1045-6.

VARIABLES:
Concentration of KOH and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Table I. Solubility of ZnO in aqueous KOH at 25°C.

C_{KOH}/wt %[a]	C_{KOH}/mol dm^{-3}[a]	C_{Zn}/mol dm^{-3}
25	5.5	0.45
30	6.9	0.64
34	8.1	0.83
36.3	8.7	0.95

[a]Values of KOH concentration before saturation with ZnO.

Table II. Effect of temperature on the solubility of ZnO in 36.3 wt % KOH.

t/°C.	C_{Zn}/mol dm^{-3}
-62	0.92
-51	0.92
-30	0.95
-30	0.94
-26	0.97
-10	0.92
0	0.94
+26	0.97

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The mixtures were agitated periodically by means of an ultrasonic bath over a three-day span. No details are given for the analytical procedures. The temperatures were controlled to within 0.5°C.

SOURCE AND PURITY OF MATERIALS:
Reagent grade materials were used. Care was taken to exclude CO_2. The solvent was deionized water.

ESTIMATED ERROR:
No details are given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

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

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

ORIGINAL MEASUREMENTS:

Gubeli, A. O.; Ste. Marie, J. *Can. J. Chem.* 1967, *45*, 827-32.

VARIABLES:

pH of the solution at 25°C

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ as a function of pH at 25°C.

pH	pZn_{tot}	pH	pZn_{tot}
6.84	2.31	9.20	5.29
6.85	2.43	9.70	5.46
6.87	2.38	10.18	5.57
6.90	2.61	10.30	5.37
7.02	2.70	10.58	5.26
7.63	3.96	10.88	4.98
7.82	4.24	11.07	4.64
8.06	4.51	11.10	4.69
8.24	4.63	11.42	4.19
8.48	4.88	11.52	4.06
8.77	5.02	11.76	3.54
9.10	5.19		

The authors assume the following general reaction

$$Zn^{2+} + x\ OH^- = Zn(OH)_x^{2-x} \qquad (1)$$

for which $$\phi_x = [Zn(OH)_x^{2-x}] / [Zn^{2+}] \cdot [OH^-]^x \qquad (2)$$

Equation (2), by substitution and rearrangement, becomes

$$[Zn(OH)_x^{2-x}] = \phi \cdot K_{so} \cdot (K_w)^{x-2} \cdot [H+]^{2-x} \qquad (3)$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

It is not clear whether mixtures were prepared using solid $Zn(OH)_2$ or whether $Zn(OH)_2$ was precipitated from solutions of Zn^{2+} ions. The solutions contained ^{65}Zn as a radioactive tracer and were all at an ionic strength of 1 mol dm^{-3} (maintained by the $NaClO_4$). The pH of the solutions was adjusted by adding either $HClO_4$ or NaOH. Mixtures were agitated for several days in a constant temperature bath. The solutions were then allowed to settle for 5 or 6 days. After this, samples were taken for analysis. Zinc content was determined by measuring the radioactivity of the solutions. pH was determined potentiometrically using calomel and glass electrodes.

SOURCE AND PURITY OF MATERIALS:

No information is given. CO_2 and O_2 were excluded from the solutions.

ESTIMATED ERROR:

No information is given except as indicated in the derived values for the various constants.

REFERENCES:

1. Gubeli, A. O.; Ste. Marie, J. *Can. J. Chem.* 1968, *46*, 1707.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Sodium perchlorate, $NaClO_4$, [7601-89-0] (3) Water, H_2O, [7732-18-5]	Gubeli, A. O.; Ste. Marie, J. *Can. J. Chem.* 1967, *45*, 827-32.

EXPERIMENTAL VALUES: con't

From equation (3)

$$\frac{d \log [Zn(OH)_x^{2-x}]}{d\ pH} = x-2 \qquad (4)$$

A plot of log $[Zn(OH)_x^{2-x}]$ vs pH is made from the solubility data, Figure 1. The slopes of the plot then indicate the pH regions where certain $Zn(OH)_x^{2-x}$ species are predominant. These species are: Zn^{2+}, $ZnOH^+$, $Zn(OH)_2$, $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$.

From the solubility data measurements and substitution in equations similar to (3) above, enough equations can be written that, when solved simultaneously, give values for ϕ_x. The values obtained at 25°C are:

$$p\phi_1 = -6.31 \pm 0.07$$

$$p\phi_2 = -11.19 \pm 0.05$$

$$p\phi_3 = -14.31 \pm 0.06$$

$$p\phi_4 = -17.70 \pm 0.05$$

The value of pK_{so} (= 16.76 ± 0.03) was obtained from similar work by the authors (1).

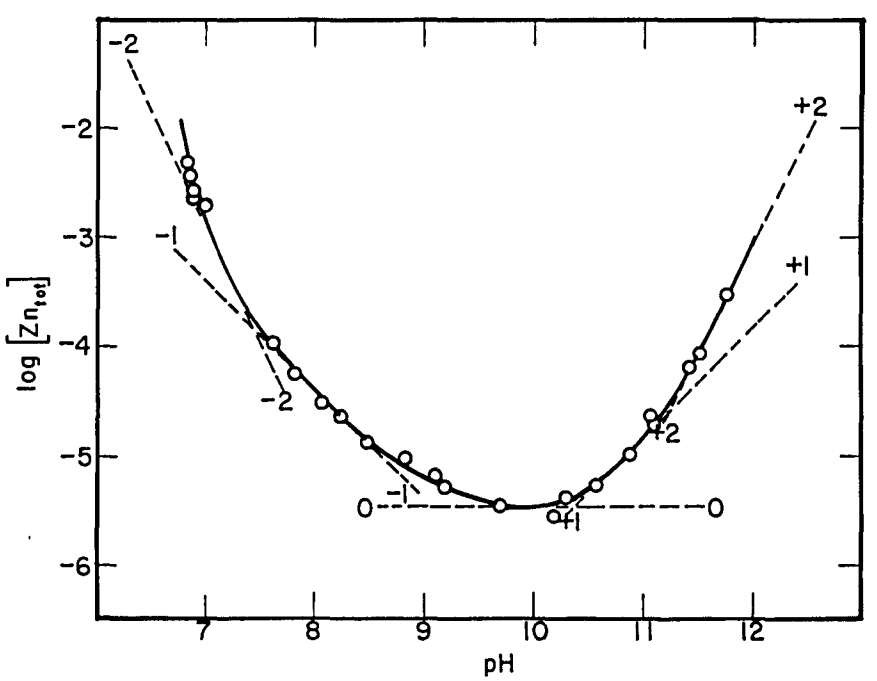

Figure 1. Solubility of $Zn(OH)_2$ as a function of pH at 25°C.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc oxide; ZnO; [1314-13-2] (2) Sodium sulfide; Na_2S; [1313-82-2] (3) Water; H_2O; [7732-18-5]	Polyvyannyi, I. R.; Milyutina, N. A. *Tr. Inst. Metal. Obogashch. AN Kaz. SSR* 1967, *21*, 3-13.
VARIABLES:	PREPARED BY:
Concentration of sodium sulfide at 60.0°C.	T. Michalowski

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous Na_2S at 60.0°C.

Initial concentration of Na_2S	1.53 mol dm^{-3}
Density of saturated solution	1.11 g ml^{-1}
Equilibrium concentration of Zn	5.5×10^{-3} mol dm^{-3}
Ionic strength	4.612 mol dm^{-3}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Equilibrium was reached isothermally by agitation for 24 hours. No information is given about the analytical procedures.	Reagent grade ZnO and Na_2S used. The Na_2S was recrystallized three times.
	ESTIMATED ERROR:
	No information is given about the reproducibility of any of the procedures.
	REFERENCES:

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Dyson, W. H.; Schrier, L. A.; Sholette, W. P. Salkind, A. J. *J. Electrochem. Soc.* 1968, *115*, 566-9.

VARIABLES:
Concentration of KOH and temperature

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous KOH at 25°C

C_{KOH}/mass %[a]	C_{ZnO}/mass %	C_{KOH}/mol kg^{-1}[b]	C_{ZnO}/mol kg^{-1}[b]
46	8.3	17.94	2.23
40	6.5	13.33	1.49
35	5.2	10.43	1.07

[a] This is the KOH concentration before the ZnO was added.

[b] Data converted to mol/kg H_2O by the compiler.

No other numerical data are included in the paper. However, solubility studies were also made at 10°, 55°, and the temperature range up to 145°C. These data are presented graphically and indicate that over this temperature range the solubility of ZnO in the KOH solutions listed in the above table is practically independent of the temperature.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Excess ZnO was added to KOH solutions saturated with ZnO at room temperature. The mixtures were agitated for at least 2 days in a water bath. At the higher temperatures, the mixtures were contained in stainless steel bombs. Zinc content was determined by titration with EDTA. Potassium content (for KOH) was determined by titrating amperometrically with tetraphenylborate.

SOURCE AND PURITY OF MATERIALS:
Reagent grade materials were used.

ESTIMATED ERROR:
Limits of experimental error were 0.05% for ZnO and 0.25% for KOH.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Ammonium hydroxide; NH_4OH; [1336-21-6]

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

ORIGINAL MEASUREMENTS:

Gubeli, A. O.; Ste. Marie, J. *Can. J. Chem.* 1968, *46*, 1707-14.

VARIABLES:

pH and concentration of ammonium hydroxide

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ as a function of pH in the presence of NH_3.

C_{NH_3}/mol dm^{-3}	pH	pZn	C_{NH_3}/mol dm^{-3}	pH	pZn
0.005	6.80	2.49	0.02	8.27	4.89
"	6.87	2.71	"	8.83	4.63
"	7.30	3.58	"	8.89	4.62
"	7.69	4.06	"	9.04	4.59
"	7.71	4.22	"	9.25	4.48
"	7.95	4.79	"	9.67	4.59
"	8.48	5.41	"	9.82	4.53
"	8.96	5.81	"	11.12	4.22
"	9.60	5.75	"	12.08	3.48
"	10.63	5.27			
"	11.35	4.76	0.04	8.64	3.74
"	11.94	4.23	"	8.76	3.68
"	12.00	4.11	"	8.87	3.64
"	12.02	4.11	"	9.08	3.55
			"	9.20	3.49
0.02	6.63	2.14	"	9.33	3.41
"	6.80	2.19	"	9.46	3.36
"	6.87	2.24	"	9.60	3.38
"	6.88	2.31	"	9.68	3.55
"	6.92	2.50	"	9.80	3.61
"	6.94	2.63	"	10.64	3.93
"	7.05	2.95	"	11.15	3.68
"	7.07	2.90	"	12.31	2.84
"	7.37	3.62	"	12.47	2.75

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Three series of solutions were prepared. These series contained NH_4OH concentrations of 0.005, 0.02 and 0.04 mol dm^{-3}. The total ionic strength of each solution was 1 mol dm^{-3} and was attained by the presence of $NaClO_4$. These solutions were equilibrated with solid $Zn(OH)_2$ by vigorous agitation for several days in a constant temperature bath at 25°C. After the solutions were quiescent for 5 or 6 days, samples were taken for analysis. pH was determined with a glass electrode. Zinc content was determined by counting of radioactivity due to ^{65}Zn. The pH was adjusted by adding either $HClO_4$ or NaOH.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Ammonium hydroxide; NH_4OH; [1336-21-6] (3) Water; H_2O, [7732-18-5]	Gubeli, A. O.; Ste. Marie, J. *Can. J. Chem.* 1968, *46*, 1707-14.

ADDITIONAL COMMENTS:

The authors analyzed these results by writing general equations for the formation of all possible $Zn(OH)_x(NH_3)_y$ compounds. From these equations they calculated the theoretical slopes of the C_{Zn}^x vs pH and C_{Zn} vs pNH_3 plots for each of these compounds. Comparing these theoretical slopes with those obtained experimentally they concluded that, within the limits of pH and pNH_3 used in this study, the main species are: $Zn(OH)_2$, $Zn(OH)_3(NH_3)^-$ and $Zn(NH_3)_4^{2+}$. Basic to this is the assumption that zinc has a coordination number of 4.

Using the appropriate experimental data, the authors then deduced values for various constants associated with these compounds.

For $Zn(OH)_2$ they deduced $pK_{s_2}^o = 16.76 \pm 0.03$ at 25°C. This was based on 15 experimental points. $K_s^o = C_{Zn^{2+}} \cdot (a_{OH^-})^2$.

The value of the formation constant of $Zn(NH_3)_4^{2+}$ was calculated from 10 experimental points and the result is given as $pK_{04} = -10.84 \pm 0.13$ at 25°C.

The value for the formation constant of $Zn(OH)_3(NH_3)^-$ was calculated from 7 experimental points and the result is given as $pK_{31} = -16.94 \pm 0.04$ at 25°C.

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Magnesium chloride; $MgCl_2$; [7786-30-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Adilova, A. A.; Taraskin, D. A. *Tr. Inst. Met. Obogashch., Akad. Nauk Kaz. SSR* 1969, *30*, 45-6.

VARIABLES:
Concentration of $MgCl_2$ at temperatures of 20, 40, 60 and 80°C.

PREPARED BY:
T. Michalowski

EXPERIMENTAL VALUES:
Solubility of $Zn(OH)_2$ in aqueous $MgCl_2$.

t/°C	C_{Zn}/g dm^{-3}	C_{MgCl_2}/g dm^{-3}	C_{Zn}/mol dm^{-3} [a]	C_{MgCl_2}/mol dm^{-3} [a]	pH
20	0.001	52.1	1.5×10^{-5}	0.547	8.05
20	0.005	128.2	7.7×10^{-5}	1.346	7.80
20	0.330	175.0	0.0050	1.838	7.09
20	3.860	283.8	0.059	2.980	6.76
40	0.001	53.3	1.5×10^{-5}	0.560	7.96
40	0.080	122.0	0.0012	1.281	7.72
40	1.530	187.4	0.023	1.968	7.03
40	4.530	288.0	0.069	3.024	6.73
60	0.002	51.8	3.1×10^{-5}	0.544	7.91
60	0.150	129.3	0.0023	1.358	7.67
60	1.780	183.9	0.027	1.931	6.75
60	4.820	289.1	0.074	3.036	6.68
80	0.003	52.3	4.6×10^{-5}	0.549	7.90
80	0.180	117.8	0.0028	1.237	7.48
80	2.070	182.5	0.032	1.916	6.61
80	5.480	287.2	0.084	3.016	6.63

[a] Calculated by the editor.

Editor's note: There is no indication that the precipitate was analyzed and shown to be $Zn(OH)_2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Mixtures of $Zn(OH)_2$ and $MgCl_2$ solutions were agitated in a thermostated (±0.1°C) flask for 11 hours. After filtration the filtrate was analyzed for zinc by polarography. No details are given as to how the pH was measured.

SOURCE AND PURITY OF MATERIALS:
$Zn(OH)_2$ was prepared by using equivalent amounts of $ZnCl_2$ (analytical grade) and NaOH. The precipitate was washed repeatedly with water. The $MgCl_2$ (a pure grade) was recrystallized before being used.

ESTIMATED ERROR:
No details are given.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Glycine; $C_2H_5NO_2$; [56-40-6]

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

ORIGINAL MEASUREMENTS:

Gorzelany, W.; Kulikow, E.; Jablonski, Z. *Rocz. Chem.* 1972, *46*, 781-6.

VARIABLES:

Concentration of glycine.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous solutions of glycine.

$C_{glycine}$/mol dm^{-3}	C_{ZnO}/mol dm^{-3}	$10^4 C_{GL^-}$/mol dm^{-3} [a]	pH
0.01	0.002	1.42	7.95
0.05	0.014	5.60	7.85
0.10	0.034	7.92	7.70
0.15	0.054	9.68	7.61
0.20	0.075	11.20	7.55
0.25	0.097	12.50	7.50
0.30	0.118	14.30	7.48

[a] GL^- is the $C_2H_4NO_2^-$ ion.

On the basis of the above results and some work with paper electrophoresis, the authors conclude that the following complexes are formed: $ZnGL_2$ and $ZnGL_2(OH)_2^{2-}$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were placed in closed flasks at 22°C and shaken. Equilibrium was reached in 8 to 10 hours. The zinc content of the saturated solutions was determined by titration with EDTA. The concentration of the $C_2H_4NO_2^-$ ion was calculated from the pH and the acid dissociation constant of glycine (1.58×10^{-10}).

SOURCE AND PURITY OF MATERIALS:

The water was doubly distilled. The glycine and ZnO were of analytical grade.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Phosphoric acid; H_3PO_4; [7664-38-2]

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

ORIGINAL MEASUREMENTS:

Kozina, T. M.; Lepilina, R. G.; *Zh. Prikład. Khim.* 1973, *46*, 812-6; *J. Applied Chem. USSR* [*Engl. transl.*] 1973, *46*, 861-4.

VARIABLES:

Concentration of phosphoric acid at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of solutions of the $ZnO-P_2O_5-H_2O$ system at 25°C.

mass % P_2O_5	mass % ZnO	$C_{P_2O_5}$/mol kg^{-1} [a]	C_{ZnO}/mol kg^{-1} [a]
60	4.0	11.73	1.37
60.5	3.4	11.80	1.16
61	2.8	11.86	0.95
64.5	2.2	13.64	0.81

[a] The data were converted to mol/kg H_2O by the compiler.

The purpose of this work was to establish the conditions under which various zinc phosphates would crystallize out of solution. For the solutions described in the above Table, the solid phase was $Zn(H_2PO_4)_2 \cdot 2H_3PO_4$. Other zinc phosphates are discussed in the article. However, the conditions described for the crystallization of these other zinc phosphates did not involve the solubilities of either ZnO or $Zn(OH)_2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was approached isothermally in a closed reactor with intensive stirring. Equilibrium was verified by chemical analysis every 3 to 6 hours. The zinc content was determined by a complexiметric titration. P_2O_5 was determined by differential colorimetry of the phosphovanadomolybdate complex (1).

SOURCE AND PURITY OF MATERIALS:

No details are given except that 95% phosphoric acid was used.

ESTIMATED ERROR:

No details are given.

REFERENCES:

1. Moizhes, I. B.; Kuz'menko, M. V.; Kushnir, V. I. *Fosfornaya Prom.* 1970, 3.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) 2,2',2''-nitrilotriethanol; $C_6H_{15}NO_3$; [102-71-6]

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

ORIGINAL MEASUREMENTS:

Mikulski, T.; Kwiecinska, A. *Pr. Nauk, Inst. Chem. Nieorg. Met. Pierwiastkow Rzadkich Politech. Wroclaw* 1973, *16*, 253-7.

VARIABLES:

Concentration of the 2,2',2''-nitrilotriethanol.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous 2,2',2''-nitrilotriethanol.

C_{TEA}/g l^{-1} [a]	C_{TEA}/mol dm^{-3} [a,b]	C_{ZnO}/g l^{-1}	C_{ZnO}/mol dm^{-3} [b]
50	0.34	0.065	8.0×10^{-4}
100	0.67	0.21	2.6×10^{-3}
200	1.34	0.65	8.0×10^{-3}

[a] TEA (triethanolamine) is the 2,2',2''-nitrilotriethanol.

[b] Calculated by the compiler.

The solubility of ZnO was also measured in aqueous solutions of ethylene diamine and of 2-aminoethanol (monoethanolamine), but these data (4 experimental points for each system) are given only in graphical form.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The samples of ZnO were placed in conical flasks, treated with solutions of the amine and shaken for 1 hour on a mechanical shaker. After centrifugation, the quantity of zinc in solution was determined by titration with EDTA. No temperature is specified.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Ponomaryeva, E. I.; Solovyeva, V. D.; Svirchevskaya, E. G.; Orlova, L.F.; Yusupova, E. N. *Tr. Inst. Metal Obogashch. Akad. Nauk Kaz. SSR* 1973, *49*, 59-65.

VARIABLES:

Concentration of NaOH and age of $Zn(OH)_2$ precipitate at 25°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in NaOH solutions at 25°C.[a]

Solid phase	5 mol NaOH dm^{-3}	7.5 mol NaOH dm^{-3}
Freshly precipitated $Zn(OH)_2$	39.2 g dm^{-3}	80.1 g dm^{-3}
$Zn(OH)_2$ aged for 1 month	32.7 g dm^{-3}	60.0 g dm^{-3}
$Zn(OH)_2$ aged for 6 months	29.9 g dm^{-3}	56.0 g dm^{-3}

In another experiment using only 7.5 mol NaOH dm^{-3} as solvent and shaking the mixture for 30 days, the following results are reported.

Freshly precipitated $Zn(OH)_2$	80.0 g dm^{-3}
$Zn(OH)_2$ aged for 1 month	78.2 g dm^{-3}
$Zn(OH)_2$ aged for 6 months	74.9 g dm^{-3}

[a] There is no indication whether the g dm^{-3} values refer to Zn, ZnO, or $Zn(OH)_2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium was reached isothermally at room temperature (said to be 25°C) by shaking for 60 days on a mechanical shaker. No information is given about any analytical procedures.

SOURCE AND PURITY OF MATERIALS:

The $Zn(OH)_2$ presumably was prepared by the addition of NaOH to a solution of $ZnSO_4$ (1). The precipitate was washed twice with distilled water. It was kept in a moist state in a closed flask.

ESTIMATED ERROR:

This cannot be estimated because of lack of sufficient information.

REFERENCES:

1. Soloveva, V. D.; Bobrova, V. V.; Orlova, L. F.; Adeyschvili, E. U. *Tr. Inst. Metal. Obogashch. Akad. Nauk Kaz. SSR* 1973, *49*, 45.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Khodakovskii, I. L.; Yelkin, A.E. *Geokhimiya* 1975, No. 10, 1490-8; *Geochem. Int. (Engl. transl.)* 1975, *12*, 127-33.

VARIABLES:

Concentration of NaOH and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of ZnO in aqueous NaOH

C_{NaOH}/mol kg^{-1}	$10^6 C_{Zn}$/mol kg^{-1} 100°C	150°C	200°C
0.00	31 ± 3	43 ± 15	49 ± 8
0.00045	1.8	4.6 ± 1.5	6.9
0.0016	2.8 ± 0.4	3.1	4.9 ± 1.0
0.005	6.1	7.6	6.9 ± 1.5
0.0095	11.5 ± 0.5	13.8	13.8 ± 2.5
0.018	-----	27.8	-----
0.0246	-----	37.4 ± 0.8	-----
0.0435	64 ± 10	-----	84 ± 8
0.058	-----	93.9	-----
0.076	-----	137.7	-----
0.087	127	164	192 ± 2

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The mixtures were contained in an autoclave and the pressure was approximately the saturated vapor pressure of pure water at the working temperature. Equilibrium was determined by analysis for zinc content. This was done by atomic absorption spectrophotometry.

SOURCE AND PURITY OF MATERIALS:

Double distilled water was used. The NaOH solutions were carbonate-free. No other details concerning purity are given.

ESTIMATED ERROR:

No details are given but the results given in the Table are averages of up to four separate determinations.

REFERENCES:

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Arsenic(V) oxide; As_2O_5; [1303-28-2]

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

ORIGINAL MEASUREMENTS:

Elghorche-Choubani, C.; Kbir-Ariguib, N.; Saugier-Cohen Adad, M. *Bull. Soc. Chim. Fr.* 1981, No. 7-8, 305-8.

VARIABLES:

Concentration of As_2O_5 at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of equilibrium solutions of the $ZnO-As_2O_5-H_2O$ system at 20°C.

mass % As_2O_5	mass % ZnO	Solid phase[a]	$C_{As_2O_5}$/mol kg^{-1}[b]	C_{ZnO}/mol kg^{-1}[b]
0.2	- - -	A	0.0087	- - -
0.3	0.2	"	0.013	0.025
0.3	0.2	A + B	0.013	0.025
0.4	0.1	B	0.017	0.012
0.4	0.1	"	0.017	0.012
0.4	0.2	B + C	0.018	0.025
0.4	0.2	C	0.018	0.025
0.5	0.3	"	0.022	0.037
0.5	0.4	C + D	0.022	0.050
0.6	0.4	D	0.026	0.050
0.7	0.3	"	0.031	0.037
0.8	0.2	"	0.035	0.025
2.5	0.4	"	0.112	0.051
3.0	0.4	"	0.135	0.051
3.7	1.3	"	0.169	0.168

[a] A = $5ZnO \cdot As_2O_5 \cdot H_2O$; B = $4ZnO \cdot As_2O_5 \cdot H_2O$; C = $3ZnO \cdot As_2O_5 \cdot 8H_2O$; D = $2ZnO \cdot As_2O_5 \cdot 3H_2O$.

[b] The data were converted to mol/kg H_2O by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Mixtures of ZnO and aqueous As_2O_5 were allowed to reach equilibrium isothermally. This sometimes required several months. Zinc content was determined by a compleximetric titration. Arsenic was determined by an iodometric titration (1). The composition of the solid phases was determined by the wet-residues method of Schreinemakers.

SOURCE AND PURITY OF MATERIALS:

The ZnO was of reagent grade quality. As_2O_5 was prepared by the oxidation of As_2O_3 (2).

ESTIMATED ERROR:

No details are given

REFERENCES:

1. Fleury, P. *J. Pharm. Chim.* 1920, *21*, 385.

2. Guerin, H. *Bull. Soc. Chim. Fr.* 1955, 1536.

COMPONENTS:

(1) Zinc oxide; ZnO; [1314-13-2]

(2) Arsenic(V) oxide; As_2O_5; [1303-28-2]

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

ORIGINAL MEASUREMENTS:

Elghorche-Choubani, C.; Kbir-Ariguib, N.; Saugier-Cohen Adad, M. *Bull. Soc. Chim. Fr.* 1981, No. 7-8, 305-8.

EXPERIMENTAL VALUES, contd.

Composition of equilibrium solutions of the $ZnO-As_2O_5-H_2O$ system at 20°C.

mass % As_2O_5	mass % ZnO	Solid phase[a]	$C_{As_2O_5}$/mol kg^{-1}[b]	C_{ZnO}/mol kg^{-1}[b]
6.3	1.2	D	0.296	0.159
14.1	3.2	"	0.742	0.475
26.8	3.5	"	1.67	0.617
38.8	3.6	"	2.93	0.768
47.5	3.9	"	4.25	0.986
56.1	2.3	"	5.87	0.679
59.6	2.3	"	6.81	0.742
62.2	2.3	D + E	7.62	0.796
64.0	0.7	E	7.89	0.244
66.3	0.5	"	8.69	0.185
67.6	0.5	"	9.22	0.193
67.8	0	F	9.16	- - -
68.6	0.3	"	9.60	0.119
69.8	0.8	G	10.33	0.334
69.0	0.	H	9.68	- - -
65.4	0.6	I	8.37	0.217

[a] D = $2ZnO \cdot As_2O_5 \cdot 3H_2O$; E = $ZnO \cdot 2As_2O_5 \cdot 8H_2O$; F = $ZnO \cdot 2As_2O_5 \cdot 6H_2O$; G = $ZnO \cdot 2As_2O_5 \cdot 3H_2O$; H = $ZnO \cdot 2As_2O_5 \cdot 1.5H_2O$; I = $ZnO \cdot 2As_2O_5 \cdot 10H_2O$.

[b] The data were converted to mol/kg H_2O by the compiler.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Ammonium nitrate; NH_4NO_3; [6484-52-2] (3) Ammonium sulfate; $(NH_4)_2SO_4$; [35089-90-8] (4) Ammonium chloride; NH_4Cl; [12125-02-9] (5) Water; H_2O; [7732-18-5]	Herz, W. Z. *Anorg. Chem.* 1900, *23*, 222-7.
VARIABLES: Solvent composition	PREPARED BY: T. P. Dirkse

EXPERIMENTAL VALUES:

Composition of equilibrium solution of $Zn(OH)_2$ dissolved in aqueous solutions of ammonium salts.

mol Zn(II) dm^{-3} [a]	mol NH_4^+ dm^{-3} [a]	Ammonium salt used
0.0038	0.58	NH_4Cl
0.0025	0.45	"
0.0015	0.30	"
0.006	0.85	NH_4NO_3
0.0038	0.64	"
0.003	0.56	"
0.002	0.43	"
0.001	0.22	"
0.012	1.47	$(NH_4)_2SO_4$
0.0045	0.74	"
0.002	0.37	"

[a]The author used the equation $Zn(OH)_2 + 2\ NH_4^+ = Zn^{2+} + 2\ NH_4OH$ to calculate these results from the analysis for free NH_3 in the solutions. He made no allowance for the possible formation of zinc-ammonia complex ions.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Solid $Zn(OH)_2$ was added to an aqueous solution of an ammonium salt. The mixture was placed in a stoppered flask and allowed to stand with frequent shaking. After equilibrium was reached a sample of saturated solution was analyzed for free NH_3. The method of analysis is not described. No temperature is specified but the work presumably was carried out at room temperature.	Pure, dry $Zn(OH)_2$ was used. There is no information about the quality or purity of any of the other materials that were used.
	ESTIMATED ERROR: No details are given.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Potassium hydroxide; KOH; [1310-58-3] (4) Water; H_2O; [7732-18-5]	Moir, J. *Proc. Chem. Soc.* 1905, *21*, 310-1.
VARIABLES: Alkali concentration.	PREPARED BY: T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in aqueous NaOH.

mol NaOH dm^{-3}	mol $Zn(OH)_2$ dm^{-3} [a]	mol $Zn(OH)_2$ dm^{-3} [b]
7.5	1.692	1.89
2.5	0.48	0.452
1.3	0.17	0.171
0.5	0.040	0.0364
0.1	0.0035	0.00265
0.05	0.0010	0.00097
0.01	0.0002	0.000135

[a]These results were obtained experimentally.

[b]These results were calculated from the equation $y = 0.004x\left[\frac{79x + 6}{x + 2}\right]$

Solubility of $Zn(OH)_2$ in aqueous KOH

mol KOH dm^{-3}	mol $Zn(OH)_2$ dm^{-3} [a]	mol $Zn(OH)_2$ dm^{-3} [b]
5.5	1.36	1.291
2.0	0.32	0.328
1.5	0.21	0.2033
1	0.110	0.1132

[a]These results were obtained experimentally.

[b]These results were calculated from the equation

$y = 0.004x\left[\frac{79x + 6}{x + 2}\right]$ where x = mol KOH dm^{-3} and y = mol $Zn(OH)_2$ dm^{-3}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
No details are given but, presumably, equilibrium was reached by two methods; (a) excess $Zn(OH)_2$ was added to the alkali solution; and (b) water was added to a saturated solution of $Zn(OH)_2$ in the aqueous alkali. The experiments apparently were carried out at room temperature, but this is not specified. No analytical procedures are described.	No details are given.
	ESTIMATED ERROR: No details are given.
	REFERENCES:

COMPONENTS:
(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Hydrochloric acid; HCl [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Reichle, R. A.; McCurdy, K. G.; Hepler, L.G.
Can. J. Chem. 1975, *53*, 3841-5.

VARIABLES:
pH of solvent and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Zn(OH)_2$ in solutions of varying pH.

pH	$10^5 C_{Zn}$/mol kg^{-1}	pH	$10^5 C_{Zn}$/mol kg^{-1}	pH	$10^5 C_{Zn}$/mol kg^{-1}
		temp., 12.5°C			
13.80	327	11.51	0.50	8.99	0.46
13.71	216	11.50	0.31	8.55	1.33
13.51	91.8	11.10	0.24	7.96	13.2
13.34	45.1	9.83	0.23	7.70	48.3
13.18	25.2	9.49	0.23	7.32	265
12.85	6.12	9.27	0.31	7.22	415
12.21	1.68	9.14	0.38	7.06	844
		temp., 25.0°C			
13.19	178	10.14	0.31	8.41	1.30
12.97	67.3	9.43	0.38	7.90	4.74
12.77	28.3	9.18	0.54	7.63	17.2
12.52	11.2	8.97	0.61	7.44	32.1
12.29	5.74	8.91	0.92	7.31	49.7
11.05	0.54	8.72	0.84	7.00	204
10.84	0.46	8.67	1.22		
		temp., 50.0°C			
12.50	261	10.75	1.38	8.27	1.45
12.24	88.7	10.25	0.92	8.04	1.84
11.99	33.7	10.02	0.84	7.82	2.43
11.76	14.8	9.55	0.76	7.54	4.97
11.55	8.03	9.08	0.87	7.26	10.7
11.25	2.92	8.77	0.99	7.05	19.6
10.99	2.14	8.52	1.15	6.75	53.4

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Equilibrium was approached isothermally by shaking the mixtures gently for about two weeks in a constant temperature bath. HCl(aq) or NaOH(aq) was added to adjust the pH of the solvent. The concentration of zinc was determined by atomic absorption spectroscopy. The pH was measured with a glass electrode.

SOURCE AND PURITY OF MATERIALS:
The crystalline ε-$Zn(OH)_2$ was prepared as described by others (1). No information is given about the source of the other materials.

ESTIMATED ERROR:
Uncertainties in the experimentally determined solubilities are about 5%.

REFERENCES:
1. Dietrich, H. G.; Johnston, J.
J. Am. Chem. Soc. 1927, *49*, 1419.

COMPONENTS:

(1) Zinc hydroxide; $Zn(OH)_2$; [20427-58-1]

(2) Sodium hydroxide; NaOH; [1310-73-2]

(3) Hydrochloric acid; HCl [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Reichle, R. A.; McCurdy, K. G.; Helpler, L. G. *Can. J. Chem.* 1975, 53, 3841-5.

EXPERIMENTAL VALUES, contd.

Solubility of $Zn(OH)_2$ in solutions of varying pH,

pH	$10^5 C_{Zn}$/mol kg^{-1}	pH	$10^5 C_{Zn}$/mol kg^{-1}	pH	$10^5 C_{Zn}$/mol kg^{-1}
		temp., 75.0°C			
12.22	1029	10.54	3.06	8.55	1.84
11.95	319	10.22	2.14	8.38	2.06
11.68	104	10.01	2.06	8.08	2.06
11.35	29.1	9.71	1.84	7.89	1.99
11.14	12.6	9.54	1.76	7.65	2.37
10.85	5.27	8.93	1.68	7.18	7.22
				6.94	13.1

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Shlyapnikov, D. S.; Shtern, E. K.
Dokl. Akad. Nauk SSSR 1975, *225*, 428-31.

VARIABLES:
NaCl concentration and pressure of CO_2.

PREPARED BY:
T. Michalowski

EXPERIMENTAL VALUES:

Solubility of ZnO at 20°C under a CO_2 pressure of 50 atm.

	in water	in 4 mol NaCl dm^{-3}
g ZnO dm^{-3}	3.8712	3.2529
mol ZnO dm^{-3} [a]	0.0475	0.040
pH of solution	5.98	5.50

[a] Calculated by compiler.

An accompanying graph shows that the solubility of ZnO at 200°C and P_{CO_2} = 100 atm increases from about 0.3 g dm^{-3} in pure water to about 0.9 g dm^{-3} in 2 mol NaCl dm^{-3}. The solubility is attributed to the transformation of ZnO to $Zn(HCO_3)_2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Solution and solid ZnO were shaken in an autoclave at the prescribed temperature for 24 hours. CO_2 was introduced as a solid. Metal analysis was done complexiметrically and spectrophotometrically. No further details are given.

SOURCE AND PURITY OF MATERIALS:
No details are given.

ESTIMATED ERROR:
This cannot be determined from the information given in the article.

REFERENCES:

COMPONENTS:
(1) Zinc oxide; ZnO; [1314-13-2]
(2) Ammonia; NH_3; [7664-41-7]
(3) Ammonium sulfate; $(NH_4)_2SO_4$; [35089-90-9]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Guy, S.; Broadbent, C. P.; Jackson, D. J. D.; Lawson, G. J. *Hydrometallurgy* 1982, *8*, 251-60.

VARIABLES:
Concentration of NH_3 and $(NH_4)_2SO_4$ at 298 K.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:
Solubility of ZnO in NH_3-$(NH_4)_2SO_4$ solutions at 25°C.

mol NH_3 dm^{-3}	mol $(NH_4)_2SO_4$ dm^{-3}	g Zn dm^{-3}	mol ZnO dm^{-3} [a]
2	2	47	0.72
3	3	81	1.24
4	3	168.3	2.57

[a] calculated by compiler.

The article contains a graph of the solubility of ZnO in a variety of NH_3-$(NH_4)_2SO_4$ solutions. However, the graphs show no data points but only smoothly drawn isosolubility curves. The solubility of ZnO increases as the concentration of NH_3 increases. It also increases with increasing $(NH_4)_2SO_4$ concentration. The authors assume that the following reaction is responsible for the solubility of ZnO is these solutions.

$$2\ NH_3 + ZnO + (NH_4)_2SO_4 = Zn(NH_3)_4SO_4 + H_2O$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Solvent and ZnO were placed in screw-capped polyethylene bottles and agitated in a thermostat for 16-18 hours. After filtration the zinc content of the filtrate was determined by atomic absorption spectrophotometry.

SOURCE AND PURITY OF MATERIALS:
Analytical reagent grade materials were used.

ESTIMATED ERROR:
The temperature was controlled to ± 0.5 K but no information is given about the control or reproducibility of any other procedures or measurements.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

CRITICAL EVALUATION:

Cadmium, like zinc, ordinarily appears only in the dipositive form in its compounds. Therefore, with respect to its oxide and hydroxide we have to consider only CdO and $Cd(OH)_2$. However, like zinc, the hydroxide, which is usually produced by adding OH^-ions to an aqueous solution of a cadmium salt, is not of uniform composition. Analysis of the products obtained shows an impurity of at least 0.5%. The impurity usually consists of the anion of the cadmium salt that was used in the preparation. This raises the question whether we are dealing with a randomly contaminated $Cd(OH)_2$ or a $Cd(OH)_2$ together with some basic salt. This question will arise again as we discuss the solubility values reported for $Cd(OH)_2$.

Solubility in water. Three papers deal with the solubility of CdO in water. In two of these the values were obtained from electrolytic conductance measurements, either by a conductimetric titration or from specific conductance values (using literature values for individual ionic conductances). In each of these papers (1, 2) concern was expressed about the possible influence of dissolved CO_2 and how to correct for it. The one author (2) was critical of the work of the others (1) with respect to the method used to correct for the presence of the dissolved CO_2. The temperature was controlled at 298 K in one instance (2) but was allowed to vary in the range 291-293 K in the other work (1). More recently, the solubility of CdO in H_2O at 298 K has been determined by chemical analysis as part of a study dealing with the effect of $(NH_4)_2SO_4$ on the solubility of CdO in water (3). Here the solubility of CdO in water at 298 K was determined to be 9×10^{-5} mol dm^{-3}. A minimum of experimental detail is given. Consequently, only a tentative value of 5.4×10^{-5} mol dm^{-3} at 298 K can be given. This is an average of the two values reported (2,3).

Six papers report a value for the solubility of $Cd(OH)_2$ in water. The results range over about an order of magnitude. This is, in some cases, a reflection of the purity or impurity of the $Cd(OH)_2$ and of the method used to make the solubility measurement. It may also be a reflection of the age of the precipitate (4).

In one paper the solubility was determined using several samples of $Cd(OH)_2$ (2). Each sample was prepared by a different method. A significant difference in the solubility values was found, although, in each case the order of magnitude was the same, i.e., 10^{-5} mol dm^{-3}. This value is very similar to that for the solubility of CdO reported above.

The recommended value for the solubility of $Cd(OH)_2$ in water at 298 K is 1.5×10^{-5} mol/kg H_2O as determined by Gayer and Woontner (5). Piater (2) reported a value of 1.2×10^{-5} mol dm^{-3} at 298 K, but this value may be in error because of impurities in the $Cd(OH)_2$ and the imprecision of the experimental work. There are two other values reported for the solubility of $Cd(OH)_2$ at 298 K. One of these is 1.75×10^{-5} mol dm^{-3} (6). (This value is taken from Chemical Abstracts. The original article was not available to us.) The other value is 8.5×10^{-6} mol dm^{-3} (7), but this value cannot be accepted because of the meager amount of information dealing with the way in which this value was obtained. The method involved the potentiometric titration of an aqueous solution of a cadmium salt with NaOH, so that the nature and purity of the precipitating phase is suspect. In one other paper the solubility of $Cd(OH)_2$ in water is given as a limiting (or extrapolated) value in which the solubility of $Cd(OH)_2$ was studied as a function of H_2O_2 concentration (8). However, it appears that the results reported are in error because calculations from the data reported show a solubility of the order of 10^{-4} mol dm^{-3} at both 273 and 293 K. This is 10 times the solubility at 298 K. It is possible that the column labelled "wt %" should be "g CdO/kg". This would give results in agreement with the work reported by others and discussed above. Because of this uncertainty the results reported in ref. (8) cannot be considered as reliable.

A value of 7.2×10^{-6} mol dm^{-3} has also been reported for the solubility of $Cd(OH)_2$ in water (9). The temperature was not controlled, but in some 40 samples it varied from 290 to 295 K. These results are not considered reliable for the following reasons:

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

CRITICAL EVALUATION:

(a) the pH of the water used varied from 5.9 to 9.0; (b) the values were dependent on the type of filtering medium that was used; (c) the $Cd(OH)_2$ was apparently a commercially available material and no information is given as to its purity; and (d) the average deviation of the individual results from the mean is about 33%.

In summary, the review of the solubilities of CdO and $Cd(OH)_2$ in water strongly suggests that these values are identical at 298 K.

The solubility product of $Cd(OH)_2$ has been evaluated by means of a variety of methods, and a wide range of values has been reported. Schindler (4) maintained that the value obtained depends on the age of the precipitate. He analyzed the saturated solutions over a period of time and found that only after about 100 hours did the solubility product value become constant. Up to this time the solid phase undergoes some subtle changes. The freshly precipitated $Cd(OH)_2$ and a sample of $Cd(OH)_2$ that had been in contact with the solution (an "aged sample") gave the same X-ray diffraction pattern, so the process of aging is not a matter of a change in crystal structure. Perhaps it is a change in particle size. Others (10) had noted this same phenomenon and suggested that perhaps during the aging process the crystallinity of the precipitate becomes more perfect. Schindler also pointed out that solubility product values that had been determined by using "aged" samples of $Cd(OH)_2$ were in general agreement with each other while solubility product values determined with the use of freshly precipitated $Cd(OH)_2$ tended to be widely scattered.

The composition of the precipitate also is a significant factor in determining the solubility product of $Cd(OH)_2$. One study (10) showed that $Cd(OH)_2$ formed by adding NaOH or KOH to a cadmium salt solution is generally contaminated with the anion of the cadmium salt. There was less contamination when the salt selected was $Cd(NO_3)_2$. This was a confirmation of earlier work (11) but even so the $OH^-:Cd^{2+}$ ratio in the precipitate was 1.96 rather than 2.

Another factor affecting the value of the solubility and the solubility product of $Cd(OH)_2$ is the total ionic strength of the solution. For example, the solubility product constant expressed as a concentration product was 1.66×10^{-14} mol^3 dm^{-9} when the total ionic strength was 0.042 mol dm^{-3} while it was 7.60×10^{-15} mol^3 dm^{-9} when the total ionic strength was 0.0025 mol dm^{-3} (10).

Thus, there are at least four factors that determine the value of the solubility and solubility product of $Cd(OH)_2$ in aqueous solutions. These factors are: temperature, purity of the precipitate, age of the precipitate, and total ionic strength of the solution. In most papers the temperature is specified and was controlled. However, in many papers very little, if anything, is said specifically about the other factors. This, doubtless, accounts for the wide range of values reported in the literature.

Three papers report a thermodynamic value for the solubility product. In one of these (10), this value was arrived at by extrapolation to zero ionic strength and also by the use of the Debye-Huckel equation for activity coefficients. This value for an "aged" precipitate is given as 5.9×10^{-15} at 298 K. Unfortunately, this paper does not give the experimental data from which the calculations and extrapolations were made. Consequently, while this value is in good agreement with other reported results, it cannot be accepted as a recommended value. In another work (12) the activity product of $Cd(OH)_2$ was determined incidentally to a study of the basic cadmium bromides. The activity of Cd^{2+} was determined with a dropping cadmium amalgam electrode. No numerical experimental data are given but it is merely stated that the activity product at 298.1 K is 8.1×10^{-15} as determined from a solution to which the quantities of Cd^{2+} and OH^- ions that had been added were equivalent to those needed for the formation of $Cd(OH)_2$. The precipitate was aged by heating it at 373 K for one hour. However, no investigation was made of the precipitate so there is some possibility that the precipitate may not have been a pure $Cd(OH)_2$.

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

CRITICAL EVALUATION:

In a somewhat similar work (13) the activity product at 291.0 K is given as -log K°_{so} = 14.5820. This was arrived at by determining the activity product of $Cd(OH)_2$ in a series of $CdSO_4$ solutions and then extrapolating to $[Cd^{2+}] = 0$. But again no analysis was made of the precipitate. Consequently, this value can at present only be considered a tentative value.

So far as thermodynamic values for the solubility product of $Cd(OH)_2$ are concerned only the following tentative values can be given at this time: 2.6×10^{-15} at 291 K (13), and 5.9×10^{-15} at 298 K (10).

There are several papers which report the solubility product as a concentration product. On the basis of calculations involving semiempirical relationships, Maijs (14) suggests a value of 10^{-14} mol^3 dm^{-9}. However, no experimental data are given nor is a temperature specified. Marcus (15) titrated solutions of cadmium salts with NaOH and measured the pH at which the first precipitate occurred. This was done at 298.1 K in solutions of constant ionic strength = 3 mol dm^{-3}. Because of imprecision in the pH data the only conclusion is a lower limit to the value of the solubility product. This lower limit is given as pK_{so} = 15.6.

From results reported in a study of the solubility of CdO in aqueous $(NH_4)_2SO_4$, a hybrid solubility product $[C_{Zn}{}^{2+} \cdot (a_{OH^-})^2]$ at 298 K is calculated to be 2.26×10^{-14} mol^3 dm^{-9} (3). Another value for this hybrid or "conventional" (10) type of solubility product is 3.1×10^{-14} mol^3 dm^{-9} at 298 K (11). Both these values may be a little large. It is not stated whether the $Cd(OH)_2$ was freshly precipitated when the measurements were made or whether the $Cd(OH)_2$ had been allowed to age first. Therefore, the recommended values for the solubility product expressed in concentration units are: log K_{so} = -14.41 > 0.05 at 298 K in 3 mol $NaClO_4$ dm^{-3} (4), and log K_{so} = -14.6 (s=>0.1) at 298 K in 1 mol $NaClO_4$ dm^{-3} (16). In the latter work the precipitate was allowed to stand about a week before measurements were made.

Where it appears that a freshly precipitated $Cd(OH)_2$ was used as the solid phase the values for the solubility product are somewhat larger than those given above. This is consistent with the general observation that the solubility of the precipitate decreases during the aging process (4,10). Such reported values (expressed as concentration products) are: 3.1×10^{-14} mol^3 dm^{-9} (11), 5.0×10^{-15} mol^3 dm^{-9} (2).

A polarographic study of the cadmium amalgam electrode in a saturated solution of $CdSO_4$ as a function of pH has been made (17). The shift in half-wave potential with pH above pH = 11 was considered to be due to control of the Cd^{2+} ion concentration at the surface of the dropping electrode by the solubility product relationship. The author says that as a result of this treatment the K_{so} for $Cd(OH)_2$ is 1.6×10^{-13} mol^3 dm^{-9} at 298 K. However, the necessary numerical data for making such a calculation are not included in the article.

De Wijs (18) studied the composition and stability of cadmium-ammonia complex ions by measuring the pressure of NH_3 in equilibrium with such solutions. Occasionally only a precipitate of $Cd(OH)_2$ was formed from such solutions. In those cases the measurements were used to calculate the solubility product constant. Again, no data are given in the article, but the author says the data she collected lead to a value of 2.5×10^{-14} mol^3 dm^{-9} for the solubility product constant of $Cd(OH)_2$ at 298 K.

An exception to the above generalization is the value 2×10^{-20} mol^3 dm^{-9} (19). This latter value was estimated from an ion exchange study using ^{109}Cd and assumed that Cd was present in solution only as $Cd(OH)^-_3$. However there is no other work in the literature that reports a value near this one.

Solubility in acid and alkaline aqueous solutions. The following reactions may represent the process of dissolution of $Cd(OH)_2$ in aqueous solutions.

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

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$$Cd(OH)_2(s) + 2\ H^+ = Cd^{2+} + 2\ H_2O \quad (1)$$
$$Cd(OH)_2(s) + H^+ = CdOH^+ + H_2O \quad (2)$$
$$Cd(OH)_2(s) = Cd(OH)_2(sln) \quad (3)$$
$$Cd(OH)_2(s) = Cd^{2+} + 2\ OH^- \quad (4)$$
$$Cd(OH)_2(s) + OH^- = Cd(OH)^-_3 \quad (5)$$
$$Cd(OH)_2(s) + 2\ OH^- = Cd(OH)^{2-}_4 \quad (6)$$

The corresponding concentration ratios or products are:

$$K_1 = C_{Cd^{2+}}/(C^{H+})^2 \quad (7)$$
$$K_2 = C_{CdOH^+}/C_{H^+} \quad (8)$$
$$K_3 = C_{Cd(OH)2} \quad (9)$$
$$K_4 = C_{Cd^{2+}} \cdot (C_{OH^-})^2 \quad (10)$$
$$K_5 = C_{Cd(OH)^-_3}/C_{OH^-} \quad (11)$$
$$K6 = C_{Cd(OH)^{2-}_4}/(C_{OH^-})^2 \quad (12)$$

Reaction (4) is the solubility product reaction which has been discussed above. The ions $Cd(OH)^-_3$ and $Cd(OH)^{2-}_4$ are sometimes written in a dehydrated form as $HCdO^-_2$ and CdO^{2-}_2, respectively.

Reactions (1) to (4) are the predominant ones in acidic and neutral solutions. Only one paper gives solubility data in acid solutions (5). The acid range was very limited because of the basicity of the $Cd(OH)_2$. As the acidity of the solvent increased it was difficult to maintain a solid phase of $Cd(OH)_2$ in equilibrium with the solution. As a result, there are no solubility data from which K_1 can be evaluated.

In the region of slight acidity the solubility of $Cd(OH)_2$ decreased with decreasing H^+ ion concentration (or increasing OH^- ion concentration). This decrease in solubility also continued on into the alkaline region until a minimum in solubility was reached in a slightly alkaline solution. This decrease in solubility can be explained by assuming that reaction (2) is the dominant one in this pH region. On the basis of this assumption the limited amount of data of Gayer and Woontner (5) gives a value of 1.5×10^4 at 298 K. for K_2. One other paper (16) contains information from which a value of K_2 can be calculated. However, this information does not consist of solubility data found in the paper but of a calculated formation constant for the ion $CdOH^+$. This value, $10^{4.7}$, was derived by solving several equations simultaneously. These equations were based on data (not given in the paper) for the solubility of $Cd(OH)_2$ in NaOH solutions. Using the value of this formation constant, K_2 is calculated to be 1.3×10^4. This is in good agreement with the value based on the data of Gayer and Woonter (5).

One other paper gives data for the solubility of $Cd(OH)_2$ in the very dilute alkaline region approaching the solubility minimum (20). The data are reported for a temperature of 297.5 K. The data are not numerous but a value for K_2 calculated from them is 3.4×10^5. This is ten times the values given above. The discrepancy between the data of Gayer and Woontner (5) and of Ryan, et al. (20) lies in the solubility values reported for $Cd(OH)_2$ in the very dilute NaOH region. While the values of Gayer and Woontner are larger than those of Ryan, et al., at most concentrations of NaOH, Figures 1 and 2, yet in the very dilute solutions (too dilute to show up on Figure 2) the values of Gayer and Woontner are the lower ones. The difference cannot be ascribed to the 0.5 K temperature difference. A possible explanation is that by maintaining a constant ionic strength (by the addition of perchlorate ions), the solubility of $Cd(OH)_2$ was increased due to the increased total ionic concentration.

The data of Gubeli and Taillon (16) serve as another indication of the difficulty in determining precise solubility values in the vicinity of pH = 7-12. While their values

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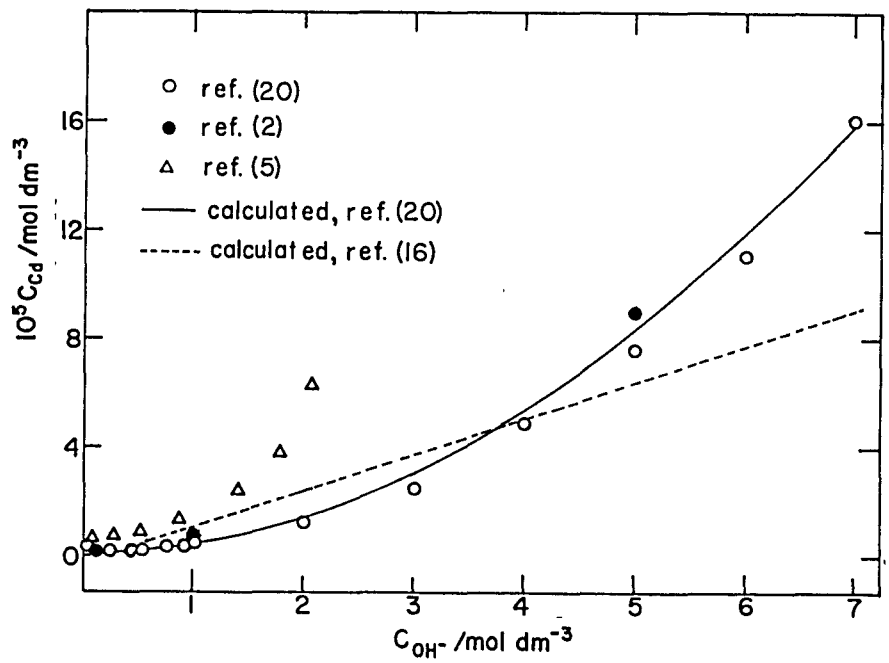

Figure 1. Solubility of $Cd(OH)_2$ in alkaline solutions at 298 K.

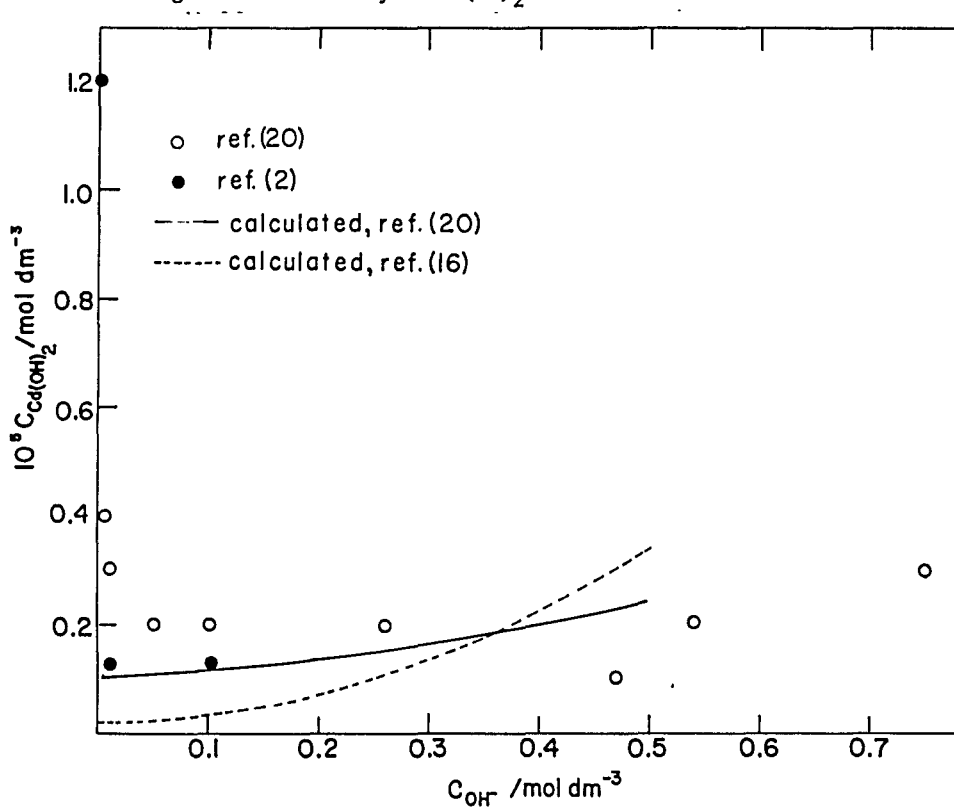

Figure 2. Solubility of $Cd(OH)_2$ in dilute alkaline solutions at 298 K.

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O, [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

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are lower at the solubility minimum, yet below pH = 9 their values tend to become at least ten times larger than those reported by others.

The tentative value for K_2 at 298 K is 1.3×10^{-4} (16) because the results in this work agree best with the tentative value for the minimum solubility to be discussed next.

The point of minimum solubility of $Cd(OH)_2$ in aqueous solutions is at a pH slightly alkaline to the pH of neutrality. However, because of the low concentrations involved it is difficult to determine exactly where the solubility minimum is. At 298 K it was found between 0.01 and 0.1 mol NaOH dm^{-3} (2) or between 10^{-4} and 10^{-2} mol NaOH dm^{-3} (5). Gubeli and Taillon (16) located the minimum solubility between pH = 11-13, or about 10^{-1} to 10^{-3} mol NaOH dm^{-3}. They present data only in graphical form but they apparently collected much more data in this region than did the others. At 297.5 K the minimum is said to be between 0.05 and 0.1 mol NaOH dm^{-3} (20). These latter investigators determined this minimum at two different total ionic strengths: 1 and 7 mol dm^{-3}. There was little difference in solubility values at these two total ionic strengths. The solubility of $Cd(OH)_2$ at this minimum is given as 1×10^{-6} mol dm^{-3} (20), 1.3×10^{-6} mol dm^{-3} (2), 3.5×10^{-6} mol dm^{-3} (5), and about 4.3×10^{-7} mol dm^{-3} (16).

A lower value of the solubility of CdO at the minimum was obtained in work at constant ionic strength of 3 mol-dm^{-3} (ionic strength was maintained by adding $NaClO_4$) at 298 K (21). The method of Schindler (4) was modified by using a solubility column (22). The data are presented only in the form of a graph from which it appears that the minimum solubility is about $10^{-6.7}$ mol dm^{-3} at pOH = 1.2 to 3.7. The authors consider the data of Schindler (4) to be the norm and admit that their data do not agree completely with his, possibly because of a slight contamination of the solid $Cd(OH)_2$ phase. In both refs. (16) and (21) there are many experimental data points around the minimum solubility. The results of these two investigations are in fairly good agreement considering the differences in total ionic strength, the small values involved, and the difficulty of interpolation from a fairly small graph. Therefore, in summary, the tentative value for the minimum solubility of $Cd(OH)_2$ is 3×10^{-7} mol dm^{-3} at 298 K and occurs in the region pH = 10 to 13.

A common assumption is that at the solubility minimum the main solute species is undissociated $Cd(OH)_2$. Consequently, the minimum solubility will be the value of K_3. This value is tentatively given as 3×10^{-7} mol dm^{-3} at 298 K.

Four papers give numerical data for the solubility of $Cd(OH)_2$ in NaOH solutions. In two of these (2, 5) the temperature was maintained at 298 K, in another (20) it was 297.5 K, and in a third (23) it was not specified. A summary of these results is given on Figures 1 and 2. The data from ref. (23) are not included on these Figures because insufficient information is given about the experimental procedure used in obtaining these values. A difference in total ionic strength (20) caused very little difference in solubility. The solubility values of Gayer and Woontner (5) are significantly higher than those in the other two papers. Therefore, in the subsequent calculations the data of ref. (20) will be used even though the temperature is 297.5 rather than 298 K.

As the alkalinity of the solvent increases beyond the point of minimum solubility, reactions (5) and (6) become more prominent. One paper (16) does not consider the $Cd(OH)_3^-$ ion to be present to any significant extent and therefore has no calculations with respect to any of its characteristics. Gayer and Woontner (5) used their experimental data to calculate equilibrium constants for different reactions and found that only reaction (5) gave a constant value for the equilibrium constant in the range 0.1 to 1 mol NaOH dm^{-3}. The value of K_5 calculated from their data is 2.1×10^{-5} at 298 K (this is a concentration ratio). However, as noted above, the solubility results reported in that paper are higher than those reported by others in the same region, see Figure 1.

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(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

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The data of ref. (20) in this same region give a value of 1.2×10^{-6} for K_5 (also a concentration ratio). This value is based on a value for a coefficient in an equation that was developed to fit the solubility data. An analysis of these data using a method described previously (24) gives a value of 2.5×10^{-6} for K_5. This value is 1/10 of that calculated by Gayer and Woontner (5), and reflects the higher solubility data reported in ref. (5). The suggested tentative value for K_5 is 2×10^{-6} at 298 K (this is a concentration ratio). The difficulty with this and other equilibrium constant values for reactions involving CdO or $Cd(OH)_2$ is the paucity of experimental data reported in the literature. This, in turn, may be a reflection of the experimental and analytical difficulties associated with this system.

Apparently reaction (6) becomes prominent only at NaOH concentrations above 1 mol dm^{-3}. The only data available here are those at 297.5 K (20). These are really insufficient on which to base a conclusion as to the value of K_6.

Two attempts have been made to develop an equation to describe the solubility of $Cd(OH)_2$ in NaOH solutions (16, 20). In each of these there is one coefficient from which a value for K_6 can be extracted. One such value is 1.3×10^{-5} mol^{-1} dm^3 (16). The other is 3.1×10^{-6} mol^{-1} dm^3 (20). An analysis of the data in the latter paper using a method described previously (24) gives a value of 1.4×10^{-6} mol^{-1} dm^3. The best tentative value for K_6 at 298 K is 2×10^{-6} mol^{-1} dm^3 based on the presumably better solubility data of ref. (20).

There has been some disagreement whether the solute species $Cd(OH)_3^-$ or $HCdO_2^-$ exists in any significant amount in solution. Ichikawa and Sato (19) measured the distribution coefficients of ^{109}Cd between an anion exchange resin and NaOH solutions. From their results they concluded that only the univalent ion existed in NaOH solutions less concentrated than 3 mol dm^{-3}. The temperature was not specified but it apparently was room temperature. On the other hand, Gubeli and Taillon (16) assumed that this ion did not exist in any appreciable quantities. Their argument was based on the values of the slopes of the solubility curve. However, these slopes were all measured in the region of minimum solubility where the concentration of $Cd(OH)_3^-$ is not significant compared to that of $Cd(OH)_2$. All the other papers dealing with solutions of CdO or $Cd(OH)_2$ in alkaline solutions consider $Cd(OH)_3^-$ to be one of the solute species present.

One equation that fits the solubility data of two papers (2, 20) in NaOH concentrations greater than 0.5 mol dm^{-3} is as follows (20).

$$[Cd]_{tot} = 1.0 \times 10^{-6} + 1.2 \times 10^{-6}[OH^-] + 3.1 \times 10^{-6}\ [OH^-]^2 \qquad (13)$$

The numerical terms on the right hand side of the equation are: concentration of undissociated $Cd(OH)_2$, K_5, and K_6, respectively. This curve is shown on Figures 1 and 2 and fits the data well for NaOH concentrations greater than 0.5 mol dm^{-3}.

Another equation was developed to fit the data in the vicinity of the minimum solubility (16). This equation is:

$$[Cd]_{tot} = \frac{2.5 \times 10\text{-}15}{[OH^-]^2} + \frac{1.3 \times 10^{-10}}{[OH^-]} + 1.6 \times 10^{-7} + 1.3 \times 10^{-5}[OH^-]^2 \qquad (14)$$

The terms on the right hand side of the equation represent the concentration of Cd^{2+}, $CdOH^+$, $Cd(OH)_2$, and $Cd(OH)_4^{2-}$, respectively. The line calculated from this equation is also shown on Figures 1 and 2. It does not fit the data very well except in the vicinity of the solubility minimum. This, no doubt, is due, at least in part, to the neglect of the presence of $Cd(OH)_3^-$ ions.

The question of whether or not polynuclear ionic species exist in solutions should also be considered. Three papers from the Department of Inorganic Chemistry, Royal

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Institute of Technology in Stockholm, Sweden, address this issue. Each of these papers (15, 21, 25) is a study of the hydrolysis of Cd^{2+} ions. Two of these papers (15, 21) state specifically that no evidence was uncovered for the existence of polynuclear species. The third paper (25) suggested that two polynuclear species existed: Cd_2OH^{3+} and $Cd_4(OH)^{4+}_4$. However, these species were said to become evident only when the total cadmium ion concentration exceeded 0.1 mol dm^{-3}. Such a concentration is not reached or exceeded in the solubility data discussed up to this point.

In one paper (26) results are given for the solubility of $Cd(OH)_2$ in NaOH solutions at 373 K. The purpose of this work was to determine whether $Cd(OH)_2$ had significant acidic characteristics, i.e., whether it would form cadmates which could be isolated. Therefore, concentrated NaOH solutions were used: 6.8 to 18.4 mol dm^{-3}. The results showed that in NaOH solutions less concentrated than 14.2 mol dm^{-3} the only solid phase was $Cd(OH)_2$. At concentrations greater than this, the solid phase appeared to be $Na_2[Cd(OH)_4]$. Similar work at 353 K gave additional solid phases but these are not described precisely. There is only one concentration of NaOH in which there are solubility data at 297.5 K (20) and 373 K (26). A comparison shows that at the higher temperature the solubility is about ten times as great.

Solovieva, et al., measured the solubility of both CdO and $Cd(OH)_2$ in concentrated NaOH solutions at elevated temperatures (27, 28). They also found that at the lower concentrations of NaOH the solid phase was $Cd(OH)_2$ but beyond a point of maximum solubility (which varies with the temperature) the solid phase changed and was probably a cadmate, $Na_2[Cd(OH)_4]$. According to their results the solubility of $Cd(OH)_2$ was significantly lower than that of CdO at comparable temperature and NaOH concentration. However, their results for the solubility of $Cd(OH)_2$ at 378 K are also lower than the results reported for 373 K (26), see Figure 3. Until more results are reported under these conditions, the results of Scholder and Staufenbiel (26) are considered the more reliable. The reason for this is that not enough is known about the experimental conditions under which the results of Solevieva, et al., (27, 28) were obtained.

Solubility in solutions containing ammonia and ammonia derivatives. Four papers deal with solutions of $Cd(OH)_2$ in aqueous ammonia solvents (16, 18, 29, 30). Only one of these papers (29) reports numerical solubility data. The solubility studies were made at 283, 293 and 303 K, but no attempts were made to determine the nature or stability of the cadmium-ammonia complex ions formed in such solutions. Furthermore, no information is given as to the purity of the materials used, nor to the reproducibility of the various experimental measurements and procedures. Nor is there any indication of the pH of the solutions. Consequently, it is not possible to develop an equation to express the solubility of $Cd(OH)_2$ in the aqueous ammonia solvents, and the results that are given must be considered as incomplete and tentative. Some of the first data on the solubility of $Cd(OH)_2$ in aqueous NH_3 solutions at 293 K (31) were not included in the Data sheets because the reproducibility was admittedly not very good and the $Cd(OH)_2$ samples used were not of uniform composition.

The other three papers dealing with this system (16, 18, 32) are primarily concerned with the composition and stability of the cadmium-ammonia complex ions. Only one of these papers (16) reports any solubility data but that is presented only in graphical form.

The reactions of interest are of the type

$$Cd(NH_3)_n^{2+} = Cd^{2+} + n\ NH_3 . \qquad (15)$$

There is no unanimity as to the composition of these ions, i.e., the value of n. That may reflect the different conditions that were used. De Wijs (18) found evidence at 298 K for only two such ions: $Cd(NH_3)_2^{2+}$ and $Cd(NH_3)_4^{2+}$. The stability constants for

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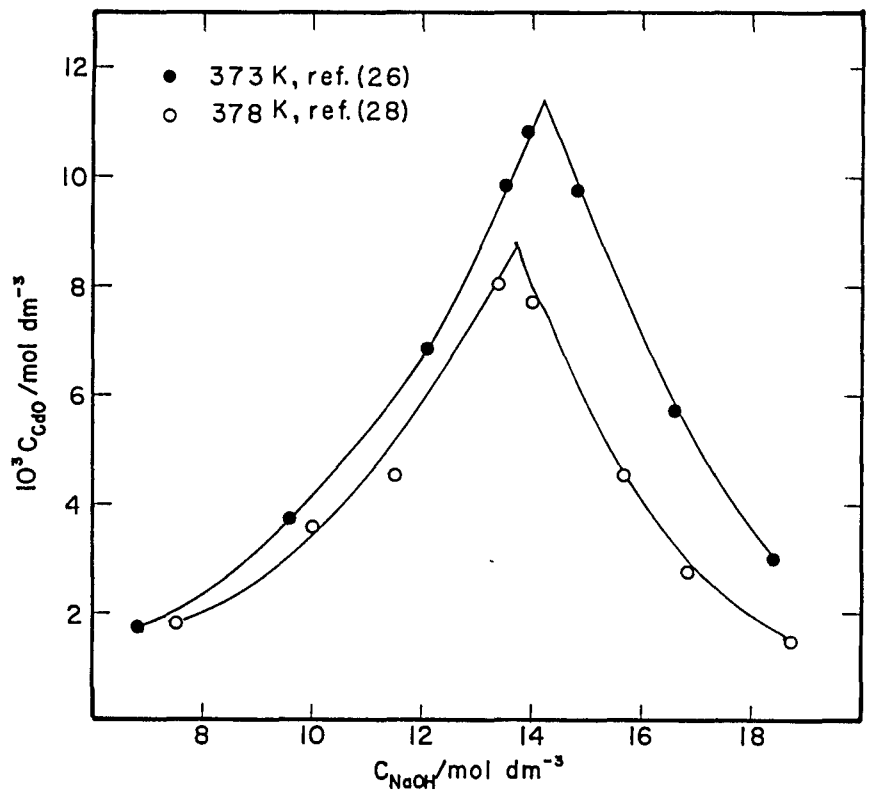

Figure 3. Solubility of $Cd(OH)_2$ in NaOH solutions at elevated temperatures.

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

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these ions are given as 2.7×10^{-5} mol^2 dm^{-6} and 2.5×10^{-7} mol^4 dm^{-12}, respectively. However, other authors reach different conclusions as to which complex ions are present and the value of the stability constant for each, Table I.

Table I

Reported stability constants for cadmium-ammonia complex ions.

Source	$Cd(NH_3)^{2+}$	$Cd(NH_3)_2^{2+}$	$Cd(NH_3)_3^{2+}$	$Cd(NH_3)_4^{2+}$
ref. (18)	---------	2.7×10^{-5}	---------	2.5×10^{-7}
ref. (16)	7.9×10^{-4}	6.3×10^{-6}	3.2×10^{-7}	1.6×10^{-8}
ref. (32)	2.2×10^{-3}	1.6×10^{-5}	3.3×10^{-8}	2.8×10^{-10}

It is difficult to determine which, if any, of these values are to be accepted. In view of the differences it seems best to consider all these values doubtful.

One paper (3) reports a few values for the solubility of CdO in aqueous $(NH_4)_2SO_4$ at 298 K. There is no other similar study reported and the solid phase is described only in general terms. Consequently, these values can only be considered as tentative.

Danilov, et al. (30) measured the solubility of CdO or $Cd(OH)_2$ in aqueous solutions containing 2-aminoethanol or 2,2'-iminodiethanol. The solubility data are reported at several temperatures, but it is impossible to evaluate the precision of the data from the meager amount of information given in the paper. The conclusions reached by the authors are: in aqueous solutions of 2-aminoethanol more concentrated than 3 mol dm^{-3} the solid phase contains 2 mol of the 2-aminoethanol per mol of $Cd(OH)_2$ while in aqueous solutions of 2,2'-iminodiethanol at concentrations up to 8 mol dm^{-3} the solid phase is $Cd(OH)_2$. In both types of solutions the solubility decreases with increasing temperature. The authors do present an equation for the total solubility of CdO in such solutions. The terms in the equation include the following factors: solubility product of $Cd(OH)_2$, mean ionic activity coefficient of $Cd(OH)_2$, ligand concentration, activity coefficient of the ligand, and the activity of water. According to the calculations of the authors this equation gives satisfactory results for aqueous solutions of 2-aminoethanol and 2,2'-iminodiethanol in which $Cd(OH)_2$ is the solid phase. However, insufficient data are included in the paper to enable one to check these calculations. Furthermore, there are no other results in the literature dealing with these systems. Consequently, the data and the conclusions can only be considered tentative, at best.

Miscellaneous. One study has been made of the $CdO-As_2O_5-H_2O$ system (33). This was a phase study and intended to show that CdO does react with weakly acidic oxides at 298 K. Five solid phases were isolated and identified: $3CdO \cdot As_2O_5 \cdot 4H_2O$, $5CdO \cdot 2As_2O_5 \cdot 5H_2O$, $2CdO \cdot As_2O_5 \cdot 2H_2O$, $CdO \cdot As_2O_5 \cdot 4H_2O$ and $CdO \cdot 2As_2O_5 \cdot 5H_2O$. The numerical data on which the phase diagram is based were not included in the paper but were supplied in a letter from Dr. N. Kbir-Arguib. These results should be considered as tentative until further work with this system is reported.

Another study is reported that deals with the reaction of CdO with hydrogen peroxide (8). The purpose of the work was to determine whether $Cd(OH)_2$, like $Zn(OH)_2$, would form peroxides. The solubility of $Cd(OH)_2$ in various H_2O_2 solutions is reported at 273 and 293 K. Besides $Cd(OH)_2$, four solid peroxides were reported to be equilibrium phases in this system: $CdO_2 \cdot 2H_2O$, $CdO_2 \cdot 1.5H_2O$, $CdO_2 \cdot H_2O$ and $CdO_2 \cdot 0.5H_2O$. Although it was stated that there is a question as to the structure of cadmium peroxides, yet the authors do not use their results to clarify this matter. There are no other solubility data reported for this aqueous hydrogen peroxide system. This fact, and the uncertainty of the results as mentioned earlier in discussing the solubility of $Cd(OH)_2$ in water, strongly indicate that these solubility results should be considered doubtful at the present time.

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One paper (34) deals with the effect of Na_2S on the solubility of CdO in water. Only one datum is given and there is no indication as to the purpose of this investigation. The one value given must be considered tentative until more work is done and reported on this system.

Solubility under hydrothermal conditions. Shlyapnikov and Shtern have presented two papers (35, 36) dealing with the effect of CO_2 and NaCl on the solubility of CdO under hydrothermal conditions. The data are rather few but, presumably, these papers are preliminary reports for a larger program of study dealing with the leaching and deposition of minerals in the earth.

In the earlier work (35) the solubility of CdO is reported for an aqueous solution containing 4 mol NaCl dm^{-3} at 293 K and under a CO_2 pressure of 50×10^5 Pa. In the later paper (36) solubility data are reported for several NaCl concentrations at two CO_2 pressures: 1×10^5 and 50×10^5 Pa. But the data in the two papers are not consistent with each other so far as can be checked. In the latter paper the solubility in a 4 mol NaCl dm^{-3} solution at 293 K and a CO_2 pressure of 50×10^5 Pa is twice that given in the earlier paper. The authors make no comment on this. Because there are no other data against which these results can be compared, the solubility data in refs. (35, 36) must be considered doubtful at the present time. However, the general conclusions are that the presence of NaCl in solution increases the rate at which CdO is converted to $CdCO_3$ under a pressure of CO_2. Furthermore, the solubility of CdO increases as the NaCl concentration increases and the CO_2 pressure increases. These phenomena are interpreted as due to the increasing formation of cadmium-chloride complexes and the formation of bicarbonates.

Several papers, e.g., (37-40) deal with the reaction of CdO with GeO_2 under hydrothermal conditions. However, these papers are primarily concerned with the formation and identification of cadmium germanates and present no numerical solubility data.

Table II

Summary of recommended values for the $CdO-H_2O$ system.

Solubility of $Cd(OH)_2$ in H_2O at 298 K	1.5×10^{-5} mol/kg H_2O
log K_{so} at 298 K in 3 mol $NaClO_4$ dm^{-3}	-14.41 ± 0.05
log K_{so} at 298 K in 1 mol $NaClO_4$ dm^{-3}	-14.6 (± 0.1)

Table III

Summary of tentative values for the $CdO-H_2O$ system

Solubility of CdO in H_2O at 298 K	5.4×10^{-5} mol dm^{-3}
K^o_{so} at 291 K	2.6×10^{-15}
K^o_{so} at 298 K	5.9×10^{-15}
$Cd(OH)_2(s) + H^+ = CdOH^+ + H_2O$	$K_2 = 1.3 \times 10^{-4}$ at 298 K
$Cd(OH)_2(s) = Cd(OH)_2(sln)$	$K_3 = 3 \times 10^{-7}$ mol dm^{-3} at 298 K
$Cd(OH)_2(s) + OH^- = Cd(OH)^-_3$	$K_5 = 2 \times 10^{-6}$ at 298 K
$Cd(OH)_2(s) + 2\ OH^- = Cd(OH)^{2-}_4$	$K_6 = 2 \times 10^{-6}$ mol^{-1} dm^3 at 298 K

COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O, [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

CRITICAL EVALUATION:

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COMPONENTS:	EVALUATOR:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. October 1983

CRITICAL EVALUATION:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Water; H_2O; [7732-18-5]	Remy, H; Kuhlman, A. *Z. anal. Chem.* 1924, *66*, 161-81.
VARIABLES: Method of measuring the solubility of CdO in water at 20°C.	PREPARED BY: T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CdO in water at 20°C.

Method	mol CdO dm^{-3}	mg CdO dm^{-3}
specific conductance	3.90×10^{-5}	5.00
conductimetric titration	3.74×10^{-5}	4.80

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Hot CdO is added to water and the mixture shaken. Two methods are used to calculate the solubility; (1) from the measured specific conductance and literature values for ionic conductances; (2) a conductimetric titration with H_2SO_4. The point of the work is to note the contribution of dissolved CO_2 to the conductance and how to correct for this.

SOURCE AND PURITY OF MATERIALS:

Reagent grade CdO and conductivity water were used.

ESTIMATED ERROR:

The temperature was not controlled but varied between 19 and 21°C. In the titration results, the uncertainty was 1% of the value reported.

REFERENCES:

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

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

ORIGINAL MEASUREMENTS:

Moeller, T.; Rhymer, P. W.; *J. Phys. Chem.* 1942, *46*, 477-85.

VARIABLES:

Composition of solvent at 25°C

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility product[a] of cadmium hydroxide at 25°C

$C_{OH^-}/C_{Cd^{2+}}$	pH	$10^{14}K_{so}$
0.2	8.13	3.1
0.4	8.18	3.4
0.6	8.21	3.3
0.8	8.23	3.0
1.0	8.26	2.8
1.2	8.32	2.8
1.4	8.40	3.0
1.6	8.52	3.3

[a] $K_{so} = C_{Cd^{2+}} \cdot (a_{OH^-})^2$

Salts other than $Cd(NO_3)_2$ were also used but $Cd(NO_3)_2$ gave the purest form of precipitated $Cd(OH)_2$.

In calculating K_{so} the ionic product constant of water at 25°C was taken as 1×10^{-14}.

Using the expression $S = \sqrt[3]{K_{so}/4}$ the solubility of $Cd(OH)_2$ in water at 25°C is calculated to be 2×10^{-5} mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

10 mol of 0.0996 mol dm^{-3} $Cd(NO_3)_2$ was diluted to 50 ml with water, thermostated at 25 ± 0.5°C, stirred vigorously, and titrated with 0.1 mol dm^{-3} carbonate-free NaOH or KOH. The pH of the solution was measured with a glass electrode. The values chosen were in the region where $Cd(OH)_2$ had precipitated from the solution.

SOURCE AND PURITY OF MATERIALS:

All materials were of reagent grade quality. The water was CO_2-free.

ESTIMATED ERROR:

No details are given about the reproducibility of any of the measurements.

REFERENCES:

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

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

ORIGINAL MEASUREMENTS:

Jenkins, S. H.; Keight, D. G.; Humphreys, R. E. *Air Water Pollution* 1964, *8*, 537-56.

VARIABLES:

Effect of successive samples of CO_2-free distilled water at room temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES: Solubility of $Cd(OH)_2$ in distilled water.

pH of H_2O	temp, °C	Bottle 1 pH of soln	Bottle 1 C_{Cd}, ppm	Bottle 2 pH of soln	Bottle 2 C_{Cd}, ppm	Bottle 3 pH of soln	Bottle 3 C_{Cd}, ppm
----	22.0	9.28	0.81	9.00	1.03	9.10	1.11
8.70	20.4	9.30	0.79	9.40	0.66	9.39	1.02
9.00	17.0	9.30	0.54	9.28	1.26	9.35	0.99
7.78	18.0	9.32	0.87	9.43	0.79	9.40	0.79
8.92	19.0	9.32	0.79	9.35	0.79	9.40	0.66
8.67	20.0	9.25	0.38	9.39	0.41	9.38	0.38
8.00	18.0	9.22	0.79	9.30	1.82	9.32	1.42
8.40	17.2	8.81	0.79	9.12	1.44	9.18	1.41
8.00	20.0	8.98	1.03	9.06	1.91	9.10	1.90
5.92	17.4	8.82	1.75	9.02	1.11	9.10	1.34
5.90	18.4	8.92	1.05	9.13	1.90	9.28	1.45
5.91	17.0	8.90	0.63	9.20	1.34	9.30	1.41
6.40	18.8	9.29	0.55	9.30	0.98	9.31	1.22

type of $Cd(OH)_2$	pH	C_{Cd}/ppm[a]	pH	C_{Cd}/ppm[b]
powder	8.7	1.0	8.5	0.485
"	8.8	0.9	8.7	0.385
"	8.8	1.1	8.8	0.425
"	9.0	0.96	8.9	0.428
freshly pptd	8.7	1.66	8.8	0.640
"	8.6	2.12	8.6	0.785

[a]These solutions were filtered through a Millipore HA filter.
[b]These solutions were filtered through a Millipore VC filter.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The $Cd(OH)_2$ was added to distilled water and the mixture was shaken intermittently for a week and then allowed to stand for about a week. A sample of the clear supernatant liquid was removed, filtered through glass paper and analyzed for cadmium content colorimetrically using diphenylthiocarbazone. Each value reported is the average of 3 replicate samples. Successive extractions were made by the addition of distilled water, shaking the mixture for 2 days, allowing the mixture to settle, and then taking samples for analysis.

SOURCE AND PURITY OF MATERIALS:

The distilled water was CO_2-free. The $Cd(OH)_2$ apparently was a commercially available product.

ESTIMATED ERROR:

No information is given about the reproducibility of any of the measurements or procedures.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	Piater, J. Z. *anorg. allgem. Chem.* 1928, *174*, 321-41.
VARIABLES: Method of preparation of $Cd(OH)_2$ and the NaOH concentration	PREPARED BY: T. P. Dirkse

EXPERIMENTAL VALUES:

Table 1

Solubility of CdO or $Cd(OH)_2$ in water at 25°C.

Preparation	mol dm^{-3}	Solubility Product ($mol^3\ dm^{-9}$)
CdO	1.79×10^{-5}	2.3×10^{-14}
$Cd(OH)_2$ [a]	1.30×10^{-5}	8.8×10^{-15}
$Cd(OH)_2$ [b]	1.14×10^{-5}	5.9×10^{-15}
$Cd(OH)_2$ [c]	1.11×10^{-5}	5.5×10^{-15}

[a] prepared by the method of De Schulten (2).

[b] prepared by the method of Bonsdorf (3).

[c] prepared by the reaction: $CdSO_4 + 2NaOH \rightarrow Na_2SO_4 + Cd(OH)_2$

The $Cd(OH)_2$ was washed by decantation and kept under water at least 3 months before use.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Apparently the solid was added to the solvent and shaken. The specific conductance of the solution was measured and the validity of the method was judged by the conductance behavior. Corrections were made for dissolved CO_2 (1) and the solubility was calculated from the specific conductance and accepted values for ionic conductances.	Analysis of each preparation showed about 0.5% impurities. Conductivity water was used, but nothing is stated about the purity of the NaOH.
	ESTIMATED ERROR: Nothing is indicated about temperature control. No information is given about reproducibility. Indications are that there may be an uncertainty of about 5% in the solubility values.

REFERENCES:

1. Laue, E. Z. *anorg. allgem. Chem.* 1927, *165*, 305.
2. De Schulten, A. *Compt. rend.* 1885, *101*, 72.
3. Bonsdorf, W. Z. *anorg. Chem.* 1904, *41*, 187.

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]

(2) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Piater, J. Z. *anorg. allgem. Chem.* 1928, *174*, 321-41.

Table 2

Solubility of $Cd(OH)_2$ in NaOH solutions at 25°C.

mol NaOH dm^{-3}	mol $Cd(OH)_2$ dm^{-3}
0.00	1.2×10^{-5}
0.01	1.3×10^{-6}
0.1	1.3×10^{-6}
1.0	0.7×10^{-5}
5.0	9.0×10^{-5}

COMPONENTS:
(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Scholder, R.; Staufenbiel, E. Z. *anorg. allgem. Chem.* 1941, 247, 259-76

VARIABLES:
Concentration of NaOH and temperature.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Table 1

Solubility of $Cd(OH)_2$ in NaOH solutions at 100.0°C.

g NaOH/100 g soln	mg CdO/100 g soln	mol NaOH dm^{-3}	(mol CdO dm^{-3}) x 10^3	solid phase
22.7[a]	18.3[a]			
22.7[b]	18.4[b]	6.8	1.72	$Cd(OH)_2$
30.0[a]	37.8[a]			
30.0[b]	37.7[b]	9.6	3.74	"
36.3[a]	65.9[a]			
36.3[b]	65.6[b]	12.1	6.84	"
39.4[a]	92.0[a]			
39.4[b]	92.5[b]	13.5	9.86	"
40.4[a]	100.0[a]			
40.4[b]	100.7[b]	13.9	10.81	"
42.3[a]	89.2[a]			
42.3[b]	89.5[b]	14.8	9.73	$Na_2[Cd(OH)_4]$
46.3[a]	51.2[a]			
46.3[b]	51.5[b]	16.6	5.75	"
50.0[a]	25.2[a]			
50.0[b]	26.5[b]	18.4	3.03	"

[a]determined after 25 hours
[b]determined after 48 hours
Work was also carried out at 80°C, but no solubility values are given for that temperature. The only information given is the composition of the solid phases.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Solid $Cd(OH)_2$ was added to the NaOH solutions in a silver vessel and refluxed for 1-2 days. In the solid phase, Cd was determined by dissolving the solid in H_2SO_4, and determining the Cd by treatment with dipyridine thiocyanate (1). In the liquid phase Cd^{2+} was determined by adding H_2SO_4, precipitating CdS, changing it to $CdSO_4$ and weighing. NaOH content was determined by titration. In some cases the solid phase was identified microscopically.

SOURCE AND PURITY OF MATERIALS:
$Cd(OH)_2$ was prepared by adding a solution of cadmium acetate to boiling concentrated KOH solution. Presumably reagent grade chemicals were used but this is not specifically stated.

ESTIMATED ERROR:
Nothing is stated. The temperature was controlled to ± 0.1°C. The solubility values appear to have an uncertainty of about 3-5%.

REFERENCES:
1. Spacu, G.; Dick, I. Z. *analyt. Chem.* 1928, 73, 279.

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

(2) Cadmium sulfate; $CdSO_4$; [10124-36-4]

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

ORIGINAL MEASUREMENTS:

Akselrud, N. V.; Fialkov, Ya. A.
Ukr. Khim. Zh. 1950, *16*, 283-95.

VARIABLES:
Concentration of $CdSO_4$ at 18.0°C

PREPARED BY:
T. Michalowski

EXPERIMENTAL VALUES:

Values of $-\log K_s o$ for $Cd(OH)_2$ at 18.0°C.

mol Cd^{2+} dm^{-3} in liquid phase	pH	$-\log K_s o$ [a]
0		14.5820[b]
0.1020	7.42	14.4203
0.1382	7.37	14.3842
0.3583	7.19	14.3255
0.5115	7.05	14.4465
1.1298	6.54	15.1198
1.4411	6.28	15.5338

[a] $-\log K_s o = -2\log K_w - \log [Cd^{2+}] - 2pH$

[b] this value was obtained by graphical extrapolation of the corresponding curve to $[Cd^{2+}] = 0$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cd(OH)_2$ was added to solutions of $CdSO_4$. The mixtures were shaken in a thermostat until equilibrium was attained. There is no information about the analytical procedures.

SOURCE AND PURITY OF MATERIALS:

$CdSO_4$ was recrystallized twice from water. The $Cd(OH)_2$ was precipitated from a $CdSO_4$ solution and then washed with hot water.

ESTIMATED ERROR:

There is insufficient information in the article to allow the possible error to be estimated.

REFERENCES:

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

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

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

ORIGINAL MEASUREMENTS:

Schindler, P. *Helv. Chim. Acta* 1959, *42*, 2736-42.

VARIABLES:

Method of reaching equilibirum at 25°C and at a constant total ionic strength of 3 mol dm^{-3}.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

$-\log [H^+]$	$-\log [H^+]^2/[Cd^{2+}]$
For solutions from which $Cd(OH)_2$ has precipitated.	
8.09 ± 0.01	14.04 ± 0.02
8.29 ± 0.01	14.03 ± 0.03
7.77 ± 0.01	14.03 ± 0.02
8.16 ± 0.01	14.06 ± 0.03
8.15 ± 0.01	14.04 ± 0.03
8.69 ± 0.01	14.04 ± 0.04
8.67 ± 0.01	14.00 ± 0.04
For solutions into which $Cd(OH)_2(s)$ dissolves.	
7.80 ± 0.01	13.99 ± 0.02
8.56 ± 0.01	14.04 ± 0.04
7.60 ± 0.01	14.02 ± 0.02

Analysis of the solution was carried out for about 450 hours. The results showed a gradual change over the first 100 hours. After that, the values remained constant.

The above values were converted to log K_{so} values using the following value.

$\log K_w = -14.22 \pm 0.02$ at 25°C in 3 mol dm^{-3} $NaClO_4$ (1).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Two solutions--one containing Cd^{2+} and the other containing OH^- were mixed to precipitate $Cd(OH)_2$. The hydrogen ion concentration (determined by an e.m.f. measurement) of the solution was measured over a period of about 20 days. The Cd^{2+} ion concentration was calculated from the volume and the concentrations of the solutions. The second method involved adding $Cd(OH)_2$ to a 3 mol dm^{-3} aqueous solution of $NaClO_4$ and again measuring the hydrogen ion concentration over a period of time.

SOURCE AND PURITY OF MATERIALS:

Chemically pure materials were used and much care was taken to exclude CO_2.

ESTIMATED ERROR:

The calculated solubility product (concentration product) has an uncertainty of about 10%.

REFERENCES:

1. Ingri, H.; Lagerstrom, G.; Frydman, M.; Sillen, L. G. *Acta Chem. Scand.* 1957, *11*, 1034.

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

(2) Hydrogen peroxide; H_2O_2; [7722-84-1]

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

ORIGINAL MEASUREMENTS:

Ladeinova, L. V.; Lozhkina, L. G.; Chernysheva, A. M. *Izv. Akad. Nauk SSR, Otd Khim. Nauk* 1961, 12-16.

VARIABLES:

Hydrogen peroxide concentration and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table 1

Data on the $Cd(OH)_2$-H_2O_2-H_2O system at 0°C.

Composition of liquid phase in wt %				Composition of liquid phase in wt%			
active O_2	H_2O_2	(CdO) x 10^3	Solid[a] phase	active O_2	H_2O_2	(CdO) x 10^3	solid[a] phase
-----	------	1.6	A	21.18	45.03	7.03	C + D
0.81	1.72	4.19	"	22.14	47.0	5.56	D
2.54	5.40	7.83	A + B	22.85	48.60	1.87	"
4.44	9.44	5.29	B	24.27	51.60	1.86	"
5.42	11.52	5.63	"	26.43	56.19	1.76	"
5.54	11.78	5.52	"	27.44	58.34	5.16	D + E
7.34	15.60	5.07	"	27.47	58.40	4.85	E
9.35	19.88	4.23	"	28.10	59.74	4.43	"
10.06	21.73	5.96	"	28.53	60.65	4.41	"
11.21	23.83	7.28	B + C	32.41	68.90	1.43	"
12.59	26.76	4.52	C	35.66	75.81	0.99	"
13.40	28.50	4.85	"	40.80	86.74	1.04	"
15.45	32.85	4.40	"	44.17	93.91	2.10	"
18.31	38.93	5.18	"				

[a] A = $Cd(OH)_2$; B = $CdO_2 \cdot 2H_2O$; C = $CdO_2 \cdot 1.5H_2O$; D = $CdO_2 \cdot H_2O$; E = $CdO_2 \cdot 0.5H_2O$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The components were mixed and stirred until equilibrium was reached. Equilibrium was determined by constancy of active oxygen analysis in both solid and liquid phases. Equilibrium was reached in 1.5 - 2 hours. Active oxygen content was determined by titration with 0.1 N $KMnO_4$ in the presence of H_2SO_4. CdO content was determined colorimetrically with dithizone in the liquid phase and gravimetrically by weighing as cadmium pyrophosphate in the solid phase.

SOURCE AND PURITY OF MATERIALS:

Chemically pure $Cd(OH)_2$ and distilled H_2O_2 without stabilizers were used.

ESTIMATED ERROR:

The temperature was controlled to within ±0.5°C. No information is given as to the reproducibility of the results.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (2) Hydrogen peroxide; H_2O_2; [7722-84-1] (3) Water; H_2O; [7732-18-5]	Ladeinova, L. V.; Lozhkina, L. G.; Chernysheva, A. M. *Izv. Akad. Nauk SSR, Otd Khim. Nauk* 1961, 12-16.

EXPERIMENTAL RESULTS, continued--------

Table 2

Data on the $Cd(OH)_2$-H_2O_2-H_2O system at 20°C.

Composition of liquid phase as wt %			
active O_2	H_2O_2[a]	(CdO) x 10^3	Solid phase[b]
-----	------	1.78	A
3.55	7.55	2.91	"
5.62	11.95	3.66	A + B
6.10	12.97	3.58	B
6.32	13.44	1.60	"
6.80	14.47	2.88	"
8.47	18.01	0.26	"
9.61	20.43	2.80	"
10.97	23.32	3.33	"
12.27	26.08	3.41	B + C
13.20	28.05	3.11	C
13.52	28.74	2.84	"
13.37	28.42	3.00	"
13.98	29.72	2.85	"
14.82	31.51	2.83	"
15.56	33.08	2.20	"
16.47	35.02	1.07	"
18.12	38.52	0.63	"
18.64	39.63	1.03	"
21.38	45.45	2.16	"
21.74	46.22	2.42	"
23.43	49.81	2.61	"
24.23	51.51	2.73	"
25.08	53.32	3.34	C + D
25.50	54.21	3.24	D
25.83	54.92	2.92	"
26.79	56.95	2.18	"
27.98	59.48	0.93	"
31.15	66.22	0.96	"
34.21	72.73	2.56	D + E
35.18	74.80	1.09	E
37.41	79.53	0.69	"
40.48	86.06	0.8	"
41.91	89.10	1.58	"

[a] recalculated by compiler

[b] A= $Cd(OH)_2$; B=$CdO_2 \cdot 2H_2O$; C=$CdO_2 \cdot 1.5H_2O$; D=$CdO_2 \cdot H_2O$; E=$CdO_2 \cdot 0.5H_2O$.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium oxide; CdO; [1306-19-0] (2) Sodium sulfide; Na_2S; [1313-82-2] (3) Water; H_2O; [7732-18-5]	Polyvyanni, I. R.; Milyutina, N.A. *Tr. Inst. Met. Obogashch. Akad. Nauk Kaz. SSR* 1967, *21*, 3-13.
VARIABLES:	PREPARED BY:
Concentration of Na_2S at 60.0°C	T. Michalowski

EXPERIMENTAL VALUES:

Solubility of CdO in aqueous Na_2S solutions at 60.0°C

mol Na_2S dm^{-3}	mol CdO dm^{-3}	density of saturated solution, g ml^{-1}
1.45	1.9×10^{-3}	1.109

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The CdO and solvent were equilibrated at 60.0°C for 26 hours.	Reagent grade CdO and Na_2S were used. The Na_2S was recrystallized three times.
	ESTIMATED ERROR:
	No information is given. The temperature was controlled to within 0.1°C.
	REFERENCES:

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]

(2) Ammonia; NH_3; [7664-41-7]

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

ORIGINAL MEASUREMENTS:

Danilov, V. V.; Martinson, I.G.; Ravdel, A. A. *Zh. Prikl ad Khim. (Leningrad)* 1971, *44*, 3-6.

VARIABLES:

Temperature and concentration of ammonia.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CdO in aqueous ammonia solutions.

mol NH_3 dm^{-3}	(mol Cd dm^{-3}) x 10^2 10°C	20°C	30°C
2.18	0.65	0.68	0.70
3.40	1.52	1.59	1.70
4.40	2.61	2.70	2.77
7.10	5.22	4.94	4.46
9.45	5.76	5.54	5.06
11.45	6.20	6.02	5.42

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were equilibrated for 30 days with intermittent stirring. Equilibrium was approached from both high and low temperatures. Cadmium content was determined by titration with Trilon B at a pH of about 10, using Eriochrome Black T as indicator.

SOURCE AND PURITY OF MATERIALS:

No indication is given.

ESTIMATED ERROR:

No information is given as to how closely the temperature was controlled, nor to how reproducible the analyses were.

REFERENCES:

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]

(2) Ammonium sulfate; $(NH_4)_2SO_4$; [7783-20-2]

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

ORIGINAL MEASUREMENTS:

Kudryaytsev, N. T.; Selivanova, G. A. Izv. *Vysšh, Ucheb. Zaved., Khim. Tekhnol.* 1971, *14*, 835-8.

VARIABLES:

Concentration of ammonium sulfate.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of CdO in aqueous $(NH_4)_2SO_4$ at 25°C.

$C_{(NH_4)_2SO_4}$/mol dm^{-3}	C_{Cd}/mol dm^{-3}	pH
0	9 x 10^{-5}	9.2
0.5	0.28	10.5
1.0	0.65	9.5
1.5	0.90	8.9
2.0	1.45	8.65
2.5	1.80	8.40
3.0	2.02	8.35

Additional results, presented only in graphical form, show that in $(NH_4)_2SO_4$ concentrations of 1 and 2 mol dm^{-3}, the solubility of CdO shows a minimum with changing pH (accomplished by adding either H_2SO_4 or NH_4OH). In the 1 mol dm^{-3} solution the minimum is about 0.7 mol dm^{-3} at a pH = 7-10. In the 2 mol dm^{-3} solution it is about 1.4 mol dm^{-3} at a pH = 6-7.

The solid phase in equilibrium with the solutions in the above Table is described as a compound of the type $CdSO_4 \cdot nCd(OH)_2 \cdot mNH_3 \cdot xH_2O$.

Using the water solubility value in the above Table, a value of 2.26 x 10^{-14} is obtained for the value of $K_{so} = C_{Zn} \cdot (a_{OH^-})^2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No information is given about the preparation and mixing of the solutions. Cadmium content was determined by a compleximetric titration or photometrically using dithizone. The pH of the solutions was measured by using a glass electrode.

SOURCE AND PURITY OF MATERIALS:

Both the CdO and the ammonium sulfate are described as chemically pure.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Soloveva, V. D.; Svirchevskaya, E. G.; Bobrova, V. V.; Eltsov, N. M. *Tr. Inst. Metal. Obogashch. AN KazSSR*, 1973, *49*, 37-44.

VARIABLES:

NaOH concentration and temperature

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of CdO in NaOH solutions.

Temperature, °C	mol NaOH dm^{-3}	Cd solubility, (mol dm^{-3}) x 10^5	Solid phase
20	2.75	4.45	$Cd(OH)_2$
20	5.10	8.9	"
20	10.25	162.0	"
20	13.08	177.0	"
40	3.0	15.0	$Cd(OH)_2$
40	5.65	57.0	"
40	8.85	131.0	"
40	10.84	320.0	"
105	3.5	71.0	$Cd(OH)_2$
105	7.5	177.0	"
105	10.0	500.0	"
105	12.0	970.0	"
200	2.75	134.0	$Cd(OH)_2$
200	5.0	223.0	"
200	7.5	339.0	"
200	10.0	900.0	"
200	12.0	1070.0	"
200	14.0	1340.0	"
200	16.5	1080.0	$Na_2Cd(OH)_4$
200	18.3	366.0	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Apparently the mixtures were equilibrated at the temperature recorded, but no explicit description of the procedure is given.

SOURCE AND PURITY OF MATERIALS:

Analytical grade CdO was used. Nothing is said about the other materials that were used.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Soloveva, V. D.; Bobrova, V. V.; Orlova, L. F.; Adeyschvili, E. U. *Tr. Inst. Met. Obogashch. AN. Kaz SSR* 1973, *49*, 45-8.

VARIABLES:

NaOH concentration and temperature.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of $Cd(OH)_2$ at different temperatures

mol NaOH dm^{-3}	Concentration of cadmium in the solution, (mol dm^{-3}) x 10^5 20°	105°	200°
3.75	4.46	44.6	44.5
5.62	9.00	71.4	125.0
7.50	71.4	178.0	250.0
10.00	90.0	357.0	543.0
11.50	180.0	455.0	580.0
13.35	340.0	803.0	759.0
14.00	338.0	770.0	1160.0
15.65	-----	455.0	990.0
16.85	-----	277.0	786.0
18.75	-----	149.0	290.0

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Apparently the mixtures were equilibrated at the temperature recorded but no explicit description of the procedure is given.

SOURCE AND PURITY OF MATERIALS:

$Cd(OH)_2$ was precipitated by the addition of a NaOH solution to a solution of $CdSO_4$. The precipitate was washed and dried and its purity was checked by X-ray diffraction diagrams.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:
(1) Cadmium oxide; CdO; [1306-19-0]
(2) Arsenic(V) oxide; As_2O_5; [1303-28-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Omezzine, B. K.; Ariguib-Kbir, N. *Compt. rend.* 1978, *286*, 197-9.

VARIABLES:
Solution composition at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:
Solubility of CdO in aqueous solutions of As_2O_5 at 25°C. [a]

As_2O_5, mass %	As_2O_5 mol/kg H_2O [b]	CdO, mass %	CdO, mol/kg H_2O [b]	Solid phase [c]
0.08	0.0035	trace	- - - - -	
3.85	0.17	0.40	0.033	A
7.85	0.37	0.75	0.064	
11.80	0.59	1.70	0.15	
11.80	0.59	1.72	0.15	A + B
11.85	0.60	1.75	0.16	A + B
11.80	0.59	1.70	0.15	
14.22	0.74	2.20	0.21	B
17.75	0.97	2.42	0.24	
22.00	1.28	3.45	0.36	
22.20	1.30	3.35	0.35	
22.15	1.30	3.42	0.36	B + C
22.10	1.29	3.39	0.35	B + C
22.10	1.29	3.30	0.34	B + C
28.40	1.81	3.40	0.39	
32.60	2.22	3.60	0.44	
39.80	3.06	3.65	0.50	
46.20	4.01	3.70	0.58	C
53.20	5.26	2.80	0.50	
59.80	6.81	2.00	0.41	
65.40	8.68	1.82	0.43	
65.52	8.74	1.85	0.44	C + D
65.50	8.74	1.87	0.45	C + D
66.20	8.84	1.20	0.29	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Mixtures were placed in polyethylene flasks and shaken in a thermostat. Equilibrium was determined by analysis. Arsenic content was determined iodometrically, and the cadmium content was determined by a complexiметric titration. The composition of the solid phases was determined by the Schreinemakers' wet-residue method.

SOURCE AND PURITY OF MATERIALS:
No information is given.

ESTIMATED ERROR:
No numerical data are given in the paper but from the data supplied in a personal communication from one of the authors it appears that the error is of the order of 1%.

REFERENCES:

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]

(2) Arsenic(V) oxide; As_2O_5; [1303-28-2]

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

ORIGINAL MEASUREMENTS:

Omezzine, B. K.; Ariguib-Kbir, N.
Compt. rend. 1978, *286*, 197-9.

EXPERIMENTAL VALUES,CONTD:

Solubility of CdO in aqueous solutions of As_2O_5 at 25°C. [a]

As_2O_5, mass %	As_2O_5 mol/kg H_2O [b]	CdO, mass %	CdO, mol/kg H_2O [b]	Solid phase [c]
68.00	9.48	0.80	0.20	D
70.20	10.25	trace	----	
71.60	10.97	trace	----	

[a] The article contains only a phase diagram. These numerical data were given in a personal communication of Sept. 11, 1982 from Prof. N. Kbir-Arguib.

[b] calculated by the compiler.

[c] A = $5CdO \cdot 2As_2O_5 \cdot 5H_2O$; B = $2CdO \cdot As_2O_5 \cdot 2H_2O$; C = $CdO \cdot As_2O_5 \cdot 4H_2O$;
D = $CdO \cdot 2As_2O_5 \cdot 5H_2O$.

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]
(2) Potassium hydroxide; KOH; [1310-58-3]
(3) Sodium hydroxide; NaOH; [1310-73-2]
(4) Lithium hydroxide; LiOH; [1310-65-2]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Rozentsveig, S. A.; Ershler, B. V.; Shtrum, E. L.; Ostanina, M. M. *Trudy Soveschaniya Elektrokhim. Akad. Nauk. SSSR, Otdel. Khim. Nauk* 1950, 571-8.

VARIABLES:

Concentration of the alkali hydroxides.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of $Cd(OH)_2$ in aqueous alkalies

$C_{alkalies}$/mol dm^{-3}	C_{Cd}/mol dm^{-3} in KOH	in NaOH	in LiOH
1	9×10^{-6}	9×10^{-6}	- - - - -
2.5	6×10^{-5}	5×10^{-5}	traces
4	9×10^{-5}	10^{-4}	4.4×10^{-5}
7	1.2×10^{-4}	1.4×10^{-4}	9×10^{-5}
10	1.5×10^{-4}	1.6×10^{-4}	1.21×10^{-4}

No temperature is specified for these results but the results appear to have been obtained at room temperature. The solubility determinations were incidental to the main purpose of the authors, which was to describe the electrochemical behavior of cadmium in these solutions.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The only statement about the procedure is that the analytical results were determined by a polarographic method. Nothing is stated about the method whereby equilibrium was attained or verified.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No information is given.

REFERENCES:

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

(2) Perchloric acid; $HClO_4$; [7601-90-3]

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Gayer, K. H.; Woontner, L. *J. Phys. Chem.* 1957, *61*, 364-5.

VARIABLES:

Alkalinity and acidity at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table 1

Solubility of $Cd(OH)_2$ in $HClO_4$ solutions at 25°C.

pH	(Activity of $HClO_4$) x 10^{8a}	(mols Cd/kg H_2O) x 10^4
8.98	(water solubility)	0.15
7.62	2.4	15.1
7.35	4.5	19.5
7.05	8.5	44

[a]presumably the activity is expressed as mol $HClO_4$/kg H_2O.

Table 2

Solubility of $Cd(OH)_2$ in NaOH solutions at 25°C.

(mol OH^- dm^{-3}) x 10^5	(mol Cd^{2+} dm^{-3}) x 10^6
1.00	15.0
1.60	7.9
2.30	7.0
66	3.5
560	3.6
5500	5.9
10100	6.2
2.8×10^6 [b]	7.5
5.4×10^4	8.8
9.0×10^4	13.0
1.4×10^5	22
1.8×10^5	38
2.1×10^5	63

[b]this is obviously a misprint in the original article and should be 2.8×10^4.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Duplicates were made of each mixture. One was shaken at 25°C for at least a week and then allowed to settle 3-5 days. The other was shaken at 35°C for at least a week and then allowed to settle at 25°C for 3-5 days. pH determination was made with a pH meter. Cd content was determined colorimetrically as a dithizone complex.

SOURCE AND PURITY OF MATERIALS:

Conductivity water, carbonate-free NaOH, and purified 70% $HClO_4$ were used. $Cd(OH)_2$ was prepared by the slow hydrolysis of a dilute solution of cadmium acetate using reagent grade materials.

ESTIMATED ERROR:

No information is given and apparently only the average results of the duplicate samples are published.

REFERENCES:

COMPONENTS:

(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

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

ORIGINAL MEASUREMENTS:

Ryan, D.E.; Dean, J.R.; Cassidy, R.M.
Can. J. Chem. 1965, *43*, 999-1003

VARIABLES:

OH^- ion concentration at 24.5° and at constant ionic strength

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table 1

Solubility of $Cd(OH)_2$ in NaOH solutions.

Ionic strength = 7 mol dm^{-3}		Ionic strenth = 1 mol dm^{-3}	
mol OH^- dm^{-3}	(mol $Cd(OH)_2$ dm^{-3}) x 10^5	mol OH^- dm^{-3}	(mol $Cd(OH)_2$ dm^{-3}) x 10^5
7.0	16.0	0.93	0.4
6.0	11.0	0.54	0.2
5.0	7.6	0.47	0.1
4.0	4.9	0.26	0.2
3.0	2.5	0.047	0.2
2.0	1.2	6.3×10^{-4}	0.6
1.0	0.5	4.1×10^{-4}	0.8
0.75	0.3	1.7×10^{-4}	2.2
0.10	0.2	6.8×10^{-5}	4.8
0.05	0.2	5.5×10^{-5}	5.5
0.01	0.3		
0.005	0.4		

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cd(OH)_2$ was prepared by dropwise addition of 1.5 M NaOH to a dilute $Cd(NO_3)_2$ solution. The precipitate was washed and allowed to stand in water for 12 hours before being used. Then it was added to the NaOH solutions and the mixture was shaken for 10-14 days. Ionic strength was maintained by adding $NaClO_4$. The analysis for Cd^{2+} was done by measuring the fluorescence when 8-hydroxyquinoline-5-sulfonic acid was added (1). At least 3 replicate samples were used each time.

SOURCE AND PURITY OF MATERIALS:

Double distilled water was used and precautions were taken to exclude carbonate ion and CO_2.

ESTIMATED ERROR:

Solubility values have an uncertainty of $\pm 1 \times 10^{-6}$ mol dm^{-3}.

REFERENCES:

1. Bishop, J.A. *Anal. Chim. Acta* 1963, *29*, 172.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cadmium hydroxide; $Cd(OH)_2$; [21041-95-2] (2) Ammonia; NH_3; [7664-41-7] (3) Sodium perchlorate; $NaClO_4$; [7601-89-0] (4) Water; H_2O; [7732-18-5]	Gubeli, A. O.; Taillon, R. *Helv. Chim. Acta* 1971, *54*, 2559-68.
VARIABLES:	PREPARED BY:
Concentration of ammonia at constant ionic strength of 1 mol dm^{-3}.	T. P. Dirkse

EXPERIMENTAL VALUES:

No numerical data are given. Equations are derived for the toal concentration of cadmium and of ammonia in terms of equilibrium constant expressions. Then, using analytical results, a set of equations is solved simultaneously to derive several equilibrium constant values. These calculated constants are then used to calculate a solubility curve of $Cd(OH)_2$ as a function of pH and of ammonia concentration. These calculated curves are then compared to the experimentally determined values.

The calculated results at 25°C are as follows (these are concentration ratios):

$Cd(OH)_2(s) = Cd^{2+} + 2OH^-$	$\log K_{so} = -14.6$
$Cd^{2+} + OH^- = CdOH^+$	$\log K_{10} = -4.7$
$Cd^{2+} + 2OH^- = Cd(OH)_2(aq)$	$\log K_{20} = -7.8$
$Cd^{2+} + 4OH^- = Cd(OH)_4^{2-}$	$\log K_{40} = -9.7$
$Cd^{2+} + NH_3 = Cd(NH_3)^{2+}$	$\log K_{01} = 3.1$
$Cd^{2+} + 2NH_3 = Cd(NH_3)_2^{2+}$	$\log K_{02} = 5.2$
$Cd^{2+} + 3NH_3 = Cd(NH_3)_3^{2+}$	$\log K_{03} = 6.5$
$Cd^{2+} + 4NH_3 = Cd(NH_3)_4^{2+}$	$\log K_{04} = 7.8$
$Cd^{2+} + 2OH^- + NH_3 = Cd(OH)_2(NH_3)$	$\log K_{21} = 9.85$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$Cd(OH)_2$ was added to the solutions and agitated for a few days and then allowed to rest for a week. pH was measured with a glass electrode. Cadmium content was measured by EDTA titration or colorimetrically using the method of Saltzman (1). The ionic strength was maintained by adding $NaClO_4$.

SOURCE AND PURITY OF MATERIALS:

The $Cd(OH)_2$ was prepared by adding aqueous NaOH to a solution of $Cd(ClO_4)_2$. Nothing is said about the purity of any of the materials used.

ESTIMATED ERROR:

Nothing is said about temperature control. The calculated equilibrium constants have a standard deviation of ±0.02.

REFERENCES:

1. Saltzman, B. E. *Anal. Chem.* 1953, *25*, 493.

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]

(2) 2-Aminoethanol; C_2H_7NO; [141-43-5]

(3) 2,2'-Iminodiethanol; $C_4H_{11}NO_2$; [111-42-2]

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

ORIGINAL MEASUREMENTS:

Danilov, V. V.,; Martinson, I. G.; Ravdel, A. A. *Zh. Obshch. Khim.* 1974, *44*, 718-21.

VARIABLES:

Solution composition and the temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CdO in the system CdO-2-aminoethanol-water

mol 2-aminoethanol dm^{-3}	mol CdO dm^{-3} 25°C	30°C	40°C	50°C	Solid phase[a]
1.00	0.0042	0.0040	0.0036	0.0033	$Cd(OH)_2$
2.00	0.018	0.017	0.016	0.014	"
3.02	0.039	0.037	0.033	0.031	$Cd(OH)_2 \cdot 2MEA$
4.01	0.066	0.060	0.054	0.052	"
5.35	0.13	0.12	0.11	0.10	"
7.10	0.29	0.28	0.27	0.24	"
11.00	0.62	0.59	0.55	0.50	"

[a]MEA represents 2-aminoethanol

Solubility of CdO in the system CdO-2,2'iminodiethanol-water

mol 2,2'-iminodiethanol dm^{-3}	mol CdO dm^{-3} 25°C	30°C	40°C	50°C	Solid phase
1.20	0.0017	0.0016	0.0014	0.0012	$Cd(OH)_2$
1.51	0.0030	0.0028	0.0024	0.0021	"
2.03	0.0048	0.0044	0.0039	0.0032	"
2.56	0.0071	0.0066	0.0057	0.0048	"
3.00	0.010	0.0093	0.0079	0.0069	"
4.02	0.022	0.020	0.018	0.015	"
5.92	0.095	0.089	0.080	0.069	"
7.80	0.19	0.18	0.17	0.15	"

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solutions were equilibrated 30 days with intermittent stirring. Equilibrium was approached from both high and low temperatures. The cadmium content was determined by titration with Trilon B at a pH of about 10 using Eriochrome Black T as indicator. The composition of the solid phase was inferred from a calculation of activity products.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

No information is given about the reproducibility of the analyses nor about the temperature control.

REFERENCES:

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Shlyapnikov, D. S.; Shtern, E. K.
Dokl. Akad. Nauk SSSR 1975, 225, 428-31; *Russ.*;
Dokl. Acad. Sci. USSR, Earth Sci. Sect. (Engl. transl.) 1975, 225, 185-8.

VARIABLES:

Sodium chloride concentration and pressure of carbon dioxide at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of CdO at 20°C and a CO_2 pressure of 50 atm.

g Cd dm^{-3} in H_2O	g Cd dm^{-3} in 4 mol NaCl dm^{-3}	mol CdO dm^{-3} in H_2O	mol CdO dm^{-3} in 4 mol NaCl dm^{-3} [a]
2.8500	4.5140	0.025	0.040

[a] calculated by the compiler.

The solubility of CdO increases linearly with increasing mol NaCl dm^{-3}.

The solubility of CdO is said to increase with increasing temperature but no quantitative data are given.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solution and solid CdO were shaken in an autoclave for 24 hours at the prescribed temperature. CO_2 was introduced as a solid. Metal analysis was done complexiметrically and colorimetrically. No further details are given.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

This cannot be determined from the information given in the article.

REFERENCES:

COMPONENTS:

(1) Cadmium oxide; CdO; [1306-19-0]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Shlyapnikov, D. S.; Shtern, E. K.
Dokl. Akad. Nauk SSSR, Ser. Geol.
1979, *249*, 457-61.

VARIABLES:

Pressure of carbon dioxide and concentration of NaCl at 20°C.

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility and composition of solid phases in the system CdO-NaCl-H_2O-CO_2 at 20°C.

P_{CO_2}	starting solution mol NaCl dm^{-3}	filtrate g Cd dm^{-3}	solid residue %Cd	%CO_2	%Cl	solid composition
1 atm	0	0.23	72.1	14.4	---	CdO + $CdCO_3$
"	1	0.88	65.8	24.4	1.5	$CdCO_3$
"	2	1.5	65.4	24.7	2.1	$CdCO_3$
"	4	3.3	66.1	23.5	2.8	$CdCO_3$
50 atm	0	0.4	65.8	24.1	---	$CdCO_3$
"	1	2.7	65.9	22.3	2.6	$CdCO_3$
"	2	5.06	65.8	24.2	2.4	$CdCO_3$
"	4	9.6	64.8	22.8	1.4	$CdCO_3$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid CdO and solvent are mixed and CO_2 is bubbled through, or the mixture is added to a rocking autoclave and solid CO_2 is added. The analytical methods were; titration with $AgNO_3$ for Cl^-; gas absorption for CO_2; titration with complexing agents for Cd^{2+}. The solid phases were identified by X-ray diffraction diagrams.

SOURCE AND PURITY OF MATERIALS:

The CdO was prepared from reagent grade materials. No information is given about the other materials that were used.

ESTIMATED ERROR:

The article contains no information about control of temperature and pressure nor about the reproducibility of the analytical procedures.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water, H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

Mercury is found in two oxidation states in its compounds: + and 2+. However, mercury does not show this dual behavior in its stable oxides. In the early literature Hg_2O was considered to be one of the oxides of mercury and several studies were carried out to determine quantitatively some of its physical properties.

Bugarszky (1) made e.m.f. measurements of cells containing Hg_2O/Hg electrodes. Later, Brodsky (2) measured the temperature dependence of the activity coefficients of $Hg_2(NO_3)_2$ in water, and the E° value for the Hg^{2+}/Hg electrode and from these results and those of Bugarszky calculated the solubility product of Hg_2O in water to be 1.8 x 10^{-24} mol^3 dm^{-9} at 298 K.

Allmand (3) attempted to repeat some of this work but found that the Hg_2O electrodes he prepared gave the same values as did HgO electrodes. Identical values were obtained whether or not light was excluded. Therefore, Allmand concluded that all calculations based on the e.m.f. of Hg_2O electrodes have dubious value because Hg_2O is unstable in aqueous solution and these electrodes then are always contaminated with an unknown quantity of HgO. Later (4) it was shown by X-ray analysis that Hg_2O is an intimate mixture of HgO and metallic mercury. Sanemasa (5) made a kinetic study of this disproportionation of Hg_2O in water.

No further data on Hg_2O are included because of this instability.

HgO crystals are red or yellow, depending on the method of preparation. When $Hg(NO_3)_2$ is heated, red crystals of HgO are obtained, while when OH^- ions are added to aqueous solutions of Hg^{2+} ions in the cold, yellow crystals of HgO precipitate. The difference between these two forms has been the subject of some disagreement. Cohen (6), as a result of some very careful work, obtained a value of 0.685 mV for the e.m.f. of the following cell:

$$\text{Hg} \mid \text{HgO(yellow)} \mid \text{alkali} \mid \text{HgO(red)} \mid \text{Hg.} \qquad (1)$$

This value remained constant for 3 days but only after a week had elapsed. From this Cohen concluded that the red and yellow forms were isomers and, at 298.2 K, the red form was the less stable and the less soluble. He stated that the red and yellow forms dissolved at different rates and he gave this as the reason it took about a week for the cell to reach equilibrium.

Ostwald (7) maintained that the difference between the red and yellow forms was merely one of particle size. This results in a difference in solubility, and Ostwald insisted that this was the cause of the e.m.f. of the cell represented in equation (1). As proof of this contention Ostwald ground up red crystals of HgO and obtained yellow ones. He also studied the extent to which the following reaction proceeded:

$$\text{HgO(s)} + \text{H}_2\text{O} + 2\ \text{KBr}\cdot\text{aq} = 2\ \text{KOH}\cdot\text{aq} + \text{HgBr}_2\cdot\text{aq.} \qquad (2)$$

He found that the amount of KOH produced depended on the particle size of the HgO.

Hulett (8) pursued this matter further. He found that by digestion and decantation he could separate the most finely divided particles (which had a yellow color) from a sample of red HgO. Although he made only qualitative measurements he also found that by grinding red HgO he could increase its solubility in water at 298 K. He concluded from this that the red and yellow forms were not isomers but merely differed in particle size.

Schoch (9) made a microscopic examination of the two forms of HgO and concluded that there were two crystal forms: prismatic (red) and square tablets (yellow). He also found that the color did change with particle size and with heating, but

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

maintained that color is no criterion of crystal form because the finely ground red form changed color on heating but the finely ground yellow form did not. He concluded that the red form is probably the less soluble one at room temperature (this is not in agreement with solubility results determined later by others).

Allmand (3) measured the e.m.f. of the following cell:

Hg | HgO(s) | aq. alkali | calomel electrode. (3)

He used both red and yellow HgO. No solubility values are given in the paper but Allmand made the following observations: (a) in general, the red HgO gives the lower e.m.f. value and, consequently, is less soluble and less stable; (b) the e.m.f.'s generally decreased with time, and while this ordinarily indicates a phase change, this cannot be the explanation here because this decrease occurred with both forms of HgO; (c) the electrodes with the highest e.m.f. values had the smallest particle size when viewed microscopically; (d) the e.m.f. of a cell such as that of equation (1) was less than the experimental uncertainty of the measurement. Consequently, Allmand concluded also that the red and yellow forms were not isomers but differed only in particle size.

Ostwald (7) determined the amount of KOH produced by reaction (2). He used both forms of HgO and found that the differences were within the experimental uncertainty. He also found that by grinding the oxides more finely a larger amount of KOH was formed. Garrett and Hirschler (10) did observe differences in the solubility of the two forms but hesitated to conclude that this difference was significant enough to warrant the assumption that the two forms are isomers. The solubility of the two forms in HNO_3 (11) show no significant differences. Schick (12) observed that mixtures of the red HgO in water sometimes deposited a yellow form of the oxide on the walls of the container. He also found that mixtures of HgO with a small amount of water became redder in color when warmed and yellower when cooled.

Consequently, it appears that the differences that have been observed can be accounted for adequately by assuming that the yellow and red forms differ in particle size and the more finely divided the particles are (yellower) the larger the solubility value. This conclusion is confirmed by careful X-ray powder diffraction measurements, which are the same for both forms of HgO (13).

Solubility in water.

Only five papers report a directly determined value for the solubility of HgO in water. Schick (12), Fuseya (14), Garrett and Hirschler (10), and Herz and Hiebenthal (15) made the determination at 298.2 K while Salem (16) made the determination at 308.2 K. Schick and Garrett and Hirschler used both red and yellow HgO while the others used only the red form. In view of the relationship between solubility and particle size the best results are those in which the system was allowed to equilibrate the longest time. Schick does not state how many days were allowed for equilibration but indications are that it was a week or more. He found very little difference between the solubilities of the red and yellow forms. Garrett and Hirschler found a larger difference but were reluctant to state the significance of this difference. The values they obtained with red HgO were less reproducible than those obtained with yellow HgO, probably because of non-uniformity of particle size. In view of all this the solubility of HgO in water is within 3% of 2.37×10^{-4} mol dm^{-3} at 298.2 K and within 3% of 3.47×10^{-4} mol dm^{-3} at 308.2 K.

Five papers report a value for the solubility product of $Hg(OH)_2$. Labendzinski (17) gives a value of 1.5×10^{-26} which was determined in his laboratory by Fulda, a colleague. However, there is no indication as to the experimental basis for this value, although it appears to be based on an e.m.f. measurement. No temperature is given. Grossmann (18) used the dissociation constants of $HgBr_4^{2-}$ and $Hg(SCN)_4^{2-}$ which

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

he and others measured and the assumed reaction (4) to derive a value of 4 x 10^{-26} mol^3 dm^{-9}

$$Hg(OH)_2 + 4\ X^- = HgX_4^{2-} + 2\ OH^- \quad (4)$$

for the value of K_{so} of $Hg(OH)_2$ at 298 K.

Allmand (3) measured the e.m.f.'s of cells containing the Hg | HgO | alkali | electrode and a calomel electrode. He does not give the values for the cell e.m.f.'s but only his derived half-cell values. In deriving these he made the following assumptions: (a) E for the normal calomel electrode is 0.283 V; (b) K_w = 0.56 x 10^{-14}; (c) E^o for the Hg^{2+}/Hg^o electrode is 0.835 V; (d) the junction potential between the NaOH and KCl solutions is 0.020 V while that between the KOH and KCl solutions is 0.015 V. All these values are at 291 K. He also made assumptions about the degree of ionization of the alkali solutions. These values differed by as much as 10% from the activity coefficients of these same solutions as determined later (19). With these assumptions he derived a value of 4 x 10^{-26} mol^3 dm^{-9} for K^o_o for $Hg(OH)_2$ at 291 K.

Maijs (20) derived a value of pK_{so} = 15-26 for $Hg(OH)_2$. This was based on calculations involving a thermochemical cycle, semiempirical relationships, and published data of the pH of complete precipitation of $Hg(OH)_2$ from aqueous solutions. No temperature is specified.

Solubility measurements at a constant ionic strength of 3 mol dm^{-3} (using perchlorate ion to maintain ionic strength) also gave a value of 10^{-26} mol^3 dm^{-9} for the solubility product constant at 298 K (21). However, in a 3 mol dm^{-3} solution of $NaClO_4$ the solubility of $Hg(OH)_2$ was 1.78 x 10^{-4} mol dm^{-3}. This is slightly less than the solubility in water and was attributed to a "salting out" effect.

Because of the divergent values reported, the solubility product of $Hg(OH)_2$ can only be said to be approximately 10^{-26} mol^3 dm^{-9} at room temperature.

Solubility as a function of pH.

Much of the interest in the solubility of HgO in aqueous solutions has as its purpose the determination of the extent to which the $Hg(OH)_2$ formed in solution acts as an acid and as a base. As an acid it may ionize as follows:

$$Hg(OH)_2 = H^+ + HHgO_2^- \quad (5)$$

$$HHgO_2^- = H^+ + HgO_2^{2-} \quad (6)$$

The equilibrium quotients are:

$$K_5 = m_{H^+} \odot m_{HHgO_2^-}/m_{Hg(OH)_2} \quad (7)$$

and

$$K_6 = m_{H^+} \odot m_{HgO_2^{2-}}/m_{HHgO_2^-} \quad (8)$$

In alkaline solutions the following reactions take place.

$$HgO(s) + OH^- = HHgO_2^- \quad (9)$$

$$HgO(s) + 2\ OH^- = HgO_2^{2-} + H_2O \quad (10)$$

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

The equilibrium constant expressions for the above reactions are:

$$K_9^o = a_{HHgO_2^-}/a_{OH^-} \quad (11)$$

and

$$K_{10}^o = a_{HgO_2^{2-}}/(a_{OH^-})^2 \quad (12)$$

and the total solubility, m_T, may then be expressed as

$$m_T = m_{Hg(OH)_2} + m_{HHgO_2^-} + m_{HgO_2^{2-}} \quad (13)$$

Making substitutions from the equilibrium constant expressions and assuming the validity of the Debye-Huckel relationship for activity coefficients in these dilute solutions, equation (13), following a procedure described earlier (22), reduces to

$$m_T = m_{Hg(OH)_2} + K_9^o \cdot m_{OH^-} + K_{10}^o \cdot (m_{OH^-})^2/\gamma_{NaOH} \cdot a_{H_2O} \quad (14)$$

Fuseya (14) and Garrett and Hirschler (10) found a linear relationship between the solubility of HgO and molality of base up to a base molality of 1 mol kg^{-1}. This indicates that the last term in equation (14) contributes less than the experimental uncertainty and the concentration of HgO_2^{2-} in these dilute solutions is negligible. Equation (14) then, in effect, becomes

$$m_T = m_{Hg(OH)_2} + K_9^o \cdot m_{OH^-} \quad (15)$$

A plot of m_T vs alkali concentration gives an intercept of 2.4×10^{-4} mol $Hg(OH)_2$ dm^{-3}. This is the solubility of $Hg(OH)_2$ at 298.2 K and the value of the equilibrium quotient, K_{16}, for reaction (16).

$$HgO(s) + H_2O = Hg(OH)_2(sln) \quad (16)$$

$$K_{16} = m_{Hg(OH)_2} \quad (17)$$

The slope of the line is 3.1×10^{-5} and this is the value of K_9^o at 298.2 K. From the values of K^o_9, K_{16}, and the ion product constant of water, K_5 can be calculated and its value at 298.2 K is 1.4×10^{-15} mol dm^{-3}.

The work of Garrett and Hirschler (10) shows that in alkalies the solubility of HgO is independent of the cation but does depend on the nature of the anion as well as on the total ionic strength. However, in the absence of alkalies, the solubility does appear to depend on the nature of the cation as well (15). In chloride solutions the increase in solubility due to the presence of the cation was $Li^+ > Na^+ > K^+$. But the solubility is not a linear function of the concentration of the salts used. No work has been reported dealing more specifically with the effect of the total ionic strength in alkaline solutions.

In neutral and acid solutions $Hg(OH)_2$ acts as a base and may ionize as follows:

$$Hg(OH)_2 = HgOH^+ + OH^- \quad (18)$$

$$Hg(OH)_2 = Hg^{2+} + 2\ OH^- \quad (19)$$

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

or

$$HgO(s) + H^+ = HgOH^+ \quad (20)$$

$$HgO(s) + 2\,H^+ = Hg^{2+} + H_2O \quad (21)$$

The corresponding equilibrium quotients are:

$$K_{18} = m_{HgOH^+} \cdot m_{OH^-}/m_{Hg(OH)_2} \quad (22)$$

$$K_{19} = m_{Hg^{2+}} \cdot (m_{OH^-})^2/m_{Hg(OH)_2} \quad (23)$$

$$K_{20} = m_{HgOH^+}/m_{H^+} \quad (24)$$

$$K_{21} = m_{Hg^{2+}}/(m_{H^+})^2 \quad (25)$$

Evaluation of the equilibrium constants for reactions (18) -(21) is complicated by the fact that the solubility of HgO in acid solutions is affected by the anions present because of the formation of complex ions involving these anions. This is particularly true of the halide ions. Another complication is that the solubility is large enough so that a significant, but unknown, amount of H^+ ions is used up in the dissolving process. Garrett and Howell (11) used a method of successive approximations to arrive at the following values: $K_{20} = 0.17$ and $K_{21} = 53$, both at 298.2 K. These values, together with the ion product constant of water and the solubility of undissociated $Hg(OH)_2$ in water give $K_{18} = 7.1 \times 10^{-12}$ mol dm^{-3} at 298.2 K and $K_{19} = 2.2 \times 10^{-23}$ mol^2 dm^{-6} at 298.2 K. The latter value is slightly less than that calculated from the solubility of HgO in alkali solutions. However, it is the better value because of the uncertainties in the $K_s^\circ O$ value for $Hg(OH)_2$.

A summary of the variation of the solubility of HgO with pH is given on Figure 1.

Oka (23) reports a value of 10^{-22} mol^2 dm^{-6} at 298 K for K_{19}. This was obviously calculated from data obtained by titrating a solution of $Hg(NO_3)_2$ in HNO_3 with NaOH. However, no indications are given as to what the calculations were or how they were made. Nor is there any indication of the experimental uncertainty. Consequently, the value of K_{19} given above is to be preferred to that of Oka.

Bilinski, et al. (24) determined values for K_{18} and K_{19} in an indirect manner. They measured the solubility of $HgCO_3 \cdot 2HgO$ at a constant ionic strength of 0.5 mol dm^{-3} over a wide range of pH. At a pH above about 9.6 yellow HgO was the only solid phase appearing at 298 K. The data are presented only in graphical form. However, the numerical data were kindly made available to us in a personal communication from Dr. H. Bilinski. The solubility of HgO at pH = 10.4 is 4.64×10^{-4} mol dm^{-3}. It is independent of the carbonate ion concentration up to a carbonate ion concentration of about 0.01 mol dm^{-3}. This solubility is slightly larger than that shown in Figure 1 at the corresponding pH. This is due to the presence of mercury-carbonato in addition to mercury-hydroxo solute species.

An equation for the total solubility of mercury in the form of the simplest polynomial in H^+ ion concentration that would fit the data was developed[24]. From this treatment a value of $K_{18} = 6.8 \times 10^{-12}$ mol dm^{-3} was obtained. This is within the experimental uncertainty of the value given above.

A value of $K_{19} = 5 \times 10^{-22}$ mol^2 dm^{-6} was also deduced from this treatment. This is about an order of magnitude larger than the value given above. However, because of the indirectness of the method used, the lower value is the preferred one.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

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

EVALUATOR:

T. P. Dirkse
Department of Chemistry
Calvin College
Grand Rapids, Michigan 49506, U.S.A.
March 1983

CRITICAL EVALUATION:

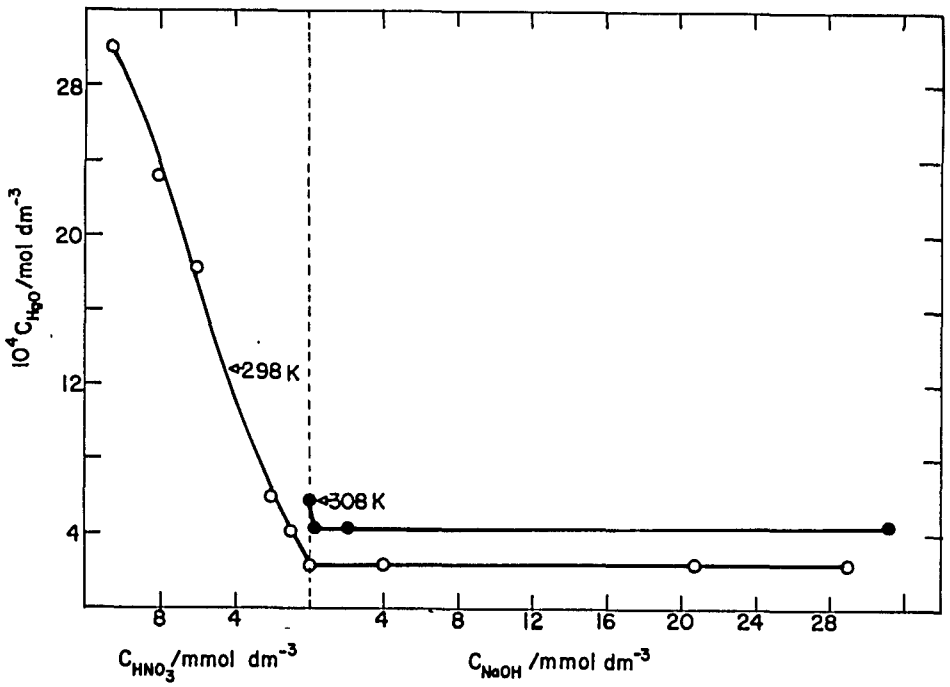

Figure 1. Solubility of HgO as a function of acidity-alkalinity.

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

A summary of the equilibrium constants for various reactions involving HgO and $Hg(OH)_2$ is given in Table I.

Table I

Tentative equilibrium constant values at 298 K for $HgO/Hg(OH)_2$ system, based on solubility measurements

$Hg(OH)_2(sln) = H^+ + HHgO_2^-$	$K_5 = 1.4 \times 10^{-15}$ mol dm^{-3}
$HgO(s) + OH^- = HHgO_2^-$	$K_9^o = 3.1 \times 10^{-5}$
$HgO(s) + H_2O = Hg(OH)_2(sln)$	$K_{16} = 2.4 \times 10^{-4}$ mol dm^{-3}
$Hg(OH)_2(sln) = HgOH^+ + OH^-$	$K_{18} = 7.1 \times 10^{-12}$ mol dm^{-3}
$Hg(OH)_2(sln) = Hg^{2+} + 2\ OH^-$	$K_{19} = 2.2 \times 10^{-23}$ mol^2 dm^{-6}
$HgO(s) + H^+ = HgOH^+$	$K_{20} = 0.17$
$HgO(s) + 2\ H^+ = Hg^{2+} + H_2O$	$K_{21} = 53$ mol^{-1} dm^3

K_{so}^o for $Hg(OH)_2$ is approximately 10^{-26} mol^3 dm^{-9}.

The above values are considered as tentative because there is a lack of corroborating work reported.

Some solubility determinations have also been made in aqueous HCl (25) and in aqueous HF (26, 27). The solubility values here tend to become erratic because of complexes formed with the acid anion. Thus, in HCl solutions a black solid phase, $2HgO \cdot HgCl_2$, was formed in molalities of HCl as low as 0.007 mol/kg. Above molalities of 0.1 mol/kg it appeared to be the only solid phase present and its solubility in water at 298 K was measured to be 11.4×10^{-4} mol/kg H_2O.

Likewise, the solubility of HgO in aqueous HF is accompanied by the formation of $HgO \cdot HF$ and $HgF_2 \cdot 2H_2O$. Jaeger (26) does not explicitly state the nature of the equilibrium solid phase but the implication is that it is HgO. Up to HF concentrations of 4 mol dm^{-3} the solubility of HgO in aqueous HF at 298 K (26, 27) can be expressed as

$$c_{HgO} = 0.103\ c_{HF} \qquad (26)$$

At HF concentrations greater than 4 mol dm^{-3} the data available are erratic, perhaps due to the appearance of more than one solid phase.

A few data are available on the solubility of HgO in aqueous solutions of sodium sulfide (28) at 298 K. However, these data cannot be evaluated because of insufficient experimental detail in the article and the lack of other work dealing with the same system.

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

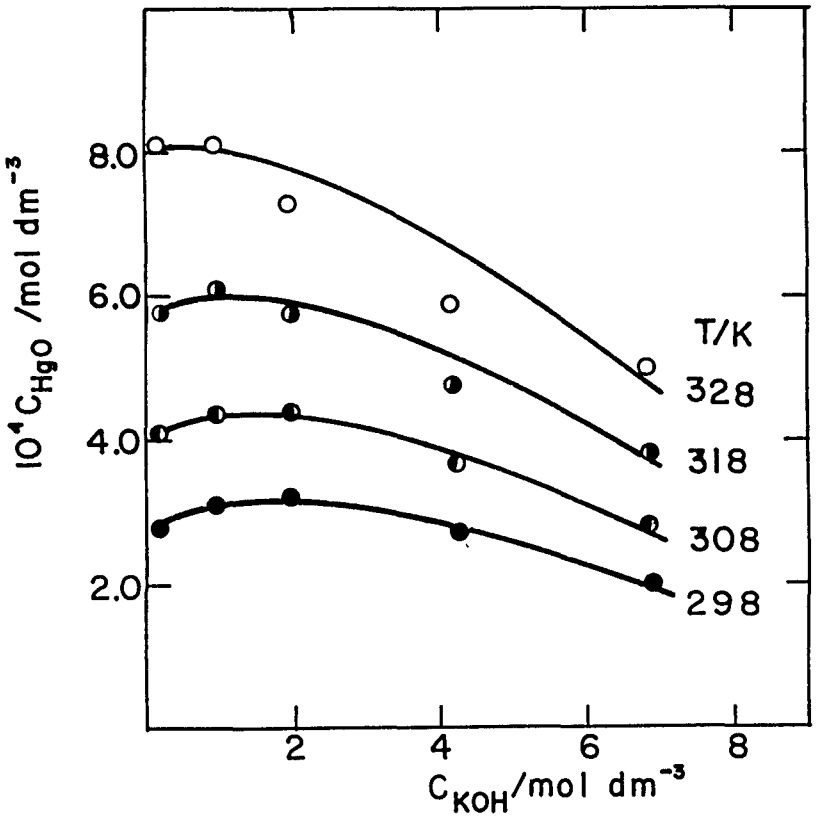

Figure 2. Solubility of HgO in aqueous KOH, ref. (35).

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

Solubility at higher temperatures

The solubility of HgO in water at 308 K is 3.5 x 10-4 mol dm^{-3}. The solubility in NaOH solutions is also larger at this temperature than at 298 K. Furthermore, the point of minimum solubility is in the very dilute alkaline region, Figure 1, rather than in water as it is at 298 K. This indicates that raising the temperature increases the basic nature of $Hg(OH)_2$ relative to its acid character.

Scholder and Staufenbiel (29) attempted to prepare mercurates in a manner similar to that by which they prepared cadmates. They were unsuccessful in their attempts to isolate solid mercurates. But in the course of this work they did measure the solubility of HgO in 18.8 mol NaOH dm^{-3} at 415 K. They obtained a value of 2.1 g HgO dm^{-3}, i.e., 9.7 x 10^{-3} mol dm^{-3}. However, this is the only value reported and only a scant bit of information is given as to the experimental details and no information about the analytical method used to obtain this value.

The solubility of HgO in aqueous KOH solutions has been measured at elevated temperatures using an e.m.f. method (35). The solubility of HgO increases with increasing temperature and has a maximum at a KOH concentration of about 1 mol dm^{-3}, Figure 2. No other work has been reported for these same conditions, and in no instance has a maximum in solubility been noted in either KOH or NaOH solutions. Therefore, although the work has been carried out carefully, the results can only be considered tentative.

Unfortunately, no pH values are given for the acetic acid-acetate mixtures used for the solubility study at 308 K (30). The data show no apparent relationship between solubility of HgO and calculated pH values. The solubility values are perhaps affected by the formation of various acetate complexes with the Hg^{2+} ions but the data are too scattered to allow for any quantitative interpretation of this possibility.

Table II

Recommended solubility values for HgO in water.

temp	Solubility
298.2 K	2.37 x 10^{-4} mol dm^{-3}
308.2 K	3.47 x 10^{-4} mol dm^{-3}

Solubility of HgO in sea water

Interest in this system is related to the fact that HgO is an ingredient of some marine antifouling paints. Two papers deal with this subject (31, 32). Only one (32) gives experimental data. These data were obtained in Baltic Sea water. Solubility data were also obtained in water and these agree with the values recommended in Table II above. However, in the article there is a disagreement in the values reported for the solubility of the oxides and nowhere is this disagreement resolved.

The other article (31) also deals with the solubility of HgO in sea water at a pH = 8.1. Only one value is reported and that value is obtained, not from experiment, but from a calculation using the solubility product of $Hg(OH)_2$ and the dissociation constant of $HgCl_2$. No temperature is specified. The one value given is 80,000 x 10^{-6} g ml^{-1}. This is equivalent to 0.37 mol dm^{-3} which is considerably larger than the value reported for Baltic Sea water (32).

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

Solubility of HgO under hydrothermal conditions.

In recent years the solubility of HgO has been of interest to those studying various geochemical processes. As yet relatively few data have been reported in this area. Shlyapnikov and Shtern (33,34) measured the solubility of HgO in NaCl solutions exposed to a CO_2 atmosphere at varying pressures. At a pressure of 50 atm CO_2 the solubility of HgO in water at 293 K is reported as 0.0010 mol dm^{-3}. This is larger than the solubility in water when exposed to ordinary atmospheres. It is also about twice as large as the value in carbonate solutions (24). However, no information is given as to the experimental uncertainty. Because of this and the fact that no other similar data have been reported, the solubility values given by Shlyapnikov and Shtern are tentative and must await further confirmation.

The solubility of HgO in solutions under a carbon dioxide atmosphere at an elevated pressure increases markedly as the concentration of NaCl in the water increases. This is due to the formation of mercury-chloro and basic mercury-carbonato solute species.

COMPONENTS:	EVALUATOR:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Water; H_2O; [7732-18-5]	T. P. Dirkse Department of Chemistry Calvin College Grand Rapids, Michigan 49506, U.S.A. March 1983

CRITICAL EVALUATION:

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35. Zhou, Weifang; Chen, Xialing *Fudan Xuebao, Ziran Kexueban* 1983, *22*, 229.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Baltic Sea water

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

ORIGINAL MEASUREMENTS:

Ragg, M. *Farbe u. Lack* 1950, *56*, 435-41

VARIABLES:

Solvent composition at 18°C and pH = 8.3-8.5

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of HgO at 18°C[b]

	distilled water		Baltic Sea water	
	g HgO dm^{-3}	mol HgO dm^{-3} [a]	g HgO dm^{-3}	mol HgO dm^{-3} [a]
yellow HgO	0.0500	2.3×10^{-4}	0.2188	1.0×10^{-3}
red HgO	0.0515	2.4×10^{-4}	0.1881	8.7×10^{-4}

[a] calculated by compiler

[b] There is a question about the reliability of the values in this Table because later in this article, Table 1 gives a summary of all the experimental results and there the following values are given.

Compound	solubility in mg dm^{-3} distilled water	Baltic Sea water
red HgO	51.5	219
yellow HgO	52.0	288

Nowhere in the article is this discrepancy discussed.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Both yellow and red HgO were used. 0.5 g of the HgO was added to 1 liter of solvent and the mixture was shaken for 48 hours at 18°C. The mixture was then filtered and the filtrate was analyzed for mercury content by adding H_2S and weighing the HgS that was formed.

SOURCE AND PURITY OF MATERIALS:

Distilled water and filtered Baltic Sea water were used as solvents.

ESTIMATED ERROR: No information is given about reproducibility of temperature control or any of the procedures. Furthermore, the data given in the body of the report do not agree with those given in a summarizing Table.

REFERENCES:

COMPONENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Hydrofluoric acid; HF; [7664-39-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Jaeger, A. Z. *Anorg. Chem.* 1901, *27*, 22-40.

VARIABLES:
Concentration of HF at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:
Solubility of HgO in aqueous HF at 25°C.

C_{HF}/mol dm^{-3}	g Hg/9.6 ccm	C_{HgO}/mol dm^{-3}
0.12	0.0242	0.01258
0.24	0.0475	0.0247
0.57	0.1210	0.0629
1.11	0.2247	0.1168
2.17	0.4976	0.2586

The solid phase is not identified but the implication is that it is HgO.

The concentration of HgO varies almost linearly with the concentration of HF. The author concludes from this that the reaction of dissolution is

$$HgO(s) + H_2F_2 = HgF_2 + H_2O,$$

i.e., the molecular formula of hydrogen fluoride is H_2F_2.

In additional experiments, details of which are not included in the article, the solubility of HgO in aqueous HF was found to decrease when KF was added to the aqueous HF. The author attributes this to the lack of formation of mercury fluoride complexes.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Mixtures of red HgO and aqueous HF were shaken in a thermostat at 25°C. The mercury content of the saturated solutions was determined by electrolysis. No information is given about the length of time the mixtures were shaken. The glass apparatus was protected from attack by the HF by coating it with bee's wax or a commercially available gelatin-like material.

SOURCE AND PURITY OF MATERIALS:
The materials were of a chemically pure grade.

ESTIMATED ERROR:
No details are given.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Barium hydroxide; $Ba(OH)_2$; [17194-00-2] (3) Water; H_2O; [7732-18-5]	Schick, K. Z. *physik. Chem.* 1903, *42*, 155-173.
VARIABLES: Red and yellow HgO were used at 25°C.	**PREPARED BY:** T. P. Dirkse

EXPERIMENTAL VALUES:

Table I

Solubility of HgO in water at 25.0°C.

yellow HgO	0.0518 g dm^{-3}	2.39×10^{-4} mol dm^{-3} [a]
red HgO	0.0513 g dm^{-3}	2.37×10^{-4} mol dm^{-3} [a]

[a] Calculated by compiler.

Table II

Solubility of yellow HgO in barium hydroxide solutions at 25.0°C.

mol $Ba(OH)_2$ dm^{-3}	g HgO dm^{-3}	mol HgO dm^{-3} [a]
0.024	0.0586	2.71×10^{-4}
0.13	0.1363	6.29×10^{-4}

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Oxide-solvent mixtures were shaken in a closed vessel in a thermostat for a week, allowed to settle for 36 hours, and filtered. The mercury content was determined by two methods: (a) add 5 g NaCl to 100 ml of solution, heat to boiling and cool to 40-50°C, add phenolphthalein and titrate the NaOH produced by this reaction with HCl; (b) evaporate an aliquot of the solution to dryness and weigh the residue. Equilibrium was approached from both supersaturation and under saturation.	Conductivity water and purified forms of the red and yellow HgO were used.
	ESTIMATED ERROR: The impurities in the oxides were estimated at less than 0.005%.
	REFERENCES:

COMPONENTS:

(1) Mercury(II)oxide; HgO: [21908-53-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Fuseya, G. *J. Am. Chem. Soc.* 1920, *42*, 368-71.

VARIABLES:

Concentration of NaOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Red HgO was used. The results are reported at 25±0.01°C.

mol dm^{-3} NaOH	mol dm^{-3} OH^- [a]	Milligrams HgS in 100 ml solution	mol dm^{-3} HgO [b]	equilibrium constant [b,c]
2.09	1.253	7.20	3.09×10^{-4}	3.06×10^{-5}
1.0758	0.7660	6.52	2.80×10^{-4}	3.25×10^{-5}
0.502	0.4257	6.17	2.65×10^{-4}	3.98×10^{-5}
0.0955	0.0863	5.79	2.49×10^{-4}	4.19×10^{-5}
0.0503	0.0465	5.75	2.47×10^{-4}	3.98×10^{-5}
0.0096	0.0091	5.73	2.46×10^{-4}	-----
0.0000	0.0000	5.43	2.33×10^{-4}	----

[a] Values obtained by multiplying the NaOH concentration by the corresponding equivalent conductance ratios (1).

[b] Calculated by the compiler. The calculations in the original paper are in error.

[c] For the reaction $OH^- + HgO(s) \rightarrow HHgO_2^-$ on the basis of the following assumptions: (1) the total concentration of the OH^- ion is not appreciably altered by the reaction with HgO; (2) the degree of ionization of $NaHgO_2$ is the same as that of NaOH; (3) the solubility of HgO in water is the extrapolated value rather than the directly determined value.

Extrapolation of the solubility values in NaOH solutions gives a value of 2.45×10^{-4} mol dm^{-3} for the solubility of HgO in water. This is significantly higher than the directly determined value. The suggested explanation was that the NaOH disperses the HgO into finer, and more soluble particles.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess HgO was sealed in tubes containing the solvent. Half the solutions were agitated at 25°C for 4 days; the other half were agitated at 40°C for 4 days and then 4 days at 25°C. For analysis, the mixtures were acidified with HCl and treated with H_2S. The HgS precipitate was dried at 110°C and weighed.

SOURCE AND PURITY OF MATERIALS:

Triple distilled Hg was dissolved in HNO_3, the solution was evaporated to dryness, and the resultant $Hg(NO_3)_2$ was heated to form HgO. The NaOH solutions were prepared by electrolytic decomposition of sodium amalgam. Conductivity water was used.

ESTIMATED ERROR: This cannot be determined from the data given. The analytical data show that the differences between individual values and the mean value range from 0.5 to 4.1% of the mean value.

REFERENCES:

1. Noyes, A. A.; Falk, K. G. *J. Am. Chem. Soc.* 1912, *34*, 454.

COMPONENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Lithium hydroxide; LiOH; [1310-65-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Garrett, A. B.; Hirschler, A. E.
J. Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:
Lithium hydroxide concentration at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of yellow HgO in LiOH solutions at 25°C.

mol LiOH/kg H_2O	(mol HgO/kg H_2O) x 10^5
0.0689	23.9
0.2019	24.6
0.4667	25.2

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other mixtures were shaken at 42°C for about 3 days and then at 25°C for 3 weeks. After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI (1).

SOURCE AND PURITY OF MATERIALS:
Two different preparations of yellow HgO were used. Reagent grade LiOH was dissolved in water and allowed to stand for a while so that the slight precipitate could settle out. Conductivity water was used throughout.

ESTIMATED ERROR:
Mercury analysis had a reproducibility within 0.5% The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:
1. Maricq, L. *Bull, soc. chim. belg.* 1928, *37*, 241.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Garrett, A. B.; Hirschler, A. E.
J. Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:

Concentration of KOH at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of yellow HgO in KOH solutions at 25°C.

mol KOH/kg H_2O	(mol HgO/kg H_2O)x 10^5
0.1082	24.0
0.3038	24.3
0.8175	25.3

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other mixtures were shaken at 42°C for about 3 days and then at 25°C for 3 weeks. After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI (1).

SOURCE AND PURITY OF MATERIALS:

Two different preparations of yellow HgO were used. The hydroxide solutions were carbonate-free. Conductivity water was used throughout.

ESTIMATED ERROR:

Mercury analysis had a reproducibility within 0.5%. The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:

1. Maricq, L. *Bull. soc. chim. belg.* 1928, *37*, 241.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Garrett, A. B.; Hirschler, A. E.
J. Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:

Sodium hydroxide concentration at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of yellow HgO in NaOH solutions at 25°C.

mol NaOH/ kg H_2O	(mol HgO/kg H_2O) x 10^5	mol NaOH/ kg H_2O	(mol HgO/kg H_2O) x 10^5
0.0000	23.7	0.2438	24.2
0.00010	23.4	0.2776	24.5
0.00042	23.7	0.3022	24.9
0.00082	23.8	0.3467	24.9
0.0018	23.2	0.5169	24.8 (u)
0.0040	23.7	0.5995	25.5
0.0100	23.7 (u)	0.7372	26.1
0.0207	23.7	0.8515	26.5
0.0290	23.9 (u)	1.006	26.8
0.0477	23.7	1.512	28.2
0.0770	24.2 (u)	1.776	28.4
0.0944	24.3	2.057	28.7 (s)
0.1015	24.4	2.562	29.6
0.1074	24.3	3.263	31.8 (u)
0.1448	24.2	3.405	30.6 (u)
0.1506	24.3 (u)	3.940	31.6
0.1513	24.2	4.460	31.2
0.2230	24.1	5.046	32.2
		5.952	31.1

(s) equilibrium approached from supersaturation only.

(u) equilibrium approached from undersaturation only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other mixtures were shaken at 42°C. for about 3 days and then at 25°C for 3 weeks. After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI (1).

SOURCE AND PURITY OF MATERIALS:

Two different preparations of yellow HgO were used. The hydroxide solutions were carbonate-free. Conductivity water was used throughout.

ESTIMATED ERROR:

Mercury analysis had a reproducibility within 0.5%. The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:

1. Maricq, L. *Bull. soc. chim. belg.* 1928, 37, 241.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Garrett, A. B.; Hirschler, A. E.
J. Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:

Sodium hydroxide concentration at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of red HgO in NaOH solutions at 25°C.

mol NaOH/kg H_2O	(mol HgO/kg H_2O) x 10^5
0.0000	22.5
0.00088	22.5
0.0050	22.5
0.0093	22.6
0.0187	22.4
0.1064	22.7 (s)
0.3398	23.1
0.4406	24.2 (s)
0.5818	24.6
0.7223	25.1 (u)
1.001	26.2
1.638	27.2
1.987	27.6 (u)
2.940	29.4
3.956	29.7
4.936	29.8

(s) equilibrium approached from supersaturation only.

(u) equilibrium approached from undersaturation only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other mixtures were shaken at 42°C for about 3 days and then at 25°C for 3 weeks After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI (1)

SOURCE AND PURITY OF MATERIALS:

Five different preparations of red HgO were used. The hydroxide solutions were carbonate-free. Conductivity water was used throughout.

ESTIMATED ERROR:

Mercury analysis had a reproducibility within 0.5%. The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:

1. Maricq, L. *Bull, soc. chim. belg.* 1928, *37*, 241.

COMPONENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Garrett, A. B.; Howell, W. W. *J. Am. Chem. Soc.* 1939, *61*, 1730-4.

VARIABLES:
Concentration of HNO_3 at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Table I

Solubility of red HgO in aqueous nitric acid solutions.

(moles HNO_3/kg H_2O) x 10^3 as samples were made up	(moles HNO_3/kg H_2O) x 10^3 from pH[a]	(moles HgO/kg H_2O) x 10^4
0.100	0.14	2.98
0.200	0.07	3.14
0.300	0.14	2.77 (u)
0.500	0.30	3.48 (s)
0.700	0.38	3.56
0.900	0.48	4.02 (u)
2.00	2.5	6.32
3.00	1.9	9.17
5.00	3.8	14.2
7.00	4.1	20.2
9.00	5.0	27.9
20.0	7.3	64.2 (s)

[a]The value of H^+ so determined was divided by the activity coefficient of HNO_3 (1).

(s) equilibrium approached from supersaturation only.

(u) equilibrium approached from undersaturation only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other such preparations were agitated for about 3 days at 42°C, then transferred to a 25°C. thermostat for 3 weeks. After the agitation the samples were allowed to sediment for about 4 days before analysis. The nitric acid solutions were prepared by dilution of standard solutions. pH was measured after equilibrium by using a glass electrode. Mercury content was determined by potentiometric titration with KI (2).

SOURCE AND PURITY OF MATERIALS:
Materials were reagent grade. Conductivity water was used to make all solutions.

ESTIMATED ERROR:
Nothing is stated and only averages of pairs of values are given.

REFERENCES:
1. Abel, E.; Redlich, D.; Lengyel, B. v. *Z. physik. Chem.* 1928, *132*, 189.
2. Maricq, L. *Bull. soc. chim. belg.* 1928, *37*, 241.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Nitric acid; HNO_3; [7697-37-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS

Garrett, A. B.; Howell, W. W.
J. Am. Chem. Soc., 1939, *61*, 1730-4

Table II
Solubility of yellow HgO in aqueous nitric acid solutions

(moles HNO_3/kg H_2O) x 10^3 as samples were made up	(moles HNO_3/kg H_2O) x 10^3 from pH[a]	(moles HgO/kg H_2O) x 10^4
0.0500	0.032	2.43
0.100	0.055	2.57
0.200	0.095	2.67
0.400	0.29	3.11
0.600	0.40	3.35
0.800	1.5	3.80
1.03		4.15
2.00	1.1	6.08
4.00	3.8	12.1
6.00		18.3
8.00		23.2
10.6		30.0
15.6		50.5
20.0	8.1	65.5
20.0		68.0
30.0		111
30.0		108
40.0		173
40.0		169
50.0	10	217
58.5	10	236
60.0		253
63.4	14	262
68.3	13	299
70.0		312
70.3	13	312
72.2	13	329
74.3	13	333
76.1	13	349
78.0	12	362
97.6	16	449
117	14	536
137		638
140	18	596
156	23	718
160	19	662

[a]The value of H^+ so determined was divided by the activity coefficient of HNO_3 (1).

REFERENCES:

1. Abel, E.; Redlich, D.; Lengyel, B. v. *Z. physik. Chem.* 1928, *132*, 189.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Hydrochloric acid; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Garrett, A.B.; Lemley, J.
J. Am. Chem. Soc., 1942, *64*, 2380-3.

VARIABLES:

Concentration of hydrochloric acid. The temperature is not stated but from comparison with other work it apparently is 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Table I

Solubility of yellow HgO in aqueous HCl solutions

(moles HCl/kg H_2O) x 10^2	(moles HgO/kg H_2O) x 10^4	(moles HCl/kg H_2O) x 10^2	(moles HgO/kg H_2O) x 10^4
0.0050	2.47(s)	0.80	18.7
0.010	2.52	0.80	36
0.030	3.7	0.82	18.1
0.030	4.1	0.84	18.6(u)
0.050	4.9	0.86	41.3
0.070	6.5	0.90	19.0
0.090	8.4	1.0	18.5
0.090	7.1	1.0	56
0.10	6.7	1.0	50.3
0.11	7.2	1.2	31
0.13	9.8	3.0	18.9
0.17	11.7	5.0	16.3
0.19	13.0	8.0	17.7
0.20	13.1	10.	19.8(u)
0.40	25.4	12.	22.8(u)
0.50	26.2	12.	34 (s)
0.50	25.8(u)	14.	47 (s)
0.60	29.6	18.	232 (u)
0.70	36.6	20.	414 (s)
0.70	28.7	28.	534 (s)
0.75	20.1(u)	40.	1490 (s)
		50.	1480 (s)

(s) equilibrium approached from supersaturation only.
(u) equilibrium approached from undersaturation only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solid HgO was added to solutions and shaken. Solubility was approached from undersaturation and from supersaturation. The general procedure is the same as that used earlier (1).

SOURCE AND PURITY OF MATERIALS:

Reagent grade chemicals and conductivity water were used.

ESTIMATED ERROR:

No estimate is given and the precision of the analyses cannot be inferred from the data given.

REFERENCES:

1. Garrett, A.B.; Howell, W. W. *J. Am. Chem. Soc.*, 1939, *61*, 1730.

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Mercury(II) oxide; HgO; [21908-53-2] (2) Hydrochloric acid; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Garrett, A.B.; Lemley, J. *J. Am. Chem. Soc.*, 1942, *64*, 2380-3.

EXPERIMENTAL VALUES continued...

Table II

Solubility of yellow HgO in aqueous HCl solutions

moles HCl/kg H_2O	(moles HgO/ kg H_2O) x 10^4	pH[a]	Solid phase color	%Hg
0.00100	9.0	5.0	yellow	
0.00300	20.8	4.9	yellow	
0.00500	3.18	4.9	yellow	
0.00700	40.7	4.7	yellow & black	
0.0090	28.9	4.9	yellow & black	
0.0120	30.9	5.1	yellow & black	
0.0160	29.1	5.0	yellow & black	
0.0200	22.1	4.8	yellow & black	
0.0300	15.0	5.0	yellow & black	
0.0400	10.0	5.2	yellow & black	
0.0500	21.6	5.1	brown	
0.1007	82	4.0	black	
0.1210	237	4.1	black	
0.1412	387	4.2	black	85.4
0.1614	545	4.0	black	
0.2018	880	3.8	black	85.5
0.2425	1150	3.9	black	85.6
0.2832	1410		black	85.4

[a]determined with a glass electrode

COMPONENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Salem, T. M. J. *Indian Chem. Soc.* 1959, *36*, 83-6.

VARIABLES:
NaOH concentration and pH at 35°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of red HgO in aqueous solutions at 35°C.

Solution	g Hg dm^{-3}	(mol HgO dm^{-3}) x 10^4	pH[a]
water	0.0696	3.47	
Buffers			
pH = 7.05	0.116	5.78	
pH = 7.55	0.0945	4.71	
pH = 8.09	0.0780	3.89	
pH = 9.11	0.0810	4.04	
NaOH mol dm^{-3}			
3.68×10^{-4}	0.0850	4.24	10.22
2.06×10^{-3}	0.0860	4.29	10.96
3.19×10^{-2}	0.0885	4.41	12.08
5.00×10^{-2}	0.0910	4.54	12.24
2.65×10^{-1}	0.0941	4.69	12.94
3.00×10^{-1}	0.0960	4.79	13.19

[a] There is no indication how these values were obtained.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Red HgO was shaken with the solution under a N_2 atmosphere for 120 hours at 50°C. and then at 35 ∓ 0.02°C. for 3 to 5 days. The clear solution was filtered through a sintered glass filter and analyzed. Mercury content was determined by potentiometric titration with KI. Buffer solutions were prepared according to the direction given by Palitzsch (1).

SOURCE AND PURITY OF MATERIALS:
Conductivity water and reagent grade chemicals were used.

ESTIMATED ERROR:
Mercury analyses had an error of not more than 1%.

REFERENCES:
1. Britton, H. T. S. *Hydrogen Ions*. 2nd Ed. Chapman and Hall, Ltd. London, 1932, p. 219.

COMPONENTS:
(1) Mercury (II) oxide; HgO; [21908-53-2]
(2) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Dyrssen, D.; Tyrrell, V. *Acta Chem. Scand.* 1961, 15, 393-402 and 1622

VARIABLES:
pH at 25°C

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Table I

Solubility of red HgO in 3 mol dm^{-3} $NaClO_4$ solutions.

Concentrations are expressed as mol dm^{-3}

-log [HgO]	-log [H^+]
1.657	2.023
2.371	2.402
2.509	2.523
2.698	2.616
2.799	2.660
2.764	2.698
2.799	2.723
2.964	2.768
3.124	2.903
3.199	3.013
3.246	3.028
3.341	3.157
3.369	3.181
3.551	3.368
3.582	3.508
3.705	3.808
3.737	3.828
3.701	4.233
3.753	4.463
3.746	4.833

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
The solvents were allowed to percolate through a column containing the solid red HgO. The solid was irradiated for 3 hours in a flux of 5.5 x 10^{11} neutrons cm^2 sec^{-1}. Mercury content was determined by taking a weighed sample, counting the gamma radiation and comparing it with a carefully prepared and analyzed standard. pH measurements were made with a glass electrode. pH was adjusted by adding 0.01 mol dm^{-3} NaOH or $HClO_4$.

SOURCE AND PURITY OF MATERIALS:
Reagent grade materials and conductivity water were used.

ESTIMATED ERROR: Analyses for individual samples had a standard deviation of 6 x 10^{-5}, but successive samples from a given system varied by 5% of the measured value. No indication is given as to how precisely the temperature was controlled.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Sodium sulfide; Na_2S; [1313-82-2]

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

ORIGINAL MEASUREMENTS:

Milyutina, N. A.; Polyvyannyi, I. R.; Sysoyev, L. N. *Tr. Inst. Metal. Obogashch. AN Kaz. SSR* 1967, *21*, 14-9

VARIABLES:

Concentration of sodium sulfide at 25°C

PREPARED BY:

T. Michalowski

EXPERIMENTAL VALUES:

Solubility of HgO in aqueous Na_2S at 25°C

mol S^{2-} dm^{-3}	mol Hg(II) dm^{-3}	Ionic Strength, mol dm^{-3}	Activity coefficient of Hg(II)
0.18	0.00727	0.899	0.1233
0.518	0.01147	1.265	0.1109
1.5	0.0174	3.634	0.100
1.67	0.01932	4.08	0.1114
2.06	0.0199	5.04	0.1245
2.06	0.0188	5.187	0.127

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No details are given, but from other work reported by these authors it appears that equilibrium was reached isothermally after agitation for about a day.

SOURCE AND PURITY OF MATERIALS:

The HgO and Na_2S were analytical grade materials.

ESTIMATED ERROR:

This cannot be estimated from the limited amount of information given in the paper.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Hydrofluoric acid; HF; [7664-39-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Polyshchuk, S. A.; Khmeliova, M. G.; Zadneprovsky, G. M.; Kaidalova, T. A.; Kuptsova, N. V. *J. Less-common Metals* 1970, *21*, 63-9.

VARIABLES:

Concentration of HF at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of red HgO in HF solutions at 25°C.

Composition of solution phase

mass % HF	mass % HgO	mol/kg[a] HF	mol/kg[a] HgO	composition of solid phase
5.9	6.4	3.4	0.34	HgOHF
6.9	7.7	4.0	0.42	"
10.6	7.5	6.5	0.42	"
15.0	13.1	10.4	0.84	"
18.4	14.6	13.7	1.01	"
23.6	15.0	19.2	1.13	$HgF_2 \cdot 2H_2O$
25.0	15.7	21.1	1.22	"
31.5	11.0	27.4	0.88	"
38.0	8.5	35.5	0.73	"
45.3	7.2	47.7	0.70	"
48.2	8.4	55.5	0.89	"
54.5	7.0	70.8	0.84	"
58.4	5.6	81.1	0.72	"
64.5	5.3	107	0.81	"
70.7	2.8	133	0.49	"

[a] molalities calculated by the compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities were determined by the isothermal method. Mixtures of red HgO and solvent were shaken in sealed polyethylene vessels at 25°C. Solid phase compositions were determined by the Schreinemakers' method of wet residues. Fluorine was determined by titration with thorium nitrate. Mercury was determined by titration with NH_4SCN.

SOURCE AND PURITY OF MATERIALS:

Reagent grade materials were used.

ESTIMATED ERROR:

Titration errors are stated as less than 0.2%. Water content is estimated to be within 2% of the correct value.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Potassium hydroxide; KOH; [1310-58-3]

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

ORIGINAL MEASUREMENTS:

Zhou, Weifang; Chen, Xialing *Fudan Xuebao, Ziran Kexueban* 1983, *22*, 229-31.

VARIABLES:

Concentration of KOH and temperature.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of HgO in aqueous KOH [a].

$10^4 C_{HgO}$/mol dm^{-3}

t/°C	A[b]	B	C	D	E
25	2.8	3.1	3.2	2.7	2.0
35	4.1	4.4	4.4	3.7	2.8
45	5.8	6.1	5.8	4.8	3.8
55	8.1	8.1	7.3	5.9	5.0

[a] These values are not included in the original article, but were supplied by the authors in a personal communication.

[b] The KOH concentrations (in mass %) for each column is: A = 1; B = 5; C = 10; D = 20; E = 30.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The e.m.f. of the following cell was measured:

Hg|Hg(II),KOH(aq)|KOH(aq)|HgO(s)|Hg

The KOH concentration was the same in both cell compartments. The concentration of Hg(II) in the left cell compartment was prepared accurately and was less than 50% of the concentration in the right cell compartment. The temperature was controlled to within 0.1°C.

SOURCE AND PURITY OF MATERIALS:

The Hg, HgO and KOH were reagent grade materials. The water was distilled twice.

ESTIMATED ERROR:

Less than 5%.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Lithium chloride; LiCl; [7447-41-8]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Potassium chloride; KCl; [7447-40-7]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Herz, W.; Hiebenthal, F. Z. *anorg. u. allgem. Chem.* 1928, *177*, 363-80

VARIABLES:

Concentration of alkali halides at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:
The solubility in water is given as 2.51×10^{-4} mol dm^{-3}
Solubility of red HgO in alkali solutions

mol LiCl dm^{-3}	normality of HgO	mol HgO dm^{-3} [a]
0.35	0.0008	0.0004
0.51	0.0011	0.0006
0.74	0.0014	0.0007
0.99	0.0020	0.0010
2.15	0.0053	0.0027
2.47	0.0061	0.0031

mol KCl dm^{-3}	normality of HgO	mol HgO dm^{-3} [a]
0.35	0.0008	0.0004
0.70	0.0011	0.0006
0.85	0.0013	0.0007
1.49	0.0023	0.0012
2.35	0.0038	0.0019
2.40	0.0040	0.0020
3.13	0.0054	0.0027

Mol NaCl dm^{-3}	normality of HgO	mol HgO dm^{-3} [a]
1.05	0.0026	0.0013
1.55	0.0036	0.0018
2.12	0.0046	0.0023
3.13	0.0074	0.0037
4.22	0.0091	0.0046
5.45	0.0158	0.0079

[a] calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Red HgO was shaken with the solvents at 25°C. Mercury was analyzed by titration and halide content was determined argimetrically. No references are given. Equilibrium was approached only from undersaturation.

SOURCE AND PURITY OF MATERIALS:
Commercially available materials were used.

ESTIMATED ERROR:
Impossible to determine from the information given.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Sodium hydroxide; NaOH: [1310-73-2]
(3) Sodium sulfate; Na_2SO_4; [7757-82-6]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Garrett, A. B.; Hirschler, A. E.
J.Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:

Solvent composition at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of yellow HgO in Na_2SO_4-NaOH solutions at 25°C.

mol NaOH/kg H_2O	(mol HgO/kg H_2O) x 10^5	mol Na_2SO_4/kg H_2O	Total ionic strength
0.1433	30.1	0.5863	1.902
0.1380	34.7	1.145	3.573
0.1649	37.0	1.668	5.169
0.1454	39.0	2.137	6.556

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 wks. at 25°C. Other mixtures were shaken at 42°C for about 3 days and then at 25°C for 3 weeks. After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI(1). The alkaline-salt solutions were made up by weight from standard solutions.

SOURCE AND PURITY OF MATERIALS:

Two different preparations of yellow HgO were used. Reagent grade Na_2SO_4 was recrystallized 2 to 4 times from conductivity water. The hydroxide solutions were carbonate-free. Conductivity water was used throughout.

ESTIMATED ERROR:

Mercury analysis had a reproducibility within 0.5%. The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:

1. Maricq, L. *Bull. soc. chim. belg.* 1928, 37, 241.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

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

(3) Sodium hydroxide; NaOH; [1310-73-2]

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

ORIGINAL MEASUREMENTS:

Garrett, A. B.; Hirschler, A. E.
J. Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:

Solvent composition at 25°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of yellow HgO in alkaline-salt solutions at 25°C.

mol NaOH/kg H_2O	(mol HgO/kg H_2O) x 10^5	mol $NaNO_3$/kg H_2O	Total ionic strength
0.1462	32.6	1.072	1.218
0.1738	49.6	2.637	2.811
0.1682	75.3	6.397	6.565

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other mixtures were shaken at 42°C for about 3 days and then at 25°C for 3 weeks. After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI (1). The alkaline-salt solutions were made up by weight from standard solutions.

SOURCE AND PURITY OF MATERIALS:

Two different preparations of yellow HgO were used. The NaOH solutions were carbonate-free. Reagent grade $NaNO_3$ was recrystallized 2 to 4 times from conductivity water. Conductivity water was used throughout.

ESTIMATED ERROR:

Mercury analysis had a reproducibility within 0.5%. The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:

Maricq, L. *Bull. soc. chim. belg.* 1928, *37*, 241.

COMPONENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Sodium hydroxide; NaOH; [1310-73-2]
(3) Potassium nitrate; KNO_3; [7757-79-1]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Garrett, A. B.; Hirschler, A. E.
J. Am. Chem. Soc. 1938, *60*, 299-306

VARIABLES:
Solvent composition at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of yellow HgO in alkaline-salt solutions at 25°C.

mol NaOH/kg H_2O	(mol HgO/kg H_2O) x 10^5	mol KNO_3/kg H_2O	Total ionic strength
0.1361	29.1	0.8143	0.950
0.1789	33.7	1.725	1.904
0.1328	38.4	2.400	2.533

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of HgO and solvent were sealed in nitrogen-filled flasks and shaken for 3 weeks at 25°C. Other mixtures were shaken at 42°C for about 3 days and then at 25°C for 3 weeks. After agitation, the samples were allowed to sediment for 4 days, then filtered through a sintered glass filter. Alkali concentration was determined by weight titration using methyl orange indicator. Mercury content was determined by potentiometric titration with KI (1). The alkaline-salt solutions were made up by weight from standard solutions.

SOURCE AND PURITY OF MATERIALS:

Two different preparations of yellow HgO were used. The NaOH solutions were carbonate-free. Reagent grade KNO_3 was recrystallized 2 to 4 times from conductivity water. Conductivity water was used throughout.

ESTIMATED ERROR:

Mercury analysis had a reproducibility within 0.5%. The alkali analysis had an error of less than 5%. Separate solubility values were within 2% of the average.

REFERENCES:

1. Maricq, L. *Bull. soc. chim. belg.* 1928, *37*, 241.

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Acetic acid; $C_2H_4O_2$; [64-19-7]

(3) Sodium acetate; $NaC_2H_3O_2$; [127-09-3]

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

ORIGINAL MEASUREMENTS:

Mahapatra, P.; Aditya, S.; Prasad, B.
J. Indian Chem. Soc. 1953, *30*, 509-513.

VARIABLES:

Concentration of acetic acid and sodium acetate at 35°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

$NaC_2H_3O_2$ mol dm^{-3}	$C_2H_4O_2$ mol dm^{-3}	HgO mol dm^{-3}	$NaC_2H_3O_2$ mol dm^{-3}	$C_2H_4O_2$ mol dm^{-3}	HgO mol dm^{-3}
0.10	1.00	0.0287	0.04	0.08	0.0192
0.50	0.50	0.1864	0.02	0.08	0.0200
1.00	0.5	0.2054	0.01	0.08	0.0198
0.04	0.32	0.0081	0.0625	0.0625	0.01636
0.50	0.25	0.08095	0.125	0.062	0.0162
0.25	0.25	0.0800	0.50	0.05	0.0098
0.0625	0.25	0.0690	0.25	0.05	0.01104
0.10	0.20	0.0674	0.100	0.05	0.00968
0.05	0.20	0.0663	0.05	0.05	0.01227
0.04	0.16	0.0488	0.04	0.04	0.0089
0.02	0.16	0.0481	0.02	0.04	0.0084
0.625	0.125	0.03757	0.01	0.04	0.0083
0.25	0.125	0.0357	0.0625	0.03125	0.00628
0.125	0.125	0.03757	0.25	0.025	0.00296
0.50	0.100	0.0266	0.125	0.025	0.005065
0.10	0.10	0.0283	0.05	0.0250	0.005095
0.05	0.10	0.0277	0.10	0.020	0.003863
			0.01	0.020	0.0034

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Excess red HgO was shaken with 100 ml of known acetic acid-sodium acetate concentration for 5 days at 25-30°C and then for 5 days at 35°C. Mercury was determined by the iodate method.

SOURCE AND PURITY OF MATERIALS:

Reagent grade materials were used.

ESTIMATED ERROR:

No information is given as to precision of temperature control nor of the analyses.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]

(2) Carbon dioxide; CO_2; [124-38-9]

(3) Sodium chloride; NaCl; [7647-14-5]

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

ORIGINAL MEASUREMENTS:

Shlyapnikov, D. S.; Shtern, E. K. *Dokl. Akad. Nauk SSSR* 1975, *225*, 428-31; *Dokl. Acad. Sci. USSR, Earth Sci. Sect. (Engl. transl.)* 1975, *225*, 185-8.

VARIABLES:

Sodium chloride concentration and pressure of carbon dioxide.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility of HgO at 293 K in aqueous solutions under a carbon dioxide pressure of 50 atm.

C_{NaCl}/mol dm^{-3}	C_{HgO}/g dm^{-3}	C_{HgO}/mol dm^{-3} [a]
0	0.22	0.0010
1	32.4	0.150
4	68.00	0.314

[a]Calculated by the compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solution and solid HgO were shaken in an autoclave at the prescribed temperature for 24 hours. CO_2 was introduced as a solid. Metal analysis was done compleximetrically and spectrophotometrically. No further details are given.

SOURCE AND PURITY OF MATERIALS:

No information is given.

ESTIMATED ERROR:

Cannot be determined from the information given in the paper.

REFERENCES:

COMPONENTS:

(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Carbon dioxide; CO_2; [124-38-9]
(3) Sodium chloride; NaCl; [7647-14-5]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Shlyapnikov, D. S.; Shtern, E. K.
Dokl. Akad. Nauk SSSR, Ser. Geol. 1979, *249*, 457-61; *Russ.*;
Dokl. Acad. Sci. USSR, Earth Sci. Sect. (*Engl. transl.*) 1979, *249*, 173-6.

VARIABLES:

Pressure of carbon dioxide, and concentration of NaCl at 20°C.

PREPARED BY:

T. P. Dirkse

EXPERIMENTAL VALUES:

Solubility and composition of solid phases in the system HgO-NaCl-H_2O-CO_2 at 20°C.

P_{CO_2}	Starting solution mol NaCl dm^{-3}	Filtrate g Hg dm^{-3}	Solid phase %Hg	Solid phase %CO_2	Solid phase %Cl	Solid phase composition[a]
1 atm	0	0.18	89.2	0.0	0.0	A
"	0.2	14.0	87.6	0.0	1.4	A+B
"	1.0	39.8	84.8	0.0	9.7	B
"	2.0	97.4	82.1	2.7	9.04	B
"	4.0	145.0	0.0	44.8	0.0	C
50 atm	0	0.21	86.8	5.4	0.0	D
"	0.2	12.9	86.0	5.7	2.4	B+D
"	1.0	32.6	85.7	2.5	4.4	B
"	2.0	92.0	82.0	4.9	7.8	B+C
"	4.0	138.0	0.12	49.2	0.22	C

[a] Identity of the solid phases:

A- HgO

B- $HgCl_2.nHgO$

C- $NaHCO_3$

D- $HgCO_3.2HgO$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Samples of yellow HgO and solvent were mixed in a rocking autoclave. The CO_2 atmosphere was produced by bubbling CO_2 through the mixture or by adding solid CO_2. Cl^- was determined by titration with $AgNO_3$, CO_2 was determined by gas absorption. The mercury content was determined by precipitation as the sulfide. The identity of the solid phases was confirmed by means of X-ray diffraction patterns.

SOURCE AND PURITY OF MATERIALS:

The HgO was prepared from reagent grade chemicals. No information is given about the other materials that were used.

ESTIMATED ERROR:

The article contains no information about control of temperature and pressure nor about the reproducibility of the analytical methods.

REFERENCES:

COMPONENTS:
(1) Mercury(II) oxide; HgO; [21908-53-2]
(2) Sodium carbonate; Na_2CO_3; [497-19-8]
(3) Sodium perchlorate; $NaClO_4$; [7601-89-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:
Bilinski, H.; Markovic, M.; Gessner, M. *Inorg. Chem.* 1980, *19*, 3440-3.

VARIABLES:
Concentration of sodium carbonate at 25°C.

PREPARED BY:
T. P. Dirkse

EXPERIMENTAL VALUES:

Equilibrium Composition of Mercury (II)-Carbonate System at 25°C.

Total ionic strength is 0.5 mol dm^{-3}
Precipitate was "aged" for 30 days.

Solution

Total CO_3^{2-} mol dm^{-3}	pH	mol Hg(II) dm^{-3}	Solid phase[a]
0.04	10.19	4.70×10^{-4}	HgO
0.05	9.80	4.55×10^{-4}	"
0.06	10.35	5.13×10^{-4}	"
0.08	10.4	4.70×10^{-4}	"
0.10	10.1	4.45×10^{-4}	"
0.14	10.5	4.67×10^{-4}	"
0.20	10.7	4.31×10^{-4}	"

[a] determined by X-ray diffraction.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:
Solid $HgCO_3 \cdot 2HgO$ was equilibrated with the solution for 30 days. Dissolved mercury content was determined polarographically (1) or compleximetrically(2). Hydrogen ion concentration was measured with a glass electrode. The ionic strength of the solutions was kept at 0.5 mol dm^{-3} by the addition of $NaClO_4$.

SOURCE AND PURITY OF MATERIALS:
Bidistilled water and commercially available chemicals were used.

ESTIMATED ERROR:
This cannot be estimated from the information in the paper.

REFERENCES:
1. Heyrovky, J.; Kuta, J. *Principles of Polarography*, Czech. Acad. Sci, Prague, 1966, p. 167.
2. *Komplexometrische Bestimmungsmethoden mit Titriplex*, AG-Darmstadt, West Germany, 1961.

SYSTEM INDEX

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