INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION COMMISSION ON SOLUBILITY DATA

SOLUBILITY DATA SERIES

Volume 18

TETRAPHENYLBORATES

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1981

SOLUBILITY DATA SERIES

Volume 18

TETRAPHENYLBORATES

Volume Editor

OREST POPOVYCH Brooklyn College City University of New York USA

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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 the most ambitious one. 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 limitedin-scope reviews exhaustively. There is a trend to preselect the literature, sometimes under the pretext of reducing it to manageable size. The crucial problem with such preselection - as far as numerical data are concerned - is that there is no indication as to whether the material was excluded by design or by a less than thorough literature search. We are equally concerned that most current secondary sources, critical in character as they may be, give scant attention to numerical data.

On the other hand, tertiary sources - handbooks, reference books, and other tabulated and graphical compilations - as they exist today, are comprehensive but, as a rule, uncritical. They usually attempt to cover whole disciplines, thus obviously are superficial in treatment. Since they command a wide market, we believe that their service to advancement of science is at least questionable. 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 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, paving equal 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 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 of both good and poor data.

It is the standard practice that any given solute-solvent system consists of two essential parts: (1) critical evaluation and recommended values, and (2) 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) whenever relevant a graphical plot of recommended data is included.

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 the numerical informat: 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.

Foreword

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 has been strongly influenced by the diversity of background of those whom we are supposed to serve. We thus deemed it right to preface the evaluation/compilation sheets in each volume with a detailed discussion of the principles of the accurate determination of relevant solubility data and related thermodynamic information.

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

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

A. S. Kertes

PREFACE

Tetraphenylborates -- compounds containing the $(C_{0H_{5}})_{\mu}B^{-}$ anion, now commonly abbreviated as BPh_{μ}^{-} , are a relatively new addition to chemistry, so that published material on their solubilities is, understandably, limited. Furthermore, the paucity of data on the solubility of tetraphenylborates is compounded by the fact that divalent and multivalent cations are not known to form tetraphenylborates, but instead cause the decomposition of the BPh_{μ}^{-} ion. A rare exception in this respect seems to be the complex salt of ruthenium o-phenanthroline, for which solubility data are included in this Volume.

The first mention of tetraphenylborates in the literature is believed to be the 1947 report by Wittig and Keicher, describing the synthesis of lithium tetraphenylborate from triphenylboron and phenyllithium (Naturwissenschaften, 1947, 34, 216). Soon thereafter, the synthesis of sodium tetraphenylborate was also accomplished in the same laboratory. (In the early literature, the tetraphenylborate ion was called simply "tetraphenylboron", to be superceded temporarily by the term "tetraphenylboride ion"). Both LiBPh, and NaBPh, are appreciably soluble in water and immediately after their synthesis attracted the attention of chemists as precipitating agents for the potassium ion, which forms a tetraphenylborate that is sparingly soluble in aqueous solutions. The fact that KBPh, is by far the least soluble potassium salt in water ($\sim 1.8 \times 10^{-4}$ mol dm⁻³ at 298 K) was probably the single most important factor that led to widespread interest in the tetraphenylborate ion and added impetus to early research on tetraphenylborate as an analytical reagent.

Soon it was discovered that rubidium, cesium, thallium(I), silver and a variety of ammonium ions formed insoluble tetraphenylborates in aqueous solution that could serve as a basis for the detection and quantitative determination of these cations. Thus, the early studies of the solubilities of tetraphenylborates were generally incidental to the development of gravimetric and other analytical procedures, where the primary focus was on the sensitivity of analysis, completeness of precipitation and thermal stability of the precipitates. Given this type of emphasis, many of the solubility data were not of the highest precision and accuracy. Furthermore, much of the analytical work, such as the spot tests for the detection of basic nitrogen compounds, was qualitative in nature, leading merely to the estimation of the orders of magnitude of the solubilities. Therefore, no compilations are provided here for published work of this type. On all aspects of the early studies on tetraphenylborates, the reader is referred to the comprehensive 1960 review by Flaschka and Barnard (in Advances in Analytical Chemistry and Instrumentation, Reilly, C. N., Ed., Interscience Publishers, Inc. New York. 1960. Vol. I).

In the 1960's and beyond, interest in tetraphenylborates was rekindled for reasons other than analytical: the BPh₄⁻ anion acquired the status of a "reference" ion for a variety of physico-chemical purposes. Thus, Fuoss proposed the estimation of limiting conductivities for single ions in nonaqueous solvents based on the assumption that the limiting conductivities of the BPh₄⁻ anion and the <u>n</u>-butyltriisopentylammonium (in the original, triisoamyl-<u>n</u>-butylammonium) cation were equal. Subsequently, we have witnessed the development and application of many analogous assumptions where a thermodynamic property of the BPh₄⁻ anion was equated to the corresponding property of the tetraphenylarsonium or the tetraphenylphosphonium cation. Such assumptions have been extensively applied particularly to the transfer free energies between pairs of solvents. Because values of solubility (ion-activity) products in different solvents are required for the calculation of the transfer free energies, the majority of recent data on the solubility of tetraphenylborates derives from studies where the ultimate objective is the evaluation of the transfer free energies. Unfortunately, also here many of the published results are not of high quality. Many investigators were satisfied with results expressed to only one or two significant digits. Many have failed to specify such crucial experimental conditions as the extent of temperature control and the method of ascertaining saturation.

Tetraphenylborates are susceptible to decomposition by water, oxygen and acids. The decomposition can be easily detected by uv-spectrophotometry in the 260-280 nm range, but may pass unnoticed when a different analytical method is employed for the determination of the tetraphenylborate. This problem must be borne in mind when evaluating literature data.

Frequently, authors have reported the solubility (ion-activity) product, but not the solubility itself. In such cases, the solubility may be estimated if the correction for the activity coefficients is known or can be neglected. Thermodynamic solubility (ion-activity) products are denoted here by the symbol K_{s0}° , while the concentration solubility products are denoted by K_{SO}. Almost invariably, the solubilities in the original literature were reported in the units of molarity, here converted to the SI equivalent of mol dm^{-3} , referring to moles of the solute per dm^3 of the saturated solution. Occasionally, the reported data were in the units of grams of solute per 100 cm^3 of solution, in which case both the original results and the correspoding values in the units of mol dm^{-3} were presented in the Volume. Temperatures have been converted to Kelvin. There are very few reliable solubility data on tetraphenylborates as a function of the temperature. Only in the case of $KBPh_4$ in water was it possible to express such data by means of a smoothing equation and to calculate the standard enthalpy and entropy from it. Names recommended by Chemical Abstracts and registry numbers were used when available. Common names used in the original literature sources were given in parentheses and sometimes retained in the text.

For this Volume, an attempt was made to survey the literature through the first half of 1978. A few later publications were included when they were specifically brought to the Editor's attention. Undoubtedly, there are errors and omissions in the compilations and evaluations and the Editor will be grateful to readers who will bring these to his attention.

The following associates and members of IUPAC Commission on Solubility Data V.8. as well as other reviewers of this Volume are gratefully acknowledged for their valuable suggestions: Abraham, Chan, Chantooni, Clifford, Kertes, Khoo, Kim, Kolthoff, Loening, Lorimer, and Scrosati. Above all, my special thanks is due to Mark Salomon for his active interest and valuable advice throughout all the phases of this project, including a critical review of the manuscript.

Orest Popovych

Brooklyn, New York.

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:

$$x_{B} = n_{B} / \sum_{i=1}^{C} n_{i}$$

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:

$$v_{\rm B} = m'_{\rm B} / \sum_{i=1}^{\rm C} m'_{i}$$
(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): $x_{S,B} = n_{B} / \sum_{i=1}^{C} n_{i} = x_{B} / \sum_{i=1}^{C} x_{i}$ (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.

(1)

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

$$m_{B} = n_{B}/n_{A} M_{A}$$
SI base units: mol kg⁻¹ (4)
where M_A is the molar mass of the solvent.
5. Concentration of solute B (1,2) in a solution of volume V:

$$c_{B} = [B] = n_{B}/V$$
SI base units: mol m⁻³ (5)
The 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 follow-
ing 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[±], will be used for the density of a mixture at t^oC, 1
atm divided by the density of water at t^oC, 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 $f_{\rm B}$ of a substance B is given by

$$RT \ln(f_{B}x_{B}) = \mu_{B} - \mu_{B}^{*}$$
(7)

where μ_B is the chemical potential, and $\mu_B{}^{\star}$ is the chemical potential of pure B at the same temperature and pressure. For any substance B in the mixture,

$$\lim_{B \to 1} f_{B} = 1$$
(8)

(b) Solutions.

(i) Solute substance, B. The molal activity coefficient $\gamma_{\rm B}$ is given by

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

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

$$\gamma_{\rm B}^{\infty} = 1 \tag{10}$$

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

$$\gamma_{\rm B} = x_{\rm A} f_{\rm x,B} = V_{\rm A}^* (1 - \sum_{\rm s} c_{\rm s}) \gamma_{\rm B}$$
(11)

or

$$f_{x,B} = (1 + M_A \sum_{s=s}^{\Sigma m}) \gamma_B = V_A * Y_B / V_m$$
(12)

or

$$y_{B} = (V_{A} + M_{A_{S}} \nabla_{s} \nabla_{s}) \gamma_{B} / V_{A}^{*} = V_{m} f_{x,B} / V_{A}^{*}$$
 (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)

$${}_{B}m_{B} = \gamma_{\pm}^{\nu}m_{B}^{\nu}Q^{\nu}$$
(14)

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

$$f_{x,B} x_{B} = v_{+}^{v_{+}} v_{-}^{v_{-}} f_{\pm}^{v_{+}} x_{\pm}^{v_{+}}$$
(15)

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

$$x_{+} = v_{+}x_{B}/[1+(v-1)x_{B}]; \qquad x_{-} = v_{-}x_{B}/[1+(v-1)x_{B}]$$
(16)

(ii) Solvent, A:

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

$$\phi = (\mu_{A}^{*} - \mu_{A}) / RT M_{A S} S$$
(17)

where μ_A^* is the chemical potential of the pure solvent. The rational osmotic coefficient, ϕ_X , is defined as (1):

$$\phi_{\mathbf{x}} = (\mu_{\mathbf{A}} - \mu_{\mathbf{A}}^{*}) / \mathrm{RT} \ln \mathbf{x}_{\mathbf{A}} = \phi M_{\mathbf{A}_{\mathbf{S}}} \sum_{\mathbf{S}} / \ln (1 + M_{\mathbf{A}_{\mathbf{S}}} \sum_{\mathbf{S}})$$
(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:

$$\sum_{i=1}^{C} x_{i}' (S_{i}' dT - V_{i}' dp + d\mu_{i}) = 0$$
(19)

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

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

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

$$d\mu_{i} = \sum_{j=2}^{C} G_{ij} dx_{j} - S_{i} dT + V_{i} dp$$
(21)

where (7)

$$G_{ij} = (\partial \mu_i / \partial x_j) T, P, x_i^{\dagger} x_j$$
⁽²²⁾

it is found that

$$\begin{array}{c} c' c \\ \Sigma & \Sigma \\ i=2 \\ j=2 \end{array} (x_{i}' - x_{i} x_{i}' / x_{1}) G_{ij} dx_{j} - (x_{1}' / x_{1}) & \Sigma & \Sigma \\ & \Sigma & \Sigma \\ i=c'+1 \\ j=2 \\ i=c' \\ i=1 \end{array} (y_{i}' - y_{i}') dT / T - C' \\ & C' \\ & i=1 \\ i=1 \end{array}$$
(23)

where

$$H_{i}-H_{i}' = T(S_{i}-S_{i}')$$

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) Sqlubility 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

$$(1/x_{B}-n/x_{A}) \{1+(\frac{\partial lnf_{B}}{\partial lnx_{B}})\} dx_{B} = (nH_{A}+H_{B}-H_{AB}^{*}) dT/RT^{2}$$
(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):

$$RT \ln f_{\rm B} = w x_{\rm h}^2$$
 (26)

(24)

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

$$nH_{A} + H_{B} - H_{AB}^{*} = \Delta H_{AB} + n(H_{A} - H_{A}^{*}) + (H_{B} - H_{B}^{*})$$
$$= \Delta H_{AB} + w(nx_{B}^{2} + x_{A}^{2})$$
(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

$$R d \ln \{x_{B}(1-x_{B})^{n}\} = -\Delta H_{AB} d(\frac{1}{T}) - w d(\frac{x_{A}^{2}+nx_{B}^{2}}{T})$$
(28)

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

$$\ln \{x_{B}(1-x_{B})^{n}\} \simeq \ln \{\frac{n^{n}}{(1+n)^{n+1}}\} - \{\frac{\Delta H_{AB}^{*} - T^{*} \Delta C_{P}^{*}}{R}\} (\frac{1}{T} - \frac{1}{T^{*}})$$

$$+ \frac{\Delta C_{P}}{R}^{*} \ln (\frac{T}{T^{*}}) - \frac{w}{R} \{\frac{x_{A} + nx_{B}}{T} - \frac{n}{(n+1)T^{*}}\}$$

$$(29)$$

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

$$\ln\{x_{B}(1-x_{B})^{n}\} = A_{1} + A_{2}/T + A_{3}\ln T + A_{4}(x_{A}^{2}+nx_{B}^{2})/T$$
(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
$$\ln f_{x,B} = w(x_A^2 - 1)$$
 (31)

and (27) becomes

$$nH_{A} + H_{B} - H_{AB} = (nH_{A} * + H_{B}^{\omega} - H_{AB}^{*}) + n(H_{A} - H_{A}^{*}) + (H_{B} - H_{B}^{\omega}) = \Delta H_{AB}^{\omega} + w(nx_{B}^{2} + x_{A}^{2} - 1)$$
(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

$$Rv(1/x_{B}-n/x_{A}) \{1+(\partial lnf_{\pm}/\partial lnx_{\pm})_{T,P}\}dx_{B}/\{1+(v-1)x_{B}\}$$
$$= \{\Delta H_{AB}^{\infty} + n(H_{A}-H_{A}^{*}) + (H_{B}-H_{B}^{\infty})\}d(1/T)$$
(33)

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

$$\ell_{n} \left\{ \frac{x_{B}^{\nu} (1-x_{B})^{n}}{1+(\nu-1)x_{D}^{n+\nu}} \right\} = \ell_{n} \left\{ \frac{n}{(n+\nu)^{n+\nu}} \right\} - \left\{ \frac{\Delta H_{AB}^{\infty} (T^{*}) - T^{*} \Delta C_{D}^{*}}{R} \right\} \left(\frac{1}{T} - \frac{1}{T^{*}} \right) + \frac{\Delta C_{D}^{*} (T^{*})}{R} \ell_{n} (T^{*})$$

A similar equation (with v=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.

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

$$\mu_{A_{n}B}^{\star} = \mu_{A_{n}B}(sln) = n\mu_{A} + \mu_{B}$$
(35)
$$= (n\mu_{A}^{\star} + \nu_{+}\mu_{+}^{\omega} + \nu_{-}\mu_{-}^{\omega}) + nRT \ln f_{A}x_{A}$$
$$+ \nu RT \ln \gamma_{\pm}m_{\pm}Q_{\pm}$$
(36)

for a salt hydrate $A_n B$ which dissociates to water, (A), and a salt, B, one mole of which ionizes to give v_+ cations and v_- 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 $K_{S_n}^{\circ}$ in

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

= -RT ln K⁰_{S0}
= -RT ln Q^V Y₊^V m₊^V m₋^V . (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_{50}° 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 $C_{V_{+}}A_{V_{-}}$ in the presence of other solutes is given by eqn (36) as

$$\nu \ln\{m_{B}/m_{B}(0)\} = -\nu \ln\{\gamma_{\pm}/\gamma_{\pm}(0)\} - n \ln(a_{H_{2}O}/a_{H_{2}O}(0))$$
(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 nonstoichiometric 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, selfexplanatory. 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 *necommended* 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 doubt jul 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 *nejected*. 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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R. Cohen-Adad, Villeurbanne, France	
JW Lorimor London Canada	
M. Salomon, Fair Haven, New Jersey, U.S.A.	1
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Lith	ium 1
COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Lithium tetraphenylborate (1-); LiC₂₄H₂₀B; [14485-20-2] (2) Water; H₂O; [7732-18-5] 	Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. <u>1968</u> , 1170-2.
VARIABLES:	PREPARED BY:
One temperature: 25.00°C	Orest Popovych
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·
The authors reported the solubi: mass %, where mass % was defined as solution. This corresponds to a solu	lity of LiBPh ₄ in water as 39.4 grams of the salt in 100 cm ³ of the ubility of 1.21 mol dm ⁻³ (compiler).
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AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Saturated solutions were prepared by shaking the suspensions in a constant-temperature bath for 6 hrs. Aliquots were removed through cotton plugs and weighed. The tetraphenyl- borate concentration was determined	SOURCE AND PURITY OF MATERIALS: KBPh ₄ needed for the preparation of LiBPh ₄ was synthesized in ether according to: $4C_{6}H_{5}MgBr + KBF_{4} \rightarrow$ KB(C ₆ H ₅) ₄ + 4MgBrF. The KBPh ₄ was doubly recrystallized from aqu. acetone, its solution in acetone

by precipitating KBPh_4 and weighing. LiBPh₄ recrystallized from water or acetone-water mixtures forms the solvate LiBPh₄·4H₂O. Double recrys-tallization of the above solvate from absolute acetone yields a new solvate having the composition: LiBPh4 · 1.5C3H60 · 2.5H20.

passed through an ion-exchange resin in Li form, the eluate evaporated under vacuum, the residue dissolved in a chilled chloroform-dichloroethane mixture and the $LiBPh_4$ precipitated by addition of cyclohexane.

ESTIMATED ERROR: Precision ±0.5%

±0.05°C Temperature control:

REFERENCES:

2 Lithi	ium	
COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Lithium tetraphenylborate (1-); LiC₂₄H₂₀B; [14485-20-2]</pre>	Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. 1968. 1170-2.	
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	<u></u> ,,	
VARTABLES :	PREPARED BY.	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:	L,,, _,	
The authors reported the solubil 52.0 mass %, where mass % was defined of the solution. This corresponds to (compiler).	lity of LiBPh ₄ in acetone as a as grams of the salt in 100 cm ³ a solubility of 1.59 mol dm ⁻³	
	1	
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE: Saturated solutions were prepared by shaking the suspensions in a con- stant-temperature bath for 6 hrs. Aliquots were removed through cotton plugs and weighed. The tetraphenyl- borate concentration was determined by precipitating KBPh4 and weighing. LiBPh4 recrystallized from water or acetone-water mixtures forms the solvate LiBPh4·4H20. Double recrys- tallization of the above solvate from absolute acetone yields a new solvate having the composition: LiBPh4·1.5C $_{3}H_{6}O\cdot2.5H_{2}O.$	SOURCE AND PURITY OF MATERIALS: KBPh4 needed for the preparation of LiBPh4 was synthesized in ether according to: $4C_{6}H_{5}MgBr + KBF_{4} \rightarrow$ KB($C_{6}H_{5}$) + 4MgBrF. The KBPh4 was doubly recrystallized from aqu. acetone and its solution in acetone passed through an ion-exchange resin in Li form. The eluate was evapor- ated under vacuum, the residue dis- solved in a chilled chloroform- dichloroethane mixture and the LiBPh4 precipitated by addition of cyclo- hexane. Absolute acetone was pre- pared by treatment with KMnO4 followed by triple fractionation. Final water content was 0.007 vol. % by Karl Fisher titration.	
	Precision ±0.5%	

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COMPONENTS:	EVALUATOR:
 (1) Sodium tetraphenylborate (1-); NaC₂₄H₂₀B; [143-66-8] (2) Water; H₂O; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. October 1979

The only datum on the solubility of sodium tetraphenylborate (NaBPh_L) in water which is backed up by detailed and unambiguous information on the experimental conditions involved is that reported by Kirgintsev and Kozitskii (1) as part of their study of the solubility in the acetone-water system (see compilation on the solubility of NaBPh4 in acetone-water mixtures). At 298.15 K, the solubility reported in the above study was 32.4 (wt./vol.)%, recalculated by the compiler to be 0.947 mol dm⁻³. Another solubility value for NaBPh, in water can be found in the chapter by Flaschka and Barnard (2) citing as the source "personal communication" from H. Buechl. It is reported to be approximately 0.88 mol dm⁻³, with the temperature being either 297 for 298 K. The determination was described as "direct analysis", presumably meaning the method of evaporation and weighing. However, as the experimental details related in the review of Flaschka and Barnard (2) are rather sketchy and an original report is in fact unavailable, no compilation sheet is provided for this original datum. In the case of KBPh4, the solubility in water increased by about 2% per degree, so that if the same temperature dependence governs the solubility of NaBPh, one could not attribute the difference between 0.947 mol dm⁻³ and 0.88 mol dm⁻³ to the possible difference of 1 K in the temperature. A third literature value related to the solubility of $NaBPh_{L}$ in water is the corresponding solubility product listed as $K_{SO}^{s} = 2.14 x$ 10^{-2} (presumably mol² dm⁻⁶) in the book by Clifford (3). Unfortunately, the original source of that value is not given there and taking simply the square root of the K_{SO}° leads to the value 0.146, suggesting that either a large activity correction had been taken into account, or it is based on very poor analytical work. Obviously, no original compilation sheet could be provided for that literature source. Considering that the work of Kirgintsev and Kozitskii (1) was carried out under good temperature control (±0.05°C), with the analysis performed both by the method of evaporation and weighing as well as by precipitation as KBPh_4 and bearing in mind the quality of other results from the same laboratory (see evaluation for KBPh in water), their solubility value can be taken as the tentative value at 298.15 K: 0.947 mol dm⁻³.

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COMPONENTS: ORIGINAL MEASUREMENTS: Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. Sodium tetraphenylborate (1-); NaC₂₄H₂₀B; [143-66-8] 1968, 1170-2. (2) 2-Propanone (acetone); $C_{3}H_{6}O; [67-64-1]$ (3) Water; H₂O; [7732-18-5] VARIABLES: PREPARED BY: Acetone-water composition Orest Popovych One temperature: 25.00°C EXPERIMENTAL VALUES: The authors reported mass % of NaBPh₄ in the saturated solutions, defined as grams of the salt in 100 cm³ of the solution. The solubilities have been recalculated to mol dm^{-3} by the compiler. % Water Solubility of NaBPh4 in acetone (Wt./vol.)% $C/mol dm^{-3}$ Vol. % 0.007 42.8 1.25 2 45.4 1.32 47.8 4 1.40 8 52.1 1.52 12 55.9 1.63 15 58.3 1.70 20 59.4 1.74 25 60.1 1.76 30 59.7 1.74 37 58.8 1.72 45 57.8 1.69 52 56.7 1.66 60 54.9 1.60 70 52.0 1.52 80 48.4 1.41 90 42.4 1.24 100 32.4 0.947 AUXILIARY INFORMATION METHOD / APPARATUS / PROCEDURE : SOURCE AND PURITY OF MATERIALS: Evaporating and weighing. Saturated Sodium tetraphenylborate of solutions prepared by shaking the "analytical grade" obtained from suspensions in a constant-temperature the Apolda Co. (GDR) was purified bath for 6 hours. Aliquots removed by recrystallization from acetonethrough cotton plugs were evaporated toluene, followed by dissolution in first under an IR lamp and then dried water and extraction with ether. The latter was removed $\frac{1}{10}$ vacuo. The purity of the salt was no less than for a week in a vacuum desiccator. Composition of the liquid phase was also checked by precipitation as 99.6%. Absolute acetone was prepared by treating with KMnO4 followed by triple fractionation. The final KBPh4. NaBPh4 recovered from acetone and its aqueous mixtures containing up to 8% water contained the solvent. water content was 0.007 vol. %, by At higher water contents in the sol-Karl Fisher titration. vent, no crystal solvates were formed. 'ESTIMATED ERROR: Precision ±0.5% Temperature control: ±0.05°C

Sodium

Sodium 5		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Sodium tetraphenylborate (1-); NaC₂₄H₂₀B; [143-66-8] (2) N-Methyl-2-pyrrolidinone; C₅H₉NO; [872-50-4] 	Virtanen, P. O. I.; Kerkelä, R. Suom. Kemistil. <u>1969</u> , B42, 29-33.	
VARIABLES: Two temperatures: 25.00°C and 45.00°C	PREPARED BY: Orest Popovych	
EXPERIMENTAL VALUES:	I	
The solubility of NaBPh ₄ in reported to be 1.19 mol dm ⁻³ at 25°C a The corresponding solubility the square of the solubility, was repo where K _{SO} units are mol ² dm ⁻⁶ .	N-methyl-2-pyrrolidinone was and 1.54 mol dm ⁻³ at 45°C. y product at 25°C, calculated as orted in the form $pK_{SO} = -0.15$,	
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
The suspensions were shaken in ther- mostatted water-jacketed flasks for one day at 50°C, followed by one day at 25°C or 45°C, respectively. Ana- lysis for BPh ₄ - concentration in the saturated solutions was carried out by precipitating KBPh ₄ or NH ₄ BPh ₄ from aliquots in aqueous solution.	N-Methyl-2-pyrrolidinone (General Aniline & Film Co.) was purified as in the literature (1).	
	ESTIMATED ERROR:	
	Not specified. Temperature control; ±0.02°C	
	REFERENCES: (1) Virtanen, P. O. I. Suom. Kemistil <u>1966</u> , B39, 257.	

Sodium

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Sodium tetraphenylborate (1-); NaC ₂₄ H ₂₀ B; [143-66-8]	Abraham, M. H.; Danil de Namor, A.F. J. Chem. Soc. Faraday Trans. 1, <u>1978</u> , 74 - 2101-10	
(2) 1-Propanol; $C_3 R_8 0$; $[71-23-3]$	/+, 2101-10.	
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of NaBPh ₄ in mol dm ⁻³ . No further calculations were	e made because of solvate formation.	
	TNEODUATION	
AUXILIARY INFORMATION		
Evaporation and weighing Saturated	The purification of the solvent was	
solutions were prepared by shaking the suspensions for several days.	described in the literature (1). The source and purification of NaBPh,	
The solvent contained no involatile material but NaBPh, formed a solvate	were not mentioned.	
Method of temperature control was not		
specified.		
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	
	A. F.; Schulz, R. A. J. Solution	
	Chem. <u>1977</u> , 6, 491.	

COMPONENTS:	EVALUATOR:
 Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] Water; H₂O; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. February 1979

A total of eleven publications dealing with the solubility of potassium tetraphenylborate (KBPh₄) in aqueous solutions have been reviewed. Nine of them report the solubility directly (1-9), while the remaining two (10, 11) report only the solubility product. Two studies report the solubility as a function of the temperature (7, 8) and only one deals with the variation of the solubility as a function of the temperature, ionic strength and pH (8). In one publication (9), the solubility was reported in a buffer solution, but not in pure water.

Three of the data had to be rejected outright (no compilation sheets provided). One was the datum of Raff and Brotz (1), who published an order-of-magnitude value for the solubility as being less than 10^{-4} mol dm⁻³. The latter was estimated from the point of incipient turbidity observed visually by contacting equal volumes of a solution of KCl and a 0.1 mol dm⁻³ solution of LiBPh₄. Aside from the fact that the observed solubility corresponds not to pure water, but to a solution containing 0.05 mol dm⁻³ LiBPh₄, the entire determination was aimed at the order of magnitude of the solubility and not its precise value. The latter point has been unfortunately overlooked by subsequent investigators, who attributed more than one significant figure to the datum of Raff and Brotz (1). Another rejected datum was the solubility at 292 K reported as 1.12×10^{-4} mol dm⁻³ by Levina and Panteleeva (2), where no method was specified. Besides, the above value is very low, as compared to other literature data in that temperature range. Also rejected was the early value of the solubility product reported as 5×10^{-9} (presumably in mol² dm⁻⁶ units) at 290 K by Rüdorff and Zannier (10). No experimental details were provided there and the authors later revised the above value themselves (3).

The relative validities of the acceptable results must be assessed not so much with respect to the inherent precisions of the analytical methods employed (which are roughly comparable) as with respect to the experimental conditions, such as the time of equilibration and the attention to possible hydrolytic decomposition of the tetraphenylborate ion.

Solubility at 298 K.

The data compiled for 298 K include one determination by electrolytic conductance (3), three determinations by ultraviolet spectrophotometry (5, 6, 9), one by the method of evaporation and weighing (7), and one employing an amperometric titration (8).

The conductometric determination by Rüdorff and Zannier (3) from which the solubility is reported as 1.82×10^{-4} mol dm⁻³ is handicapped by the lack of data on the nature of the conductance apparatus employed and the precision of the temperature control as well as insufficient time of equilibration (4 hours). However, even if we assume that the experimental precision was consistent with the reported value, the latter was calculated from erroneous data. The authors used the value of 21 S cm² mol⁻¹ for the molar conductivity of the tetraphenylborate ion and combined it with the known (unspecified) value for the λ^{∞} of the potassium ion to calculate the Λ^{∞} (KBPh₄). If the value λ^{∞} (K⁺) = 73.50 S cm² mol⁻¹ was used, the resulting Λ^{∞} (KBPh₄) was 94.50 S cm² mol⁻¹. However, if one uses the correct value for λ^{∞} (BPh₄⁻), which is 19.69 S cm² mol⁻¹ (12), the correct value for Λ^{∞} (KBPh₄) becomes 93.19 S cm² mol⁻¹. Presumably the authors calculated the solubility from the measured electrolytic conductivity κ and the calculated Λ^{∞} (KBPh₄) using the relationship C = 1000 κ/Λ^{∞} . On this basis, the correct solubility from their data would be 1.85 x 10⁻⁴ mol dm⁻³. This value, however, is based on the limiting molar conductivity, which even at that low concentration applies only approximately. No data are available on the variation of the molar conductivity of KBPh₄ with concentration in water, but using the corresponding constants

COMPONENTS:	EVALUATOR:
 Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] Water; H₂O; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. February 1979

for the variation of the molar conductivity of NaBPh₄ with concentration (12), it can be estimated that at 1.8 x 10^{-4} mol dm⁻³ the molar conductivity of KBPh₄ would be about 92.2. This would raise the calculated solubility further to 1.87 x 10^{-4} mol dm⁻³.

In the opinion of this evaluator, the best method for determining tetraphenylborate concentration is ultraviolet spectrophotometry, as the spectra are very sensitive to decomposition, so that appreciable changes in the shape of the spectral bands and particularly in the ratio of the heights of the 266-nm and 274-nm peaks occur long before any yellow or brown color betrays the presence of decomposition. Thus, decomposition in the course of solubility determinations can be detected when UVspectrophotometry is the analytical method employed, which is not true of the other analytical methods cited here.

Of the two solubility determinations in pure water by the method of uv-spectrophotometry, that by Popovych and Friedman (6) was carried out under more reliable experimental conditions, namely a temperature control to ±0.01°C in the bath from which water was circulated and an equilibration period of two weeks. The reported value is 1.74 x 10^{-4} mol dm^{-3} with a relative precision of ±1%. The second uv determination, by Pflaum and Howick (5), reports no information on the temperature control and the length of equilibration. Its further shortcoming is that the authors used the peak molar absorption coefficients $\varepsilon_{m\,ax}$ determined in acetonitrile to analyze aqueous solutions. The acetonitrile ε_{max} values were 3.225 x 10³ and 2.110 x 10³ at 266 and 274 nm, respectively. For aqueous solutions, Popovych and Friedman (6) report the molar absorption coefficients as 3.25×10^3 and 2.06×10^3 at 266 and 274 nm, respectively (all molar absorption coefficients are in the units of dm^3 (cm mol)⁻¹). Nevertheless, the solubility reported by Pflaum and Howick (5), 1.78 x 10⁻⁴ mol dm⁻³, agrees with the Popovych and Friedman (6) value, within experimental error. This agreement may be due to certain compensating errors and other mitigating factors. Thus, the solubility of KBPh4 in the temperature range of 293-298 K varies only by 0.04 x 10^{-4} mol dm⁻³ per degree (7). Therefore, a temperature control to only ±0.5°C would suffice to keep the error within the limits of precision imposed by the analytical method ($\pm 1\%$ relative). The e_{max} value for the BPh_4 anion used by Pflaum and Howick (5) in their calculation of the solubility was 2.5% too high at 274 nm and 1% too low at 266 nm. If the solubility value was determined as the average from the two wavelengths, what we may be seeing here is a compensation of errors.

In the uv-determination by McClure and Rechnitz (9), the solubility of KBPh₄ was not measured in pure water, but in a buffer solution consisting of 0.1 mol dm⁻³ tris(hydroxymethyl)aminomethane and 0.01 mol dm⁻³ acetic acid adjusted to pH 5.1 with $HClO_4$. Thus, the solubility value of 2.3 x 10^{-4} mol dm⁻³ reported by them is not comparable with the results at zero ionic strength. However, it may be compared with Siska's (8) data obtained at an ionic strength of 0.1 mol dm⁻³, which we discuss later.

In excellent agreement with the uv-determined solubilities reported for pure water is the value obtained by evaporation of a saturated solution and weighing of the residue (7). Here, two solubility values are reported at 298 K, one resulting from a continuous equilibration at the stated temperature for 12 hours: 1.74×10^{-4} mol dm⁻³ (1.75×10^{-4} mol dm⁻³ in the original, due to an error in converting from wt %) and the other, resulting from a preliminary equilibration at 40°C for 6 hours, followed by 12 hours at 25°C: 1.79×10^{-4} mol dm⁻³. This study is characterized by good temperature control (± 0.05 °C) and a reasonable time of equilibration.

CO	MPONENTS:	EVALUATOR:
(:	L) Potassium tetraphenylborate (1-); KC ₂₄ H ₂₀ B; [3244-41-5] 2) Water: H ₂ O: [7732-18-5]	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
``	2) water; h20; [//32-18-5]	rebruary 1979

Recommended Values_at 298.15 K

Combining the average value reported by Kozitskii (7), 1.76×10^{-4} mol dm⁻³, by Popovych and Friedman (6), 1.74×10^{-4} mol dm⁻³, and by Pflaum and Howick (5), 1.78×10^{-4} mol dm⁻³, we obtain the overall average from three studies by two different methods as:

Solubility = $(1.76 \pm 0.02) \times 10^{-4} \text{ mol dm}^{-3}$

The absolute error derives from the relative precision of a uv-determination of the tetraphenylborate concentration, which is $\pm 1\%$ (6).

The solubility product can be calculated as $K_{s0}^{\circ} = (Cy_{\pm})^2$, where the mean molar ionic activity coefficient y_{\pm}^2 is estimated from the Debye-Hückel limiting law: log $y_{\pm}^2 = -1.18(1.76 \times 10^{-4})^{\frac{1}{2}}$. This yields $y_{\pm}^2 = 0.969$ and

 $K_{e0}^{\circ} = (3.00 \pm 0.04) \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$

The absolute error in the $K_{\rm SO}^{\circ}$ was calculated assuming the 1% error in C as its only source.

Solubility at Other Temperatures

At 293 K, the solubility can be found in two literature sources (4,7), reported directly and in another source where it is reported in the form of the solubility product (11). Closest agreement exists between the value published by Kozitskii (7), 1.56×10^{-4} mol dm⁻³, which was determined by evaporation and weighing, and the radiometrically determined value of 1.48 x 10^{-4} mol dm⁻³ reported by Geilmann and Gebauhr (4). Unfortunately, even these two values are not quite close enough to merit averaging for a recommended value. Considering that Kozitskii specified an equilibration time of 24 hours and that his solubility at 298 K is equal to the recommended value at that temperature, this evaluator chooses 1.56×10^{-4} mol dm⁻³ as the tentative value for the solubility at 293 K. Geilman and Gebauhr (4), on the other hand, did not specify the time of equilibration.

The other solubility values reported for 293 K-appear to be too low. From a potentiometric titration, Havir (11) reports a solubility product of 1.6 x 10^{-8} (presumably in mol² dm⁻⁶ units), from which the solubility taken simply as the square root would be 1.3 x 10^{-4} mol dm⁻³. No equilibration time was specified here, but considering that the solubility of AgBPh₄ reported in the same article was determined after only 4 hours of equilibration, it is likely that a similar time was used for KBPh₄. It should be noted that the intention of the author in this case was to demonstrate the concentration limit to which a potentiometric titration of the BPh₄⁻ ion was feasible and that the determination of the solubility of KBPh₄ was incidental. Similarly, Siska's (8) value of 1.25 x 10^{-4} mol dm⁻³, which was determined after only 3 hours of equilibration, must be too low due to absence of saturation.

Both Siska (8) and Kozitskii (7) reported the solubility at several temperatures. Siska also showed tables of the solubility as a function of ionic strength and the pH. Most of his values were determined at an ionic strength of 0.1 mol dm⁻³ and are therefore not directly comparable with other literature data. However, judging from the one datum given for zero ionic strength at 293 K (1.25×10^{-4} mol dm⁻³) and from the fact that Siska's data at other temperatures at 0.1 ionic strength are of approximately the same magnitude as other literature data at zero ionic strength, it seems that all the results in this most comprehensive study of the solubility of KBPh₄ in aqueous solutions are too low due to

COMPONENTS:	EVALUATOR:
(1) Potassium tetraphenylborate $(1-)$; KC ₂₁ H ₂₀ B; [3244-41-5]	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College,
(2) Water; H ₂ O; [7732-18-5]	Brooklyn, N. Y. 11210, U. S. A. February 1979

undersaturation. This conclusion seems also to be corroborated by the fact that the solubility of KBPh₄ in a 0.1 mol dm⁻³ buffer solution reported by McClure and Rechnitz (9) at 298 K, $(2.3 \times 10^{-4} \text{ mol dm}^{-3})$ is higher than the solubility reported by Siska at 303 K (2.13 $\times 10^{-4}$ mol dm⁻³). Consequently, we are again limited to stating as <u>tentative values</u> those solubilities that were reported by Kozitskii (7) at other temperatures as well. Below we tabulate these solubilities as well as the solubility products derived from them using mean molar activity coefficients y_{\pm} estimated from the Debye-Huckel limiting law. It should be noted that in the concentration range involved, the use of a Debye-Huckel expression with ion-sized parameters would result in a change of about one part per thousand only.

Solubility at Different Temperatures (8)

Т/К	10^{4} C/mol dm ⁻³	10 ⁸ K [°] _{s0} /mol ² dm ^{-6*}	A (Debye-Hückel)
273.15	1.29	1.62	0.490
293.15	1.56	2.36	0.505
298.15	1.76	3.00	0.509
323.15	3.71	13.1	0.537

Calculated by the evaluator as $K_{SO}^{} = C^2 y_{\pm}^2$, where log $y_{\pm}^2 = -2A(C)^{\frac{1}{2}}$ and the units of A are mol^{-1/2} dm^{3/2}.

A plot of log K_{SO}° vs. T^{-1} is linear only in the range of 293-323 K, for which the smoothing equation obtained by the method of least squares is: log $K_{SO}^{\circ} = -2387/(T/K) + 0.501$, with $\sigma_y = 0.013$ (absolute) and a correlation coefficient of -0.999. The highly tentative values for the thermodynamic constants calculated from the above slope and intercept are:

 $\Delta H^{\circ} + 45.7 \pm 1.8 \text{ kJ mol}^{-1} \text{ and } \Delta S^{\circ} = 9.6 \pm 6.1 \text{ JK}^{-1} \text{ mol}^{-1}.$

All four points can be described by the equation:

 $\log K_{S0}^{\circ} = 30.97 - 2.121 - 10^{4}/(T/K) + 2.903 \times 10^{6}/(T/K)^{2} \text{ with } \sigma_{y} = 0.006 \text{ (abs.)},$

References:

Raff, P.; Brotz, W. Z. anal. Chem. 1951, 133, 241. 1. 2. Levina, N. D.; Panteleeva, N. I. Zavod. Lab. 1957, 23, 285. Rüdorff, W.; Zannier, H. Z. Naturforsch. 1953, 8b, 611. 3. Geilmann, W.; Gebauhr, W. Z. anal. Chem. <u>1953</u>, 139, 161. Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u>, 28, 1542. Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u>, 70, 4. 5. 1956, 28, 1542. 1966, 70, 1671. 6. 7. Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. 1970, 8. Siska, E. Magy. Kem. Foly. <u>1976</u>, 82, 275. McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u>, 38, 136. Rüdorff, W.; Zannier, H. Angew. Chem. <u>1952</u>, 64, 613. Havir, J. Collect. Czech. Chem. Commun. <u>1959</u>, 24, 1955. 8. 9. 10. 11. Skinner, J. F.; Fuoss, R. M. J. Phys. Chem. 1964, 68, 1882. 12.

Potassium

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium tetraphenylborate (1-);	Rüdorff, W.; Zannier, H.
KC ₂₄ H ₂₀ B; [3244-41-5]	Z. Naturforsch. <u>1953</u> , 8b, 611-2.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES: The solubility of (KBPh4) was repor and the solubilit	potassium tetraphenylborate ted as 1.82 x 10^{-4} mol dm ⁻³ sy product, K _{SO} , as 3.3 x 10^{-8} mol ² dm ⁻⁶ .
The authors determined the limiting m phenylborate to be 71 S cm ² mol ⁻¹ , fr 21 S cm ² mol ⁻¹ for the λ^{∞} of the tetr latter with the known (unspecified) w calculated the solubility from the co of potassium tetraphenylborate, presu C = 1000 κ/Λ^{∞} , where C is the solubil tivity of the solution corrected for specified). The calculation method, article. The present results were reported previously published by the same auth (presumably in units of mol ² dm ⁻⁶), w	toolar conductivity of sodium tetra- tom which they derived the value of aphenylborate anion. Combining the alue for the $\lambda^{\infty}(K^+)$, the authors unductance of the saturated solution solution the relationship: fity and κ , the electrolytic conduc- solvent conductance (magnitude not however, was not explained in the end as an improvement over the for (1) value of $K_{SO} = 5 \times 10^{-9}$ which was also derived from conduc-
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Electrolytic conductance on unspecified apparatus. Temperature controlled, but within unspecified limits. Saturated solutions of KBPh ₄ were prepared by bubbling nitrogen through its suspensions in conductivity water for 4 hours.	SOURCE AND PURITY OF MATERIALS: NaBPh ₄ from the Heyl Co. of Hildesheim, Germany, was purified in the absence of air by just dis- solving it in chloroform-acetone mixture and precipitating with petroleum ether. After repeated treatment, it was recrystallized under N_2 from chloroform and vacuum dried. KBPh ₄ was recrystallized from acetone-ethyl acetate.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:
	Rüdorff, W.; Zannier, H.
	Angew. Chem. <u>1952</u> , 64, 613.

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Potassium tetraphenylborate (1-); 	Geilmann, W.; Gebauhr, W.		
KC ₂₄ H ₂₀ B; [3244-41-5]	Z. anal. Chem. <u>1953</u> , 139, 161-81.		
(2) Water; H_2O ; [7732-18-5]			
VARIABLES:	PREPARED BY:		
One temperature: 20°C	Orest Popovych		
EVERTIMENTAL VALUES.			
EXTERIMENTAL VALUES:			
water and as 1.5×10^{-4} mol dm ⁻³ . Re the above solubility would be 1.48 x	th as $C_{\rm K}$ = 0.578 mg/100 m1 of taining three significant figures, 10^{-4} mol dm ⁻³ (compiler).		
The solubility product of KBPh ₄ is reported as $K_{\rm SO} = 2.25 \times 10^{-8}$ mol ² dm ⁻⁶ . Because the latter is simply $C_{\rm K}^2$, the value calculated from the solubility expressed to three significant figures is $K_{\rm SO} = 2.19 \times 10^{-8}$ mol ² dm ⁻⁶ (compiler).			
Also reported is the rate of borate in water:	dissolution of potassium tetraphenyl-		
Time, hours	µg K/10 ml of water		
0.5	55.7		
2.0	57.0		
5.0	57.4		
16.0	57.5		
	•		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE: Radiometric,	SOURCE AND PURITY OF MATERIALS:		
using liquid-scintillation counting of ⁴² K. Apparatus not specified. The radioactive potassium obtained as the carbonate from the Harwell nuclear reactor was purified by pre-	Nothing specified.		
cipitation with $HClO_4$ in the presence of 2 mg of Na_2HPO_4 and recrystalli- zation. The KClO ₄ solution was re- acted with NaBPh ₄ , the resulting			
KBPh4 precipitate washed with water, mechanically shaken in water at 20°C			
and the filtrate analyzed radiometri- cally to constant activity.	ESTIMATED ERFOR-		
	Not specified. However, given the		
	temperature control to ± 0.5 °C, the relative precision cannot be better		
	than ±1-2% (compiler). REFERENCES:		
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Potassium

COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Potassium tetraphenylborate (1-);	Pflaum, R. T.; Howick, L. C.		
KC ₂₄ H ₂₀ B; [3244-41-5]	Anal. Chem. <u>1956</u> , 28, 1542-44.		
(2) Water;H ₂ O ; [7732-18-5]			
VADT IN TO			
VARIABLES:	PREPARED BY:		
one temperature: 25°C	Orest Popovych		
EXPERIMENTAL VALUES:			
	•		
The solubility of potassium reported as 1.78×10^{-4} mol dm ⁻³ .	tetraphenylborate (KBPh ₄) was		
Also reported were the molar absorption coefficients of the tetraphenylborate ion in acetonitrile at 266 nm and 274 nm as 3225 and 2100 dm^3 (cm mol) ⁻¹ , respectively.			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE: Ultraviolet	SOURCE AND PURITY OF MATERIALS:		
spectrophotometry on a Cary Model 11 recording spectrophotometer.	NaBPh ₄ (J. TBaker Chemical Co.) was used as received for pptns, but was		
Saturated solutions were prepared in conductivity water by an unspecified	recrystallized from acetone-hexane mixt for detn of absorption coeffi-		
Procedure. Method of controlling the temperature was not stated. The	cients. KBPh, was prepd by metathesi of KC1 and NaBPh, and purified by re-		
concentration of BPh_{4} in saturated solutions was obtained from spectro-	crystallization from a CH_3CN-H_2O mixt CH_2CN (Matheson, Coleman & Bell) was		
photometric measurements at 266 and 274 nm by applying the molar	treated with cold satd KOH, dried		
absorption coefficients specified	refluxed over P_2O_5 in an all-glass		
	81-81.5 °C was retained. All other		
	ity.		
	ESTIMATED ERROR:		
	Nothing specified. Precision is		
	(compiler).		

Potassium

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Potassium tetraphenylborate (1-); 	Popovych, O.; Friedman, R. M.		
$KC_{24}H_{20}B;$ [3244-41-5]	J. Phys. Chem. <u>1966</u> , 70, 1671-3.		
(2) Water; H ₂ O; [7732-18-5]			
VARIABLES:	PREPARED BY:		
One temperature: 25.00°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility of potas was reported as the concentration of saturated solution:	sium tetraphenylborate (KBPh ₄) total tetraphenylborate in its		
$C = 1.74 \times 10^{-4}$	mol dm ⁻³		
The solubility product $K_{SO}^{\circ} = (Cy_{\pm})^2$ was computed by the authors from the above solubility C and the activity coefficient y_{\pm} calculated from the Debye-Hückel equation in the form:			
$\log y_{\pm} = \frac{-0.509 \ C^{\frac{1}{2}}}{1 + 0.328 \& C^{\frac{1}{2}}}$			
Values of the ion-size parameter å were taken as 0.3 nm for the K ⁺ ion (1) and 1.0 nm for the tetraphenylborate ion (2). The solubility product computed in this manner was:			
$K_{s0}^{\circ} = 2.94 \times 10^{-10}$	⁸ mol ² dm ⁻⁶		
Complete dissociation was assumed. The molar absorption coefficient of the tetraphenylborate ion in water was reported as 3.25×10^3 at 266 nm and as 2.06×10^3 at 274 nm. The units of the absorption coefficient were dm ³ (cm mol) ⁻¹ .			
ΔΊΙΧΤΙ.ΤΑΡΥ	ΙΝΕΩΡΜΑΤΙΩΝ		
METUOD /ADDADATIIS /DDOCEDIIDE			
spectrophotometry using a Cary Model 14 recording spectrophotometer. Saturated solutions were prepared by shaking suspensions of KBPh4 in water on a Burrell wrist-action shaker in water-jacketed flasks with water cir- culated from a constant-temperature bath maintained at 25.00 ±0.01°C. After about 2 weeks of shaking, the suspensions were filtered and the filtrates analyzed spectrophotometri- cally. The molar absorption coeffi- cients stated above were used to	KBPh4 was prepared from NaBPh4 (Fisher, 99.7%) by metathesis with KC1; it was recrystallized 3 times from 3:1 acetone-water and dried <u>in vacuo</u> at 80°C. Deionized water was redistilled.		
compute the concentration of tetra- phenylborate. All work was carried out in deaerated containers and solvents.	Not stated by the authors, but relative precision in known to be of the order of 1% (compiler). <u>Temperature: ±0.01°C</u> REFERENCES: (1) Kielland J. J. Am. Chem. Soc.		
	1937, 39, 1675. (2) Nightingale, E. R. J. Phys. Chem. <u>1959</u> , 63, 1381.		

COMPONENTS:	ORIGINAL MEASUREMENTS:			
(1) Potassium tetraphenylborate (1-); $KC_{24}H_{20}B$; [3244-41-5]	Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. <u>1970</u> , 8-11.			
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]				
(3) Water; H ₂ O; [7732-18-5]				
VARIABLES: Acetone-water composition	PREPARED BY:			
2 temperatures: 0.00°C and 50.00°C	Orest Popovych			
range of 0.00-97.50°C for water.				
EXPERIMENTAL VALUES: The author reports	the solubility of potassium			
tetraphenylborate (KBPh ₄) in water i In acetone-water mixtures, the solub in saturated solutions. The mass $\%$ the salt in 100 ml of the solution. recalculated to the units of mol dm ⁻	n the units of mg/l and in mol dm ⁻³ . ility is reported as mass % of the salt is defined as the number of grams of The latter solubilities have been ³ by the compiler.			
Solubility of K	BPh ₄ in water			
t/°C mg dm ⁻³ 10^4 mol dm ⁻³ p	ydrolysis Time of roducts, mg dm ⁻³ saturation, pH hrs			
0 46.1 1.29	0 24 6.6			
25 62.5 1.75 ⁺	0 12 6.5			
25* 64.0 1.79 50 133 3.7 ^x	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$			
75 301 8.1	14.4 1.1 7.40			
97.5 426 13	23.2 6 7.82 238 0.6 7.90			
546	94 1.5 8.85			
*Preliminary equilibration at 40°C for 6 hours. [†] Should be 1.74 (compiler). ^x Should be 3.71 (compiler).				
The above table also illustrates the extent of hydrolytic decomposi- tion of the tetraphenylborate anion as a function of the temperature and the time of equilibration.				
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing	SOURCE AND PURITY OF MATERIALS; Absolute acetope (0,0065 vol % H_0)			
Saturated solutions were prepared by	was prepd by the same method as			
in thermostatted baths for the lengt	for KBPh4 in acetone-water at 25°C.			
of time indicated in the above Table One liter of the filtrate from the	KBPh, obtained by metathesis of KCl			
saturated solution was dried by	recrystallization from 3:1 acetone-			
the temperature no higher than 40°C)	water, evaporation of the acetone, washing of the crystals with water			
The residue and the column were rinsed out many times with small	and ether and vacuum drying at 60°C.			
portions of acetone, which was then				
residue, weighed.	ESTIMATED ERROR:			
	None stated			
	Temperature: ±0.05°C			
	REFERENCES:			

COMPÓNENTS:	ORIGINAL MEASUREMENTS: (continued)
<pre>(1) Potassium tetraphenylborate (1-); KC24H20B; [3244-41-5]</pre>	Kozitskii, V. P. Izvest. Akad. Nauk: SSSR, Khim. Ser. <u>1970</u> , 8-11.
<pre>(2) 2-Propanone (acetone): C₃H₆O; [67-64-1] (3) Water: H₂O; [7732-18-5]</pre>	

Potassium

COMMENTS AND/OR ADDITIONAL DATA:

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The author reports the solubility of potassium tetraphenylborate in acetone-water mixtures at 0, 25 and 50°C, but the values at 25°C were taken from a previous study in the same laboratory (1) compiled on the sheet for KBPh₄ in acetone-water mixtures at 25°C, with the exception of the value for pure water, which is now reported as 0.0063 wt %, corresponding to 1.76×10^{-4} mol dm⁻³ (compiler).

Solubility of KBPh4 in Acetone-Water Mixtures

Temperature	,	0 ° C	50	o°c
Vol.% H ₂ O in acetone	(wt/vol)%	mol dm ⁻³ (compiler)	(wt/vol)%	mol dm ⁻³ (compiler)
0.007 2 4 8 12 15	7.04 7.59 7.67 7.18 6.45 5.87	0.196 0.212 0.214 0.200 0.180 0.164	5.15 6.04 6.58 7.14 7.05 6.77	0.144 0.169 0.184 0.199 0.197 0.189
20 25 33.3 37	4.88 3.81 2.19	$\begin{array}{c} 0.136\\ 0.106\\ 6.11 \times 10^{-2}\\ \end{array}$	6.24 5.56 4.24 3.69	0.174 0.155 0.118 0.103
40 45 52 60 70 80 100	0.86 0.389 0.116 0.031 0.0096 0.0046	$\begin{array}{c} 3.82 \times 10^{-2} \\ 2.4_0 \times 10^{-2} \\ 3.24 \times 10^{-3} \\ 8.6 \times 10^{-4} \\ 2.6_8 \times 10^{-4} \\ 1.3 \times 10^{-4} \end{array}$	2.42 1.50 0.82 0.26 0.0992 0.0133	6.75×10^{-2} 4.19×10^{-2} 2.29×10^{-2} 7.3×10^{-3} 2.77×10^{-3} 3.71×10^{-4}

REFERENCES:

 Kirgintsev, A. N. Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. <u>1968</u>, 1170. ;

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v 1
COMPONENTS:	ORIGINAL MEASUREMENTS:		
 Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] Sodium sulfate; Na₂SO₄; [7757-82-6] 	Siska, E. <i>Magy. Kem. Foly.</i> <u>1976</u> , 82, 275-8.		
(3) Water; H_20 ; [7732-18-5]			
VARIABLES:	PREPARED BY:		
Temperature range 10-45°C	Orest Popovych		
Concentration of Na ₂ SO ₄ PH			
EXPERIMENTAL VALUES:			
The solubility of potassium tetraphenylborate (KBPh ₄) at 20 ± 1°C was reported for distilled water to be C = 1.35×10^{-4} mol dm ⁻³ and the corresponding solubility product, calculated at K _{SO} = C ² , was reported as K _{SO} = 1.72×10^{-8} mol ² dm ⁻⁶ . With ionic strength varied by means of Na ₂ SO ₄ , the following solubilities C were reported for potassium tetraphenylborate in aqueous solutions at 20 ± 1°C:			
Ionic strength, mol d	m ⁻³ 10 ⁴ C/mol dm ⁻³		
0	1.25		
0.1	1.50		
0.3	1.34		
0.5	1.25		
1.0	0.79		
2.0	0.43		
	、		
AUXILIARY	INFORMATION		
METHOD /APPAPATUS /PROCEDURE +	COURCE AND BUDITY OF MATERIALS.		
Amperometric titration of the tetraphenylborate ion with $AgNO_3$ or TINO ₃ solutions using a Radeikis OH-102 polarograph and a graphite- calomel electrode system with an agar-agar bridge. The calomel elect-	Not specified.		
rode contained 0.1 mol dm ⁻³ NaCl. The titration was carried out in 5-10 cm ³ of acetic acid-sodium acetate buffer mixed with 5 cm ³ of acetone. KBPh ₄ was prepared by metathesis of KCl and NaBPh ₄ .			
Prepared by magnetically stimutes its	ESTIMATED ERROR:		
suspensions for up to 3 hours.	±2% is the precision in the solubility determination. Temperature ±1°C		
	REFERENCES:		

Potassium

COMBONERNES.	ORIGINAL MEASUREMENTS: (continued)		
COMPONENTS:	ORIGINAL MERSONSMENTS. (Concerneed)		
 Potassium tetraphenylborate (1-); 	Siska, E. <i>Magy. Kem. Foly.</i> 1976, <i>82</i> , 275-8.		
$KC_{24}H_{20}B; [3244-41-5]$			
(2) Sodium sulfate; Na ₂ SO ₄ ; [7757-82-6	1		
(3) Water; H ₂ O; [7732-18-5]			
COMMENTS AND/OR ADDITIONAL DATA:			
Keeping the ionic strength constant at 0.1 mol dm ⁻³ with sodium sulfate, the following solubilities C were obtained as a function of the tempera- ture:			
t/°C	10^{4} C/mol dm ⁻³		
10	1.19		
20	1.50		
30	2.13		
40	2.45		
Keeping the ionic strength constant at 0.1 mol dm^{-3} , with sodium sulfate, the following solubilities C were obtained as a function of the pH varied by means of acetic acid and sodium hydroxide at 20 ± 1°C:			
pH 10 ⁴ C/mol dm ⁻³ pH	10^{4} C/mol dm ⁻³		
1.3 0.30 11.5	1.40		
1.8 0.94 11.6	1.40		
2.8 1.54 11.6	1.42		
3.0 1.42 11.7	1.50		
4.6 1.48 3.7	1.42		
5.7 1.44 3.9	1.40		
6.6 1.45			
6.9 1.44 The auth	The authors report at an ionic strength of		
7.8 1.42 0.1 and	the pH range of 2.8-11.7, the		
8.8 1.42 IOIIOWIN	tollowing solubility value for potassium		
10.2 1.50 certaple	tetraphenylborate in aqueous solution:		
10.6 1.50 The error	r in the above value was stated as		
11.2 1.46 0.046 (1	0^{-4} mol dm ⁻³), presumably referring		
to the p	recision.		

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] (2) Tris(hydroxymethyl)aminomethane; C₄H₁₁NO₃; [77-86-1] (3) Acetic acid; C₂H₄O₂; [64-19-7] (4) Water; H₂O; [7732-18-5] 	McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u> , 38, 136-139.
VARIABLES:	PREPARED BY:
One temperature: 24.8°C	Orest Popovych
EXPERIMENTAL VALUES:	1
The solubility of potassium tetr tris(hydroxymethyl)aminomethane (THAM) 2.3 x 10 ⁻⁴ mol dm ⁻³ .	raphenylborate (KBPh4) in aqueous) buffer at a pH 5.1 was reported as
	INFORMATION
METHOD (LDD LD	
UV-spectrophotometry according to the Procedure of Howick and Pflaum (1). No other details.	The buffer solution was composed of 0.1 mol dm ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO4. The source of BPh ₄ was a solution of Ca(BPh ₄) ₂ in THAM prepared from Fisher Scientific reagent-grade NaBPh ₄ by the procedure of Rechnitz et al. (2) and standardized by potentiometric titrn with KCl and RbCl. Baker reagent-grade KCl was the source of K ⁺ . ESTIMATED ERROR: Not stated
	Not stated. Temperature: ±0.3°C
	 REFERENCES: 1. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u>, 19, 342. 2. Rechnitz, G. A.; Katz, S. A.; Zamochnick, S. B. Anal. Chem. <u>1963</u>, 35, 1322.

Potassium			
COMPONENTS :	ORIGINAL MEASUREMENTS:		
(1) Potassium tetraphenylborate	(1-); Havir, J. Collect. Czech. Chem.		
KC ₂₄ H ₂₀ B; [3244-41-5]	Commun. <u>1959</u> , 24, 1955-9.		
(2) Water; H ₂ 0; [7732-18-5]			
VARIABLES:	PREPARED BY:		
One temperature: 20°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility product of potassium tetraphenylborate (KBPh ₄) in water is reported to be: $K_{s0} = 1.6 \times 10^{-9}$ presumably in mol ² dm ⁻⁶ units (compiler). The corresponding solubility calculated as $(K_{s0})^2$ is: $C = 1.3 \times 10^{-4}$ mol dm ⁻³ (compiler).			
AUX	ILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE: Potentiome titration of the tetraphenylbora ion in saturated KBPh ₄ solutions AgNO ₃ using a freshly plated sil indicator electrode and a satura calomel reference electrode dipp in a solution of 10% NaNO ₃ . The salt bridge was a 2% Agar-Agar solution in a 10% NaNO ₃ solution An Ionoskop potentiometer was us	tric SOURCE AND PURITY OF MATERIALS: NaBPh4 was obtained from the Heyl Co. (Berlin), but the method of preparation and purification of the potassium salt was not specified. ed.		
	ESTIMATED ERROR:		
	Nothing specified.		
	DEFEDENCIO		
	REFERENCES:		

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COMPONENTS:	EVALUATOR:
<pre>(1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5]</pre>	Orest Popovych, Department of Chemistry, City University of
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
(3) Water; H ₂ 0; [7732-18-5]	September 1979

CRITICAL EVALUATION:

The solubility of potassium tetraphenylborate (KBPh4) in acetonewater mixtures was determined at 301 K by Scott et al. (1) and at 298.15 K by Kirgintsev and Kozitskii (2). This difference in the temperature and, to a smaller degree, the fact that the acetone in the first study was of reagent grade and may have contained up to 0.5% water preclude a comparison of the two sets of data. Only for pure acetone was it possible to make a comparison between the results obtained from the above two studies, but the agreement was very poor. Thus, according to Scott et al. (1) the solubility in acetone at 301 K was 0.117 mol dm⁻³, while a smoothing equation based on the data of Kirgintsev and Kozitskii (2, 3) predicted a solubility of 0.165 mol dm⁻³ at 301 K (see evaluation for $KBPh_4$ in acetone). Of course, it is impossible to tell whether or not the two sets of data would similarly disagree at other solvent compositions, since data for the solubility as a function of the temperature are not available for acetone-water mixtures. At this time, the solubilities reported for acetone-water mixtures by Kirgintsev and Kozitskii (2) should be regarded as the <u>tentative values at 298.15 K</u>. They were obtained under good tem-perature control (±0.05°C), but the equilibration time of 6 hours may have been insufficient for complete saturation.

REFERENCES:

- Scott, A. D.; Hunziker, H. H.; Reed, M. G. Chemist-Analyst <u>1959</u>, 48, 11.
- 2. Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim.
- Ser. <u>1968</u>, 1170. 3. Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. <u>1970</u>, 8.

(The compilation based on this reference is included among the aqueous systems).

COMPONENTS: ORIGINAL MEASUREMENTS: (I) Potassium tetraphenylborate Scott, A. D.; Hunziker, H. H.; Reed, M. G. Chemist-Analyst 1959, $(1-); KC_{24}H_{20}B; [3244-41-5]$ 48, 11-12. (2) 2-Propanone (acetone); C₃H₆O; [67 - 64 - 1](3) Water; H_20 ; [7732-18-5] VARIABLES: PREPARED BY: Acetone-water composition. Orest Popovych One temperature: 28°C EXPERIMENTAL VALUES: The solubility of $\rm KBPh_4$ in acetone-water mixtures at 28°C was reported in mg cm^3 by the authors and recalculated to mol dm^3 units by the compiler. Vol % Acetone in Solubility of KBPh4 mol dm^{-3} mg cm⁻³ Mixture* 1.1×10^{-3} 0.4 16 1.7×10^{-3} 25 0.6 3.4×10^{-3} 32 1.2 3.1×10^{-3} 33 1.1 8.1×10^{-3} 38 2.9 $\begin{array}{c} 7.0 \times 10^{-3} \\ 1.4 \times 10^{-2} \\ 2.93 \times 10^{-2}, 2.49 \times 10^{-2} \end{array}$ 2.5 40 44 4.9 50 10.5, 8.9 5.14×10^{-2} 60 18.4 7.54×10^{-2} 27.0 70 1.13×10^{-1} 40.6 80 1.48×10^{-1} 90 53.0 1.67×10^{-1} 59.8 95 1.38×10^{-1} 99 49.3 1.17×10^{-1} 41.8 100 *Percentage by volume based on combined volumes of the solvents. AUXILIARY INFORMATION METHOD / APPARATUS / PROCEDURE : SOURCE AND PURITY OF MATERIALS: KBPh4 was shaken for 16 hours in Reagent-grade acetone was used undried, and its water content (0.5% 20-ml portions of acetone-water mixtures or finely-ground samples max.) was neither determined, nor shaken for 48 hours. Solutions with corrected for. ${\rm KBPh}_4$ prepared by metathesis of KCl and ${\rm NaBPh}_4$ in 50% acetone or more were analyzed by evaporation and weighing. In other solution acidified with HCl (presumsolutions, the ${\rm KBPh}_{\rm 4}$ was destroyed with aqua regia and the potassium ably aqueous), washed with water saturated with KBPh4 and air dried. determined by flame photometry. ESTIMATED ERROR: Nothing specified. **REFERENCES:**

1 otasaan 25			
COMPONENTS :	ORIGINAL MEASUREMENTS .		
(1) Potassium tetraphenylborate (1-); $KC_{24}H_{20}B$; [3244-41-5]	Kirgintsev, A. N.; Kozitskii, V. J Izvest. Akad. Nauk SSSR, Khim. Ses		
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	<u>1968</u> , 1170-2.		
(3) Water; H ₂ O; [7732-18-5]			
VARIABLES:	PREPARED BY:		
Acetone-water composition One temperature: 25.00°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The authors reported mass $\%$ of KBPh ₄ in the saturated solutions, defined as grams of the salt in 100 cm ³ of the solution. The solubilities have been recalculated to mol dm ⁻³ by the compiler.			
% Water So in acetone*	lubility of KBPh ₄		
<u>vol % (Mass/v</u>	<u>o1.)%</u> <u>mol_dm⁻³</u>		
0.007 2 4 7.04 8 7.02	0.171 0.188 0.196 0.196		
12 6.60	·· 0.184		
15 $6.1720 5.38$	0.172 0.150		
25 4.55	0.127		
30 3.81 37 2.60	0.106 7.26 x 10 ⁻²		
45 1.60	4.47×10^{-2}		
52 0.81 60 0.35	2.26×10^{-2} 9.8×10^{-3}		
70 0.11	3.1×10^{-3}		
*Determined by weighing. Solvent volume was taken as the sum of the volumes of acetone and water, neglecting the effect of mixing.			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions were prepared by shaking the suspensions in a constant-tem- perature bath for 6 hours. Aliquots were removed through cotton plugs, weighed and the solvent removed by evaporation first under an IR lamp and then by oven-drying to constant weight at 105°C. The solid phase contained no solvent when recrystal- lized from acetone or acetone-water mixtures. SOURCE AND PURITY OF MATERIALS: SOURCE AND PURITY OF MATERIALS: NaBPh ₄ ("analytical grade" : Apolda Co., GDR) was purifi recrystallization from aceto toluene, followed by dissolt water, extraction with ether purity of the final NaBPh ₄ with less than 99.6%. KBPh ₄ was by metathesis of NaBPh ₄ with from 20% water 80% acetone by vol.). The acetone was se evaporated and the precipit for a long time under high ' Acetone was treated with KMI lowed by triple fractionatic water content was 0.007 vol Karl Fisher titration. ESTIMATED ERROR: Precision ±0.5% Temperature control: ±0.05'			

COMPONENTS:	ORIGINAL MEASUREMENTS:		
<pre>(1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5]</pre>	Kundu, K. K.; Das, A. K. J. Solution Chem. 1979, 259-65.		
(2) Water; H ₂ O; [7732-18-5]			
<pre>(3) Dimethylsulfoxide; C₂H₆OS; [67-68-5]</pre>			
VARIABLES:	PREPARED BY:		
Composition of solvent at 25.0°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility of potassium tetr ubility (ion-activity) product were re (DMSO)-water mixtures:	aphenylborate (KBPh ₄) and its sol- eported for three dimethylsulfoxide		
Mass % DMSO 10 ³ C/mo	ol dm ⁻³ pK ^o _{SO} (volume units)		
20 0.0 40 2.1 60 20.4	59 6.35 18 5.37 3 3.49		
The activity coefficients y_{\pm} were calc in the extended form: $-\log y_{\pm} = \frac{1}{2}AC^{\frac{1}{2}}$	culated from the Debye-Hückel equation $\left[(1 + a_{BC^{\frac{1}{2}}})^{-1} + (1 + a_{BC^{\frac{1}{2}}})^{-1} \right] + \frac{1}{2}$		
Where <u>C</u> is the solubility in mol dm ⁻³ , <u>A</u> and <u>B</u> are the Debye-Hückel constants, 1.824 x $10^{6} (\varepsilon_{s}T)^{-3/2}$ and $50.29 (\varepsilon_{s}T)^{-1/2}$, respectively, <u>a</u> is the ion-size parameter for the K ⁺ ion, taken as 0.3 nm, and <u>a</u> is the ion-size parameter for the BPh ₄ ion, taken as 0.5 nm. M is the formula weight of the salt, M _s is the mean molecular weight of the solvent, <u>d</u> is the density of the solution, assumed to be approximately equal to that of the pure solvent d _s .			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;		
Saturated solutions were prepared by shaking for 3-4 h followed by equili- bration in a thermostat. Filtered, weighed aliquots, after proper dilu- tion with water, were analyzed by uv- spectrophotometry using a Beckman DU 2400 spectrophotometer. The shak- ing followed by thermostatting was repeated at 3-4-day intervals until constant absorption was obtained, which required 2-4 weeks.	DMSO was purified by a literature method (1). KBPh4 was prepared and purified as described by Popovych and Friedman (2) (see compilation for KBPh4 in water).		
	ESTIMATED ERROR:		
	Temperature ±0.1°C Precision in solubility: ±2%		
	 REFERENCES: (1) Das, A. K.; Kundu, K. K. J. Chem. Soc. Faraday Trans. 1 <u>1973</u>, 69, 730. (2) Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u>, 70, 1671. 		

COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Potassium tetraphenylborate (1-); KC., H., B: [3244-41-5]	Dill, A. J.; Popovych, O. J. Chem. Eng. Data 1969, 14, 240-3		
(2) Lithium chloride; LiCl; [7447-41-8]	5. 6.6 Dug. Dava <u>1969</u> , 11, 246 5.		
(3) Ethanol; C_2H_60 ; $[64-17-5]$			
(4) water; n_20 ; $[7732-10-5]$			
VARIABLES:	PREPARED BY:		
concentration varied from 0 to 200	Orest Popovych		
times molar solubility of KC ₂₄ H ₂₀ B. One temperature: 25.00°C			
EXPERIMENTAL VALUES:			
The authors report the solubility C of potassium tetraphenylborate (KBPh ₄) in ethanol-water mixtures without added LiCl. The solubilities with added LiCl are not reported, only the activity coefficients calculated from the variation of the above solubility as a function of ionic strength varied by means of LiCl.			
Mass% ethanol Solubility of KBPh4, 10 ³ C/mol dm ⁻³			
100.0	0.504		
90.0	1.09		
80.0	2.11		
78.1	2.35		
70.0	2.89		
60.0 50.0*	2.80		
46.0	2.08		
40.0	1.33		
30.0	0.670		
20.0	0.340		
10.0	0.220		
* Graphically interpolated			
	continued		
AUXILIARY	INFORMATION		
METHOD (ADDADATUS (DDOGEDUDE)	COUDCE AND DUDITY OF MATERIALC.		
III traviolat areatrophotomotry using	KBPh was prepared from NaBPh		
a Carv Model 14 enectrophotometer.	(Fisher, 99.7%) by metathesis with		
Saturated solutions were prepared by	KC1; it was recrystallized three		
shaking suspensions of KBPh4 in	times from 3:1 acetone-water and		
Water-jacketed flasks. A solution	dried <u>in vacuo</u> at 80°C. Baker ana-		
was considered saturated when suc-	lyzed LiC1 was doubly recrystallized		
cessive weekly analses agreed to about	from conductivity water and dried		
1%. This required about 2 weeks of	and transferred in a dry box USP		
added LiCl and one month for solutions	95% ethanol was doubly distilled.		
with added LiCl. Saturated solutions	USP absolute ethanol was refluxed		
were filtered and analyzed spectro-			
Photometrically using absorption	FSTIMATED FREQR.		
coefficients characteristic of each	Provision +1%		
solvent. All work was carried out	rrecision IIA Accuracy +3% (authors)		
ueaerated containers and solvents.	Temperature: ±0.01°C.		
COMMENTS :	REFERENCES :		
The results reported in this study			
can be considered as tentative values.			
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26 Potas	ssium		
COMPONENTS: (1) Potassium tetraphenylborate (1-); KC ₂₄ H ₂₀ B; [3244-41-5] (2) Lithium chloride; LiCl; [7447-41-8] (3) Ethanol; C ₂ H ₆ O; [64-17-5] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Dill, A. J.; Popovych, O. J. Chem. Eng. Data <u>1969</u> , 14, 240-3.		
COMMENTS AND/O	R ADDITIONAL DATA		
EXPERIMENTAL VALUES:			
The authors determined the mean molar activity coefficients of potassium tetraphenylborate $(KBPh_4)$ in ethanol-water mixtures from the variation of solubility as a function of the ionic strength varied by means of LiCl. The following equations were used:			
$\log \frac{\alpha_{I}C_{I}}{\alpha_{O}C_{O}} = \log y_{\pm,O} - \log y_{\pm,I} \text{ and } \cdot$	$-\log y_{\pm,I} = A_1 I^{\frac{1}{2}} + A_2 I + A_3 I^{\frac{3}{2}} + \dots$		
where α 's are the degrees of ionic as vity coefficient (f _± in the original) pure solvent and ionic strength <u>I</u> as KBPh ₄ . At any ionic strength <u>I</u> , the from the known A-coefficients. Value association constant K _A (1) using the for KBPh ₄ in methanol (2). C _o is the	sociation, y_{\pm} is the mean molar acti- , and the subscripts <u>o</u> and <u>I</u> denote determined by the sum of LiCl and activity coefficient can be calculated s of α were calculated from the same equation as in the compilation solubility in the pure solvent.		
Mass% ethanol α _o y _{±,o} A _l in water	$A_{2} \qquad K_{s0}^{\circ} = (C_{0}^{\alpha} y_{\pm,0})^{2},$ $mol^{2} dm^{-6} (compiler)$		
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$		
*Activity coefficients calculated from the Debye-Hückel limiting law.			
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:continued over magnesium ethoxide for 12 hours under nitrogen and then distilled, collecting the middle fraction. De- ionized water with a specific con- ductance of 3 x 10 ⁻⁷ ohm ⁻¹ cm ⁻¹ was used. The exact mass% composition of ethanol-water mixtures was deter- mined from the densities of the mixture and literature data (2).		

ESTIMATED ERROR:

REFERENCES:
(1) Dill, A. J.; Popovych, O. J. Chem. Eng. Data <u>1969</u>, 14, 156.
(2) Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u>, 70, 1671.
(3) Osborne, N. S.; McKelvey, E. C.; Bearce, H. W. J. Wash. Acad. Sci. <u>1912</u>, 2, 95.

<pre>COMPONENTS: (1) Potassium tetraphenyl- borate (1-); KC₂₄H₂₀B; [3244-41-5] (2) Lithium chloride; LiC1; [7447-41-8] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Methano1; CH₄O; [67-56-1]</pre>	ORIGINAL MEASUREMENTS: LaBrocca, P. J.; Phillips, R.; Goldberg, S. S.; Popovych, O. J. Chem. Eng. Data <u>1979</u> , 24, 215-8. (including Supplementary Material).
(5) Water; H ₂ 0; [7732-18-5]	
VARIABLES: Methanol-water composition.	PREPARED BY:
10^3 times the solubility of KBPh ₄ in mol dm ⁻³ . One temperature:	Orest Popovych
25.00°C.	L
TAFERIMENTAL VALUES.	
The solubility of KBPh ₄ in the p was reported in the absence of LiCl : mixtures:	presence of 2 x 10^{-5} mol dm ⁻³ NaOH in the following methanol-water
Mass % methanol in water	Solubility of KBPh ₄ , 10^{3} C/mol dm ⁻³
89.4	2.22
69.6	1.92
58.8	1.20
40.0	0.586
29.8	0.261
9.8	0.220
	-
AUXILIARY	INFORMATION
AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometer. Saturated solutions were prepared by shaking the suspensions in water-jacketed flasks. A solution was considered saturated when successive weekly analyses agreed to about 1%. Satur- ated solutions were filtered and analyzed spectrophotometrically using absorption coefficients characteristic of each solvent. All work was carried out in deaerated containers and solvents. COMMENTS: The result in this study can be designated as <u>tentative values</u> . SOURCE AND PURITY OF MATERIALS: KBPh4 y prepared from NaBPh4 (Fisher, 99 by metathesis with KCl; it was r crystallized three times from 3: acetone-water and dried in vacuo 80°C. Baker analyzed LiCl was doubly recrystallized from condu- tivity water and dried for 48 hr; in a dry box. Certified ACS spentra lized methanol (Fisher Scien ic Co.) was used without further purification. The densities of methanol-water mixtures were detain mined gravimetrically and their % obtained from literature data ESTIMATED ERROR: Precision ±1% (the solubility) Temperature control: ±0.01°C REFERENCES: (1) Bates, R. C.; Robinson, R. A <i>Chemical Physics of Ionia</i> <i>Solutions</i> Conway, B. E.; Barradas, R. C., Eds. Wiley.	
	Solutions Conway, B. E.; Barradas, R. G., Eds. Wiley.

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Potassium

COMPONENTS: (1) Potassium tetrapher (1-); KC ₂₄ H ₂₀ B; [32 (2) Lithium chloride; I [7447-41-8] (3) Sodium hydroxide; N [1310-73-2] (4) Methanol; CH ₄ 0; [67 (5) Water; H ₂ 0; [7732-1]	Aylborate 244-41-5] .1C1; MaOH; 7-56-1] 8-5]	ORIGINAL MEAS LaBrocca, 1 Goldberg, S J. Chem. Er (including	SUREMENTS: P. J.; Phillip S. S.; Popovyc <i>ng. Data</i> <u>1979</u> , Supplementary	os, R.; ch, O. 24, 215-8. Material).
EXPERIMENTAL VALUES:	Supplementa	ary Material		
Solubility of Potassium Tetraphenylborate in Methanol-Water Mixtures, $C_{\rm BPh}_{\mu}$, as a Function of LiCl Concentration (all concentrations in mol dm ⁻³)				
89.4 Mass % Methanol	79.7 Mass 🔅	% Methanol	58.8 Mass %	Methanol
10 ³ C _{BPh4} 10 ¹ C _{LIC1}	10 ³ C _{BPh4}	10 ¹ C _{LiC1}	$10^{3}C_{BPh_{4}}$	10 ¹ C _{LiC1}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1.919 2.378 2.690 2.826 2.927 3.069 3.143 3.105 2.970 2.860 2.594	0 0.2049 0.6147 1.024 1.434 2.049 4.098 6.147 8.196 10.24 14.34	1.191 1.349 1.458 1.532 1.565 1.624 1.682 1.702 1.698 1.671 1.646 1.505	0 0.1108 0.3324 0.5540 0.7756 1.108 2.216 3.324 4.432 5.540 7.756 11.08
50.8 Mass % Methanol	40.0 Mass %	% Methanol	29.8 Mass %	Methanol
10 ³ C _{BPh4} 10 ² C _{LiC1}	10 ⁴ C _{BPh4}	10 ² C _{LiC1}	10 ⁴ C _{BPh4}	10 ² C _{LiCl}
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5.693 6.104 6.328 6.538 6.686 6.881 7.134 7.272 7.277 7.301 7.158 7.072	0 0.5902 1.771 2.951 4.131 5.902 11.80 17.71 23.61 29.51 41.31 47.22	3.714 4.025 4.146 4.224 4.428 4.545 4.608 4.584	0 1.059 1.765 2.471 7.060 10.59 14.12 17.65
20.0 Mass	% Methanol	9.8 Mass	% Methanol	
10 ⁴ C _{BPh4}	10 ² C _{LiCl}	$10^4 C_{BPh_4}$	10 ² C _{LiC1}	
2.571 2.728 2.846 2.831 2.949 2.935 3.033 3.072 3.131 3.195 3.171	0 0.2817 0.8451 1.409 1.972 2.817 5.634 8.451 11.27 14.09 22.54	2.177 2.344 2.373 3.388 2.486 2.491 2.604 2.589 2.648	0 1.032 1.465 2.064 4.128 6.192 8.256 10.32 14.45	

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<pre>COMPONENTS: (1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] (2) Lithium chloride; LiC1; [7447-41-8] (3) Sodium hydroxide; NaOH;</pre>	ORIGINAL MEASUREMENTS: LaBrocca, P. J.; Phillips, R.; Goldberg, S. S.; Popovych, O. J. Chem. Eng. Data <u>1979</u> , 24, 215-8. (including Supplementary Material)		
[1310-73-2] (4) Methano1; $CH_{4}0$; [67-56-1] (5) Water; $H_{2}0$; [7732-18-5]			
continuation COMMENTS AND	/OR ADDITIONAL DATA		
EXPERIMENTAL VALUES:			
From the variation of the solubility of KBPh_4 as a function of ionic strength varied by means of LiCl, the authors determined the mean ionic activity coefficients of KBPh_4 in the methanol-water mixtures using the following equations:			
$\log C_{I}/C_{o} = \log y_{\pm,o} - \log y_{\pm,I} \text{ and } -$	$-\log y_{\pm,I} = A_1 I^{\frac{1}{2}} + A_2 I + A_3 I^{\frac{3}{2}} + \dots$		
where y_{\pm} is the mean molar activity coefficient (f ₊ in the original) and the subscripts <u>o</u> and <u>I</u> denote solutions without and with added LiC1. Complete dissociation was assumed for all methanol-water mixtures, since KBPh ₄ is practically unassociated even in pure methanol (1). At any ionic strength I (in mol dm ⁻³), the solubility C _I and the activity coeffi- cient can be calculated from the A-coefficients characteristic of the methanol-water mixture, which are tabulated:			
Mass % methanol y _{±,0} A ₁ A ₂ in water	$A_3 A_4 K_{s0}^{\circ}/mol^2 dm^{-6*}$		
$ \begin{cases} 89.4 & 0.882 \pm 0.032 & 1.38 & -2.0 \\ 79.7 & 0.854 \pm 0.020 & 1.21 & -1.7 \\ 69.6 & 0.913 \pm 0.004 & 1.06 & -2.2 \\ 58.8 & 0.935 \pm 0.029 & 0.905 & -1.7 \\ 50.8 & 0.918 \pm 0.038 & 0.847 & -0.8 \\ 40.0 & 0.964 \pm 0.003 & 0.697 & -1.7 \\ 29.8 & 0.976 \pm 0.006 & 0.688 & -1.6 \\ 20.0 & 0.988 \pm 0.014 & 0.558 & -1.1 \\ 9.8 & 0.981 \pm 0.017 & 0.585 & -2.6 \\ *K_{60}^{\circ} = (C_{0}Y_{+,0})^{2} . \end{cases} $	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;		
	-		
	ESTIMATED ERROR: The absolute precision in the y_{\pm}		
	and K_{s0}° values is indicated abo $\bar{\nabla} e^{0}$.		
	REFERENCES: (1) Popovych, O.; Friedman, R.M. J. Phys. Chem. <u>1966</u> , 70, 1671-3.		

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5]</pre>	Kundu, K. K.; Das, A. K. J. Solution Chem. 1979, 259-65.
(2) Water; H ₂ O; [7732-18-5]	<u></u> , 207 051
(3) Urea; CH ₄ ON ₂ ; [57-13-6]	
VARIABLES:	PREPARED BY:
Composition of solvent at 25.0°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of potassium teth solubility (ion-activity) product we mixtures:	raphenylborate (KBPh ₄) and its re reported for three urea-water
Mass % Urea 10 ⁴ C/mol o	im ⁻³ pK [°] _{SO} (volume units)
11.52 1.3	7.77
29.64 1.8	7.55
36.83 1.9	7.45
The activity coefficients y_{\pm} were called equation in the form: -log $y_{\pm} = \frac{1}{2}AC^{\frac{1}{2}}$ + log	Lculated from an extended Debye-Hückel [(1 + å_BC ^{1/2}) ⁻¹ + (1 + å_BC ^{1/2}) ⁻¹] + g [(d - 0.001CM + 0.002CM _g)/d _g] ···
size parameter for the BPh_4^- ion, tal weight of the salt, M_S is the mean mu the density of the solution, assumed the pure solvent, \underline{d}_S .	cen as 0.5 nm. M is the formula olecular weight of the solvent, <u>d</u> is to be approximately equal to that of
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Saturated solutions were prepared by shaking for 3-4 h followed by equili- bration in a thermostat. Filtered, weighed aliquots, after proper dilu- tion with water, were analyzed by uv-spectrophotometry using a Beckman DU 2400 spectrophotometer. The shak- ing followed by thermostatting was repeated at 3-4 day intervals until constant absorption was obtained, which required 2-4 weeks.	Urea was purified by a literature method (1). KBPh ₄ was prepared and purified as described by Popovych and Friedman (2) (see compilation for KBPh ₄ in water).
	ESTIMATED ERROR:
	Temperature: ±0.1°C Precision in solubility: ±2%
	 REFERENCES: (1) Kundu, K. K.; Majumdar, K. J. Chem. Soc. Faraday Trans. 1 1973, 69, 807. (2) Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u>, 70, 1671.

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COMPONENTS:	EVALUATOR:
 Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] Acetonitrile; C₂H₃N; [75-05-8] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

The solubility of potassium tetraphenylborate $(KBPh_4)$ in acetonitrile was reported as such by Kolthoff and Chantooni (1) as well as by Popovych et al. (2). The solubility products of $KBPh_4$ in acetonitrile were reported in the above two studies and also in the two articles by Alexander and Parker (3, 4). All determinations were at 298 K.

Excellent agreement exists between the solubility value obtained by Kolthoff and Chantooni (1) from evaporation and weighing, $C = 5.40 \times 10^{-2}$ mol dm⁻³ and the value $C = 5.33 \times 10^{-2}$ mol dm⁻³ determined by UV-spectro-photometry by Popovych et al. (2). The latter study was carried out under temperature control to 0.01°C in the constant-temperature bath from which water was circulated through jacketed flasks containing the suspensions. Saturation was ascertained by successive analyses days apart until the solubilities agreed to 1% or better. Unfortunately, no experimental details are available in the Kolthoff and Chantooni (1) article as far as the temperature control and saturation attainment is concerned. Nevertheless, if we accept the number of significant figures retained in the result, it is possible to average the values 5.33×10^{-2} mol dm⁻³. The indicated precision is that governing the UV-analysis for the BPh₄⁻ concentration. There are no data on the precision of the analysis by the method of evaporation and weighing.

Alexander and Parker report the formal (concentration) solubility product of $KBPh_4$ in acetonitrile as $pK_{SO} = 2.7$ (3) and 2.4 (4) (in volume units) in the two successive studies. Because these are concentration products, the values of the corresponding solubilities can be calculated from them simply as $(K_{SO})^{2}$. When $pK_{SO} = 2.7$, the solubility is 4.5 x 10^{-2} mol dm⁻³. The solubility corresponding to the $pK_{SO} = 2.4$ is 6.3 x 10^{-2} mol dm⁻³. However, it should be noted that in the second study the authors estimate a precision of ± 0.2 pK units, which means that the solubility derived from it could range from 5 x 10^{-2} to 8 x 10^{-2} mol dm⁻³. Clearly, these results cannot be compared in precision with the recommended values stated above. While in the case of solubility of KBPh4 in acetonitrile it is possible to recommend a value, this is unfortunately not so in the case of the thermodynamic solubility product. The latter was estimated both by Kolthoff and Chantooni (1) as well as by Popovych et al. (2) using calculated activity coefficients and at the concentration involved the differences in the activity corrections can be appreciable. By employing an unspecified form of the Guggenheim equation, Kolthoff and Chantooni calculated a $pK_{s0}^{s} = 3.2$ (K_{s0}^{s} units are mol² dm⁻⁶ in this evaluation). Popovych et al. (2) by suing a Debye-Hückel equation shown on the compilation sheet obtained for the mean ionic activity coefficient $y_{\pm}^2 = 0.298$, from which $K_{S0}^\circ = 8.47 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ and the $pK_{S0}^\circ = 3.07$. The above activity coefficient was calculated using ion-size parameters $a^\circ = 0.3$ nm for the K^+ ion and $a^{\circ} = 0.5$ nm for the BPh₄ ion. The latter, however, may be too small. For example, Kolthoff and Chantooni (5) used an ion-size parameter of 1.2 nm for the BPh4. Applying this value, the mean ionic activity coefficient in acetonitrile becomes y_{+}^2 = 0.359, the K $_{\rm SO}^{\circ}$ becomes 1.02 x 10⁻³ and the pK_{s0}^{*} = 2.99. Thus, for approximate work, one can choose a pK_{s0}^{*} value of about 3.1 \pm 0.1, but it can be described as no better than tenta-A recommended value for solubility product of KBPh4 in acetonitrile tive. must await an experimental determination of the activity coefficients.

Potassium

COMPONENTS:	EVALUATOR:
 Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] Acetonitrile; C₂H₃N; [75-05-8] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION: (continued)

REFERENCES:

Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024.
 Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u>, 44, 811.
 Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 5549.
 Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313.
 Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194.

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Potassium

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Potassium tetraphenylborate (1-); $KC_{24}H_{20}B$; [3244-41-5]	Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u> , 76, 2024-34.	
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The authors report the solubility of potassium tetraphenylborate $({\tt KBPh}_4)$ in acetonitrile as:		
$C = 5.40 \times 10$	$^{-2}$ mol dm ⁻³ .	
Assuming complete dissociation, and calculating the mean ionic activity coefficient from the Guggenheim equation*, the authors report as the solubility product of KBPh4:		
$pK_{s0}^{\circ} = 3.2 (K_{s0}^{\circ} \text{ units are mol}^2 \text{ dm}^{-6}).$		
*Not shown.		
AUXILIARY	INFORMATION	
ME THOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:	
Evaporation of a saturated solution and weighing. No other details.	Acetonitrile was purified very thoroughly by a literature method (1). Sodium tetraphenylborate (Aldrich puriss. grade) was purified according to the method of Popov and Humphrey (2). KBPh ₄ was prepared by metathesis of KC1 with NaBPh ₄ , referring to the procedure described in the compilation for KBPh ₄ in methanol.	
	ESTIMATED ERROR:	
	 REFERENCES: (1) Kolthoff, I. M.; Bruckenstein, S. Chantooni, M. K., Jr. J. Am. Chem. Soc. 1961, 83, 3927. (2) Popov, A. I.; Humphrey, R. J. Am. Chem. Soc. 1959, 81, 2043. 	

ORIGINAL MEASUREMENTS:

 (1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] (2) Acetonitrile; C₂H₃N; [75-05-8] 	Popovych, O.; Gibofsky, A.; Berne, D. H. <i>Anal. Chem</i> . <u>1972</u> , 44, 811-17.	
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility was reported as ($S_{BPh4} = 5.33 \times 10^{-2} \text{ mol } dm^{-3}.$	
The mean molar ionic activity coefficient was calculated using the relationship:		
$-\log y_{\pm}^{2} = \frac{1}{1+2}$	64C ¹²	
1 + 0.	485aC ²	
Adopting $a^{\circ} = 0.5$ nm for BPh ₄ ⁻ and $a^{\circ} = 0.3$ nm for K ⁺ , the value of $y_{\pm}^{2} = 0.298$ and the pK _{\$0} derived from it is 2.85 (molal scale), i. e., K _{\$0} units are mol ² kg ⁻² . pK _{\$0} value on the molar scale (K _{\$0} units of mol ² dm ⁻⁶) was not reported, but can be calculated from the molal value via the solvent density, which was 0.777 g ml ⁻¹ . pK _{\$0} (molar scale) = 3.07. Complete dissociation was assumed, which is generally true for most electrolytes in acetonitrile. Also reported were the molar absorption coefficients for the BPh ₄ ⁻ ion: 3203 and 2082 dm ³ (cm mol) ⁻¹ at 266 nm and 274 nm, respectively.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. Saturation achieved by shaking the salt suspensions for 2 weeks in water-jacketed flasks. Solutions filtered and analyzed at 266 and 274 nm using the absorption coefficients specified above. All solutions and containers were deaerated. Differential thermal analysis showed absence of crystal solvates.	Acetonitrile (Matheson, spectroqua- lity) was refluxed for 24 hrs over CaH ₂ and fractionally distilled. KBPh ₄ was prepared from NaBPh ₄ (Fisher, 99.7%) and KCl by metathesis in aqueous solution. It was recrys- tallized three times from 3:1 ace- tone-water and dried <u>in vacuo</u> at 80°C.	
	ESTIMATED ERROR:	
	Precision ±1% (rel.) Accuracy ±3% (rel.) Temperature control: ±0.01°C	
	REFERENCES:	

COMPONENTS:

FOR	3
COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium tetraphenylborate (1-); $KC_{24}H_{20}B$; [3244-41-5]	Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> , 89, 5549-51.
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product was can The authors reported $pK_{s0} = 2.7$, where units of mol ² dm ⁻⁶ .	alculated using concentrations. e the solubility product is in
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry of the solutions saturated under nitrogen or potentio- metric titration of the anion with AgNO ₃ . No details.	Not stated, "
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

ORIGINAL MEASUREMENTS: COMPONENTS: (1) Potassium tetraphenylborate (1-); Parker, A. J.; Alexander, R. KC₂₄H₂₀B; [3244-41-5] J. Am. Chem. Soc. 1968, 90, 3313-9. (2) Acetonitrile; C_2H_3N ; [75-05-8] VARIABLES: PREPARED BY: One temperature: 25°C Orest Popovych EXPERIMENTAL VALUES: The formal (concentration) solubility product of KBPh4 in acetonitrile was reported as: $pK_{s0} = 2.4 (K_{s0} \text{ units are mol}^2 \text{ dm}^{-6}).$ AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: UV spectrophotometry on solutions The purification of materials has saturated under nitrogen, using a been described in the literature Unicam SP500 spectrophotometer. (1-3). Saturated solutions were prepared by shaking for 24 hours at 35°C and then for a further 24 hours at 25°C. ESTIMATED ERROR: Absolute precision was estimated to be ±0.2 pK units. Temperature control unspecified. REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J.
J. Am. Chem. Soc. <u>1966</u>, 88, 1911.
(2) Alexander, R.; Ko, E. C. F.; Mac,
Y. C.; Parker, A. J. J. Am. Chem. Soc. 1967, 89, 3703. (3) Parker, A. J. J. Chem. Soc. A <u>1966</u>, 220.

COMPONENTS	OPTOTNAL MEASUDEMENTS.		
	CRIGHAL READURERENTS.		
(1) Potassium tetraphenylborate $(1-)$; $KC_{24}H_{20}B$; [3244-41-5]	Farker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.		
(2) Formamide; CH ₃ NO; [75-12-7]			
VARIABLES:	PREPARED BY:		
One temperature: 25°C	Orest Popovych		
ond temperature. 25 C			
EXPERIMENTAL VALUES:			
The formal (concentration) so formamide was reported as:	The formal (concentration) solubility product of KBPh ₄ in formamide was reported as:		
BK_0 = 2.8 (K_0 u	nits are $mol^2 dm^{-6}$).		
AUXILIARY	INFORMATION		
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:		
UV spectrophotometry on solutions	The purification of the materials		
saturated under nitrogen, using a	has been described in the literature $(1-3)$.		
Saturated solutions were prepared			
by shaking for 24 hours at 35°C and then for a further 24 hours at 25°C.			
Linen for a fullher 24 hours at 25 of			
	ESTIMATED ERROR:		
	Absolute precision was estimated to		
	be ±0.2 pK units.		
	DEDEDEN QUA		
	REFERENCES: (1) Clare, B. W.; Cook, D.;		
	J. Am. Chem. Soc. <u>1966</u> , 88, 1911.		
	(2) Alexander, R.; Ko, E. C. F.; Mac,		
	Soc. <u>1967</u> , 89, 3703.		
	(3) Parker, A. J. J. Chem. Soc. A		
	1700, 220.		

Potassium

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5]</pre>	Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u> , 70, 1671-3.	
(2) Methanol; CH ₄ O; [67-56-1]		
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The colubility of KBPb, in methanol was reported to be		
$C = 3.11 \times 10^{-3}$	3 mol dm ⁻³ .	
The solubility product, K_{s0}° , was calculated by the authors as $(C\alpha y_{\pm})^2$, where α is the degree of dissociation and y_{\pm} , the mean ionic activity coefficient on the molar scale. α was calculated from a literature calue of the ion-pair association constant $K_A = 22 \text{ mol}^{-1}\text{dm}^3$ (1), using the relationship: $-1 \pm (1 \pm 4K_{b}Cy_{a})^{\frac{1}{2}}$		
2K _A Cy _± ²		
estimated from the Debye-Hückel equation in the form:		
$-\log y_{\pm}^2 = 3.803 (C\alpha)^{\frac{3}{2}}$		
using 0.55 nm as the value for the ion-size parameter \mathring{a} . The above calculations yielded $\alpha = 0.958$ and $y_{\pm}^2 = 0.660$, from which the reported $K_{S0}^{\circ} = 5.86 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$. Also reported were the molar absorption coefficients of the tetraphenylborate ion in methanol: $3.00 \times 10^3 \text{ dm}^3(\text{cm mol})^{-1}$ and $2.12 \times 10^3 \text{ dm}^3(\text{cm mol})^{-1}$ at 266 and 274 nm, respectively.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. Saturation achieved by shaking the salt suspensions for 2 weeks in water-jacketed flasks. Solutions fil- tered and analyzed at 266 and 274 nm using the above absorption coeffi- cients. All solutions and containers were deaerated.	KBPh ₄ was prepared from NaBPh ₄ (Fisher, 99.7%) and KCl by metathesis in aqueous solution. It was recry- stallized three times from 3:1 acetone-water and dried <u>in vacuo</u> at 80°C. Methanol (Matheson, spectro grade) was refluxed over Al amalgam and distilled, rejecting the initial and final 10%.	
COMMENTS: The solubility and the K_{SO}° in this study can be designated as <u>tentative</u> <u>values</u> . However, the 3 significant digits in K_{SO}° are not justified in view of the uncertainty in the value of K_A , which was reported (1) as rang- ing from 6 to 35, with an average of 22. Taking this into account, the K_{SO}° should be expressed as (5.9 ± 0.3) x 10 ⁻⁶ mol ² dm ⁻⁶ .	ESTIMATED ERROR: Not stated by the authors, but rel. precision in the solubility is known to be about ±1%. Temperature control: ±0.01°C. REFERENCES: (1) Kunze, R. W.; Fuoss, R. M. J. Phys. Chem. <u>1963</u> , 67, 911.	

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COMPONENTS :	ORIGINAL MEASUREMENTS:
<pre>(1) Potassium tetraphenylborate (1-); KC₂₄H_{2C}B; [3244-41-5]</pre>	Virtanen, P. O. I.; Kerkela, R. Suomen Kemistilehti <u>1969</u> , B42, 29-33.
(2) N-Methyl-2-pyrrolidinone	
(N-Methy1-2-pyrrolidone); C ₅ H _g NO; [872-50-4]	
VARIABLES:	PREPARED BY:
Two temperatures: 25.00° C and	Orest Popovych
45.00°C	
EXPERIMENTAL VALUES:	
The solubility of KBPh4 in N-met	thy1-2-pyrrolidone was reported to
be 1.01 mol dm^{-3} at 25° C and 1.03 mo	ol dm ⁻³ at 45°C.
The corresponding solubility pro	oduct at 25° C, calculated as the
square of the solubility, was report K_{cO} units are mol ² dm ⁻⁶ . The pK _{sO} va	alue at 45° C was not reported.
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.	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The suspensions were shaken in	N-Methyl-2-pyrrolidone (General Aniline & Film Co.) was purified as
thermostatted water-jacketed flasks	in the literature (1). KBPh4 was
for I day at 50°C, followed by I day at 25°C or 45°C, respectively.	NaBPh4 in water, followed by double
Saturated solutions were anayzed	recrystallization from an acetone-
aliquots in aqueous solution.	water mixture and drying in vacuo.
	ESTIMATED ERROR:
	Not specified.
	Temperature control: ±0.02°C
	REEDENCIO
	REFERENCES:
	(1) Virtanen, P. O. I. Suomen Kemistilehti 1966, B39, 257
	<u> </u>

COMPONENTS:	EVALUATOR:
 Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5] 2-Propanone (acetone); C₃H₆O; [67-64-1] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

The solubility of potassium tetraphenylborate (KBPh₄) in acetone has been reported in three publications (1-3). Scott et al. (1) determined the solubility in acetone as part of their study of the solubility in acetone-water mixtures at 301 K (see compilation for acetone-water mixtures). Similarly, Kirgintsev and Kozitskii (2) included the acetone datum in their report on the solubilities of KBPh₄ in acetone-water mixtures at 298.15 K (see compilation for acetone-water mixtures). Subsequently, Kozitskii (3) published the solubilities of KBPh₄ in acetone at 273.15 K and 323.15 K. Thus, no comparison is available between data from two laboratories at any one temperature. However, solubilities at three different temperatures are available from the same laboratory (2, 3). All the available data are summarized in the Table below.

Tentative Values

Solubilities of KBPh₄ in Acetone at Different Temperatures

т/к	Solubility/mol dm ⁻³
273.15 298.15 301 323.15	0.196 (3) 0.171 (2) 0.117 (1)* 0.144 (3)

*Doubtful value

All of the above solubilities were determined by the method of evaporation and weighing, but the purity of the acetone employed and the temperature control were not the same in the different studies. The solubilities at the temperatures other than 301 K came from the same laboratory and were measured in thoroughly dried acetone (0.007 vol % of water), observing a temperature control of ± 0.05 °C (2, 3). On the other hand, the datum of Scott et al. (1) at 301 K was determined in acetone which may have contained up to 0.5% water (by volume?) and the solubility value of 0.117 mol dm⁻³ obtained by them clearly does not belong to the same population as the remaining three data points in the Table.

Since the activity correction would be too uncertain at the solubilities involved here, the corresponding solubility products were not estimated. Instead, a smoothing equation was obtained for the logarithm of the solubility S as a function of reciprocal absolute temperature, using the three data points at 273.15 K, 298.15 K and 323.15 K (all from the same laboratory (2, 3)):

log S = 235/(T/K) - 1.56, with a $\sigma_{\rm y}$ = 0.0062 and a correlation coefficient of 0.994. The solubility value calculated from the above equation for 301 K is 0.165 mol dm⁻³. This differs considerably from the 0.117 mol dm⁻³ value reported by Scott et al. (1). Since low concentrations of water in acetone lead to an <u>increase</u> in the solubility (2) (see compilation) for KBPh₄ in acetone-water mixtures based on Reference (2)), the low solubility value in the study by Scott et al. (1) cannot be rationalized on the basis of the wetness of their acetone. Of course, the unspecified degree of the temperature control and saturation control in the last study, as well as differences between the amounts of residue obtained from the solvent in different studies could account for the discrepancy between the results from the laboratory of Kirgintsev and Kozitskii (2,3) on the one hand and those of Scott et al. (1) on the other hand.

COMPONENTS:	EVALUATOR:
 Potassium tetraphenylborate (1-) KC₂₄H₂₀B; [3244-41-5] 2-Propanone (acetone); C₃H₆O; [67-64-1] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION: (continued)

In conclusion, the only thing that prevents this evaluator from designating the solubility data of Kirgintsev and Kositskii (2) and of Kositskii (3) as the recommended values is the fact that equilibrium for only 6 hours may have been insufficient for complete saturation. Thus, the solubility values at all temperatures except 301 K listed in the Table on the preceeding page should be considered as tentative values at this time.

REFERENCES:

- Scott, A. D.; Hunziker, H. H.; Reed, M. G. Chemist-Analyst <u>1959</u>, 48, 11.
 Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser.
- 1968, 1170.
- 3. Kozitskii, V. P. Izvest. Akad. Nauk. SSSR, Khim. Ser. 1970, 8.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Potassium tetraphenylborate (1-); KC₂₄H₂₀B; [3244-41-5]</pre>	Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. <u>1970</u> , 8-11.
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	
VARIABLES:	PREPARED BY:
Two temperatures: 0.00°C and 50.00°C	Orest Popovych ,
EXPERIMENTAL VALUES:	
The author reported the solubil: of mass %, defined as grams of the sa solution. The solubility was conver- compiler.	lty of KBPh4 in acetone* in units alt in 100 cm ³ of the saturated ted to units of mol dm ⁻³ by the
Solubility o	f KBPh4 in Acetone
 0°C 7 04 %	$ar + 6 + 10^{-1} = -1 + -3$
	or 1.96 x 10 - moi dm -
50°C 5.15 mass %	or $1.44 \times 10^{-1} \text{ mol dm}^{-3}$
AUXILIARY	INFORMATION
ME THOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
Evaporation and weighing. Saturated solutions were prepared by stirring mechanically the suspensions in the thermostatted baths for the length of time indicated in the above Table. One liter of the filtrate from the saturated solution was dried by vacuum distillation (~5 hrs keeping the temperature no higher than 40°C). The residue and the column were rinsed out many times with small portions of acetone, which was then collected, evaporated and the residue, weighed.	Absolute acetone (0.0065 vol % H ₂ O) was prepd by the same method as des- cribed on the compilation sheet for KBPh4 in acetone-water at 25°C. KBPh4 obtained by metathesis of KC1 and NaBPh4 was purified by double recrystallization from 3:1 acetone- water, evaporation of the acetone, washing of the crystals with water and ether and vacuum drying at 60°C. Water was doubly distilled.
	Temperature control: ±0.05°C
	REFERENCES:
	 Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. <u>1968</u>, 1170.

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Rubidium

COMPONENTS:	EVALUATOR:
 (1) Rubidium tetraphenylborate (1-); RbC₂₄H₂₀B; [5971-93-7] (2) Water; H₂0; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

Five publications containing original data on the solubility of rubidium tetraphenylborate (RbBPh4) in aqueous solutions have been reviewed (1-5). Historically the first datam, the conductometrically determined solubility product of RbBPh₄, $K_{SO} = 8 \times 10^{-10}$ (presumably mol² dm⁻⁶) at 290 K, was rejected (no compilation sheet provided), because nothing was specified in that communication (1). Next was the radiometric determination by Geilman and Gebauhr (2), in which the solubility was reported as 4.4 x 10^{-5} mol dm⁻³ at 293.2 K. (The last value was recalculated from raw data in the article by the compiler). In pure water at 298 K, there are the data of Pflaum and Howick (3), where the solubility is given as 2.33×10^{-5} mol dm⁻³ and of Popovych et al. (4), where it is reported as $5.4_2 \times 10^{-5}$ mol dm⁻³. The last two studies were carried out by UV-spectrophotometry, but their results are unfortunately in poor agreement. Because care was taken in the latter study to control the temperature in the bath to 0.01°C and to ensure saturation by successive analyses days apart until the results checked to 1% or better, the solubility value of 5.4×10^{-5} mol dm⁻³ is the most reliable we have at the moment at 298.15 K and it should be regarded as the tentative value. Pflaum and Howick (3), on the other hand, gave no details on the temperature control or the saturation procedure. The only other solubility datum at 298 K was determined in a buffer solution, not in pure water (5).

REFERENCES:

- 1.
- 2.
- 5.
- з.
- Rüdorff, W.; Zannier, H. Angew. Chem. <u>1952</u>, 64, 613, Geilman, W.; Gebauhr, W. Z. anal. Chem. <u>1953</u>, 139, 161. Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u>, 44, 1542. Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u>, 44, 811. 4.
- McClure, J. E.; Rechnitz, G. A. Anal. Chem. 1966, 38, 136.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Rubidium tetraphenylborate (1-); RbC₂₄H₂₀B; [5971-93-7]</pre>	Geilman, W.; Gebauhr, W. Z. anal. Chem. <u>1953</u> , 139, 161-81.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 20°C	Orest Popovych
EXPERIMENTAL VALUES: The solubility is reported both as $C_{\rm Rb} = 0.380 \text{ mg cm}^{-3}$ and as 4.5 x 10 ⁻⁵ mol dm ⁻³ . However, inspection of the raw data (below) suggests that the authors consider only two figures to be significant, i. e. 0.38 mg cm ⁻³ should be the solubility. Using 85.48 for the atomic mass of Rb, this compiler obtains for the solubility $C_{\rm Rb} = 4.4 \times 10^{-5} \text{ mol dm}^{-3}$. Correspondingly, the solubility product, which the authors report simply as $C_{\rm Rb}^2 = 2.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$, should be $K_{\rm SO} = 1.9 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6}$ (compiler). Also reported is the rate of dissolution of RbBPh ₄ in water:	

Time, hours	μg Rb/10 cm ³ of water
0.5	31.5
1.0	33.6
3.0	34.2
8.0	35.5
20.0	37.9
33.0	37.8

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Radiometric, using liquid-scintilla- tion counting of 86 Rb. The radio- active rubidium obtained as the carbonate from the Harwell nuclear reactor was purified by precipitation with HClO ₄ in the presence of 2 mg of Na ₂ HPO ₄ followed by recrystallization The RbClO ₄ solution was reacted with NaBPh ₄ , the resulting RbBPh ₄ precipi- tate washed with water, mechanically shaken in water at 20°C and the filtrate analyzed radiometrically to	SOURCE AND PURITY OF MATERIALS: Not stated.
specified.	ESTIMATED ERROR: Not specified. However, given the temperature control to ±0.5°C, the relative precision cannot be better than ±1-2% (compiler). REFERENCES:

COMPONENTS: (1) Rubidium tetraphenylborate (1-); RubC24H20B: [5971-93-7] (2) Water: H20; [7732-18-5] VARIABLES: One temperature: 25°C PREPARED BY: One temperature: 25°C Drest Popovych EXPERIMENTAL VALUES: The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . MARIABLES: The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . MARIABLES: Diterviolet spectrophotometry on a Cary Model II recording spectro Controlling the temperature was not photometer. Saturated solutions was obtained in saturated solutions was obtained a started solutions was obtained a started solutions was obtained a started solutions was obtained to dat 266 and 274 m by applying the solar absorption coefficients of Solar absorption coefficients was obtained to dat 2100 di (cm moth, how end Stated. The concentration of Bho Solar absorption coefficients of Solar absorption coefficients was obtained to dat 2100 di (cm moth, how end Solar absorption coefficients was obtained tated and 274 m by applying the solar absorption coefficients was obtained tated and 274 m by applying the solar absorption coefficients was obtained tated and 274 m by applying the solar absorption coefficients was obtained tated and 274 m by applying the solar absorption coefficients was obtained tated and actonitrile solutions. Hand a actonitrile solutions. Hand a scenditrile solutions.		4
(1) Rubidium tetraphenylborate (1-): RBC2_HZ_23: [5971-93-7] Pflaum. R. T.: Howick, L. C. AndZ. Chem. 1956, 23, 1542-44. (2) Water; Hz_0; [7732-18-5] PREPARED BY: Orest Popovych VARIABLES: One temperature: 25°C PREPARED BY: Orest Popovych EXFERIMENTAL VALUES: PREPARED BY: Orest Popovych The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . WITMOUAPPARATUS/PROCEDURE: Ultraviolet spectrophotometry on a Cary Model 11 recording spectro- Photometer. Sturated solutions was obtained in saturated solutions was obtained in aburytical give another in the concentration of Pha. Naturated solutions was obtained stated. TAt econcenties were obtained stated af274 may applying the stated on acetonitrile solutions. SUBACE AND PURITY OF MATERIALS: Ultraviolet was not stated. The concentration of Pha. Naturated solutions was obtained stated on acetonitrile solutions. WITMOUAPPARATUS/FROCEDURE: Ultraviolet spectrophotometry on Cartoling the temperature was not stated. The concentration of Pha. Distance in the distilled from Plog in an all-glass apparatus. The feasing in the distilled in the chemicals were of for 24 hrs., refluxed over Phylore F.CO for 24 hrs., refluxed over Phylore F.Co for 24 hrs., refluxed over Phylores F.Co in the distilled in the chemicals were of for agene grade quality. ESTIMATED ERROR: Nothing was specified, but the precision fo likely to be ziz (compiler).	COMPONENTS:	ORIGINAL MEASUREMENTS:
(2) Water; H ₂ 0; [7732-18-5] VARIABLES: One temperature: 25*C Drest Popovych EXFERNMENTAL VALUES: The solubility of RbBFh ₄ in water was reported as 2.33 x 10 ⁻⁵ nol dm ⁻³ . EXFERIMENTAL VALUES: The solubility of RbBFh ₄ in water was reported as 2.33 x 10 ⁻⁵ nol dm ⁻³ . BETHOD/APPAANUS/PROCEDORE: Ultraviolet spectrophotometry on a Cary Model 11 recording spectro-photometric measuremetrs and properile from according spectro-photometric measuremetrs at 266 and 274 mm by applying the themistic of Bh ₇ and sturated solutions. Mastria absorption coefficients were determined from spectrophotometric measuremetr absorption coefficients were determined on acetonitrile solutions. EXTIMATED EEROR: Noting was specified, but the precision is likely to be zi% (compiler).	<pre>(1) Rubidium tetraphenylborate (1-); RbC₂₄H₂₀B; [5971-93-7]</pre>	Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u> , 28, 1542-44.
VARIABLES: PREPARED BY: One temperature: 25°C Orest Popovych EXPERIMENTAL VALUES: The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . WILLARY INFORMATION WETHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry on a Cary Model 11 recording spectro-pherometry in controlling the temperature was reported as a received for pres, but was recystallized from acctone-hexane numpecified procedure. Method of the spectrophotometris and outcometer to a solutions was outcaneated in sturing the temperature was reported by the spectrophotometris and outcaneated in sturing file into a shore the spectrophotometris and outcaneated in a sturated solutions was outcaneated in the difficients of the spectrophotometris and outcaneated in the spectrophotometris and outcaneated in the spectrophotometris and the shore the spectrophotometris spectrophotometris and the shore the spectrophotometris and the shore the spectrophotometris spectrophotometris and the shore the spectrophotometris spectrophotometris and the shore the shore the outcometal was been the shore the solutions. ESTIMATED EROR: Nothing was specified, but the precision is likely to be ±12 (compiler).	(2) Water; H ₂ O; [7732-18-5]	
One temperature: 25°C Orest Popovych EXTERIMENTAL VALUES: The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . WILLIARY INFORMATION WILLIARY INFORMATION WETHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry on a Cary Model II recording spectro-photometer by an unspecified procedure. Method of controlling the temperature was not stated solutions was obtained from acetorophotometric measurement of BPh, in saturated solutions was not stated. The concentration of BPh, in statistical solutions was obtained to absorption coefficients. RbBPh, vas prepd by Cathering the temperature was not stated solutions. SOURCE AND FURITY OF MATERIALS: NaBPh, (J. T. Baker Chemical Co.) was concentration of BPh, in saturated solutions was obtained to absorption coefficients. RbBPh, was prepd by Cathering the temperature was not stated to absorption coefficients were determined on acetonitrile solutions. WILLIARY INFORMATION ESTIMATED EROR: Nothing was specified, but the precision is likely to be ±12 (compiler).	VARIABLES:	PREPARED BY:
EXTERIMENTAL VALUES: The solubility of RbBPh, in water was reported as 2.33 x 10 ⁻⁵ mol dm ⁻³ . AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry on a Cary Model 11 recording spectro- photometer. Saturade solutions were prepared in conductivity water by an unspecified procedure. Method of controlling the temperature was notained to add 2100 dm ³ (cm mol) ⁻¹ . respectively. However, the above absorption coefficients were deter- mined on acetonitrile solutions. Moting was specified, but the precision is likely to be ±12 (compiler).	One temperature: 25°C	Orest Popovych
AUXILIARY INFORMATION METROD/APPARATUS/PROCEDURE: SUBJECT AND PURITY OF MATERIALS; METROD/APPARATUS/PROCEDURE: SUBJECT AND PURITY OF MATERIALS; METROD/APPARATUS/PROCEDURE: SUBJECT AND PURITY OF MATERIALS; METROD/APPARATUS/PROCEDURE: SUBJECT AND PURITY OF MATERIALS; METROD/APPARATUS/PROCEDURE: SUBJECT AND PURITY OF MATERIALS; SUBJECT AND PURITY OF MATERIALS; METROD/APPARATUS/PROCEDURE: SUBJECT AND PURITY OF MATERIALS; SUBJECT AND PURITY OF ANTERIALS; SUBJECT AND P		
AUXILIARY INFORMATION METROD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry on a Cary Model 11 recording spectro- photometer. Saturated solutions was obtained from specified procedure. Method of controlling the temperature was not stated. The concentration of BPh_ in saturated solutions was obtained from specifion procedure. Method of controlling the temperature was not stated. The concentration of BPh_ in saturated solutions was obtained from specifion procedure. Method of controlling the temperature was not stated. The concentration of BPh_ in saturated solutions was obtained from specified procedure. Method of controlling the temperature was not stated. The concentration of BPh_ in saturated solutions was obtained from specified procedure. Method of controlling the temperature was not stated. The concentration of BPh_ in saturated solutions was obtained from specified procedure. Method of controlling the temperature was not stated. The concentration of BPh_ in saturated solutions was obtained from specified procedure. Method of colsom & Bell) was treated with colso for 24 hrs., refluxed over Plog for 225 and 2100 dm ³ (cm mol) ⁻¹ . Colsom & Bell) was treated with colso for 24 hrs., refluxed over Plog for 2325 and then discilled from specified by recrystallized from plogs in an all-glass apparatus. The fraction boiling at 81-81.570 was respecified, but the precision is likely to be ±12 (compiler).	EXPERIMENTAL VALUES:	
$\begin{array}{lllllary INFORMATION \\ \hline \begin{tabular}{llllary INFORMATION \\ \hline \begin{tabular}{lllllary INFORMATION \\ \hline \begin{tabular}{llllllary Model 11 recording spectro-photometer. Saturated solutions were prepared in conductivity water by an unspecified procedure. Method of controlling the temperature was not stated. The concentration of BPh_{1}^{-1} in saturated solutions was obtained from spectrophotometric measurements at 266 and 274 nm by applying the molar absorption coefficients of 3225 and 2100 dm3 (cm mol)^{-1}, respectively. However, the above absorption coefficients were determined on acetonitrile solutions. \\ \hline \begin{tabular}{lllllllllllllllllllllllllllllllllll$	The solubility of RbBPh4 in water wa	as reported as 2.33 x 10^{-5} mol dm ⁻³ .
 METHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry on a Cary Model 11 recording spectro- photometer. Saturated solutions were prepared in conductivity water by an unspecified procedure. Method of controlling the temperature was not stated. The concentration of BPh₄⁻ in saturated solutions was obtained from spectrophotometric measurements at 266 and 274 nm by applying the molar absorption coefficients of 3225 and 2100 dm³ (cm mol)⁻¹, respectively. However, the above absorption coefficients were deter- mined on acetonitrile solutions. SOURCE AND PURITY OF MATERIALS: NaBPh₄ (J. T. Baker Chemical Co.) was used as received for pptns, but was recrystallized from acetone-hexane mixt for detn of absorption coeffi- cients. RbBPh₄ was prepd by metathesis of RbCl and NaBPh₄ and purified by recrystallization from a COleman & Bell) was treated with cold satd KOH, dried over anhydrous K₂CO₃ for 24 hrs., refluxed over P₂O₅ for 2-3 hrs. and then distilled from P₂O₅ in an all-glass apparatus. The fraction boiling at 81-81.5°C was retained. All other chemicals were of reagent grade quality. ESTIMATED ERROR: Nothing was specified, but the precision is likely to be ±1% (compiler). 		ΙΝΕΩΡΜΑΤΙΩΝ
Ultraviolet spectrophotometry on a Cary Model 11 recording spectro- photometer. Saturated solutions were prepared in conductivity water by an unspecified procedure. Method of controlling the temperature was not stated. The concentration of BPh ₄ ⁻ in saturated solutions was obtained from spectrophotometric measurements at 266 and 274 nm by applying the molar absorption coefficients of 3225 and 2100 dm ³ (cm mol) ⁻¹ , respectively. However, the above absorption coefficients were deter- mined on acetonitrile solutions. ESTIMATED ERROR: Nothing was specified, but the precision is likely to be $\pm 1\%$ (compiler).	METHOD /APPARATUS / PROCEDURE •	SOURCE AND PURITY OF MATERIALS.
	Ultraviolet spectrophotometry on a Cary Model 11 recording spectro- photometer. Saturated solutions were prepared in conductivity water by an unspecified procedure. Method of controlling the temperature was not stated. The concentration of BPh ₄ ⁻ in saturated solutions was obtained from spectrophotometric measurements at 266 and 274 nm by applying the molar absorption coefficients of 3225 and 2100 dm ³ (cm mol) ⁻¹ , respectively. However, the above absorption coefficients were deter- mined on acetonitrile solutions.	 NaBPh₄ (J. T. Baker Chemical Co.) was used as received for pptns, but was recrystallized from acetone-hexane mixt for detn of absorption coefficients. RbBPh₄ was prepd by metathesis of RbCl and NaBPh₄ and purified by recrystallization from a CH₃CN-H₂O mixt. CH₃CN (Matheson, Coleman & Bell) was treated with cold satd KOH, dried over anhydrous K₂CO₃ for 24 hrs., refluxed over P₂O₅ for 2-3 hrs. and then distilled from P₂O₅ in an all-glass apparatus. The fraction boiling at 81-81.5°C was retained. All other chemicals were of reagent grade quality. ESTIMATED ERROR: Nothing was specified, but the precision is likely to be ±1% (compiler).

6 Rubidium	
COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Rubidium tetraphenylborate (1-);</pre>	Popovych, O.; Gibofsky, A.; Berne, D. H. <i>Anal. Chem.</i> <u>1972</u> , 44, 811-7.
VARIABLES:	PREPARED BY:
One temperature: 25.00°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of RbBPh ₄ was	s reported as:
$C_{BPh_4} = 5.4_2 \times 10^{-10}$	0^{-5} mol dm ⁻³ .
Combining the above value with the mean molar activity coefficient calculated from the Debye-Hückel limiting law -log $y_{\pm} = 0.509C^{\frac{1}{2}}$, the authors reported as the solubility product: $pK_{s0}^{\circ} = 8.54$ (K_{s0}° units are mol ² kg ⁻²).	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry using a Cary Model 14 spectrophotometer. Saturated	RbBPh ₄ was prepared from NaBPh ₄ (Fisher, 99.7%) by metathesis with
solutions were prepared by shaking suspensions of RbBPh, in water-jacket-	RbCl; it was recrystallized three times from 3:1 acetone-water and
ed flasks. After about two weeks of	dried in vacuo at 80°C. Deionized water was redistilled.
tered and the filtrates analyzed spec-	
tion coefficients of 3.25×10^3 and 2.06×10^3 km s	
and 274 nm, respectively, were used	
to compute the concentration of tetra- phenylborate. All work was carried	ECTIMATED FREADA
out in deaerated containers and sol- vents. Differential thermal analysis	Precision ±2% (rel.)
showed absence of crystal solvates.	Temperature control: ±0.01°C
	REFERENCES:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Rubidium tetraphenylborate (1-); RbC24H20B; [5971-93-7] (2) Tris(hydroxymethyl)aminomethane; C4H11N03; [77-86-1] (3) Ethanoic acid (acetic acid); 	McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u> , 38, 136-9.
$C_{2}H_{4}O_{2}; [64-19-7]$ (4), Water; $H_{2}O; [7732-18-5]$	
VARIABLES:	PREPARED BY:
One temperature: 24.8°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of rubidium tetra tris(hydroxymethyl)aminomethane (THA)	aphenylborate (RbBPh ₄) in aqueous M) buffer at pH 5.1 was reported as:
6.7 x 10 ⁻⁵ mol dm	-3.
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV-spectrophotometry using a Cary Model 11 spectrophotometer according to the procedure of Howick and Pflaum (1). No other details. In the cited procedure, saturated solutions were prepared both by agitating the sus- pensions at 25°C continuously and by agitating them first for a 0.5 hr at 40-50°C and then cooling to 25°C. The equilibrated solutions were filtered prior to analysis.	The buffer solution consisted of $0.1 \mod dm^{-3}$ THAM and $0.01 \mod dm^{-3}$ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO ₄ . The source of BPh ₄ ⁻ was a solution of Ca(BPh ₄) ₂ in THAM prepared from Fisher Scientific reagent-grade NaBPh ₄ by the procedure of Rechnitz et al. (2) and standardized by poten- tiometric titration with KCl and RbCl. RbCl was from the Fisher Scientific Co.
	ESTIMATED ERROR: Not stated. Temperature: ±0.3°C
	REFERENCES :
	 Howick, L. C.; Pflaum, R. T. Anal. Chem. Acta <u>1958</u>, 19, 342. Rechnitz, G. A.; Katz, S. A.; Zamochnick, S. B. Anal. Chem. <u>1963</u>, 35, 1322.

Kirgintal Measurements: Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. 1968, 1170-72. REPARED BY: Orest Popovych BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
REPARED BY: Orest Popovych BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
REPARED BY: Orest Popovych BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
REPARED BY: Orest Popovych BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
Orest Popovych BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
BPh4 in the saturated solutions, ³ of the solution. The solubilities y the compiler. Solubility of RbBPh4 t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
Solubility of RbBPh_ t./vol.)% 10 ² C/mol dm ⁻³ 1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
1.56 3.85 1.81 4.47 1.98 4.89 2.10 5.19 2.05 5.07		
2.10 5.19 2.05 5.07		
2.05 5.07		
1.97 4.87		
1.73 4.27 1.47 3.63		
1.20 2.97		
0.75 1.85		
0.214 0.529		
0.113 0.030 0.074		
0.013 0.032		
*Determined by weighing. Solvent volume was taken as the sum of the volumes of acetone and water, neglecting the effect of mixing. The authors provided no density data.		
IFORMATION		
OURCE AND PURITY OF MATERIALS: NaBPh ₄ ("analytical grade" from the Apolda Co., GDR) was purified by recrystallization from acetone- toluene, followed by dissolution in water, extraction with ether, and removal of the latter <u>in vacuo</u> . The purity of the final NaBPh ₄ was no less than 99.6%. RbBPh ₄ was pre- pared by metathesis of NaBPh ₄ with RbCl and purified by double recrys- tallization from 20% water 80%		

COMPONENTS :	ORIGINAL MEASUREMENTS:
 Rubidium tetraphenylborate (1-); RbC₂₄H₂₀B; [5971-93-7] Acetonitrile; C₂H₃N; [75-05-8] 	Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u> , 44, 811-7.
VARIABLES:	PREPARED BY:
One temperature: 25.00°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility was reported The mean molar ionic activity coeffic relationship:	as $C_{BPh4} = 1.70 \times 10^{-2} \text{ mol dm}^{-3}$. ient was calculated using the

 $-\log y_{\pm} = \frac{1.64C^{\frac{1}{2}}}{1 + 0.485\&C^{\frac{1}{2}}}$

Adopting å = 0.5 nm for BPh₄⁻ and å = 0.3 nm for Rb⁺, the value of y_{\pm}^{2} =0.455 and the pK_{\$0}[°] derived from it was reported as 3.66 (molal scale), i. e., K_{\$0}[°] units are mol² kg⁻². pK_{\$0}[°] values on the molar scale (K_{\$0}[°] units of mol² dm⁻⁶) was not reported, but can be calculated from the molal value via the solvent density, which was 0.777 g ml⁻¹. On the molar scale, K_{\$0}[°] = 1.31 x 10⁻⁴ mol² dm⁻⁶ and the corresponding pK_{\$0}[°] = 3.88 (compiler). Complete dissociation was assumed, which is generally true for most electrolytes in acetonitrile (1). The molar absorption coefficients for the BPh₄⁻ ion were determined to be 3203 and 2082 dm³ (cm mol)⁻¹ at 266 nm and 274 nm, respectively.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: UV spectrophotometry using a Cary Model 14 spectrophotometer. Satd solutions were prepd by shaking the suspensions in water-jacketed flasks. After about two weeks of shaking, the suspensions were filtered and the filtrates analyzed spectrophotometrically. The molar absorption coefficients stated above were used to compute the concentration of tetraphenylborate. All work was carried out in deaerated containers and solvents. Differential thermal analysis detected no crystal solvates.

COMMENTS:

The ion-size parameter used for the BPh_4 ion in this study was probably too small. If the literature value of 1.2 nm (2) is used instead, y_{\pm}^2 becomes 0.500, the $K_{SO}^\circ = 1.44 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ and $pK_{SO}^\circ = 3.84$. Probably a tentative value of $K_{SO}^\circ = 1.4 \times 10^{-4} \text{ mol}^2 \text{ dm}^{-6}$ can be adopted until the activity coefficients are determined experimentally.

SOURCE AND PURITY OF MATERIALS: Acetonitrile (Matheson, spectroquality) was refluxed for 24 hrs over CaH₂ and fractionally distilled. RbBPh₄ was prepared from NaBPh₄ (Fisher, 99.7%) by metathesis with RbCl; it was recrystallized three times from 3:1 acetone-water and dried <u>in</u> vacuo at 80°C.

ESTIMATED ERROR:

Precision ±1% (rel.) Accuracy ±3% (rel.) Temperature control: ±0.01°C

REFERENCES: (1) Kay, R. L.; Hales, B. J.; Cunningham, G. P. J. Phys. Chem. <u>1967</u>, 71, 3925.

(2) Kolthoff, I. M.; Chantooni, M. K. Jr. Anal. Chem. <u>1972</u>, 44, 194.

COMPONENTS :	ORIGINAL MEASUREMENTS:
<pre>(1) Rubidium tetraphenylborate (1-); RbC₂₄H₂₀B; [5971-93-7]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 1976, 72, 955-62.
<pre>(2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reported the solubility of RbBPh4 in 1,2-dichloroethane as:	
9.90 x 10^{-6} mol dm ⁻³ .	
They used an association constant $K_A = 1.70 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ and the extended Debye-Hückel equation for the mean ionic activity coefficient with an ion-size parameter $\&$ = 0.56 nm to calculate the standard Gibbs free energy of solution: $\Delta G_S^\circ = 13.76 \text{ kcal mol}^{-1} = 57.60 \text{ kJ mol}^{-1}$ (compiler). From the relationship: $\Delta G_S^\circ = -\text{RT} \ln K_{SO}^\circ$, the solubility product can be calculated as $pK_{SO}^\circ = 10.088$ where the units of K_{SO}° are mol}2 dm ⁻⁶ (compiler).	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Saturated solutions prepared by shaking the suspensions at 25°C for several days and analyzing aliquots by evaporation and weighing. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into a distillation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. RbBPh ₄ was recryst. from aqueous acetone and dried in a vacuum oven at 60-80°C for several days.
	ESTIMATED ERROR:
COMMENTS:	Precision of 0.1 kcal mol ⁻¹ in ΔG_S° .
be regarded as a <u>tentative</u> value.	REFERENCES:

Rubidium	
COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Rubidium tetraphenylborate (1-);</pre>	 Popovych, O.; Gibofsky, A.; Berne D. H. Anal. Chem. <u>1972</u>, 44, 811-7. Berne, D. H. Ph.D. Thesis. City
(3) Ethanol; C_2H_60 ; [64-17-5]	University of New York. 1972 (1).
VARIABLES:	PREPARED BY:
LiCl concentration varied from 2 to 200 times that of RbBPh, in mol dm ⁻³ . One Temperature: 25.00°C.	Orest Popovych
EXPERIMENTAL VALUES: The solubility (ion-activit reported as:	:y) product of $RbBPh_4$ in ethanol was
$pK_{s0}^{\circ} = 7.60 \ (K_{s0}^{\circ})$) units are mol ² kg ⁻²).
The value of the ion-activity product, determined from the variation of the solubility with ionic strength, was not reported, but it is listed as $K_{s0}^{\circ} = 1.56 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$ in the Ph.D. thesis by Berne (1).	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry using a Cary Model 14 spectrophotometer. Satura- ted solutions were prepared by shak- ing suspensions of RbBPh ₄ in water- jacketed flasks. After about two weeks of shaking, the suspensions were filtered and the filtrates ana- lyzed spectrophotometrically. The molar absorption coefficients of 2.97 x 10 ³ and 2.10 x 10 ³ dm ³ (cm mol) ⁻¹ at 266 nm and 274 nm, respec- tively (2), were used to compute the	RbBPh, was prepared from NaBPh, (Fis- her, 99.7%) by metathesis with RbCl; it was recrystallized three times from 3:1 acetone-water and dried <u>in</u> <u>vacuo</u> at 80°C. The purification of LiCl and ethanol have been described (3).
concentration of tetraphenylborate.	ESTIMATED ERROR:
containers and solvents.	Precision ±1% (rel.) in solubility. Accuracy ±3% (rel.) in solubility. Temperature control: ±0.01°C.
	REFERENCES: (1) Berne, D. H. Ph. D. Thesis. City University of New York. 1972. (Dissertation index No. 73- 02829). (2) Dill, A. J.; Popovych, O. J. Chem.
	Eng. Data <u>1969</u> , 14, 240. (3) Dill, A. J.; Popovych, O. J. Chem. Eng. Data <u>1969</u> , 14, 240.

Cesium

COMPONENTS:	EVALUATOR:
 (1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9] (2) Water; H₂O; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. October 1979

CRITICAL EVALUATION:

There are seven publications dealing with original data pertaining to the solubility of cesium tetraphenylborate (CsBPh₄) in aqueous solutions (1-7). Two of them, however, report only the solubility product (1,2). Only one of the studies deals with the solubility as a function of the temperature, ionic strength and pH (3). In one publication (7) the solubility was reported in a buffer solution, but not in pure water. What seems to be historically the first datum, the solubility product of CsBPh₄ reported as 5×10^{-10} (presumably mol² dm⁻⁶) at 290 K by Rüdorff and Zannier (1), must be rejected because of lack of any experimental details provided, except for the statement that the determination was conductometric. Since the result was reported to one significant figure, no compilation sheet was provided for that original source.

Solubility at 298 K.

At 298 K, we have the solubility data of Pflaum and Howick (4), Alexander and Parker (2), expressed in the form of a solubility product, and of Popovych, Gibofsky and Berne (5). All three determinations were by UV-spectrophotometry for the BPh₄⁻ ion, but they differ in their reported degree of temperature control and saturation control. Alexander and Parker in reporting a pK_{SO} of 8.7 (all solubility products in this evaluation have units of mol² dm⁻⁶) failed to specify how the temperature was controlled and how the existence of saturation was ascertained. However, if we make the usual assumption that the error is 0.1 pK units, the solubility derived from the above $K_{\rm SO}$ by simply taking the square root is (4.5 ± 0.5) x 10^{-5} mol dm⁻³. This calculation is justified since the above solubility product was reported to be a product of concentrations, not activities. As we can see, the solubility value derived from the datum of Alexander and Parker does not agree with the value of $2.79 \ \mathrm{x}$ 10^{-5} mol dm⁻³ reported by Pflaum and Howick. In the latter study, there is also no indication of how the temperature and the saturation were controlled. Furthermore, the authors used the molar absorption coefficients determined in acetonitrile to analyze the spectra obtained on aqueous solutions. While this procedure may have resulted in a compensation of errors (see evaluation for KBPh4 in water), a combination of all those shortcomings cannot inspire confidence in the reported solubility value. The work of Popovych et al. (5), on the other hand, was characterized by temperature control to ± 0.01 °C and repeated analyses days apart until a constant solubility value was attained. The relative precision of determining the solubility of CsBPh4 in water turned out to be a little lower than the normal $\pm 1\%$ associated with the UV-analysis for tetraphenylborates -- it was $\pm 4\%$. The solubility was reported as 4.0 x 10^{-5} mol dm⁻³ (the last, uncertain, digit dropped by the evaluator). If we restirct the recommendation to two significant digits in the solubility value, it may be just barely justified to average the value of Alexander and Parker (2) and that of Popovych et al. (5) to arrive at the recommended solubility value at 298 K as:

Solubility = $(4.2 \pm 0.2) \times 10^{-5} \text{ mol dm}^{-3}$.

The solubility product calculated as $K_{SO}^{\circ} = C^2 y_{\pm}^2$, where C is the solubility and y_{\pm}^2 is the mean ionic activity coefficient calculated from the Debye-Hückel limiting law, was reported by Popovych et al. (5) as $pK_{SO}^{\circ} = 8.80$. It is within 0.1 log units of the value reported by Alexander and Parker (2), but the latter contains no activity correction.

Solubility at Other Temperatures

There are two reported solubility values at 293 K. From the work of Geilman and Gebauhr (6), the solubility calculated by the compiler is 3.2×10^{-5} mol dm⁻³. At zero ionic strength (presumably meaning in the absence of added inert eletrolyte) the solubility value reported by Siska (3) is 3.50×10^{-5} mol dm⁻³. Although one might be tempted to average
COMPONENTS:	EVALUATOR:
(1) Cesium tetraphenylborate (1-);	Orest Popovych, Department of Chemistry, City University of
CsC ₂₄ H ₂₀ B; [3087-82-9]	New York, Brooklyn College, Brooklyn N. Y. 11210 U.S. A
(2) Water; H ₂ 0; [7732-18-5]	October 1979

CRITICAL EVALUATION:

these two results at 293 K, the problem with Siska's data is the very short time of equilibration (3 hours). This length of equilibration proved to be sufficient for the saturation of CsBPh₄ in the rate-of-disso-lution study by Geilman and Gebauhr (6), but it is not so as a general rule, in the experience of this evaluator. We have noted in the evaluation for KBPh4 in water that Siska's (3) solubility values seemed to be too low. If undersaturation did not occur for CsBPh4, much valuable information might be salvaged, because Siska's is the only study to date that reported the solubility of CsBPh4 in water as a function of ionic strength and pH at 293 K as well as the solubility at other temperatures in solutions with ionic strength maintained at 0.1 mol dm⁻³. The latter solubility determinations were reported at 283 K, 303 K, 313 K and 318 K (3). Unfortunately, the only other literature datum on the solubility of CsBPh₄ in a 0.1 mol dm⁻³ buffer solution, which is 5.4×10^{-5} mol dm⁻³ at 298 K (7), tends to confirm the undersaturation of Siska's solution.

REFERENCES:

- 1. Rüdorff, W.; Zannier, H. Angew. Chem. 1952, 64, 613.
- 2. Alexander, R.; Parker, A. J. J. Am. Chem. Soc. 1967, 89, 5549.
- з.
- Siska, E. Magy. Kem. Foly. <u>1976</u>, 82, 275. Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u>, 28, 1542. 4.
- Popovych, O; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u>, 44, 811. Geilman, W.; Gebauhr, W. Z. anal. Chem. <u>1953</u>, 139, 161. 5.
- 6.
- McClure, J. E.; Rechnitz, G. A. Anal. Chem. 1966, 38, 136. 7.

Gesium		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Cesium tetraphenylborate (1-); 	Alexander, R.; Parker, A. J.	
CsC ₂₄ H ₂₀ B; [3087-82-9]	J. Am. Chem. Soc. <u>1967</u> , 89, 5549-51.	
(2) Water; H_20 ; [7732-18-5]		
-		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The formal (concentration) solu was reported as:	ubility product of CsBPh4 in water	
pK _{s0} = 8.7 (K _{s0} un:	its are $mol^2 dm^{-6}$).	
The solubility can be calculated as	$(K_{s0})^{\frac{1}{2}} = (4.5 \pm 0.5) \times 10^{-5} \text{ mol dm}^{-3}$	
	(00.1.91101)	
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions	Not stated.	
saturated under nitrogen. No other details.		
	ESTIMATED ERROR:	
	Precision of ±0.1 pK is assumed by the compiler.	
	REFERENCES:	

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Cesium tetraphenylborate (1-); $CsC_{24}H_{20}B$; [3087-82-9]	Siska, E. Magy. Kem. Foly. <u>1976</u> , 82, 275-8.		
(2) Sodium sulfate; Na ₂ SO ₄ ; [7757-82-6]			
(3) Water; H ₂ O; [7732-18-5]			
VARIABLES:	PREPARED BY:		
Temperature range 10-45°C Concentration of Na ₂ SO ₄ pH	Orest Popovych		
EXPERIMENTAL VALUES:			
In distilled water at 20°C, the solubility of CsBPh ₄ was reported to be: 3.49×10^{-5} mol dm ⁻³ and the corresponding solubility product, K_{s0} , as 1.22×10^{-9} mol ² dm ⁻⁶ . The K_{s0} is simply the square of the solubility, without activity corrections.			
With ionic strength varied by m solubilities, C, were reported for Cs	neans of Na ₂ SO ₄ , the following BPh ₄ in aqueous solution at 20°C:		
Ionic strength/mol dm ⁻³	10 ⁵ C/mol dm ⁻³		
0 0.05 0.1 0.3 0.5 0.7 1.0 2.0	3.50 3.00 2.98 2.55 2.35 2.03 1.58 0.86		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Amperometric titration. For details see compilation for KBPh ₄ in water based on the same reference. CsBPh ₄ was prepared from the chloride by metathesis with NaBPh ₄ .	Not specified.		
	ESTIMATED ERROR:		
	Precision in solubility deter- mination is ±2%. Temperature control: ±1°C.		
	REFERENCES:		

bo Cesium		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Siska, E. <i>Magy. Kem. Foly.</i> <u>1976</u> , 82, 275-8.	
(2) Sodium sulfate; Na ₂ SO ₄ ; [7757-82-6]		
(3) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
COMMENTS AND/OR	ADDITIONAL DATA	
EXPERIMENTAL VALUES:	tant at $0.1 \text{ mol} \text{ dm}^{-3}$ with No. 60.	
the following solubilities of CsBPh4,	C, were obtained as a function of	
t/°C	10 ⁵ C/mol dm ⁻³	
10	2.02	
30	3.90	
40	5.72	
45	680	
Keeping the ionic strength constant a lowing solubilities of CsBPh ₄ , C, wer pH varied by means of acetic acid and	at 0.1 mol dm^{-3} with Na_2SO_4 , the fol- re obtained at 20°C as a function of a sodium hydroxide:	
pH 10 ⁵ C/mol dm ⁻³ pH	10^5 C/mol dm ⁻³	
1.7 1.48 10.9 2.3 2.52 11.3	2.87 2.82	
2.7 2.74 2.9 2.72 $A \neq 20^{\circ}$	C ionic strongth of 0.1 mol dm^{-3} and	
4.4 2.78 in the	pH range of 2.7-11.3, the authors	
5.4 2.85 report 6.5 2.79	the solubility of CsBPh ₄ in water as:	
7.3 2.87 $C = (2)$	2.82 ± 0.047) x 10^{-5} mol dm ⁻³ .	
8.5 2.84		
9.3 2.82 10.1 2.82		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
	ESTIMATED ERROR:	
	REFERENCES:	
	1	

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u> , 28, 1542-4.	
(2) Water: H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
	[
EXPERIMENTAL VALUES:		
The solubility of CsBPh ₄ in water was reported as 2.79 x 10^{-5} mol dm ⁻³ .		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Ultraviolet spectrophotometry. For details see the compilation for KBPh ₄ in water based on the same reference.	See the compilation for KBPh ₄ in water based on the same reference. CsBPh ₄ was prepared by metathesis of CsCl and NaBPh ₄ and recrystallized from an acetonitrile-water mixture.	
	ESTIMATED ERROR:	
	Nothing is specified, but the precision is likely to be ±1% (compiler).	
	REFERENCES:	

57

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u> , 44, 811-7.	
(2) Water; H ₂ 0; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of CsBPh4 was reported	as: $C_{BPh} = 4.0_1 \times 10^{-5} \text{ mol } dm^{-3}$.	
Combining the above value with the mean molar activity coefficient calculated from the Debye-Hückel limiting law -log $y_{\pm} = 0.509C^2$, the authors reported as the solubility product: $pK_{S0}^{\circ} = 8.80$ (K_{S0}° units are mol ² kg ⁻²).		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;	
Ultraviolet spectrophotometry. Procedure identical with that described for KBPh4 in methanol. Differential thermal analysis showed absence of crystal solvates.	CsBPh ₄ was prepared and purified by a method analogous to that employed for KBPh ₄ and described in the com- pilation for KBPh ₄ in methanol.	
	ESTIMATED ERROR:	
	Precision ±4% (rel.) Temperature control: ±0.01°C	
	REFERENCES:	

Cesium			
COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Cesium tetraphenylborate (1-); CsC ₂₄ H ₂₀ B; [3087-82-9]	Geilman, W.; Gebauhr, W. Z. anal. Chem. <u>1953</u> , 139, 161-81.		
(2) Water; H ₂ O; [7732-18-5]			
VARIABLES:	PREPARED BY:		
One temperature: 20°C	Orest Popovych		
EXPERIMENTAL VALUES:	L		
The solubility is reported both 2.9 x 10^{-5} mol dm ⁻³ . The correspondisimply as C_{Cs}^2 , is reported as 8.4 x J	as C _{Cs} = 0.430 mg cm ⁻³ and as ing solubility product, calculated 10 ⁻¹⁰ .		
However, inspection of the raw data (below) suggests that the authors consider only two figures to be significant, i. e., the solubility should have been reported as 0.43 mg cm ⁻³ . Using the value of 132.91 for the relative atomic mass of Cs, this compiler obtains somewhat different results from the authors: $C_{CS} = 3.2 \times 10^{-5}$ mol dm ⁻³ and $K_{SO} \equiv C_{CS}^2 = 1.0 \times 10^{-9}$ mol ² dm ⁻⁶ .			
Also reported is the rate of dis	ssolution of CsBPh4 in water:		
Time, hours	μg Cs/10 cm ³ of water		
0.5 1.0 3.0 6.0 12.0 20.0	28.0 34.0 44.0 43.5 43.5 43.2		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Radiometric, using liquid-scintilla- tion counting of ¹³⁴ Cs. The radio- active cesium obtained as the carbonate from the Harwell nuclear reactor was purified by precipitation with HClO ₄ in the presence of 2 mg of NaHPO ₄ followed by recrystallization. The CsClO ₄ solution was reacted with NaBPh ₄ , the resulting CsBPh ₄ precipi- tate washed with water, mechanically shaken in water at 20°C and the filtrate analyzed radiometrically to constant activity. Apparatus was not specified.	Not stated. ESTIMATED ERROR: Not specified. However, given the temperature control to ±0.5°C, the relative precision cannot be better		
	REFERENCES:		

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60 Ces	Cesium	
COMPONENTS: (1) Cesium tetraphenylborate (1-); $CsC_{24}H_{20}B$ [3087-82-9] (2) Tris(hydroxymethyl)aminomethane $C_{4}H_{11}NO_{3}$; [77-86-1] (3) Acetic acid; $C_{2}H_{4}O_{2}$; [64-19-7] (4) Water; $H_{2}O$; [7732-18-5]	ORIGINAL MEASUREMENTS: McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u> , 38, 136-9.	
VARIABLES: One temperature: 24.8°C	PREPARED BY: Orest Popovych	
EXPERIMENTAL VALUES: The solubility of cesium tetraph tris(hydroxymethyl)aminomethane (THAM 5.4 x 10 ⁻⁵ mol	enylborate (CsBPh ₄) in aqueous) buffer at pH 5.1 was reported as: dm ⁻³ .	
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details.	SOURCE AND PURITY OF MATERIALS: The buffer solution consisted of 0.1 mol dm ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO4. The source of BPh4 ⁻ was a solution of Ca(BPh4) ₂ in THAM prepared from Fisher Scientific reagent-grade NaBPh4 by the procedure of Rechnitz et al. (2) and standardized by potentiometric titration with KCl and RbCl. CsCl was from the Fisher Scientific Company. ESTIMATED ERROR: Not stated. Temperature: ±0.3°C REFERENCES: 1) Howick, L. C.; Pflaum, R. T. Anal. Chem. Acta <u>1958</u> , 19, 342. 2) Rechnitz, G. A.; Katz, S. A.; Zamochnick, S. B. Anal. Chem. <u>1963</u> , 35, 1322.	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cesium tetraphenylborate (1-);	Berne, A; M. A. Inests. Brooklyn College 1976
(2) Lithium chloride: LiCl:	biookiyn bollege. 1970.
[7447-41-8]	
(3) Sodium hydroxide; NaOH;	
[1310-73-2]	
(4) Methanol; CH ₄ O; [67-56-1]	
(5) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Methanol-water composition. Lici	Orest Benevych
times the solubility of CaBPh.	blest topových
Lone temperature: 25.00°C	
EXPERIMENTAL VALUES:	
The author reported the mean	ionic activities of CsBPh4 in
saturated solutions, which were deter	mined from the variation of the
solubility of CsBPh ₄ as a function of 1401 dr the masses of $5 \times 10^{-5} \text{ mol}$	10nic strength varied by means of
sition the presence of 5 x 10 ° mol	am " Nauh. For each solvent compo-
sition, the activity in saturated sol	delon without added inert electrolyte,
at, o, was computed from the functions.	
$\log C_{T} = \log \alpha - \log T$ and -	$\log x = A_T \frac{1}{2} + A_T + A_T \frac{3}{2} +$
-05 0I - 10g at,o - 10g yt,I and -	
where y_+ is the mean molar activity c	pefficient (f $_{\pm}$ in the original)
and the subscripts o and I denote solu	itions without and with added inert
electrolyte. Complete dissociation wa	as assumed. The solubilities at
different ionic strength were not rep	orted, but their values, as well
as those of the activity coefficients	at any ionic strength I (in mol dm^{-3})
can be calculated from the A-coeffici	ents characteristic of the methanol-
water mixture tabulated below.	
The colubility of CeBPh, in	the nure solvents was not measured
due to the extensive decomposition in	the absence of added LiCl, but
ade to the extensive decomposition in	
the corresponding ionic activity, ar	, should be a very good approximation
the corresponding ionic activity, a_{\pm} , of the solubility in the concentration	, should be a very good approximation range involved,
the corresponding ionic activity, a_{\pm} , of the solubility in the concentration	, should be a very good approximation range involved.
the corresponding ionic activity, $a_{t'}$, of the solubility in the concentration	, should be a very good approximation range involved.
the corresponding ionic activity, $a_{t',i}$ of the solubility in the concentration	, should be a very good approximation range involved.
the corresponding ionic activity, $a_{I'}$, of the solubility in the concentration	, should be a very good approximation range involved.
the corresponding ionic activity, a _f , of the solubility in the concentration	, should be a very good approximation range involved.
the corresponding ionic activity, a _f , of the solubility in the concentration	, should be a very good approximation range involved. continued
the corresponding ionic activity, a _f , of the solubility in the concentration	, should be a very good approximation range involved. continued
the corresponding ionic activity, a _f , of the solubility in the concentration AUXILIARY	, should be a very good approximation range involved. continued INFORMATION
the corresponding ionic activity, a _f , of the solubility in the concentration AUXILIARY	, should be a very good approximation range involved. continued
the corresponding ionic activity, a _f , of the solubility in the concentration AUXILIARY METHOD/APPARATUS/PROCEDURE:	, should be a very good approximation range involved. continued INFORMATION SOURCE AND PURITY OF MATERIALS: CSRPh. was prepared by materials
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AUXILIARY METHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry using a Cary Model 17 spectrophotometer. Saturation was achieved by subjecting the suspensions for 20 minutes to ultrasonic waves (E/MC Corp. Model 450 Ultrasonic Generator) followed by agitation in a thermostatted bath	, should be a very good approximation range involved.
AUXILIARY METHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry using a Cary Model 17 spectrophotometer. Saturation was achieved by subjecting the suspensions for 20 minutes to ultrasonic waves (E/MC Corp. Model 450 Ultrasonic Generator) followed by agitation in a thermostatted bath for at least 3 days until constant	continued continued INFORMATION SOURCE AND PURITY OF MATERIALS: CsBPh ₄ was prepared by metathesis of NaBPh ₄ and CsCl (both from Alfa Inorganic) and purified by triple recrystallization from a 3:1 acetone- water mixture. It was dried <u>in vacuo</u> at 80°C for 24 hours. LiCl (Baker Analyzed Reagent) was used without purification after drying in vacuo
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62	Ces	ium			
COMPONENTS: (1) Cesium tetraphenyl: CSC ₂₄ H ₂₀ B; [3087-8 (2) Lithium chloride; [7447-41-8] (3) Sodium hydroxide; [1310-73-2] (4) Methanol; CH ₄ O; [6 (5) Water; H ₂ O; [7732-	borate (1-); 2-9] LiCl; NaOH; 7-56-1] 18-5]	EVALUATOR: Orest Popov Chemistry, New York, H Brooklyn, N Sept	yych, Depar The City U Brooklyn Co W. Y. 11210 Cember]979	tment of University Dilege, D, U. S. A	of
CRITICAL EVALUATION:	MMENTS AND/OR AD	DITIONAL DATA	A		
Mass% methanol 10 ⁴ a _± in water	,o/mol dm ⁻³ Rel	ative error, ^a ±,0 ^{/a} ±,0	% A ₁ A ₂	A ₃	A ₄
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	5.04 4.43 4.07 3.34 3.09 1.83 1.22 0.749 0.474	3.6 2.0 2.4 5.4 7.0 21 6.2 5.8 4.0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9 4.22 31 1.49 8 0.487 9 1.34 40 0.0864 77 -3.91 78 0.432 98 0.167 34 0.660	-2.17 -0.564 4.45
<u>b</u> The data in this reliable value for the ion. In the original, $a_{\pm,0} = 4.49 \times 10^{-4}$ $A_4 = -0.724$.	row were recalcu absorption coef mol dm ⁻³ ; A ₁ =	lated by the ficient for t 1.25; A ₂ = -1	compiler u che tetraph 97; A ₃ =	enylborat	re

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser. 1968, 1170-2.
(2) 2-Propanone (acetone); $C_{3}H_{6}O;$	
(3) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Acetone-water composition One temperature: 25.00°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reporte solutions, defined as grams of salt solubilities have been recalculated t	ed mass % of CsBPh ₄ in the saturated In 100 cm ³ of the solution. The to mol dm ⁻³ by the compiler.
Vol. % water in acetone* (V	Solubility of CsBPh ₄ Nt./vol.)% 10 ² C/mol dm ⁻³
0.007	1.50 3.32
2 4	1.09 3.74 1.82 4.03
8	1.92 4.25
12	1.80 3.98
20	1.56 3.45
30	1.32 $2.921.05$ 2.32
37	0.71 1.57
45	0.38 0.84
60	0.077 0.170
70 80	0.034 0.075
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. For de- tails see compilation for KBPh ₄ in acetone-water, based on the above reference.	SOURCE AND PURITY OF MATERIALS: See compilation for KBPh ₄ in acetone- water based on the above reference. CsBPh ₄ was prepared and purified as KBPh ₄ , starting with CsCl.
	ESTIMATED ERROR:
	Temperature control: ±0.05°C
	REFERENCES:

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COMPONENTS:	EVALUATOR:
 (1) Cesium tetraphenylborate (1-); CsC₂₊H₂₀B; [3087-82-9] (2) Acetonitrile; C₂H₃N; [75-05-8] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. October 1979

CRITICAL EVALUATION:

There are only two original data on the solubility of cesium tetraphenylborate (CsBPh4) in acetonitrile, both at 298 K. Alexander and Parker (1) reported the solubility in the form $pK_{80} = 3.1$, where the K_{80} was a product of ionic concentrations, not activities (all K_{80} values in this evaluation have units of mol² dm⁻⁶). On the assumption that the above pK_{80} has a precision of ±0.1 units, the compiler estimated the solubility to be $(K_{80})^{\frac{1}{2}} = (2.8 \pm 0.3) \times 10^{-2}$ mol dm⁻³. The analytical method was either UV-spectrophotometry, or titration of BPh4- with Ag⁺. Unfortunately, no experimental details are provided by the authors as to the extent of temperature control and the manner in which the attainment of saturation was ascertained. Popovych, Gibofsky and Berne (2) reported a solubility value of 1.68 x 10⁻² mol dm⁻³, which differs greatly from that of Alexander and Parker (1). Considering that Popovych et al. (2) controlled the temperature of the bath to 0.01°C and that saturation (as well as possible decomposition) were monitored by successive analyses days apart until the results checked to 1% or better, their solubility value would seem to be the preferred one of the two. However, the solubility of 1.68 x 10⁻² mol dm⁻³ should be considered no better than tentative at this time.

The thermodynamic solubility product estimated by Popovych et al. (2) was reported in the form $pK_{SO}^{\circ} = 3.67$ (weight basis), i. e., K_{SO}° units of mol² kg⁻². Based on volume units, i. e., mol dm⁻³, the pK_{SO}° would be 3.89 (evaluator). The activity correction was made via the calculated activity coefficient of $y_{\pm}^{2} = 0.456$ derived from the Debye-Hückel equation with ion-size parameter shown on the compilation sheet. One could argue, however, that using a = 0.5nm for the BPh₄⁻ ion is not realistic; for example, Kolthoff and Chantooni (3) preferred a value of a = 1.2nm. Using the latter value in our calculation leads to a $y_{\pm}^{2} = 0.501$ and a $pK_{SO}^{\circ} = 3.85$ (volume basis).

REFERENCES:

1.	Alexander,	R.;	Parker,	Α.	J.	J.	Am.	Chem.	Soc.	<u>1967,</u>	89,	5549.	
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- 2. Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u>, 44, 811.
- 3. Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cesium tetraphenylborate (1-); CsC ₂₄ H ₂₀ B; [3087-82-9]	Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> , 89, 5549-51.
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]	
VARIABLES:	PREPARED BY:
One Temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration)	solubility product of CsBPh ₄ in
$pK_{-0} = 3.1 (K_{-0})$	units are $mol^2 dm^{-6}$).
The solubility is therefore $(K_{-0})^{\frac{1}{2}} =$	$(2.8 \pm 0.3) \times 10^{-2} \text{ mol } dm^{-3} \text{ (compiler)}.$
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AUXILIARY	INFORMATION
METHOD / APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen, or titra- tion for the BPh_4^- anion with silver nitrate. No other details.	Not stated.
	ESTIMATED ERROR:
	Nothing is specified. A precision of ±0.1 pK units can be
	assumed (compiler). REFERENCES:

66 Ces	ium		
COMPONENTS:	ORIGINAL MEASUREMENTS:		
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u> , 44, 811-7.		
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]			
VARIABLES:	PREPARED BY:		
One temperature: 25.00°C	Orest Popovych		
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·		
The solubility was reported as ($C_{\rm BPh_4} = 1.68 \times 10^{-2} \text{ mol } dm^{-3}.$		
The mean molar ionic activity coeffic relationship:	ient was calculated using the		
$-\log y_{\pm} = \frac{1.0}{1-100}$	54 c ^{¹⁄₂} ⊦ 0.485åc ^{1⁄2}		
Adopting $a^{\circ} = 0.5$ nm for BPh ₄ ⁻ and $a^{\circ} = 0.3$ nm for Cs ⁺ , the value of $y_{\pm}^{2} = 0.456$, and the pK _{\$0} [°] = 3.67 (weight basis), i. e., K _{\$0} [°] units are mol ² kg ⁻² . pK _{\$0} [°] value on the volume basis (K _{\$0} [°] units of mol ² dm ⁻⁶) was not reported, but can be calculated from the above value via the solvent density, which was 0.777 g ml ⁻¹ . Complete dissociation was assumed, which is generally true for most electrolytes in acetonitrile.			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE: Ultraviolet spectrophotometry. Procedure identical with that described for KBPh4 in methanol. Differential thermal analysis showed absence of crystal solvates.	SOURCE AND PURITY OF MATERIALS; Acetonitrile (Matheson, spectroqua- lity) was refluxed for 24 hours over CaH ₂ and fractionally distilled. CsBPh ₄ was prepared and purified in a manner analogous to that described in the compilation for KBPh ₄ in methanol.		
	ESTIMATED ERROR: Precision ±1% (rel.) Accuracy ±3% (rel.) Temperature control: 0.01°C REFERENCES:		

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cesium tetraphenylborate (1-); $CsC_{24}H_{20}B$; [3087-82-9]	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 1976, 72, 955-62.
<pre>(2) 1,1-Dichloroethane; C₂H₄Cl₂; [75-34-3]</pre>	<u></u> ,,
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

EXPERIMENTAL VALUES:

The authors reported the solubility of \mbox{CsBPh}_4 in 1,1-dichloro-ethane as:

 $5.30 \times 10^{-5} \text{ mol } dm^{-3}$.

Using an estimated association constant of $1.20 \times 10^4 \text{ mol}^{-1} \text{ dm}^3$ and an ionsize parameter of å = 0.57 nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained for the standard Gibbs free energy of solution:

 $\Delta G_{S}^{\circ} = 12.21 \text{ kcal mol}^{-1} = 51.11 \text{ kJ mol}^{-1} \text{ (compiler)}.$

The solubility (ion-activity) product of CsBPh_4 can be calculated from the relationship:

 $\Delta G_{s}^{\circ} = -RT \ ln \ K_{s0}^{\circ}, \ yielding \ pK_{s0}^{\circ} = 8.952, \ where \ K_{s0}^{\circ} \ units are \ mol^{2} \ dm^{-6} \ (compiler).$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into a distillation flask and fractionated under N_2 through a three-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. CsBPh ₄ was recrystallized from aqueous acetone and vacuum dried at 60-80°C for several days. ESTIMATED ERROR: Precision of 0.1 kcal mol ⁻¹ in ΔG_s° .

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COMPONENTS :	ORIGINAL MEASUREMENTS:
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1
<pre>(2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2]</pre>	<u>1370</u> , 72, 933-02.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reported the so ethane as:	lubility of CsBPh4 in 1,2-dichloro-
3.09 x 10	$5 \text{ mol } dm^{-3}$.
Using an estimated association consta size parameter of $a = 0.57$ nm with wh activity coefficient from the extende at the value for the standard Gibbs f	ent of 2.00 x 10 ³ mol ⁻¹ dm ³ and an ion- tich to calculate the mean ionic ad Debye-Hückel equation, they arrived tree energy of solution:
$\Delta G_{S}^{\circ} = 12.51 \text{ kcal mol}^{\circ}$	$1 = 52.37 \text{ kJ mol}^{-1}$ (compiler).
The solubility (ion-activity) product relationship:	of $CsBPh_4$ can be calculated from the
$\Delta G_{s}^{\circ} = -RT \ln K_{s0}^{\circ}, yie$ are mol ² dm ⁻⁶ (compiler).	elding $pK_{s0}^{\circ} = 9.172$, where K_{s0}° units
	-
AUXILIAR	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into a dis- tillation flask and fractionated under N_2 through a three foot column. At least 10% of the distillate was rejected, the rest collected over freshly activated molecular sieve. CsBPh ₄ was recrystallized from aqueous acetone and vacuum dried at 60-80°C for several days.
	Precision of 0.1 kcal mol ⁻¹ in ΔG_{s}° ,
	REFERENCES:
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COMPONENTS:	ORIGINAL MEASUREMENTS:		
<pre>(1) Cesium tetraphenylborate (1-); CsC₂₄H₂₀B; [3087-82-9]</pre>	Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u> , 44, 811-7.		
(2) Lithium chloride; LiCl; [7447-41-8]			
(3) Ethanol; C ₂ H ₅ O; [64-17-5]			
VARIABLES:	PREPARED BY:		
LiCl concentration varied from 2 to 200 times that of CsBPh, in mol dm ⁻³ . One temperature: 25.00°C.	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility (ion-activit reported as:	y) product of CsBPh ₄ in ethanol was		
$pK_{s0}^{\circ} = 7.65 \ (K_{s0}^{\circ})$	s_0 units are mol ² kg ⁻²).		
The value of the ionic activity, dete solubility with ionic strength, was r	ermined from the variation of the not reported.		
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AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY- OF MATERIALS;		
UV spectrophotometry. Procedure	CsBPh, was prepared and purified by		
Identical with that described for KBPh, in methanol. Differential	for KBPh _u and described in the com-		
thermal analysis showed absence of	pilation for KBPh, in methanol. The purification of LiCl and ethanol have		
crystal bolvates.	been described (1).		
	ESTIMATED ERROR:		
	Presiden +1% (rel) dr. 1 1111		
COMMENTS: CsBPh, is susceptible to decomposi-	Accuracy ±3% (rel.) in solubility.		
tion in solution.	Temperature control: ±0.01°C		
	$\mathbf{AEFEAENUES}:$		
	J. Chem. Eng. Data <u>1969</u> , 14, 240.		
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COMPONENTS .	ORIGINAL MEASUREMENTS.
 Cesium tetraphenylborate (1-); 	Alexander, R.; Parker, A. J.
CsC ₂₄ H ₂₀ B; [3087-82-9]	J. Am. Chem. Soc. <u>1967</u> , 89, 5549-51.
(2) Formamide; CH ₃ NO; [75-12-7]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) s formamide was reported as:	olubility product of CsBPh ₄ in
$pK_{s0} = 3.6 (K_{s0})$	units are $mol^2 dm^{-6}$).
The solubility can be estimated as (K	$1^{\frac{1}{2}} = (1 + 0)^{\frac{1}{2}} = 10^{-2}$ mol dm ⁻³
(compiler).	0) - (1.0 - 0.2) x 10 mol um
AUXILIARY	INFORMATION
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions	Not stated.
saturated under nitrogen, or titra- tion for the BPh anion with silver	
nitrate. No other details.	
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	ESTIMATED ERROR:
	Nothing is specified. A precision
	or ±0.1 pK units can be assumed (compiler).
	REFERENCES :

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Cesium tetraphenylborate (1-); CsC ₂₄ H ₂₀ B; [3087-82-9]	Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> , 89, 5549-51.
(2) Methanol; CH ₄ O; [67-56-1]	
VARIABLES ·	DEEDADED BV.
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) methanol was reported as;	solubility product of $CsBPh_4$ in
$pK_{s0} = 6.1 (K_{s0} un)$	its are $mol^2 dm^{-6}$).
The solubility can be estimated as (9 \pm 1) x 10 ⁻⁴ mol dm ⁻³ (compiler).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen, or titra- tion for the BPh_4^- anion with silver nitrate. No other details.	Not stated.
	FSTIMATED EDDOD.
	Nothing is specified
	A precision of ±0.1 pK units can be assumed (compiler).
	REFERENCES:

COMPONENTS:	EVALUATOR:
 (1) Ammonium tetraphenylborate (1-); C₂₄H₂₀BN; [14637-34-4] (2) Water; H₂0; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. November 1979

CRITICAL EVALUATION:

The solubility of ammonium tetraphenylborate (NH_4BPh_4) in aqueous solutions was published in four articles (1-4). In the two studies by Pflaum and Howick (1,2), the solubility was determined at 298 K by uv-spectrophotometry, but the two reported results differed drastically, being 1.07×10^{-4} mol dm⁻³ and 2.88 x 10^{-4} mol dm⁻³, respectively. Such huge discrepancy cannot be rationalized on the basis of any of the obvious shortcomings in the reported work. Thus, while it is true that the method and the precision of the temperature control were not specified in either of the articles, we can readily see from Siska's (3) data that the solubility of $\mathrm{NH_4BPh_4}$ in aqueous solutions varies on the average by about 7 x 10^{-6} mol dm^{-3} per degree in the 293-303 K range. It is also true that in their first study Pflaum and Howick (1) used absorption coefficients ε_{max} for the BPh₄⁻ ion which were characteristic of acetonitrile solutions. Although nothing was specified with respect to the absorption coefficients in their subsequent article (2), it is probable that the ε_{max} values characteristic of acetonitrile solutions were used to calculate solubilities in aqueous solutions from absorption data throughout their work. The molar ϵ_{max} values used by Pflaum and Howick (1) were 3.225 x 10³ and 2.110 x 10³ at 266 nm and 274 nm, respectively, while the corresponding values reported for aqueous solutions are 3.25×10^3 and 2.06×10^3 , respectively (5). (All molar absorption coefficients are in the units of dm^3 (cm mol)⁻¹). Thus, if Pflaum and Howick averaged the solubility values determined at the two wavelengths, they benefitted from a compensation of errors, which in the case of the solubility of KBPh4 in water (1) led to a result in excellent agreement with other literature data (see critical evaluation for KBPh4 in water). Certainly, the discrepancies between aqueous and acetonitrile ε_{max} values, which are of the order of 1-3%, could not account for the unreasonably large difference between the two solubility values reported in the two studies by Pflaum and Howick (1,2).

The third source of information on the solubility of NH_4BPh_4 in aqueous solutions -- the article by Siska (3) -- can offer only an indirect check on the validity of the results from the previous two studies. This is so because at zero ionic strength Siska reported a solubility only at 293 K, which was 2.52×10^{-4} mol dm⁻³. An estimate of the solubility at 298 K can be made from Siska's data on the variation of the solubility as a function of the temperature, but at an ionic strength of 0.1 mol dm⁻³ maintained by sodium sulfate. If we use a linear interpolation in the function of log C vs. T⁻¹, where C is the solubility, the interpolated solubility value at 298.15 K turns out to be 3.27×10^{-4} mol dm⁻³ (at the ionic strength of 0.1 mol dm⁻³). If the Davies equation is used to estimate the activity coefficient: $-\log y_{\pm} = [0.509 \ I^2/(1 + I^2)] + 0.1 I$, where I is the ionic strength, we obtain for a 0.1 mol dm⁻³ solution the value $y_{\pm} = 0.771$, from which the solubility at zero ionic strength is estimated to be 2.52×10^{-4} mol dm⁻³.

McClure and Rechnitz (4) measured the solubility of NH_4BPh_4 in a 0.1 mol dm⁻³ tris(hydroxymethyl)aminomethane buffer solution at 298.0 K and reported it as 3.4×10^{-4} mol dm⁻³. This is in fair agreement with the result interpolated above from Siska's data, but a precise comparison and a calculation of the solubility at zero ionic strength from the data of McClure and Rechnitz is impossible, because the ionic strength of their buffer solution is not known exactly. Unfortunately, Siska's solubility values are very likely to be too low due to undersaturation (the suspensions were agitated for only 3 hours). They were definitely too low in the case of KBPh₄ in water. Nevertheless, the data of Siska as well as of McClure and Rechnitz suggest that it must be the second reported solubility value

COMPONENTS:	EVALUATOR:
 (1) Ammonium tetraphenylborate (1-); C₂₄H₂₀BN; [14637-34-3] (2) Water; H₂O; [7732-18-5] 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. November 1979

CRITICAL EVALUATION: (continued)

by Howick and Pflaum (2), i.e., $2.88 \times 10^{-4} \text{ mol dm}^{-3}$, that we should place our reliance on at 298 K. Of course, the above value should be regarded as <u>tentative</u> at best. At other temperature, the only available solubility values are those reported by Siska (3), which are probably too low due to undersaturation.

REFERENCES:

- 1.
- Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u>, 28, 1542. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u>, 19, 343. Siska, E. Magy. Kem. Foly. <u>1976</u>, 82, 275. McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u>, 38, 136. Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u>, 70, 1671. 2.
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COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Ammonium tetraphenylborate (1-); C ₂₄ H ₂₄ BN; [14637-34-4]	Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u> , 28, 1542-4.	
(2) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of NH4BPh4 in water was reported as:		
$1.07 \times 10^{-4} \text{ mol}$. dm ⁻³ .	
The authors also reported the molar absorption coefficients for the BPh ₄ ion in <u>acetonitrile</u> solutions to be 3.225 x 10^3 and 2.110 x 10^3 dm ³ (cm mol) ⁻¹ at 266 and 274 nm, respectively.		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Cary Model 11 recording spectrophoto-	used as received for pptns, but was	
prepared in conductivity water by an	recrystallized from acetone-hexane mixt for detn of absorption coeffi-	
unspecified procedure. Method of controlling the temperature was not	cients. NH ₄ BPh ₄ was prepared by metathesis of NH4Cl and NaBPh, and	
stated. The concentration of BPh4	recrystallized from an acetonitrile-	
from spectrophotometric measurements	water mixture.	
not and 2/4 nm by applying the molar absorption coefficients		
specified above.		
	Nothing is specified but the	
	precision is likely to be ±1% (com- piler).	
	REFERENCES :	

Amn	nonium . 7
COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Ammonium tetraphenylborate (1-); $C_{24}H_{24}BN$; [14637-34-4]	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.
(2) Water, H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of NH_4BPh_4 in 2.88 x 10 ⁻⁴ mol dm ⁻³ .	water was reported to be
AUXILIANI	INFORMATION
Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the fil- tered solutions were analyzed for the BPh ₄ - anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not stated.	NaBPh ₄ (J. T. Baker Chemical Co.) was used as received. Other chem- icals were of reagent grade. De- ionized water was used. NH_4BPh_4 was prepared by reacting a 5% excess of freshly prepared $NaBPh_4$ solution with NH_4Cl . The product was recry- stallized from acetone-water and analyzed for purity both by UV-spec- trophotometry in acetonitrile and by titration with $HClO_4$ in HAc gla- cial to the crystal violet end point in anhydrous acetone (1). ESTIMATED ERROR: Nothing specified.
-	REFERENCES: (1) Flaschka, H. Chemist Analyst <u>1955</u> , 44, 60.

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Ammonium		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 Ammonium tetraphenylborate (1-); C₂₄H₂₄BN; [14637-34-4] Sodium sulfate; Na₂SO₄; [7757-82-6] Water; H₂O; [7732-18-5] 	Siska, E. <i>Magy. Kem. Foly.</i> <u>1976</u> , 82, 275-8.	
VARIABLES: Temperature range: 3-50°C Concentration of Na ₂ SO ₄ pH	PREPARED BY: Orest Popovych	
EXPERIMENTAL VALUES:		
In distilled water at 20°C, the solubility of NH_4BPh_4 was reported to be: $C = 2.39 \times 10^{-4} \text{ mol } dm^{-3}$ and the corresponding solubility product, $K_{SO} = C^2$, as 5.71 x 10^{-8} mol ² dm ⁻⁶ . With ionic strength varied by means of Na_2SO_4 , the following solubilities, C, were reported for NH_4BPh_4 at 20°C in water:		
Ionic strength/mol dm ⁻³	10^4 C/mol dm ⁻³	
0 0.05 0.1 0.3 0.5 0.7 1.0 2.0	2.52 2.84 2.84 2.80 2.52 2.08 1.92 0.88	
Keeping the ionic strength constant at the following solubilities C were obta	0.1 mol dm ⁻³ with sodium sulfate, ined as a function of the temperature: Continued	
	INFORMATION	
METHOD/APPARATUS/PROCEDURE: Amperometric titration. For details see compilation for KBPh ₄ in water based on the same reference.	SOURCE AND PURITY OF MATERIALS: Not specified. NH4BPh4 was prepared from the chloride by metathesis with NaBPh4. ESTIMATED ERROR: Precision in solubility determination is ±2%. Temperature control: ±1°C. REFERENCES:	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Ammonium tetraphenylborate (1-);	Siska, E. Magy. Kem. Foly. <u>197</u> 6,
$C_{24}H_{24}BN; [14637-34-4]$	82, 275-8.
(2) Sodium sulfate; Na ₂ SO ₄ ;	
[7732-6]	
(0) water, n ₂ 0, [//52 10 5]	
VARIABLES:	PREPARED BY:
COMMENTS AND/OR ADDITIONAL DATA:	
t/°C	$10^{4}C/mol dm^{-3}$
	1.06
3	2.40
20	2.76
30	3.44
40	4.32
50	6.00
Keeping the ionic strength constant a	t 0.1 mol dm^{-3} with sodium sulfate
and the temperature at $20 \pm 1^{\circ}C$, the	following solubilities C were
obtained as a function of pH varied b	y means of acetic acid and sodium
ayaroxide:	
рН	10^{4} C/mol dm ⁻³
	2 57
2.7	2.57
4.0	2,75
4.4	2,60
4.7	2.74
4.8	2.64
6.5	2.74
The authors summarize their findings of $0.1 \text{ mol} dm^{-3}$, a pH range of $2.7-6$.	5 and a temperature of 20 \pm 1°C.
the solubility of NH _h BPh _h in aqueous	solution is $(2.67 \pm 0.067) \times 10^{-4}$
mol dm-3. The error apparently refer	s to precision.
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
	l
	l
1	ESTIMATED ERROR:
	}
	REFERENCES:
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	ODICINAL MELCUDING	
<pre>(1) Ammonium tetraphenylborate (1-); NH₄ C₂₄ H₂₀ B; [14637-34-4]</pre>	McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u> , 38, 136-9.	
(2) Tris(hydroxymethyl)aminoethane;		
(3) Acetic acid; $C_2 H_4 O_2$; [64-19-7] (4) Water; $H_2 O_3$; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 24.8°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of ammonium tetraphenylborate $(NH_4 BPh_4)$ in an aqueous solution of tris(hydroxymethyl)aminoethane (THAM) buffer at pH 5.1 was reported as: 3.4 x 10^{-4} mol dm ⁻³ .		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE: UV- spectrophotometry according to the procedure of Howick and Pflaum (1). No other details.	SOURCE AND PURITY OF MATERIALS: Baker reagent-grade NH ₄ Cl was the starting material. The buffer solu- tion was prepared to contain 0.1 mol dm ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO ₄ . The source of BPh ₄ ⁻ was a solution of Ca(BPh ₄) ₂ in THAM prepared from Fisher Scientific reagent-grade NaBPh ₄ by the procedure of Rechnitz et al. (2) and standardized by poten- tiometric titrn with KCl and RbCl. ESTIMATED ERROR: Not stated.	
	Temperature: ±0.3°C	
	REFERENCES: 1. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 342.	
	2. Rechnitz, G. A.; Katz, S. A.; Zamochnick, S. B. Anal. Chem. <u>1963</u> , 35, 1322.	

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Ammonium tetraphenylborate (1-); $C_{24}H_{24}BN;$ [14637-34-4]	Kirgintsev, A. N.; Kozitskii, V. P. Izvest. Akad. Nauk SSSR, Khim. Ser.	
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	<u>1968</u> , 1170-2.	
(3) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
Acetone-water composition	Orest Popovych	
One temperature: 25.00°C		
EXPERIMENTAL VALUES:		
The authors reported mass $\%$ of NH ₄ BPh ₄ in the saturated solutions, defined as grams of the salt of 100 cm ³ of the solution. The solubilities have been recalculated to mol dm ⁻³ by the compiler.		
Vol. % water So in acetone* (mass/v	vol.)% C/mol dm ⁻³	
0.007 5.6	0 0.166	
	6 0.224 7 0.253	
8 10.0	0 0.205	
12 9.9	1 0.294	
15 9.5	1 0.282	
20 8.7	0 0.258	
30 5.8	8 0.174	
37 4.3	6 0.129	
45 . 2.7	0 0.0801	
52 1.4	4 0.0427	
	0.01/9	
80 0.0	$\begin{array}{c} 4.54 \times 10^{-3} \\ 1.30 \times 10^{-3} \end{array}$	
*Determined by weighing. Solvent volume was taken as the sum of the volumes of acetone and water, neglecting the effect of mixing.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Evaporation and weighing. Saturated solutions were prepared by shaking the suspensions in a constant-temper- ature bath for 6 hours. Aliquots were removed through cotton plugs and weighed. Solvent was removed by evaporation in a stream of air, followed by desiccation under P ₂ O ₃ and under vacuum. The solid phase contained no solvent when recrystal- lized from acetone or acetone-water	See compilation sheet for $KBPh_4$ in acetone-water, based on the above reference. NH_4BPh_4 was prepared and purified as $KBPh_4$ by metathesis of NaBPh ₄ and NH_4Cl .	
mixtures.		
	EDIIMAIED EKKUK:	
	Temperature control: ±0.05°C	
	REFERENCES:	

COMPONENTS .	ORTGINAL MEASUREMENTS.	
(1) Ammonium tetraphenylborate (1-); $C_{24}H_{24}BN$; [14637-34-4]	Virtanen, P. O. I.; Kerkelä, R. Suom. Kemistil. <u>1969</u> , B42, 29-33.	
<pre>(2) 1-Methyl-2-pyrrolidinone (N-Methyl-2-pyrrolidone); C₅H₉NO; [872-50-4]</pre>		
VARIABLES:	PREPARED BY:	
Two temperatures: 25.00°C and 45.00°C.	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of NH ₄ BPh ₄ in reported to be:	N-methyl-2-pyrrolidone was	
1.21 mol dm^{-3} at 25°C and 1.	24 mol dm ⁻³ at 45°C.	
The corresponding solubility product at 25°C, calculated as the square of the solubility, was reported in the form $pK_{SO} = -0.16$, where K_{SO} units are mol ² dm ⁻⁶ . The pK_{SO} value at 45°C was not reported.		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE: The suspensions were shaken in thermostatted water-jacketed flasks for 1 day at 50°C, followed by 1 day at 25°C or 45°C, respectively.	SOURCE AND PURITY OF MATERIALS: N-Methyl-2-pyrrolidone (General Aniline and Film Co.) was purified as in the literature (1). NH ₄ BPh ₄ was prepared by metathesis of NH ₄ Cl	
Saturated solutions were analyzed by precipitating the NH4BPh4 from aliquots in aqueous solution.	and NaBPh ₄ in water, followed by double recrystallization from an acetone-water mixture and drying <u>in</u> <u>vacuo</u> .	
	ESTIMATED ERROR:	
	Not specified. Temperature control: ±0.02°C	
	REFERENCES: (1) Virtanen, P. O. I. Suom. Kemistil. <u>1966</u> , B39, 257.	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) <u>N,N'- bis(3-aminopropyl)-1,4- butanediamine (spermine) tetrakis-tetraphenylborate (1-); C₁₀₆H₁₁₀B₄N₄;</u></pre>	Zeidler, L. Hoppe-Seyler's 2. Physiol. Chem. <u>1952</u> , 291, 177-8.	
(2) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
Presumably room temperature	Orest Popovych	
EXPERIMENTAL VALUES:	L, , , , , , , , , , , , , , , , , , ,	
The solubility of spermine tetrakis-tetraphenylborate was reported as 0.02%, probably meaning 0.02 g in 100 cm ³ of saturated solution. If this interpretation is correct, the solubility corresponds to 13×10^{-4} mol dm ⁻³ (compiler).		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Nothing specified.	The salt was prepared by reacting the amine in neutral or weakly acidic solution with a freshly prepared solution of NaBPh ₄ ("Kalignost" from Heyl & Co.). Analysis of the product yielded 3.69% N, as compared to 3.78% theoretical.	
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	

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82	1,4-Butar	nediamine
COMPONENTS:		ORIGINAL MEASUREMENTS:
(1) 1,4-Butanediam bis-tetrapheny $C_{52}H_{54}B_2N_2$;	ine (putrescine) lborate (l-);	Zeidler, L. Hoppe-Seyler's Z. Physiol. Chem. <u>1952</u> , 291, 177-8.
(2) Water; H ₂ O; [7	732-18-5]	
VARIABLES:		PREPARED BY:
Presumably room te	mperature	Orest Popovych
EXPERIMENTAL VALUES:		
The solubilit 0.027%, probably m this interpretatio mol dm ⁻³ (compiler	y of putrescine bis eaning 0.027 g in 1 n is correct, the s).	s-tetraphenylborate was reported as 100 cm ³ of saturated solution. If solubility corresponds to 3.7 x 10 ⁻⁴
	AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCED Nothing specified.	URE:	SOURCE AND PURITY OF MATERIALS: The salt was prepared by reacting the amine in neutral or weakly acidic solution with a freshly pre- pared solution of NaBPh ₄ ("Kalig- nost" from Heyl & Co.). Analysis of the product yielded 3.62% N, as compared to 3.85% theoretical.
		ESTIMATED ERROR: Nothing specified.
		REFERENCES :

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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Butylammonium tetraphenylborate (1-); C₂₈H₃₂BN; [69502-97-2]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of butylammonium reported as: 1.12×10^{-3} methods for a critical evaluation of the data for NH ₄ BPh ₄ in water.	tetraphenylborate in water was nol dm ⁻³ . a from this study, see the evaluation
AUXILIARY	INFORMATION
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS
Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the fil- tered solutions were analyzed for the BPh ₄ anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not stated.	See the compilation for NH ₄ BPh ₄ in water based on the same reference. The amine hydrochloride from which the tetraphenylborate was prepared was an Eastman White Label product. ESTIMATED ERROR: Nothing specified.
	REFERENCES:

Butyltriisopentyl

<pre>COMPONENTS: (1) Butyltriisopentylammonium tetraphenylborate (1-); (Triisoamyl-n-butylammonium tetraphenylborate (1-); C₃₃H₆₂BN; [16742-92-0] (2) Sodium hydroxide; NaOH:</pre>	ORIGINAL MEASUREMENTS: Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u> , 70, 1671-3.	
[1310-73-2] (3) Water: H ₂ O: $[7732-18-5]$		
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The authors report the solubility of triisoamyl-n-butylammonium tetraphenylborate (TAB BPh ₄) in water determined directly by uv-spectro- photometry in the presence of 10 ⁻⁵ mol dm ⁻³ NaOH as an uncertain value:		
$C = 1.4 \times 10^{-10}$	-7?mol dm -3 .	
Because of the tendency of TAB BPh ₄ to decompose upon prolonged equilibration with water, the authors also calculated the solubility indirectly from the transfer activity coefficients (medium effects) as follows:		
$\log_{m} y_{\pm}^{2} (TAB BPh_{\downarrow}) = \log_{m} y_{\pm}^{2} (TAB Pi)$	+ $\log_{m}y_{\pm}^{2}(KBPh_{\mu}) - \log_{m}y_{\pm}^{2}(KPi)$ (1)	
and $\log_m y_{\pm}^2 = 1c$	$\frac{K_{SO}^{\circ} (water)}{K_{SO}^{\circ} (methanol)} $ (2)	
Substituting on the rhs of Equation (1) values of $_{m}y_{\pm}^{2}$ obtained from experimental determinations of solubilities and Equation (2), the authors obtained:		
$\log_{m}y_{\pm}^{2}$ (TAB BPh ₄) = -5.398	+ (-2.300) - 1.101 = -8.799	
Using the above result as well as K_{s0}° (methanol) = 7.36 x 10^{-6} in Equ. (2), they obtained K_{s0}° (water) = 1.17 x 10^{-14} mol ² dm ⁻⁶ (units by compiler), from which the solubility C = 1.08 x 10^{-7} mol dm ⁻³ .		
In the above equations, the transfer activity coefficients refer to the transfer from water to methanol. Pi = picrate ion.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. Saturation achieved by shaking the salt suspensions for 2 weeks in water- jacketed flasks. Solutions filtered and analyzed at 266 and 274 nm. All solutions and containers were deaerated.	TAB BPh ₄ was synthesized and purified by the method of Coplan and Fuoss (1).	
	ESTIMATED ERROR:	
	Not specified. Temperature: ±0.01°C.	
	REFERENCES	
	 (1) Coplan, M. A.; Fuoss, R. M. J. Phys. Chem. <u>1964</u>, 68, 1177. 	

COMPONENTS: (1) Butyltriisopentylammonium tetra- phenylborate (1-) (Triisoamyl-n- butylammonium tetraphenylborate); CapheaBN: [16742-92-0]	Dill, A. J.; Popovych, O. J. Chem. Eng. Data <u>1969</u> , 14, 240-3.
 (2) Lithium chloride; LiCl; [7447-41-8] (3) Ethanol; C₂H₆O; [64-17-5] 	
(4) water; H ₂ U; [//32-18-5]	
VARIABLES: Ethanol-water composition.	PREPARED BY:
200 times molar solubility of	Orest Popovych
C ₃₃ H ₆₂ BN. One temperature: 25.00°C	
EXPERIMENTAL VALUES:	
The authors report the solubility of triiscamyl- <u>n</u> -butylammonium tetraphenylborate (TAB BPh ₄) in ethanol-water mixtures without added LiCl. The solubilities with added LiCl are not reported, but they were used to calculate the activity coefficients of TAB BPh ₄ by a procedure identical with that described in the compilation for KBPh ₄ in ethanol-water mixtures.	
Mass % ethanol in water	Solubility of TAB BPh ₄ , 10^{4} C/mol dm ⁻³
	11 0
	11.8 7.30
80.0	5.94
78.1	4.50
70.0	2.97
60.6	1.48
60.0	1.21
46.0	0.512
40.0	0.210
*Graphically interpolated. Activity of products are tabulated below. The unit Mass % ethanol $\alpha_0(1)$ y_{\pm}, A_1 in water 100.0 0.886 0.842 2.44 78.1 0.986 0.946 0.703 60.6 0.998 0.957 1.17 (The above symbols are from equations methanol)	coefficient data and solubility its of K_{SO}° are mol ² dm ⁻⁶ (compiler) A_2 A_3 $K_{SO}^{\circ} = (C_0 \alpha_0 y_{\pm})^2$ -5.86 8.38 7.74×10^{-7} $$ 1.76×10^{-7} -0.985 $$ 2.00×10^{-8} in the compilation for KBPh ₄ in
methanol.)	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. A solution was considered saturated when successive weekly analyses agreed to about 1%. This required 2 weeks of equilibration for solutions with- out added LiCl and one month for solutions with added LiCl. Solutions filtered and analyzed at 266 and 274 nm. All solutions and containers were deaerated.	TAB BPh ₄ was synthesized and puri- fied by the method of Coplan and Fuoss (2). Purification of ethanol and the preparation of ethanol- water mixtures is described on the compilation sheet for KBPh ₄ in ethanol-water mixtures.
	ESTIMATED ERROR: (For the solubility)
	Precision $\pm 1\%$ Accuracy: $\pm 3\%$ (authors) Temperature: ± 0.01 °C.
	REFERENCES:
	 (1) Dill, A. J.; Popovych, O. J. Chem. Eng. Data <u>1969</u>, 14, 156. (2) Coplan, M. A.; Fuces, R. M.
	J. Phys. Chem. <u>1964</u> , 68, 1177.

ORIGINAL MEASUREMENTS: COMPONENTS: (1) Butyltriisopentylammonium tetraphenylborate (1-) Popovych, O. Anal. Chem. 1966, 38, (Triisoamy1-n-butylammonium tetra-558-63. phenylborate (1-); C33H62BN; [16742-92-0] (2) Toluene; C₇H₈; [108-88-3] (3) Isopropyl alcohol; C₃H₈O; [67-63-0](4) Water; H₂0; [7732-18-5] VARIABLES: PREPARED BY: One temperature: 25.00°C Orest Popovych EXPERIMENTAL VALUES: The author reports as the solubility of triisoamyl-n-butylammonium tetraphenylborate (TAB BPh₄) in the toluene-isopropyl-alcohol-water mixture known as the ASTM medium:* C = 1.09×10^{-4} mol dm⁻³. From a K = 5.62 x 10^{-6} mol dm⁻³, the degree of dissociation α in saturated solution was calculated to be 0.238 and the mean ionic activity coefficient (volume basis) was estimated from the limiting Debye-Huckel law as $y_{\perp}^2 = 0.691$. Combining these, the author arrived at the solubility product of TAB BPh₄ in the ASTM solvent: $K_{s0}^{\circ} = 4.67 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$, (where $K_{s0}^{\circ} = (C_{\alpha} y_{\pm})^2$). *American Society for Testing Materials specifies this solvent for acid-base measurements on petroleum products. AUXILIARY INFORMATION METHOD / APPARATUS / PROCEDURE : SOURCE AND PURITY OF MATERIALS: Electrolytic conductance of diluted TAB BPh₄ was synthesized and purified essentially by the method of Coplan and Fuoss (1). For the purification saturated solutions, using a calibration curve for TAB BPh4 concentration. The conductance apparatus was a Wayne-Kerr Universal Bridge B221 of the solvents, the authors referred with a platinum cell. Saturation was to a literature source (2). achieved by shaking for at least 2 weeks on a Burrell wrist-action shaker in water-jacketed flasks. ESTIMATED ERROR: Not specified. Temperature: ±0.01°C. **REFERENCES**: (1) Coplan, M. A.; Fuoss, R. M. J. Phys. Chem. <u>1964</u>, 68, 1177. (2) Popovych, O. J. Phys. Chem. <u>1962</u>, 66, 915.

CONDONENTES	ODICINAL MEASUDEMENTS.	
<pre>(1) Butyltriisopentylammonium tetra- phenylborate (1-); (triisoamyl- <u>n</u>-butylammonium tetraphenyl- borate (1-); C₃₃H₆₂BN; [16742-92-0]</pre> (2) Lithium ahlarida: LiCl:	Dill, A. J.; Popovych, O. J. Chem. Eng. Data <u>1969</u> , 14, 240-3.	
[7447-41-8] (3) Etherol: CoHeO: [64-17-5]		
VARIABLES:	PREPARED BY:	
200 times the solubility of $C_{3,3}H_{6,2}BN$. One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of triisoamyl- <u>n</u> -butylammonium tetraphenylborate in ethanol without added LiCl was reported as 1.18 x 10^{-3} mol dm ⁻³ . Solubilities with added LiCl were not reported as such, only the activity coefficient derived from the variation of the solubility as a function of ionic strength varied by means of LiCl (for details see compilation for KBPh ₄ in ethanol-water mixtures based on the same literature reference). Using an association constant $K_A = 192 \text{ mol}^{-1} \text{ dm}^3$ (1) the authors computed the degree of dissociation in saturated solution to be $\alpha_s = 0.886$. The experimentally determined mean ionic activity coefficient in saturated solution was reported to be $y_{\pm^{+,0}} = 0.842$. Combining these: $K_{SO}^{\circ} = (1.18 \times 10^{-3} \text{ mol} \text{ dm}^{-3} \times 0.886 \times 0.842)^2 = 7.74 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$.		
METHOD/APPARATOS/PROCEDORE: Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. A solution was considered saturated when successive weekly analyses agreed to about 1%. This required 2 weeks of equilibration for solu- tions without added LiCl and one month for solutions with added LiCl. Solutions filtered and analyzed at 266 and 274 nm. All solutions and containers were deaerated.	Sobker AND Poking of MATERIALS: Triisoamyl- <u>n</u> -butylammonium tetra- phenylborate was synthesized and purified by the method of Coplan and Fuoss (2). Purification of ethanol was described in the compilation for KBPh ₄ in ethanol-water system based on the same reference.	
	ESTIMATED ERROR: (For the solubility) Precision ±1% Accuracy ±3% (authors) Temperature control: ±0.01°C	
	REFERENCES: (1) Dill, A. J.; Popovych, O. J. Chem. Eng. Data 1969, 14, 156. (2) Coplan, M. A.; Fuoss, R. M. J. Phys. Chem. <u>1964</u> , 68, 1177.	

Butyltriisopentyl

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Butyltriisopentylammonium tetra- phenylborate (1-) (Triisoamyl-<u>n</u>- butylammonium tetraphenylborate (1-)); C₃₃H₆₂BN; [16742-92-0] 	Popovych, O.; Friedman, R. M. J. Phys. Chem. 1966, 70, 1671-3.	
(2) Methanol; CH ₄ O; [67-56-1]		
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The authors report the solubility of triisoamyl- <u>n</u> -butylammonium tetraphenylborate (TAB BPh ₄) as:		
$C = 3.60 \times 10^{-3} \text{ mol } dm^{-3}.$		
The solubility (ion-activity) product, K_{SO}° , was calculated by the authors as $(C\alpha y_{\pm})^2$, where the degree of dissociation α was calculated from the following relationship using a literature value (1) for the ion-pair dissociation constant K_A :		
$\alpha = \frac{-1 + (1 + 4K_A Cy_{\pm}^2)^{\frac{1}{2}}}{2}$		
$2K_A Cy \pm^2$ The activity coefficient y _± was estimated from the Debye-Hückel equation in the form:		
$-\log y_{+}^{2} = 3.803 (C\alpha)^{\frac{1}{2}}$ using $a^{2} = 0.7$ nm.		
1 + 0	.5099 $a^{1/2}$	
The above calculations yielded $\alpha = 0.930$ and $y_{\pm}^2 = 0.657$ from which $K_{S0}^{\circ} = 7.36 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$ (compiler's units). The molar absorption coefficients of the tetraphenylborate ion used to calculate the solubilities were reported to be 3.00 x 10^3 and 2.12 x 10^3 dm ³ (cm mol) ⁻¹ at 266 and 274 nm, respectively.		
AUXILIARY	INFORMATION	
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS;	
Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. Saturation achieved by shaking the salt suspensions for 2 weeks in water-jacketed flasks. Solutions filtered and analyzed at 266 and 274 nm. All solutions and containers were deaerated.	Source and purification of methanol the same as described in the compila- tion for potassium tetraphenylborate. TAB BPh ₄ was synthesized and purified by the method of Coplan and Fuoss (1)	
	ESTIMATED ERROR: None stated, but the precision is known to be about ±1% for the solu- bility. Temperature: +0.01°C.	
	REFERENCES: (1) Coplan, M. A.; Fuoss, R. M. J. Phys. Chem. <u>1964</u> , 68, 1177.	
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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Dimethylammonium tetraphenyl- borate (1-); C₂₆H₂₈BN; [69502-98-3]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.	
(2) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of dimethylammon: reported as:	ium tetraphenylborate in water was	
1.63×10^{-5} r	iol dm ⁻³ .	
For a critical evaluation of the data for NH_4BPh_4 in water.	a from this study, see the evaluation	
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
-Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the fil- tered solutions were analyzed for the BPh ₄ - anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not stated.	See the compilation for NH4BPh4 in water based on the same reference. The amine hydrochloride used to pre- pare the tetraphenylborate was an Eastman White Label product.	
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	
	1	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Ethylammonium tetraphenylborate (1-); C₂₆H₂₈BN; [53694-97-6]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.	
(2) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of ethylammonium reported as: 2.83 x 10 ⁻³	tetraphenylborate in water was mol dm ⁻³ .	
For a critical evaluation of the data from this study, see the evaluation for $\mathrm{NH}_4\mathrm{BPh}_4$ in water.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the fil- tered solutions were analyzed for the BPh ₄ ⁻ anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not	See the compilation for NH, BPh, in water based on the same reference. The amine hydrochloride from which the tetraphenylborate was prepared was an East White Label product.	
stated.	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Guanidine tetraphenylborate (1-); C₂₅H₂₆BN₃;</pre>	Zeidler, L. Hoppe-Seyler's Z. Physiol. Chem. <u>1952</u> , 291, 177-8.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Presumably room temperature	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of guanidine tetraphenylborate was reported as 0.14%, probably meaning 0.14 g in 100 cm ³ of saturated solution. If this interpretation is correct, the solubility corresponds to 3.7×10^{-3} mol dm ⁻³ (compiler).	
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AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Nothing specified.	The salt was prepared by reacting the amine in neutral or weakly acidic solution with a freshly prepared solution of NaBPh ₄ ("Kalignost" from Heyl & Co.). Analysis of the product gave 10.43% N as compared to 11.08% theoretical.
	Nothing specified.
	REFERENCES:

2 ⊦	listamine
OMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Histamine bis-tetraphenylborat (1-); C₅₃H₅₁B₂N₃;</pre>	e Zeidler, L. <i>Noppe-Seyler's Z.</i> <i>Physiol. Chem.</i> <u>1952</u> , 291, 177-8.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Presumably room temperature	Orest Popovych
XPERIMENTAL VALUES:	

A	UXILIARY INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Nothing specified.	The salt was prepared by reacting the amine in neutral or weakly acidic solution with a freshly prepared solution of NaBPh4 ("Kalignost" from Heyl & Co.). Analysis of the product gave 5.50% N, as compared to 5.59% theoretical.
	Nothing specified.
	REFERENCES:

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CONDONENTES	ODICINAL MEACHDENGUTC.
COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) lH-Imidazole-4-ethanamine (histidine) tetraphenylborate (1-); C₃₀H₃₀BN₃O₂;</pre>	Zeidler, L. Hoppe-Seyler's Z. Physiol. Chem. <u>1952</u> , 291, 177-8.
(2) Water; H ₂ 0; [7732-18-5]	
VARIABLES:	PREPARED BY:
Presumably room temperature	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of histidine tetr probably meaning 0.24 g in 100 cm ³ of pretation is correct, the solubility (compiler).	raphenylborate was reported as 0.24%, saturated solution. If this inter- corresponds to 5.1 x 10 ⁻³ mol dm ⁻³
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Nothing specified.	The salt was prepared by reacting the amine in neutral or weakly acidic solution with a freshly prepared solution of NaBPh ₄ ("Kalignost" from Heyl & Co.). Analysis of the product yielded 8.01% N, as compared to 8.64% theoretical.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

04 Methylammonium		nmonium
COMPON	ients:	ORIGINAL MEASUREMENTS:
(1)	Methylammonium tetraphenylborate (1-); C ₂₅ H ₂₆ BN; [60337-02-2]	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.
(2)	Water; H ₂ 0; [7732-18-5]	
VARIA	BLES:	PREPARED BY:
One	temperature: 25°C	Orest Popovych
EXPERI	IMENTAL VALUES:	
rep	The solubility of methylammonium orted as:	n tetraphenylborate in water was
For for	3.63×10^{-3} a critical evaluation of the data NH ₄ BPh ₄ in water.	³ mol dm ⁻³ . a from this study, see the evaluation
	AUXILIARY	INFORMATION
METHO	DD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Satu both at 2 ther and equa tere BPh, usin	urated solutions were prepared h by agitating the suspensions 25°C continuously and by agitating m first for a 0.5 hr at 40-50°C then cooling to 25°C. When ilibrium was attained, the fil- ed solutions were analyzed for the anion by UV spectrophotometry, ng a Cary Model 11 recording spec- photometer. The method of temper-	See the compilation for NH4BPh4 in water based on the same reference. Methylammonium tetraphenylborate, prepared from the hydrochloride (Eastman White Label) was <u>not</u> re- crystallized before use.
atui	re control was not stated.	
		ESTIMATED ERROR:
		Nothing specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) 1,5-Pentanediamine (cadaverine) bis-tetraphenylborate (1-); C₅₃H₅₆B₂N₂;</pre>	Zeidler, L. Hoppe-Seyler's Z. Physiol. Chem. <u>1952</u> , 291, 177-8.
(2) Water, H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Presumably room temperature	Orest Popovych
EXPERIMENTAL VALUES:	1

The solubility of cadaverine bis-tetraphenylborate was reported as 0.031%, probably meaning 0.031 g in 100 cm³ of saturated solution. If this interpretation is correct, the solubility corresponds to 4.2×10^{-4} mol dm⁻³ (compiler).

AUXILIARY	INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Nothing specified.	The salt was prepared by reacting the amine in neutral or weakly acidic solution with freshly prepared solu- tion of NaBPh ₄ ("Kalignost" from Heyl & Co.). Analysis of the product gave 3.45% N as compared to 3.77% theoretical.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

so riopyiammonium		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Propylammonium tetraphenylborate (1-); C₂₇H₃₀BN; [6928-94-5]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.	
(2) Water; H ₂ 0; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of propylammonium tetraphenylborate in water was reported as: 9.03 x 10^{-4} mol dm ⁻³ .		
For a critical evaluation of the data from this study, see the evaluatio for $\mathrm{NH}_4\mathrm{BPh}_4$ in water.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the fil- tered solutions were analyzed for the BPh ₄ ⁻ anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not stated.	See the compilation for NH4 BPh4 in water based on the same reference. The amine hydrochloride from which the tetraphenylborate was prepared was an Eastman White Label product.	
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES :	

Pyridinium		
COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Pyridinium tetraphenylborate (1-); C_{29H26}BN; [50328-28-4]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.	
(2) Water, H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of pyridinium tetraphenylborate in water was reported as:		
1.99 x 10 ⁻⁴	mol dm^{-3} .	
For a critical evaluation of the data from this study, see the evaluation for $\mathrm{NH}_4\mathrm{BPh}_4$ in water.		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the filtered solutions were analyzed for the BPh ₄ ⁻ anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not stated.	See the compilation for NH ₄ BPh ₄ in water based on the same reference. To an ethanolic solution of pyridine (Eastman White Label) HClO ₄ was added slowly and the perchlorate recrystal- lized from the water-ethanol was used to prepare the tetraphenylborate.	
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Tetra-<u>n</u>-butylammonium tetra- phenylborate (1-); C₄₀H₅₆BN; [15522-59-5] (2) Sodium hydroxide; NaOH; [1310-73-2] (3) Water; H₂O; [7732-18-5] 	Popovych, O; Friedman, R. M. <i>J. Phys. Chem</i> . <u>1966</u> , 70, 1671-3.	
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES: The authors report the solubility of tetra-n-butylammonium tetra- phenylborate ($Bu_4N BPh_4$) in water determined directly by uv-spectro- photometry in the presence of 10^{-5} M NaOH as an uncertain value:		
$C = 3.4 \times 10^{-6}$? m	ol dm ⁻³ .	
Because of the tendencey of Bu ₄ N BPh ₄ to decompose upon prolong equilibra- tion with water, the authors also calculated the solubility indirectly, via transfer activity coefficients (medium effects) as follows:		
$\log_{m} y_{\pm}^{2} (Bu_{4} N BPh_{4}) = \log_{m} y_{\pm}^{2} (Bu_{4} N P)$	L) + $\log_{m}y_{\pm}^{2}(KBPh_{4}) - \log_{m}y_{\pm}^{2}(KPi)$ (1)	
where $_{m}y_{\pm}$ is the mean molar medium effect for the eletrolyte in methanol (i.e., the activity coefficient for the transfer water \rightarrow methanol) and Pi is the picrate ion.		
Values of log $_{m}y_{\pm}$ for the electrolytes on the rhs of the above equation were obtained from the experimentally determined solubility products:		
$\log_{m} y_{\pm}^{2} = \log \frac{K_{\$0} \text{ (water)}}{K_{\$0} \text{ (methanol)}} $ (2)		
then: $\log_{m}y_{\pm}^{2}(Bu_{4}N BPh_{4}) = -4.438 + (-2.300) - 1.101 = -7.839$		
introducing in equation (2) the above result as well as $K_{SO}^{\circ} = 4.62 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$ in methanol, the authors obtained $K_{SO}^{\circ} = 6.69 \times 10^{-14}$ (water) from which the solubility C = 2.59 x 10^{-7} mol dm ⁻³ .		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry using a Cary Model 14 spectrophotometer. Satura- tion achieved by shaking the salt suspensions for 2 weeks in water- jacketed flasks. Solutions filtered and analyzed at 266 and 274 nm. All solutions and containers were deaerated.	Bu ₄ N BPh ₄ was synthesized and purified as described in the literature (1).	
	ESTIMATED ERROR:	
	Not specified. Temperature: ±0.01°C	
	REFERENCES:	
	(1) Accascina, F.; Petrucci, S. Fuoss, R. M. J. Am. Chem. Soc. <u>1959</u> , 81, 1301.	

Tetra- <i>n</i> -butylammonium	
COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tetra- <u>n</u> -butylammonium tetra- phenylborate (1-); C ₄₀ H ₅₆ BN; [15522-59-5]	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
(2) 1,1-Dichloroethane; C ₂ H ₄ Cl ₂ ; [75-34-3]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES: The authors reported the solubility of Bu_4NBPh_4 in 1,1-dichloroethane as: 5.09 x 10 ⁻³ mol dm ⁻³ . Using an estimated association constant of 1.03 x 10 ⁴ mol ⁻¹ dm ³ and an ion-size parameter of $a = 0.68$ nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained for the standard Gibbs free energy of solution: $\Delta G_S^{\circ} = 8.78$ kcal mol ⁻¹ = 36.8 kJ mol ⁻¹ (compiler). The solubility (ion-activity) product of Bu_4NBPh_4 can be calculated from the relationship: $\Delta G_S^{\circ} = -RT$ ln K_{SO}° , yielding $pK_{SO}^{\circ} = 6.437$, where K_{SO}° units are mol ² dm ⁻⁶ (compiler).	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distillation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Bu ₄ NBPh ₄ was recrystallized from aqueous acetone and vacuum dried at 60-80°C for several days.
	ESTIMATED ERROR:
	Precision of 0.1 kcal mol ⁻¹ in ΔG_{S}° .
	REFERENCES:

ORIGINAL MEASUREMENTS: COMPONENTS: Abraham, M. H. Danil de Namor, A. F. (1) Tetra-n-butylammonium tetra-J. Chem. Soc. Faraday Trans. 1 1976, phenylborate (1-); C40H56BN; [15522-59-5] 72, 955-62. (2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2] VARIABLES: PREPARED BY: One temperature: 25°C Orest Popovych EXPERIMENTAL VALUES: The authors reported the solubility of Bu, NBPh, in 1,2-dichloroethane as: $2.24 \times 10^{-1} \text{ mol } \text{dm}^{-3}$. Using an association constant of $1.715 \times 10^3 \text{ mol}^{-1} \text{ dm}^3$ (1) and an ion-size parameter of $a^{2} = 0.68$ nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained for the standard Gibbs free energy of solution: $\Delta G_{s}^{\circ} = 5.76 \text{ kcal mol}^{-1}$ $= 24.1 \text{ kJ mol}^{-1} \text{ (compiler)}.$ The solubility (ion-activity) product of Bu4NBPh4 can be calculated from the relationship: $\Delta G_{s}^{\circ} = -RT \ln K_{s0}^{\circ}$, yielding $pK_{s0}^{\circ} = 4.223$, where K_{s0}° units are mol² dm⁻⁶ (compiler). AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS: Evaporation and weighing. Saturated The solvent was shaken with anhydrous solutions prepared by shaking the K_2CO_3 , passed through a column of suspensions for several days at 25°C. basic activated alumina into distil-No solvate was detected. Method of lation flask and fractionated under temperature control was not N2 through a 3-foot column. At least 10% of distillate was rejected, the specified. rest collected over freshly activated molecular sieve. Bu4NBPh4 was recrystallized from aqueous acetone and vacuum dried at 60-80°C for several days. ESTIMATED ERROR: Precision of 0.1 kcal mol⁻¹ in ΔG_c° . **REFERENCES:** (1) D'Aprano, A.; Fuoss, R. M. J. Solution Chem. <u>1975</u>, 4, 175.

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Tetra- <u>n</u> -butylammonium tetra- phenylborate (1-); $C_{40}H_{56}BN$; [15522-59-5]	Popovych, O.; Friedman, R. M. J. Phys. Chem. <u>1966</u> , 70, 1671-3.	
(2) Methanol; CH ₄ 0; [67-56-1]		
VARIABLES :	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES:	1	
The authors report the solubility of tetra-n-butylammonium tetraphenylborate (Bu ₄ N BPh ₄) in methanol as		
$C = 2.58 \times 10^{-3} \text{ mol } dm^{-3}.$ The solubility product, K_{SO}° , was calculated by the authors as $(C\alpha y_{\pm})^2$ where the degree of dissociation α was obtained using a literature value of the ion-pair dissociation constant K_A (1) and the following expression:		
$\alpha = \frac{-1 + (1 + 4K_A Cy_{\pm}^2)^{\frac{1}{2}}}{2}$. The mean $\alpha = \frac{-1}{2}$	an ionic activity coefficient	
$x = \frac{2K_A Cy_2^2}{2K_A Cy_2^2}$ y ₊ was estimated from the Debye-Hückel equation in the form:		
$-\log y_{\pm}^2 = 3.803 (C_{\alpha})^{\frac{1}{2}}$ using $\frac{a}{2}$	= 0.7 nm.	
$1 + 0.5099 a(C\alpha)^{\frac{1}{2}}$		
The above calculations yielded $\alpha = 0.940$ and $y_{\pm}^2 = 0.786$ from which $K_{SO}^{\circ} = 4.62 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}$ (compiler's units). The molar absorption coefficients of the tetraphenylborate ion used to calculate the solubilities were reported to be 3.00 x 10^3 and 2.12 x 10^3 dm ³ (cm mol) ⁻¹ at 266 and 274 nm, respectively.		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry using a Cary Mo- del 14 spectrophotometer. Saturation achieved by shaking the salt suspen- sions for 2 weeks in water-jacketed flasks. Solutions filtered and ana- lyzed at 266 and 274 nm. All solu- tions and containers were deaerated.	Source and purification of methanol the same as described in the com- pilation for potassium tetraphenyl- borate in methanol. Bu N BPh, was synthesized and purified as described in the literature (1).	
	ESTIMATED ERROR:	
	Not specified, but the precision is known to be about ±1% for solubility. Temperature: ±0.01°C.	
	 REFERENCES: (1) Coplan, M. A.; Fuoss, R. M. J. Phys. Chem. <u>1964</u>, 68, 1177. (2) Accascina, F.; Petrucci, S.; Fuoss, R. M. J. Am. Chem. Soc. <u>1959</u>, 81, 1301. 	

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetra-n-butylammonium tetra- phenylborate (1-); C₄₀H₅₆BN; [15522-59-5]</pre>	Virtanen, P. O. I.; Kerkelä, R. Suom. Kemistil. <u>1969</u> , B49, 29-33.
<pre>(2) l-Methyl-2-pyrrolidinone (N-methyl-2-pyrrolidone) C₅H₉NO; [872-50-4]</pre>	
VARIABLES:	PREPARED BY:
Two temperatures: 25.00°C and 45.00°C.	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of <u>n</u> -Bu ₄ NBPh ₄ reported to be 0.964 mol dm ⁻³ at 25°C The corresponding solubility square of the solubility, was reported units are mol ² dm ⁻⁶ . The solubility p	in N-methyl-2-pyrrolidone was and 1.08 mol dm ⁻³ at 45°C. product at 25°C, calculated as the in the form pK _{SO} ⁼ 0.03, where K _{SO} roduct at 45°C was not reported.
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
The suspensions were shaken in thermo- statted water-jacketed flasks for one day at 50°C, followed by one day at 25°C or 45°C, respectively. Saturated solutions were analyzed gravimetric- ally after precipitation of KBPh ₄ or NH ₄ BPh ₄ from aliquots in aqueous solution.	N-methyl-2-pyrrolidone (General Aniline & Film Co.) was purified as in the literature (1). <u>n</u> -Bu ₄ NBPh ₄ was prepared by metathesis of aqueous NaBPh ₄ with methanolic <u>n</u> -Bu ₄ NI, followed by double recrystallization from an acetone-water mixture and drying <u>in vacuo</u> .
	ESTIMATED ERROR:
	Not specified. Temperature control: ±0.02°C
	REFERENCES :
	(1) Virtanen, P. O. I. Suom. Kemistil. <u>1966</u> , B39, 257.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraethylammonium tetraphenyl- borate (1-); C₃₂H₄₀BN; [12099-10-4]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
(2) 1,1-Dichloroethane; $C_2H_4Cl_2$; [75-34-3]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

The authors reported the solubility of Et_4NBPh_4 in 1,1-dichloroethane as: 4.14 x 10⁻⁴ mol dm⁻³. Using an estimated association constant of 1.50 x 10⁴ mol⁻¹ dm³ and an ion-size parameter a = 0.64 nm with which to calculate the mean ionic activity coefficient from the extended Debye-Huckel equation, they obtained for the standard Gibbs free energy of solution:

 $\Delta G_{s}^{\circ} = 10.64 \text{ kcal mol}^{-1} = 44.54 \text{ kJ mol}^{-1} \text{ (compiler)}.$

The solubility (ion-activity) product of Et_4NBPh_4 can be calculated from the relationship: $\Delta G_s^{\circ} = -RT \ln K_{s0}^{\circ}$, yielding $pK_{s0}^{\circ} = 7.801$, where K_{s0}° units are mol² dm⁻⁶ (compiler).

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not speci- fied.	SOURCE AND PURITY OF MATERIALS: The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Et ₄ NBPh ₄ was re- crystallized from aqueous acetone and vacuum dried for several days at 60-80°C. ESTIMATED ERROR: Precision of 0.1 kcal mol ⁻¹ in ΔG_s . REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraethylammonium tetraphenyl- borate (1-); C₃₂H₄₀BN; [12099-10-4]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
<pre>(2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
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EXPERIMENTAL VALUES:	
The authors reported the solubility of Et_4NBPh_4 in 1,2-dichloroethane as: 8.40 x 10 ⁻³ mol dm ⁻³ . Using an estimated association constant of 2.50 x 10 ³ mol ⁻¹ dm ³ and an ion-size parameter of $\mathring{a} = 0.64$ nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained for the standard Gibbs free energy of solution: $\Delta G_S^\circ = 7.88$ kcal mol ⁻¹ = 33.0 kJ mol ⁻¹ (compiler). The solubility (ion-activity) product of Et ₄ NBPh ₄ can be calculated from the relationship: $\Delta G_S^\circ = -RT \ln K_{SO}^\circ$, yielding $pK_{SO}^\circ = 5.777$, where K_{SO}° units are mol ² dm ⁻⁶ (compiler).	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS.
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Et ₄ NBPh ₄ was re- crystallized from aqueous acetone and vacuum dried for several days at 60-80°C.
	ESTIMATED ERROR:
	Precision of 0.1 kcal mol ⁻¹ in ΔG_{S}° .
	REFERENCES:

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COMPONENTS: (1) Tetraethylammonium tetraphenyl- borate (1-); C ₃₂ H ₄₀ BN; [12099-10-4]	ORIGINAL MEASUREMENTS: Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1978</u> , 74, 2101-10.
(2) 1-Propanol; C ₃ H ₈ O; [71-23-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	I
The solubility of Et_4NBPh_4 i	n l-propanol was reported as:
4.03×10^{-4}	mol dm- ³ .
Using an estimated association consta ion-size parameter of 0.65 nm with wh activity coefficient from the extende obtained for the standard Gibbs free	nt of 800 mol ⁻¹ dm ³ (1) and an ich to calculate the mean ionic d Debye-Hückel equation, the authors energy of solution:
$\Delta G_{s}^{\circ} = 9.66 \text{ kcal mol}^{-1}$, which is 40	.42 kJ mol ⁻¹ (compiler).
The solubility (ion-activity) product of Et_4NBPh_4 can be calculated from the relationship $\Delta G_S^\circ = -RT \ln K_{SO}^\circ$, yielding $pK_{SO}^\circ = 7.082$, where K_{SO}° units are mol ² dm ⁻⁶ (compiler).	
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AUXILIARY	
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions were prepared by shaking the suspensions for several days. The solvent contained no involatile material and the solute formed no solvate. Method of temperature control was not specified.	SOURCE AND PURITY OF MATERIALS: The purification of the solvent was described in the literature (2). Et ₄ NBPh ₄ was recrystallized from aqueous acetone and vacuum dried for several days at 60-80°C.
	ESTIMATED ERROR.
	Precision of 0.15 kcal mol ⁻¹ in ΔG_s° .
	REFERENCES: (1) Abraham, M. H.; Lee, W. H.; Wheaton, R. S. J. Solution Chem. in press.
	 (2) Abraham, M. H.; Danil de Namor, A. F.; Schulz, R. A. J. Solution Chem. 1977, 6, 491.

COMPONENTS:	EVALUATOR:
<pre>(1) Tetramethylammonium tetraphenyl- borate (1-); C₂₈H₃₂BN; [15525-13-0]</pre>	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn N. Y. 11210 U.S. A
(2) Water; H ₂ 0; [7732-18-5]	March 1980

CRITICAL EVALUATION:

Although the solubility of tetramethylammonium tetraphenylborate in water was reported from two different studies (1,2), there is no doubt as to which of them is the more reliable. Thus, the solubility reported by Zeidler (1) as 0.05% is not only ambiguous and expressed to one significant digit, but also was determined by an unspecified analytical method at an unspecified (presumably room) temperature. On the other hand, the value reported by Howick and Pflaum (2) as 4.3×10^{-5} mol dm⁻³ was obtained by uv-spectrophotometry at 298 K under conditions where saturation was ascertained.

There are unfortunately two drawbacks in the latter study as well. First, the extent to which the temperature was controlled is not specified. Second, it is not clear which values of the absorption coefficients ε_{max} for the tetraphenylborate ion were used to calculate the solubilities. This question arises because of the fact that in an earlier study Pflaum and Howick (3) used ε_{max} values characteristic of a cetonitrile solutions to calculate solubilities in aqueous solutions from their absorption data. The molar ε_{max} values used by Pflaum and Howick (3) were 3.225×10^3 and 2.110×10^3 at 266 nm and 274 nm, respectively, while the corresponding values reported for aqueous solutions are 3.25×10^3 and 2.06×10^3 , respectively (4). (All molar absorption coefficients are in the units of dm³ (cm mol)⁻¹). Thus, if Howick and Pflaum (2) averaged the solubility values determined at the two wavelengths, they benefitted from a compensation of errors, which in the case of the solubility of KBPh4 in water (3) led to excellent agreement with other literature data (see critical evaluation for KBPh4 in water). However, one cannot be certain that a similar compensation of errors was involved in the case of tetramethylammonium tetraphenylborate. Consequently, the solubility of 4.3 x 10^{-5} mol dm⁻³ at 298 K must be regarded as a highly <u>tentative value</u>.

REFERENCES:

- 1. Zeidler, L. Hoppe-Seyler's Z. Physiol. Chem. 1952, 291, 177.
- 2. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta 1958, 19, 343.
- 3. Pflaum, R. T.; Howick, L. C. Anal Chem. 1956, 28, 1542.
- 4. Popovych, O.; Friedman, R. M. J. Phys. Chem. 1966, 70, 1671.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetramethylammonium tetraphenyl- borate (1-); C₂₈H₃₂BN; [15525-13-0]</pre>	Zeidler, L. Hoppe-Seyler's Z. Physiol. Chem. <u>1952</u> , 291, 177-8.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
Presumably room temperature	Orest Popovych

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The solubility of tetramethylammonium tetraphenylborate was reported as 0.05%, probably meaning 0.05 g in 100 cm³ of saturated solution. If this interpretation is correct, the solubility corresponds to $1._3 \times 10^{-3}$ mol dm⁻³ (compiler).

A	UXILIARY INFORMATION
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS; The salt was prepared by reacting
Nothing specified.	tetramethylammonium hydroxide (it isn't clear whether its solution was adjusted to neutrality or slight acidity as in the case of other bases in this study) with a freshly pre- pared solution of NaBPh4 ("Kalignost" from Heyl & Co.). Analysis of the product yielded 3.28% N, as compared to 3.56% theoretical.
	ESTIMATED ERROR: Nothing specified.
ς.	REFERENCES:

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		Tetran	nethylammonium
S:			ORIGINAL M

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetramethylammonium tetraphenyl- borate (1-); C₂₈H₃₂BN; [15525-13-0]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.
(2) Water, H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of tetramethy water was reported as:	lammonium tetraphenylborate in
4.3×10^{-5}	$5 \text{ mol } dm^{-3}$.
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Saturated solutions were prepared both by agitating the suspensions at 25°C continuously and by agitat- ing them first for a 0.5 hr at 40- 50°C and then cooling to 25°C. When equilibrium was attained, the fil- tered solutions were analyzed for the BPh ₄ anion by UV spectrophoto- metry, using a Cary Model 11 record- ing spectrophotometer. The method of temperature control was not stated.	See the compilation for NH4BPh4 in water based on the same reference. The amine hydrochloride used to pre- pare the tetraphenylborate was an Eastman White Label product.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES :

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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetramethylammonium tetraphenyl- borate (1-); C₂₈H₃₂BN; [15525-13-0]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
<pre>(2) 1,1-Dichloroethane; C₂H₄Cl₂; [75-34-3]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reported the solution ethane as: $7.21 \times 10^{-5} \text{ mol dm}^{-3}$. Using an estimated association constation size parameter of $\&$ = 0.62 nm with white activity coefficient from the extended for the standard Gibbs free energy of	ubility of Me ₄ NBPh ₄ in 1,1-dichloro- nt of 7.44 x 10 ⁴ mol ⁻¹ dm ³ and an ion- ich to calculate the mean ionic d Debye-Hückel equation, they obtained solution:
$\Delta G_{s}^{\circ} = 12.59 \text{ kcal mol}^{-1} =$	52.70 kJ mol ⁻¹ (compiler).
The solubility (ion-activity) product the relationship:	of Me_4NBPh_4 can be calculated from
$\Delta G_s^\circ = -RT$ 1n K_{s0}° , yielding $pK_{s0}^\circ = 9.23$ (compiler).	30, where K _{SO} units are mol ² dm ⁻⁶
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Me ₄ NBPh ₄ was recrystallized from acetone and vacuum dried at 60-80°C for several days.
	ESTIMATED ERROR:
	Precision of 0.1 kcal mol ⁻¹ in ΔG_S° .
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetramethylammonium tetraphenyl- borate (1-); C₂₈H₃₂BN; [15525-13-0]</pre>	Abraham, M. H.; Danil de Namor A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
(2) 1,2-Dichloroethane; C ₂ H ₄ Cl ₂ ; [107-06-2]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reported the solubil as: 4.12×10^{-4} mol dm ⁻³ . Using an estimated association consta- ion-size parameter of a = 0.62 nm with activity coefficients from the extend obtained for the standard Gibbs free $\Delta G_s^2 = 10.56$ kcal mol ⁻¹ = The solubility (ion-activity) product	lity of Me_4NBPh_4 in 1,2-dichloroethane ant of 1.24 x 10^4 mol ⁻¹ dm ³ and an th which to calculate the mean ionic ded Debye-Hückel equation, they energy of solution: 44.20 kJ mol ⁻¹ (compiler).
the relationship: $\Delta G_S^{\circ} = -RT \ln K_{SO}^{\circ}$, units are mol ² dm ⁻⁶ (compiler).	yielding pK _{SO} = 7.742, where K _{SO}
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	SOURCE AND PURITY OF MATERIALS: The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Me ₄ NBPh ₄ was re- crystallized from acetone and vacuum dried for several days at 60-80°C.
	ESTIMATED ERROR: Precision of 0.1 kcal mol ⁻¹ in ΔG_{s}° .
	REFERENCES :

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetramethylammonium tetraphenyl- borate (1-); C₂₈H₃₂BN; [15525-13-0]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1978</u> , 74, 2101-10.
(2) 1-Propanol; C ₃ H ₈ O; [71-23-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

The solubility of Me_4NBPh_4 in 1-propanol was reported as:

 $1.07 \times 10^{-4} \text{ mol } dm^{-3}$.

Using an estimated association constant of $1300 \text{ mol}^{-1} \text{ dm}^3$ (1) and an ionsize parameter of 0.60 nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, the authors obtained for the standard Gibbs free energy of solution:

 $\Delta G_{S}^{\circ} = 11.06 \text{ kcal mol}^{-1}$, which is 46.28 kJ mol}^{-1} (compiler).

The solubility (ion-activity) product of Me_4NBPh_4 can be calculated from the relationship $\Delta G_s^\circ = -RT \ln K_{s0}^\circ$, yielding $pK_{s0}^\circ = 8.109$, where K_{s0}° units are mol² dm⁻⁶ (compiler).

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions were prepared by shaking the suspensions for several days. The solvent contained no involatile material and the solute formed no solvate. Method of temperature control was not specified.	SOURCE AND PURITY OF MATERIALS: The purification of the solvent was described in the literature (2). Me ₄ NBPh ₄ was recrystallized from acetone and vacuum dried for several days at 60-80°C.
	 ESTIMATED ERROR: Precision of 0.15 kcal mol⁻¹ in ΔG^o_S. REFERENCES: (1) Abraham, M. H.; Lee, W. H.; Wheaton, R. S. J. Solution Chem., in press. (2) Abraham, M. H.; Danil de Namor, A. F.; Schulz, R. A. J. Solution Chem. 1977, 6, 491.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetrapropylammonium tetraphenyl- borate (1-); C₃₆H₄₈BN; [15556-39-5]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
<pre>(2) 1,1-Dichloroethane; C₂H₄Cl₂; [75-34-3]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reported the solubil as: 2.61 x 10^{-3} mol dm ⁻³ . Using an estimated association consta- ion-size parameter $a = 0.66$ nm with v activity coefficient from the extender for the standard Gibbs free energy of $\Delta G_s^2 = 9.30$ kcal mol ⁻¹ = The solubility (ion-activity) product the relationship: $\Delta G_s^2 = -RT \ln K_{SO}^2$, units are mol ² dm ⁻⁶ (compiler).	<pre>lity of Pr₄NBPh₄ in 1,1-dichloroethane ant of 1.26 x 10⁴ mol⁻¹ dm³ and an which to calculate the mean ionic ed Debye-Hückel equation, they obtained solution: 38.9 kJ mol⁻¹ (compiler). of Pr₄NBPh₄ can be calculated from yielding pK^o_{SO} = 6.818, where K^o_{SO}</pre>
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Evaporation and weighing. Saturated solutions were prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distillation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Pr_4NBPh_4 was recrystallized from aqueous acetone and vacuum dried for several days at 60-80°C.
	ESTIMATED ERROR:
	Precision of 0.1 kcal mol ⁻¹ in ΔG_{g}° .
	REFERENCES:

Tetrapropylammonium		113	
COMPON	JENTS :	ORIGINAL MEASUREMENTS:	
(1)	Tetrapropylammonium tetraphenyl- borate (1-); C ₃₆ H ₄₈ BN; [15556-39-5]	Abraham. M. H.; Danil de Namor A. F. J. Chem. Soc. Faraday Trans. <u>1976</u> , 72, 955-62.	1
(2)	1,2-Dichloroethane; C ₂ H ₄ Cl ₂ ; [107-06-2]		
VARIAE	BLES:	PREPARED BY:	
One	temperature: 25°C	Orest Popovych	
as: Usin ion- acti for The rela are	The authors reported the solubil 1.01 x 10 ⁻¹ mol dm ⁻³ . ag an estimated association constant size parameter of $a = 0.66$ nm with vity coefficient from the extended the standard Gibbs free energy so $G_s^\circ = 6.33$ kcal mol ⁻¹ = solubility (ion-activity) product tionship: $\Delta G_s^\circ = -RT$ ln K_{s0}° , yiel mol ² dm ⁻⁶ (compiler).	Lity of Pr_4NBPh_4 in 1,2-dichloroethan ant of 2.10 x 10 ³ mol ⁻¹ dm ³ and an th which to calculate the mean ionic ed Debye-Hückel equation, they obtain fution: 26.5 kJ mol ⁻¹ (compiler). to of Pr_4NBPh_4 can be calculated from ding $pK_{SO}^* = 4.640$, where K_{SO}^* units	e

AUXILIARY INFORMATION

METHOD / APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS.
Evaporation and weighing. Saturated	The solvent was shaken with aphydrous
solutions prepared by shaking the	K_2CO_3 , passed through a column of
suspensions for several days at 25°C.	basic activated alumina into distil-
No solvate was detected. Method of	lation flask and fractionated under
temperature control was not	N ₂ through a 3-foot column. At least
specified.	10% of distillate was rejected, the
•	rest collected over freshly activated
	molecular sieve. Pr. NBPh, was re-
	crystallized from aqueous acetone and
	vacuum dried for several days at
	60-80°C.
	ESTIMATED ERROR:
	Precision of 0.1 kcal mol ⁻¹ in ΔG_s° .
	5
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetrapropylammonium tetraphenyl- borate (1-); C₃₆H₄₈BN; [15556-39-5]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1978</u> , 74, 2101-10.
(2) 1-Propanol; C ₃ H ₈ O; [71-23-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of $\mathtt{Pr}_4\mathtt{NBPh}_4$ in	1-propanol was reported as:
$6.40 \times 10^{-4} m$	ol dm ⁻³ .
Using an estimated association constant ion-size parameter of 0.50 nm with whith activity coefficient from the extended obtained for the standard Gibbs free	nt of 670 mol ⁻¹ dm ³ (1) and an ich to calculate the mean ionic d Debye-Hückel equation, the authors energy of solution:
ΔG_{s}° = 9.19 kcal mol ⁻¹ , which is 3	8.45 kJ mol ⁻¹ (compiler).
The solubility (ion-activity) product from the relationship $\Delta G_{s}^{\circ} = -RT \ln K_{SO}^{\circ}$ units are mol ² dm ⁻⁶ (compiler).	of $Pr_4 NBPh_4$ can be calculated , yielding $pK_{SO}^{\circ} = 6.738$, where K_{SO}°
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions were prepared by shaking the suspensions for several days. The solvent contained no involatile material and the solute formed no solvate. Method of temperature control was not specified.	SOURCE AND PURITY OF MATERIALS: The purification of the solvent was described in the literature (2). Pr ₄ NBPh ₄ was recrystallized from aqueous acetone and vacuum dried for several days at 60-80°C.
	ESTIMATED ERROR:
	rectation of 0.13 Keat mot - in 20g.
	REFERENCES :
	 Abraham, M. H.; Lee, W. H.; Wheaton, R. S. J. Solution Chem. in press. Abraham, M. H.; Danil de Namor, A. F.; Schulz, R. A. J. Solution Chem. <u>1977</u>, 6, 491.

Trimethy	lammonium	115
COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Trimethylammonium tetraphenyl- borate (1-); C₂₇H₃₀BN; [51016-92-3]</pre>	Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 343-7.	
(2) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
The solubility of trimethylammo reported as: 3.87×10^{-4}	nium tetraphenylborate in water was mol dm ⁻³ .	
The solubility of trimethylammo reported as:	nium tetraphenylborate in water was	
For a critical evaluation of the dat for $\mathrm{NH}_4\mathrm{BPh}_4$ in water.	a from this study, see the evaluatio	n

ATTATA DV	INFORMATION
AUXILIARI	INFORMATION

Saturated solutions were prepared both by agitating the suspensions continuously at 25°C and by agitating them first for a 0.5 hr at 40-50°C and then cooling to 25°C. When equilibrium was attained, the filtered solutions were analyzed for the BPh₄- anion by UV spectrophotometry, using a Cary Model 11 recording spectrophotometer. The method of temperature control was not stated. SOURCE AND PURITY OF MATERIALS:

See the compilation for $NH_{4}BPh_{4}$ in water based on the same reference. The amine hydrochloride used to prepare the tetraphenylborate was an Eastman White Label product.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
 Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆; Organic Solvents 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. October 1979

CRITICAL EVALUATION:

There is only one published value for the solubility of tris(o-phenanthroline)ruthenium(II) tetraphenylborate in each of the 22 organic solvents at 298 K as given in the compilations that follow (1). Unfortunately, the accuracy of these solubility values is probably adversely affected by two shortcomings: 1) The molar absorption coefficient of the cation, which was used to calculate the solubiluty in different organic solvents was characteristic of aqueous solutions and 2) the precision of the temperature control was not specified. Consequently, the reported solubility values must be disignated as no better than <u>tentative</u>.

REFERENCE:

1. Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u>, 47, 1285.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Benzyl alcohol; C ₇ H ₈ O; [100-51-6]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

The solubility of $Ru(phen)_3(BPh_4)_2$ in benzyl alcohol was reported as: 2.68 x 10^{-4} mol dm⁻³.

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
<pre>(2) 2-Butanone (ethyl methyl ketone); C₄H₈O; [78-93-3]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (BPh ₄) ₂ in 2-butanone was reported as:
2.45 x 10 ⁻³	mol dm ⁻³ .
AUXILIARY	INFORMATION .
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) in acetone based on the same lit. ² reference.
	ECTIMATED EDDODA
	LOTITUTED ERROR;
	Nothing specified.
	REFERENCES:

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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan 1974, 47, 1285-6.
(2) <u>sec</u> -Butyl alcohol (2-butanol); $C_{4}H_{10}$; [78-92-2]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (BPh	4) ₂ in 2-butanol was reported as:
2.05×10^{-6}	mol dm^{-3} .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) (BPh) in acetone based on the same lit. ⁴ 2 reference.
	ESTIMATED ERROR:
	Nothing specified.
-	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthernium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) <u>n</u> -Butyl ethanoate (<u>n</u> -butyl ace- tate); $C_6H_{12}O_2$; [123-86-4]	
VARIABLES:	PREPARED BY:
	Orest Popovych
One temperature: 25°C	
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (BPh ₄) ₂ in <u>n</u> -butyl acetate was reported as:
5.94×10^{-7}	mol dm ⁻³ .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

COMPON	IENTS:	ORIGINAL MEASUREMENTS:
(1)	Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC ₈₄ H ₆₄ B ₂ N ₆ ;	Takamatsu, T. Bull Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2)	Chlorobenzene; C ₆ H ₅ Cl; [108-90-7]	
VARIAB	BLES:	PREPARED BY:
One	temperature: 25°C	Orest Popovych
EXPERI	MENTAL VALUES:	1

The solubility of $Ru(phen)_3(BPh_4)_2$ in chlorobenzene was reported as: 7.03 x 10^{-6} mol dm⁻³.

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR: Nothing specified.
	REFERENCES :

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) bis-2-Chloroethyl ether; C ₄ H ₈ Cl ₂ O; [111-44-4]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ was reported as:	(BPh ₄) ₂ in bis-2-chloroethyl ether
$1.26 - 10^{-2}$	3
$1.26 \times 10^{-2} \text{ mc}$)1 dm ⁻³ .
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:
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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Chloroform; CHCl ₃ ; [67-66-3]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

The solubility of $Ru(phen)_3(BPh_4)_2$ in chloroform was reported as:

 $1.29 \times 10^{-4} \text{ mol } dm^{-3}$.

AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	SOURCE AND PURITY OF MATERIALS: See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR: Nothing specified. REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
<pre>(2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of $Ru(phen)_3(BPh_4)_2$ in 1,2-dichloroethane was reported as:	
$4.18 \times 10^{-4} \text{ mol } dm^{-3}$.	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES -
	INT EVENCES ;
Tris(o-phenanthroline)ruthenium(II)

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
<pre>(2) 3,3-Dimethyl-2-butanone (methyl isobutyl ketone); C₆H₁₂O; [75-97-8]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (was reported as: 6.92 x 10	$BPh_4)_2$ in methyl isobutyl ketone ⁻⁴ mol dm ⁻³ .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ROMINATED DDDOD
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:
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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Ethanol; C ₂ H ₆ O; [64-17-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
	The other of the reported act
The solubility of $Ru(phen)_3(B)$	rn4)2 in ethanoi was reported as:
1.30 x 10	D^{-5} mol dm ⁻³ .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see	See compilation for $\operatorname{Ru}(\operatorname{phen})_3(\operatorname{BPh}_4)_2$
acetone based on the same lit.	reference.
reference.	
	ESTIMATED ERROR:
	Nothing specified.
	KEFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Ethyl ethanoate (ethyl acetate); $C_4H_8O_2$; [141-78-6]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

EXPERIMENTAL VALUES:

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The solubility of $Ru(phen)_3(BPh_4)_2$ in ethyl acetate was reported as:

5.41 x 10^{-7} mol dm⁻³.

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	SOURCE AND PURITY OF MATERIALS: See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR: Nothing specified. REFERENCES:

COMPONENTS: (1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC ₈₄ H ₆₄ B ₂ N ₆ ;	ORIGINAL MEASUREMENTS: Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Isopropyl alcohol; C ₃ H ₈ O; [67-63-0]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ () reported as:	3Ph ₄) ₂ in isopropyl alcohol was
5.41 x 10 ⁻⁰	⁵ mol dm ⁻³ .
AUXILIARY	INFORMATION
METHOD / AP PARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see	See compilation for Ru(phen) ₃ (BPh ₄) ₂
acetone based on the same lit.	in acetone based on the same lit. reference.
reference.	
	RETIMATED EDDOD.
	LOTIMATED ERROR:
	Nothing specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Isopropyl ether; C ₆ H ₁₄ O; [108-20-3]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	

The solubility of $Ru(phen)_3(BPh_4)_2$ in isopropyl ether was reported as:

 $4.32 \times 10^{-7} \text{ mol } dm^{-3}$.

AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ECTIMATED EDDAD
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Methanol; CH ₄ 0; [67-56-1]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	<u> </u>
The colubility of Du(phon) ()	PPh) in methanol was reported as
ine solubility of ku(phen) ₃ ()	^{brn} 4 ² in methanol was reported as:
3.84 x 10	D^{-5} mol dm ⁻³ .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry, For details see	See compilation for Ru(phen) (BPh)
compilation for Ru(phen) (BPh.) in	in acetone based on the same lit.
acetone based on the same lit.	reference.
reference.	
	1
	ESTIMATED ERROR:
	ESTIMATED ERROR:
	ESTIMATED ERROR: Nothing specified.
	ESTIMATED ERROR: Nothing specified.
	ESTIMATED ERROR: Nothing specified.
	ESTIMATED ERROR: Nothing specified. REFERENCES:

COMPONENTS .	ORTGINAL MEASUREMENTS.	
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.	
(2) 3-Methyl-1-butanol (isoamyl alcohol); C ₅ H ₁₂ O; [123-51-3]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:	L	
The solubility of Ru(phen) ₃ (BPh ₄) ₂ in isoamyl alcohol was reported as:		
$3.78 \times 10^{-6} \text{ mol } \text{dm}^{-3}$.		
ÀUXTLIARY	τηξορματίου	
	COURCE AND DUDTTY OF MATERIALS.	
Spectrophotometry, For details see	See compilation for $Ru(phen)_3(BPh_4)_2$	
compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	in acetone based on the same lit. reference.	
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.	
(2) Y-Methyl-butyl ethanoate (iso- amyl acetate); C ₇ H ₁₄ O ₂ ; [123-92-2]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of $Ru(phen)_3(BPh_4)_2$ in isoamyl acetate was reported as:		
$\sim 10^{-7}$ mol dm ⁻³ .		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Spectrophotometry. For details see compilation for $Ru(phen)_3(BPh_4)_2$ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	
	ESTIMATED ERROR:	
	Nothing specified.	
	REFERENCES:	

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.	
(2) β-Methyl-propyl ethanoate (isobutyl acetate); C ₆ H ₁₂ O ₂ ; [110-19-0]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of $Ru(phen)_3(BPh_4)_2$ in isobutyl acetate was reported as:		
$1.08 \times 10^{-7} \text{ mol } \text{dm}^{-3}$.		
a 		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE: Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	SOURCE AND PURITY OF MATERIALS: See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	
	ESTIMATED ERROR:	
	Nothing specified	
	Nothing Specificut	
	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.	
(2) 1-Nitropropane; C ₃ H ₇ NO ₂ ; [25322-01-4]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility of $Ru(phen)_3(BPh_4)_2$ in 1-nitropropane was reported as:		
4.22 x 1	0^{-3} mol dm ⁻³ .	
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
compilation for $Ru(phen)_3(BPh_4)_2$ in acetone based on the same lit. reference.	in acetone based on the same lit. reference.	
	ESTIMATED ERFOR-	
	Nothing specified.	
	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych

EXPERIMENTAL VALUES:

The solubility of $Ru(phen)_3(BPh_4)_2$ in acetone was reported as:

 $2.02 \times 10^{-3} \text{ mol } \text{dm}^{-3}$.

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;
The suspensions were shaken in a thermostat for 7-8 days and analyzed for Ru(phen)3 ⁺⁺ spectrophotometrical- ly at 448 nm using a previously determined value for the molar absorptivity of 18,500 dm ³ cm ⁻¹ mol ⁻¹ (1). Method of temperature control not specified.	The solvent was repeatedly distilled using a 1-m column packed with heli- cal steel wire. The salt was pre- pared by reacting 200 mg of RuCl ₃ H ₂ O, 526 mg of o-phenanthroline and 218 mg of hydoxylammonium sulfate in 50 cm ³ of 1:1 ethanol-water and the pH adjusted to 6 with satd. Ba(OH) ₂ . After refluxing for 2 days at 100°C, the BaSO ₄ was filtered out, and the excess o-phenanthroline was removed by washing the solution several times with CHCl ₃ and then with <u>n</u> -hexane. The resulting solu- tion was dried <u>in vacuo</u> , the residue
	continued
	ESTIMATED ERROR: Nothing specified.
	REFERENCES: Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 118.

AUXILIARY INFORMATION

COMPONENTS :	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	
VARIABLES:	PREPARED BY:
COMMENTS AND/OR	ADDITIONAL DATA
EXPERIMENTAL VALUES:	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:continued was dissolved in a minimum of aceto-
	nitrile and remaining precipitate filtered out. Ru(phen) ₃ Cl was
	crystallized by adding CHCl ₃ to the filtrate. Ru(phen) ₃ (BPh ₄) ₂ was pre-
	pared by adding a slight excess of
	cipitate was dried for 2 days in
	$\frac{Vacuo}{C-78.81\%}$; H- 5.03%; N- 6.56%.
	Found: C- 78.78; H- 4.81; N- 6.60.
	ESTIMATED ERROR:
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) <u>n</u> -Propyl acetate; C ₅ H ₁₀ O ₂ ; [109-60-4]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (reported as:	BPh ₄) ₂ in <u>n</u> -propyl acetate was
1.62 x 1	0^{-6} mol dm ⁻³ .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for $Ru(phen)_3(BPh_4)_2$ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES .

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆; 	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
(2) Tetramethylene oxide (tetra- hydrofuran); C ₄ H ₈ O; [26249-20-7]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (B reported as:	Ph ₄) ₂ in tetrahydrofuran was
6.03 x 10 ⁻⁴	mol dm ⁻³ .
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AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see	See compilation for $Ru(phen)_3(BPh_4)_2$
compilation for $Ru(phen)_3(BPh_4)_2$ in	in acetone based on the same lit.
reference.	
(
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES :
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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tris(o-phenanthroline)ruthenium (II) tetraphenylborate (1-); RuC₈₄H₆₄B₂N₆;</pre>	Takamatsu, T. Bull. Chem. Soc. Japan <u>1974</u> , 47, 1285-6.
<pre>(2) 2,2,4,4-tetramethyl-3-pentanone (diisobutyl ketone); C₉H₁₈0; [815-24-7]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of Ru(phen) ₃ (reported as:	BPh ₄) ₂ in diisobutyl ketone was
1.19 x 10	$-5 \text{ mol } dm^{-3}$.
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Spectrophotometry. For details see compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.	See compilation for Ru(phen) ₃ (BPh ₄) ₂ in acetone based on the same lit. reference.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

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COMPONENTS:	EVALUATOR:
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Water; H₂0; [7732-18-5] 	Orest Popovych, Department of Chemistry, The City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

The solubility of silver tetraphenylborate (AgBPh4) in water proved to be exceptionally elusive. It is too low for reliable direct determination by UV-spectrophotometry, since the molar absorptivity of the BPh4 ion in water at the characteristic 266-nm peak is only 3.25 x $10^3\ \rm dm^3$ $(\text{cm mol})^{-1}$, while the reported solubility generally ranges between 10^{-7} and 10^{-9} mol dm⁻³. Furthermore, the reduction of the silver ion in AgBPh₄ suspensions by light and possibly by organic impurities creates additional difficulties regardless of the analytical method employed.

Historically, the first to report a solubility product for AgBPh, in water was Havir (1). Noting that direct potentionmetry with a silver electrode in saturated AgBPh4 solutions led to irreproducible results, he resorted to potentiometric determinations in the presence of ~ 0.01 mol dm⁻³ NaBPh₄, which at 293 K yielded a K_{s0} = 4.0 x 10⁻¹⁴ (all solubility products in this evaluation have units of mol² dm⁻⁶). Popovych (2) repeated Haviř's work at several concentrations of NaBPh₄ at 298 K, obtaining a K_{SO}^{s} = 4.07 x 10^{-14} . (The pK_{s0} values from the work of both Havir (1) and Popovych (2) are 13.4). Alexander et al. (3) reported a $pK_{\rm SO}$ = 11.1 at 298 K and at an ionic strength of 0.01 mol dm⁻³ on the basis of a potentiometric titration of a tetraphenylborate solution with silver ion.

Kolthoff and Chantooni (4) questioned all of the above results on the grounds that the values for the transfer activity coefficients (medium effects) for the transfer of silver and tetraphenylborate ions from water to methanol required a pK_{s0}° value of $AgBPh_4$ in water of the order of 17.5. They repeated Popovych's (2) experiments, obtaining a pK_{s0}° value of 14.3 \pm 0.2, from which they concluded that the silver-silver tetraphenylborate electrode behaves abnormally in aqueous solutions, probably because it is not wetted by water (4). Instead, Kolthoff and Chantooni (4) deter-mined the solubility product of AgBPh4 in water from the chemical-exchange experiments in which a solution of NaBPh4 was equilibrated with solid AgI and a solution of NaI was equilibrated with solid AgBPh4. On this basis they reported a $pK_{SO}^{\circ} = 17.2 \pm 0.2$ at 298K. The latter is probably the best value available to date, but in view of the fact that it has not yet been corroborated by another method or by work from another laboratory that value must be described for now as tentative.

Since the activity correction in this case is certainly negligible, the solubility of AgBPh₄ in water can be estimated as $(K_{SO}^{\circ})^{\frac{1}{2}}$, which leads to the value of <u>Solubility = (2.5 ± 0.3) x 10⁻⁹ mol dm⁻³ at 298 K</u>. It is, of course, also <u>tentative</u>. In view of this, the solubility of 7.6 x 10⁻⁶ mol dm^{-3} reported by McClure and Rechnitz (5) for a THAM buffer solution is much too high.

REFERENCES:

- 1. Havir, J. Collect. Czech. Chem. Commun. 1959, 24, 1955.
- Popovych, O. Anal. Chem. 1966, 38, 558. 2.
- Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. з. Soc. <u>1967</u>, 89, 3703. Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194. McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u>, 38, 136.
- 4.
- 5.

AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Fifty cm ³ of a 0.01 mol dm ⁻³ solution of NaBPh ₄ were reacted with 2 drops of 0.01 mol dm ⁻³ AgNO ₃ and the resulting suspension shaken in the dark for 4 hrs. A silver electrode dipping in the above suspension was connected via an Agar bridge to another silver electrode in a 0.01 mol dm ⁻³ solution of AgNO ₃ . The resulting emf was 0.545 V.	SOURCE AND PURITY OF MATERIALS: NaBPh ₄ was from the Heyl & Co. (Berlin).
	ESTIMATED ERROR: Not specified. Temperature control: ±0.5°C
	REFERENCES:

COMPONENTS: (1) Silver tetraphenylborate (1-); AgC ₂₄ H ₂₀ B; [14637-35-5] (2) Sodium tetraphenylborate; NaC ₂₄ H ₂₀ B; [143-66-8] (3) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Havíř, J. Collect. Czech. Chem. Commun. <u>1959</u> , 24, 1955-9.
VARIABLES:	PREPARED BY:
One temperature: 20°C	Orest Popovych

EXPERIMENTAL VALUES:

The solubility product of $AgBPh_4$ in water determined in the presence of ${\rm \sim}0.01~mo1~dm^{-3}~NaBPh_4$ was reported as:

 $K_{SO}^{\circ} = 4.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}.$

Assuming a Nernstein response in the emf cell specified below, the author obtained $a_{Ag} = 4.5 \times 10^{-12}$ mol dm⁻³ and presumably multipled that value by the BPh₄ activity though no value for the activity coefficient was mentioned specifically.

<pre>COMPONENTS: (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium tetraphenylborate; NaC₂₄H₂₀B; [143-66-8] (3) Water; H₂0; [7732-18-5]</pre>	ORIGINAL MEASUREMENTS: Popovych, O. <i>Anal. Chem</i> . <u>1966</u> , <i>38</i> , 558-63.
VARIABLES:	PREPARED BY:
One temperature: 25.00°C	Orest Popovych
EXPERIMENTAL VALUES:	
The author reports the solubilit	y product of AgBPh ₄ in water as:
$K_{s0}^{\circ} = (4.07 \pm 0.50)$	$x 10^{-14} mol^2 dm^{-6}$.
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Potentiometric determination of silver-ion activity in suspensions of AgBPh, containing BPh, concen- trations in the range of 10 ⁻⁴ -10 ⁻² mol dm ⁻³ added as the sodium salt. The potential difference was measured between two silver electrodes, one of which was immersed in the above suspensions and the other, in 10 ⁻² mol dm ⁻³ AgNO ₃ solution. No bridge solution was specified. Saturation was achieved by shaking for at least 2 weeks on a Burrell wrist-action shaker in water-jacketed flasks.	SOURCE AND PURITY OF MATERIALS: AgBPh ₄ was prepared by metathesis of exactly stoichiometric amounts of aqueous AgNO ₃ and purified KBPh ₄ dissolved in a minimum of acetone. The precipitate was washed thorough- ly by decantation. ESTIMATED ERROR: Relative precision of $\pm 12\%$ in the determination of a_{Ag} . Temperature: $\pm 0.01^{\circ}$ C. REFERENCES:

<pre>COMPONENTS: (1) Silver tetrapheny1- borate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium nitrate; NaNO₃; [7631-99-4] (3) Sodium tetrapheny1borate; NaC₂₄H₂₀B; [143-66-8] (4) Water; H₂O; [7732-18-5]</pre>	ORIGINAL MEASUREMENTS: Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1967</u> , <i>89</i> , 3703-12.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product of AgBPh ₄ in water was reported as a product of ionic concentrations determined at ionic strengths in the range of 0.01-0.005 mol dm ⁻³ maintained by NaBPh ₄ : $PK_{RO} = 11.1 (K_{RO} units are mol2 dm-6).$	
-	
	-
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Potentiometric titration of 0.01 mol dm ⁻³ solution of NaBPh ₄ with AgNO ₃ using a silver indicator electrode and a silver-silver nitrate reference cell connected by a bridge of NEt ₄ picrate. A radiometer pH meter, Type PHM22r was used. Cell was thermostatted, but limits of temperature control were not specified.	The salts were of Analar grade and were used as received.
	ESTIMATED ERROR:
	±0.1 pK units is assumed by the compiler.
	REFERENCES:

COMPONENTS: (1) Silver tetraphenyl- borate (1-); AgC ₂₄ H ₂₀ B; [14627-35-5] (2) Sodium tetraphenylborate; NaC ₂₄ H ₂₀ B; [143-66-8] (3) Sodium iodide; NaI; [7681-82-5] (4) Water; H ₂ O; [7732-18-5]	ORIGINAL MEASUREMENTS: Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u> , 44, 194-5. PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
to be:	oduct of Agbrn ₄ in water was reported	
$pK_{S0}^{\circ} = 17.2 \ (K_{S0}^{\circ})^{\circ}$	units are $mol^2 dm^{-6}$).	
The above value was derived from cheme by the equilibrium:	nical-exchange experiments described	
NaBPh ₄ + AgI(s) ‡ AgI	BPh ₄ (s) + NaI	
from which the ratio: $K_{s0}^{\circ}(AgBPh_{4})$	[BPh4] was measured.	
K _{ŝO} (AgI)	[1-]	
coefficients were calculated from the limiting Debye-Hückel law. The relevant experimental data are shown on the next page.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE: A suspension of AgI in a solution of NaBPh ₄ or a suspension of AgBPh ₄ in a solution of NaI were shaken under deaerated conditions for 5 days. In the former case, AgBPh ₄ solid was added as seed. The filtered saturated solutions were analyzed spectrophotometrically for the BPh ₄ in the 260-280-nm range, after subtracting the iodide absorb- ance, and potentiometrically for the I ⁻ , using a silver electrode. UV spectra were recorded on a Cary Model 15 spectrophotometer. Emf measure- ments were made with a Corning Model 10 pH meter on the millivolt scale.	SOURCE AND PURITY OF MATERIALS: Conductivity water was used. NaI was Mallinckrodt AR Grade, recrystal- lized from water. NaBPh4 was Aldrich puriss. product, purified according to a literature method (2). AgBPh4 was prepared by metathesis of AgNO3 and 2% excess of NaBPh4. The product was washed well with methano1, dried <u>in vacuo</u> at 50°C for 3 hrs., all preparation and storage taking place in the dark. AgI was prepared and handled analogously. ESTIMATED ERROR: Accuracy ±0.2 pK units (3). A precision of ±0.1 pK units is assumed by the compiler. Temperature control: ±1°C	
	 REFERENCES: (1) Buckley, P.; Hartley, H. Phil. Mag. <u>1929</u>, 8, 320. (2) Popov, A. I.; Humphrey, R. J. Am. Chem. Soc. <u>1959</u>, 81, 2043. (3) Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024. 	

	Si	ilver	·	145
COMPONENTS: (1) Silver tetra $AgC_{24}H_{20}B;$ [(2) Sodium tetra $NaC_{24}H_{20}B;$ [(3) Sodium iodid (4) Water; $H_{20};$	phenylborate (1-); 14627-35-5] phenylborate; 143-66-8] e; NaI; [7681-82-5] [7732-18-5]	ORIGINAL MEAS Kolthoff, Jr. Anal.	UREMENTS: I. M.; Chantoo <i>Chem.</i> <u>1972</u> , 49	oni, M. K., 4, 194-5.
VARIABLES:		PREPARED BY:		
One temperature:	25°C	Orest Pop	ovych	
EXPERIMENTAL VALUES	: (continued)			
	<u>Exchange</u> exp	eriments	с. С	
Initial C/mol	dm ⁻³ [BPh ₄ ⁻]	[I-]	K [°] _{s0} (AgBPh ₄)	pK°o
NaBPh ₄ or NaI	mol dm^{-3}	mol dm^{-3}	K [°] _{SO} (AgI)	(AgBPh ₄)
	NaBPh ₄ +	Agl(ș)		
0.00740 0.00817 0.0155	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	6.94×10^{-3} 7.66 x 10 ⁻³ 1.43 x 10 ⁻²	0.066 0.067 0.082	17.2 17.2 17.1
	NaI + AgB	Ph ₄ (s)		
0.0107 0.0214	5.48 x 10^{-4} 1.0 ₇ x 10^{-3}	1.01×10^{-2} 2.03 x 10 ⁻²	0.054 0.053	17.3 17.3
	AUXILIARY	INFORMATION		
METHOD/APPARATUS/PRO)CEDURE :	SOURCE AND PU	RITY OF MATERIALS	2
		ESTIMATED ERR	OR:	<u> </u>
		REFERENCES :		

Silver

CMMCDENTS: (1) filver tetraphenylborate (1-); AGQ_HEQB; [14637-35-5] (2) Tria(hydroxymethyl)aminomethane; CRH_1NAS; [7738-1] (3) Acetic acid; CgHoQ; [64-19-7] (4) Water; H_QO; [7732-18-5] VARIABLES: One temperature: 24.8 C VARIABLES: One temperature: 24.8 C The solubility of silver tetraphenylborate (AgBPh_) in aqueous solution of the tria(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ .			
VARIABLES: PREPARED BY: One temperature: 24.8 C Orest Popovych EXPERIMENTAL VALUES: The solubility of silver tetraphenylborate (AgBPh ₀) in aqueous solution of the tris(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details. Source AND FURITY OF MATERIALS: Baker reagent-grade AgNO ₂ was the storing day by otention metric titrn with KCl and RPGL. Ca(BPh ₀) zoution in THAM was the source of Rechnitz et al. (2) and was standardized by potention metric titrn with KCl and RDCl. Ca(BPh ₀). Soution in THAM was the source of Ph ₀ - The buffer contained 0.1 mol am ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with 0.7. Smith reagent-grade INON: Ket Stated. RefPRENCES: Not stated. Temperature: 10.3°C	<pre>COMPONENTS: (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Tris(hydroxymethyl)aminomethane; C₄H₁₁NO₃; [77-86-1] (3) Acetic acid; C₂H₄O₂: [64-19-7] (4) Water; H₂O; [7732-18-5]</pre>	ORIGINAL MEASUREMENTS: McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u> , 38, 136-9.	
VARIABLES: One temperature: 24.8 C EXPERIMENTAL VALUES: The solubility of silver tetraphenylborate (AgBPh _a) in aqueous solution of the tris(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . AUXILLARY INFORMATION METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details. Scientific reagent-grade AgNO ₃ was the scientific reagent-grade AgNO ₄ was the scientific reagent			
One temperature: 24.8 C Orest Popovych EXPERIMENTAL VALUES: The solubility of silver tetraphenylborate (AgBPh _b) in aqueous solution of the trig(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . Main terms of the trig(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . Main terms of the trig(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . Main terms of the trig(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . Main terms of the trig(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . Main terms of the trig(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ . Main terms of the tetraphenylborate terms of the tetraphenylborate tetraphenylboratetet	VARIABLES:	PREPARED BY:	
AUXILLARY INFORMATION AUXILLARY INFORMATION METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details. Source AND PURITY OF MATERIALS: Baker reagent-grade AgNO, was the starting material for the AgPth, . Scientific reagent-grade AgPth, by otherico- source of BPh, . The buffer con- tained 0.1 mol dm ⁻³ THAM was the Source SPh, . The buffer con- tained 0.1 mol dm ⁻³ THAM was the Source SPh, . The buffer con- tained 0.1 mol dm ⁻³ THAM and 0.01 metric tirthe FRMCRE; Not stated, Temporature; 10.3*C REFERENCES: Howick, L. C.; Pflaum, R. T. AMAL OF MALE ARD AGE	One temperature: 24.8 C	Orest Popovych	
AUXILIARY INFORMATION AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details. Source AND PURITY OF MATERIALS: Baker reagent-grade AgNO ₃ was the Scientific reagent-grade AgNO ₃ was the Ca(BPh ₃) ₂ was prepared from Fisher Scientific reagent-grade AgBPh ₄ by the procedure of Rechnicz et al. (2) and was standardized by potentio- metric titrn with KCl and RBCl. Ca(BPh ₃) ₂ solution in THM was the source of BPh ₄ . The buffer con- tained 0.1 mol am ⁻³ TAM and 0.01 mol am ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade KFFERNCES: 1. Howick, L. C.; Fflaum, R. T. Amat. Chim, Acta 1955, 19, 342. 2. Rechnicz, G. A.; Kates, S. A.; Temporature; 20.3°C	EXPERIMENTAL VALUES:		
AUXILIARY INFORMATION METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details. SOURCE AND PURITY OF MATERIALS: Baker reagent-grade AgNO, was the starting material for the AgBPh4. Ca(BPh4)2 was prepared from Fisher Scientific reagent-grade NaBPh4 by the procedure of Rechnitz et al. (2) and was standardized by potentio- metric titrn with KCl and RbCl. Ca(BPh4)2 solution in THAM was the source of BPh4 ⁻ . The buffer con- tained 0.1 mol dm ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HCl04. ESTIMATED ERROR: Not stated. Temperature: ±0.3°C REFERENCES: 1. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 342. 2. Rechnitz, G. A.; Katz, S. A.; Zamonick G. P. dwaf.	The solubility of silver tetraphenylborate (AgBPh ₄) in aqueous solution of the tris(hydroxymethyl)aminomethane (THAM) buffer at pH 5.1 was reported to be 7.6 x 10 ⁻⁶ mol dm ⁻³ .		
METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details. SOURCE AND PURITY OF MATERIALS: Baker reagent-grade AgDO ₃ was the starting material for the AgBPh ₄ . Ca(BPh ₄) ₂ was prepared from Fisher Scientific reagent-grade NaBPh ₄ by the procedure of Rechnitz et al. (2) and was standardized by potentio- metric titrn with KCl and RbCl. Ca(BPh ₄) ₂ solution in THAM was the source of BPh ₄ ⁻ . The buffer con- tained 0.1 mol dm ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO ₄ . ESTIMATED ERROR: Not stated. Temperature: ±0.3°C REFERENCES: 1. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 342. 2. Rechnitz, G. A.; Katz, S. A.; Temperature, S. M. (2)	AUXILIARY	INFORMATION	
<pre>UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details.</pre> Baker reagent-grade AgNO ₃ was the starting material for the AgBPh ₄ . Ca(BPh ₄) ₂ was prepared from Fisher Scientific reagent-grade NaBPh ₄ by the procedure of Rechnitz et al. (2) and was standardized by potentio- metric titrn with KCl and RbCl. Ca(BPh ₄) ₂ solution in THAM was the source of BPh ₄ ⁻ . The buffer con- tained 0.1 mol dm ⁻³ THAM and 0.01 mol dm ⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO ₄ . ESTIMATED ERROR: Not stated. Temperature: ±0.3°C REFERENCES: 1. Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta <u>1958</u> , 19, 342. 2. Rechnitz, G. A.; Katz, S. A.; Zapochnick, C. D. Amed. Chem.	METHOD /APPARATUS / PROCEDURE +	SOURCE AND PURITY OF MATERIALS	
<u>1963</u> , 35, 1322.	WE THOD/APPAKATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum (1). No other details.	<pre>SOURCE AND PURITY OF MATERIALS: Baker reagent-grade AgNO₃ was the starting material for the AgBPh₄. Ca(BPh₄)₂ was prepared from Fisher Scientific reagent-grade NaBPh₄ by the procedure of Rechnitz et al. (2), and was standardized by potentio- metric titrn with KC1 and RbC1. Ca(BPh₄)₂ solution in THAM was the source of BPh₄⁻. The buffer con- tained 0.1 mol dm⁻³ THAM and 0.01 mol dm⁻³acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HC10₄. ESTIMATED ERROR: Not stated. Temperature: ±0.3°C REFERENCES: 1. Howick, L. C.; Pflaum, R. T. <i>Anal. Chim. Acta</i> <u>1958</u>, 19, 342. 2. Rechnitz, G. A.; Katz, S. A.; Zamochnick, S. B. <i>Anal. Chem.</i> <u>1963</u>, 35, 1322.</pre>	

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COMPONENTS :	ORIGINAL MEASUREMENTS:		
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Isopropyl alcohol; C₃H₈O; [67-63-0] (3) Toluene; C₇H₈; [108-88-3] (4) Water; H₂O; [7732-18-5] 	Popovych, O. Anal. Chem. <u>1966</u> , 38, 117-9.		
VARIABLES:	PREPARED RV.		
One temperature: 25.00°C	Orest Popových		
EXPERIMENTAL VALUES:			
The solubility of AgBPh4 in th 49.5% isopropyl alcohol and 0.5% water was reported as:	he mixture consisting of 50.0% toluene, r by volume known as the ASTM medium [*]		
$C = 5.40 \times 10^{-5} r$	nol dm ⁻³ .		
The corresponding ionic concentration reported to be:	in the saturated solution was		
$C_{\alpha} = 2.48 \times 10^{-5}$	mol dm ⁻³ .		
The molar activity coefficient for the 25°C is given by the limiting Debye-Hi	e electrolyte in the ASTM medium at ickel expression as:		
$\log y_{\pm}^{2} = -31.446$	(Cα) ^{1/2} .		
The solubility product for AgBPh ₄ in the ASTM medium calculated from the above results in the form: $K_{SO}^{\circ} = (C\alpha y_{\perp})^2$ was reported as:			
$K_{s0}^{\circ} = 4.29 \times 10^{-1}$	l ⁰ mol ² dm ⁻⁶ .		
The degree of dissociation α was calculated from the Wirth equation (1):			
$\alpha = 1000 \kappa ,$			
$C[\Lambda^{\infty} - S(1000 \kappa/\Lambda^{\infty})]^{\frac{1}{2}}$			
	continued		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Electrolytic conductivity of saturated and diluted solutions in conjunction with equations developed in this article. The measurements were car- ried out on a Wayne-Kerr Universal Bridge B221 with a platinum cell. Saturated solutions were prepared by shaking for at least 2 weeks on a Burrell wrist-action shaker in water- jacketed flasks.	AgBPh ₄ was prepared by metathesis of exactly stoichiometric amounts of aqueous AgNO ₃ and purified KBPh ₄ dissolved in a minimum of acetone. The precipitate was washed by decan- tation first with water, then with ASTM solvent. The purification of solvents was described elsewhere (2).		
	ESTIMATED ERROR:		
	None specified, but the precision in the solubility was about ±6% (compiler). Temperature: ±0.01°C.		
	REFERENCES :		
	(1) Wirth, H. E. J. Phys. Chem. <u>1961</u> , 65, 1441.		
	(2) Popovych, O. J. Phys. Chem. <u>1962</u> , 66, 915.		

Silver

COMPONENTS :	ORIGINAL MEASUREMENTS:	
 Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] Isopropyl alcohol; C₃H₈O; [67-63-0] 	Popovych, O. Anal. Chem. <u>1966</u> , 38, 117-9.	
(3) Toluene; C ₇ H ₈ ; [108-88-3] (4) Water; H ₂ O; [7732-18-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25.00°C	Orest Popovych	
EXPERIMENTAL VALUES: (Continued)		
where <u>S</u> is the Onsager coefficient and κ and Λ [∞] are the electrolytic and limiting molar conductivities, respectively.		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS: ESTIMATED ERROR: REFERENCES:	
	1 1	

COMPONENTS:	EVALUATOR:
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Acetonitrile; C₂H₃N; [75-05-8] 	Orest Popovych, Department of Chemistry, The City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

The solubility product of silver tetraphenylborate (AgBPh_b) in acetonitrile was reported in three studies, all determinations being at 298 K (1-3). In their first publication, Alexander et al. (1) reported a $pK_{SO} = 7.2$ (all K_{SO} units are $mol_2^2 dm^{-6}$). It was determined by potentiometric titration of BPh_4^- with Ag at a constant ionic strength of 0.01 mol dm⁻³ using a silver electrode. The revised value from the same laboratory was $pK_{s0}^{\circ} = 7.5$ (2). It was also derived from analogous potentiometric titrations, but was based on additional measurements and activity corrections from the Davies equation (see compilation). Unfor-Unfortunately, neither temperature control, nor a method of ascertaining saturation were mentioned in the above two publications. Fortunately, at the low levels of precision involved, fine temperature control is not likely to be critical.

Kolthoff and Chantooni (3) published a pK_{SO}° value of 7.7, using the same potentiometric method as for AgBPh4 in methanol (see compilation). Although one cannot be sure of the specifics, this implies that activity coefficients may have been calculated by the Debye-Hückel equation with ion-size parameters and that a temperature control of $\pm 1^{\circ}C$ was probably maintained, since both measures were observed in the methanol study (4). The analysis was carried out on saturated solutions.

Although the pK_{s0}° of 7.7 may be the best available datum to date, its accuracy was estimated by the authors as not better than ± 0.2 pK units. In view of this we may feel justified to average their result with the pK_{s0}° of 7.5 reported by Alexander et al. (2), obtaining as the <u>tentative</u> value $pK_{s0}^{\circ} = 7.6$.

Assuming as usual an error of 0.1 pK_{s0}° units, we can estimate the solubility as $(K_{s0})^{\frac{1}{2}}$: Solubility = $(1.6 \pm 0.2) \times 10^{-4} \mod dm^{-3}$. This, of course, is an estimate which neglects the unknown activity correction introduced originally in the calculation of K_{SO}° , so that the solubility of AgBPh, in acetonitrile cannot even be designated as tentative at this time.

REFERENCES:

- Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. 1. Soc. 1967, 89, 3703.
- Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. 2. Chem. Soc. 1972, 94, 1148.
- Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024. Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194. з.
- 4.

COMPONENTS: (1) Silver tetraphenyl- borate (1-); $AgC_{24}H_{20}B$; [14637-35-5]	ORIGINAL MEASUREMENTS:
$\begin{bmatrix} (2) & \text{Sodium nitrate; Nand}_3; \\ & [7631-99-4] \end{bmatrix}$	Y. C.; Parker, A. J. J. Am. Chem.
(3) Sodium tetraphenylborate; NaC., H., B: [143-66-8]	<i>Soc</i> . <u>1967</u> , <i>89</i> , 3703-12.
(4) Acetonitrile; C_2H_3N ; [75-05-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product of AgBPh a product of ionic concentrations det range of 0.10-0.05 mol dm ⁻³ , maintain	4 in acetonitrile was reported as ermined at ionic strengths in the ed by NaBPh4:
$pK_{s0} = 7.2 (K_{s0} u)$	nits are mol² dm=°).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS.
Potentiometric titration of 0.01	Acetonitrile was purified by a
mol dm^{-3} solution of NaBPh ₄ with	literature method (1). The salts
AgNO ₃ using a silver indicator electrode and a silver-silver	were of Analar grade and were used as received.
nitrate reference cell connected by a bridge of NEt, picrate, A	
radiometer pH meter, Type PHM22r was	
limits of temperature control were	
not specified.	
	ESTIMATED ERFOR-
	None specified. A precision of
	±0.1 pK units is assumed by the compiler.
	DEFEDENCES.
	G. P.; McGuire, D. K.;
	Padmanabhan, G. R.; Anal. Chem. <u>1962</u> , 34, 1139.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver tetraphenylborate (1-); AgC ₂₄ H ₂₀ B; [14637-35-5]	Alexander, R.; Parker, A. J.; Sharp,
[7601-89-0]	<i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.
(3) Sodium tetraphenylborate; NaCo, Hora B: [143-66-8]	
(4) Acetonitrile; C_2H_3N ; [75-05-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
	l
EXPERIMENTAL VALUES:	
The solubility (ion-activity) p was determined in the presence of 0. reported as:	roduct of $AgBPh_4$ in acetonitrile 01-0.005 mol dm ⁻³ NaBPh ₄ and
pK _{\$0} ≈ 7.5 (K _{\$0}	units are $mol^2 dm^{-6}$).
The mean ionic activity coefficient	was calculated from the Davies
equation in the form: $\log \gamma_{\pm} = -A [$ <u>I</u> is the ionic strength in mol dm ⁻³ mol ^{-1/2} dm ^{3/2} .	$(I)^{1/2}/(1 + (I)^{1/2}) - (1/3) I]$, where and the value of <u>A</u> used was 1.543
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
dm^{-3} NaBPh ₄ with 0.01 mol dm ⁻³	Not stated.
AgClO ₄ . The ionic strength at the midpoint of the titration curve was	
used to calculate the activity	
coefficient.	
	ESTIMATED ERROR:
	Not specified. A precision of ± 0.1
	pr units is assumed by the compiler.
	REFERENCES :
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152 Silv	Silver	
COMPONENTS:	ORIGINAL MEASUREMENTS:	
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium tetraphenylborate; NaC₂₄H₂₀B; [143-66-8] (3) Acetonitrile; C₂H₃N; [75-05-8] 	Kolthoff, I. M.; Chantooni, M. K., Jr. <i>J. Phys. Chem.</i> <u>1972</u> , 76, 2024-34.	
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·	
The solubility product of AgB pK [°] _{SO} = 7.7 (K [°] _{SO} uni	Ph ₄ in acetonitrile was reported as: .ts are in mol ² dm ⁻⁶).	
AUXILIARY	INFORMATION	
METHOD /APPARATUS / PROCEDURE · SOURCE AND DURITY OF METERALS		
Potentiometric determination of paAg in saturated solution in the pre- sence of NaBPh ₄ , as described for methanol (1). It should be noted, however, that the reference cited by the authors (Kolthoff, I. M.; Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1971</u> , 93, 7104.) does not per- tain to the methanol study. The au- thors reported that AgBPh ₄ does not form solvates with acetonitrile. (See compilation for AgBPh ₄ in	Literature methods were used to puri- fy acetonitrile (2) and NaBPh ₄ (Al- drich puriss. grade) (3). The pre- paration of AgBPh ₄ was not outlined in this article and was probably accomplished by metathesis of NaBPh ₄ and AgNO ₃ as described earlier (1).	
metnanoi based on Ker. (1)).	 ESTIMATED ERROR: Only an accuracy of ±0.2 pK units was mentioned. A precision of ±0.1 pK units is assumed by the compiler. REFERENCES: (1) Kolthoff, I. M.; Chantooni, M. K. Jr. Anal. Chem. 1972, 44, 194. (2) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. J. Am. Chem. Soc. 1961, 83, 3927. (3) Popov, A. I.; Humphrey, R. J. Am. Chem. Soc. 1959, 81, 2043. 	

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<pre>COMPONENTS: (1) Silver tetraphenyl- borate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium nitrate; NaNO₃; [7631-99-4] (3) Sodium tetraphenylborate; NaC₂₄H₂₀B; [143-66-8] (4) N,N-Dimethylacetamide; C₄H₉NO; [127-19-5]</pre>	ORIGINAL MEASUREMENTS: Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. <i>J. Am. Chem.</i> Soc. <u>1967</u> , 89, 3703-12.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product of AgBPh reported as a product of ionic concen- strengths in the range of $0.10-0.05$ m $pK_{s0} = 5.9$ (K _{s0} units	4 in N,N-dimethylacetamide was trations determined at ionic ol dm ⁻³ , maintained by NaBPh ₄ : are mol ² dm ⁻⁶).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: Potentiometric titration of 0.01 mol dm^{-3} solution of NaBPh ₄ with AgNO ₃ using a silver indicator electrode and a silver-silver nitrate reference cell connected by a bridge of NEt ₄ picrate. A radiometer pH meter, Type PHM22r was used. Cell was thermostat- ted, but limits of temperature control were not specified.	N,N-Dimethylacetamide was dried with Type 4A molecular sieves and fractionated twice under a reduced pressure of dry nitrogen. The salts were of Analar grade and were used as received.
COMMENTS AND/OR ADDITIONAL DATA:	
The above solubility product seems to be a combination of Ag ⁺ activity and BPh ₄ ⁻ concentration. The validity of the reported value is therefore <u>doubtful</u> .	ESTIMATED ERROR: Nothing specified. A precision of ±0.1 pK units is assumed by the compiler.
	REFERENCES :

<pre>COMPONENTS: (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>	EVALUATOR: Orest Popovych, Department of Chemistry, The City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

The solubility product of silver tetraphenylborate (AgBPh,) in N.N-dimethylformamide at 298 K was published in three literature sources (1-3). Both values reported by Alexander et al. (1, 2) were derived from potentiometric titrations of BPh_{L}^{-} with Ag^{+} using a silver electrode. In their first study, a concentration solubility product was reported in the form $pK_{SO} = 6.7$ (1). (All K_{SO} units are mol² dm⁻⁶). In the follow-up study from the same laboratory, which involved additional determinations and activity corrections via the Davies equation (see compilation), the revised value was $pK_{0}^{\circ} = 7.1$ (2). Unfortunately, neither temperature control, nor a method of ascertaining saturation were mentioned in the above two publications. However, at the low levels of precision involved, a fine temperature control may not be critical.

Kolthoff and Chantooni (3) reported a $pK_{s0}^{\circ} = 7.5$ determined by the same potentiometric procedure as for AgBPh4 in methanol (see compilation). If this means that activity coefficients were calculated from the Debye-Hückel equation with ion-size parameters and that temperature was controlled to $\pm 1^{\circ}$ C, as was done on both counts in methanol (4), their result may be slightly more reliable than that of Alexander et al. (2). At least the analysis was carried out in definitely saturated solutions, as opposed to the assumed saturation at an electrode in the course of a potentiometric precipitation titration. Thus the $pK_{s0}^{\circ} = 7.5$ may be described as the tentative value for $AgBPh_{L}$ in N,N-dimethylformamide. The corresponding solubility taken as $(K_{SO}^{*})^{\frac{1}{2}} = (1.8 \pm 0.2) \times 10^{-4} \text{ mol dm}^{-3}$, assuming a precision of 0.1 units in pK_{SO}^{*} . Of course, this estimate neglects an unknown activity correction contained in the K_{s0}° , so that it cannot even be described as tentative. For example, if we use the above estimate of the solubility to compute the activity coefficient from the Davies equation, the result is $y_{\pm} = 0.954$ and the "corrected" solubility value becomes 1.9 x 10^{-4} mol dm⁻³.

REFERENCES:

- Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. 1. Soc. <u>1967</u>, 89, 3703. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am.
- 2. Chem. Soc. 1972, 94, 1148.
- Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024. Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194. 3. 4.

COMPONENTS: (1) Silver tetraphenyl- borate (1-); $AgC_{24}H_{20}B$; [14637-35-5] (2) Sodium nitrate; $NaNO_3$; [7631-99-4] (3) Sodium tetraphenylborate; $NaC_{24}H_{20}B$; [143-66-8] (4) N, N-Dimethylformamide; C_3H_7NO ; [68-12-2]	ORIGINAL MEASUREMENTS: Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1967</u> , <i>89</i> , 3703-12.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product of AgBPh reported as a product of ionic concen- strengths in the range of $0.10-0.05$ m $pK_{s0} = 6.7$ (K_{s0} u)	4 in N,N-dimethylformamide was trations determined at ionic ol dm ⁻³ , maintained by NaBPh ₄ : nits are mol ² dm ⁻⁶).
AUXILIARY	INFORMATION
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
Potentiometric titration of 0.01 mol dm ⁻³ solution of NaBPh ₄ with AgNO ₃ using a silver indicator electrode and a solver-silver nitrate reference cell connected by a bridge of NEt ₄ picrate. A radiometer pH meter, Type PHM22r was used. Cell was thermostatted, but limits of temperature control were not specified.	N,N-Dimethylformamide was dried with Type 4A molecular sieves and fractionated twice under a reduced pressure of dry nitrogen. The salts were of Analar grade and were used as received.
	ESTIMATED ERROR: None specified. A precision of ±0.1 pK units is assumed by the compiler.
	REFERENCES :

NTS:	(1)	Silver	te

156 Sil	Silver		
<pre>COMPONENTS: (1) Silver tetraphenyl- borate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium perchlorate; NaClO4; [7601-89-0] (3) Sodium tetraphenylborate; NaC₂₄H₂₀B; [143-66-8] (4) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>	ORIGINAL MEASUREMENTS: Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.		
VARIABLES:	PREPARED BY:		
One temperature: 25°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility (ion-activity) product of AgBPh ₄ in N,N-dimethylfor-mamide was determined in the presence of 0.01-0.005 mol dm ⁻³ NaBPh ₄ and reported as:			
$pK_{s0} = 7.1 (K_{s0})$ ur	nits are mol ² dm ⁻⁰).		
The mean ionic activity coefficient we equation in the form: $\log \gamma_{\pm} = -A$ [<u>I</u> is the ionic strength in mol dm ⁻³ and $m^{-1/2}$ dm ^{3/2} .	vas calculated from the Davies $(I)^{1/2}/(1 + (I)^{1/2}) - (1/3)I]$, where and the value of <u>A</u> used was 1.551		
AUXILIARY INFORMATION			
METHOD/APPARATUS/PROCEDURE: Potentionmetric titration of 0.01 mol dm ⁻³ NaBPh ₄ with 0.01 mol dm ⁻³ AgClO ₄ . The ionic strength at the midpoint of the titration curve was used to calculate the activity coefficient.	SOURCE AND PURITY OF MATERIALS: Not stated.		
	ESTIMATED ERROR: Not specified. A precision of ±0.1 pK units is assumed by the compiler.		
	REFERENCES:		

COMPONENTS:	ORIGINAL MEASUREMENTS:		
(1) Silver tetraphenylborate (1-); AgC ₂₄ H ₂₀ B; [14637-35-5]	Kolthoff, I. M.; Chantooni, M. K., Jr. <i>J. Phys. Chem.</i> <u>1972</u> , 76, 2024-34.		
(2) Sodium tetraphenylborate; NaC ₂₄ H ₂₀ B; [143-66-8]			
<pre>(3) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>			
VARIABLES:	PREPARED BY:		
One temperature: 25°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility product of $AgBPh_4$ in N,N-dimethylformamide was reported as:			
$pK_{s0}^{\circ} = 7.5 (K_{s0}^{\circ} \text{ units are in mol}^2 \text{ dm}^{-6}).$			

AUXILIAR	(INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Potentiometric determination of P _{Ag} on filtered saturated solutions in the presence of NaBPh ₄ as de- scribed for methanol (1). (See com- pilation for methanol based on Ref. 1) However, the reference cited by the authors (Kolthoff, I. M.; Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1971</u> , 93, 7104.) does not pertain to the methanol study. The authors detected no crystal solvates of AgBPh ₄ with N,N-dimethylformamide.	N,N-Dimethylformamide was purified as described in the literature (2) as was NaBPh ₄ (Aldrich puriss. grade) (3). The preparation of AgBPh ₄ was not described, but most likely in- volved the metathesis of AgNO ₃ and NaBPh ₄ as in an earlier study (1).
	ESTIMATED ERROR:
	Nothing specified, except an accuracy of ± 0.2 pK units. A precision of ± 0.1 pK units is assumed by the compiler.
	REFERENCES:
	 Kolthoff, I. M.; Chantooni, M. K. Jr. Anal. Chem. <u>1972</u>, 44, 194. Kolthoff, I. M.; Chantooni, M. K. Jr.; Smagowski, H. Anal. Chem. <u>1970</u>, 42, 1622. Popov, A. I.; Humphrey, R. J. Am. Chem. Soc. <u>1959</u>, 81,2043.

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COMPONENTS:	EVALUATOR:
 Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] Dimethylsulfoxide;C₂H₆OS; [67-68-5] 	Orest Popovych, Department of Chemistry, The City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

The solubility product of silver tetraphenylborate (AgBPh₄) in dimethylsulfoxide was reported in three literature sources, all determinations being at 298 K (1-3). Using either potentiometry or UV-spectro-photometry, Alexander et al. (1) determined a $pK_{SO} = 4.6$ from the product of ionic concentrations (all K_{SO} units are mol² dm⁻⁶). A subsequent report from the same laboratory (2) based upon potentiometric titration of BPh_4 with Ag^+ using a silver electrode and activity corrections by the Davies equation (see compilation) gave a $pK_{SO}^{\circ} = 5.1$. It is difficult to evaluate these results, as neither temperature control, nor a method for ascertaining saturation have been specified.

Kolthoff and Chantooni (3) reported a potentionmetric pK_{SO}^{s} value of 4.7, and a conductometric value of 4.7, with an estimated accuracy of ± 0.2 pK units. The analysis was carried out on filtered saturated solutions in both cases, but nothing is mentioned about activity corrections or temperature control. In analogous work reported from the same laboratory (4), the temperature control was ±1°C and activity coefficients were calculated from a Debye-Hückel equation with ion-size parameters. Thus, the value $pK_{00}^{\circ} = 4.7_{5}$ can be considered no better than <u>tentative</u> at this time.

In view of the uncertainty in the activity corrections incorporated in the above pK_{g0} value, the solubility must be derived from the concentration pK_{g0} determined by Alexander et al. (1). Assuming an error of 0.1 pK units in the value 4.6, we obtain for the <u>solubility (5.0 \pm 0.6) x 10⁻³</u> mol dm⁻³. (evaluator). This solubility value must be described as highly tentative.

REFERENCES:

- Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. 1. Soc. 1967, 89, 3703.
- 2. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. 1972, 94, 1148.
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- Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024. Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194. 4.

Silver

COMPONENTS	ORIGINAL MEASUREMENTS.		
(1) Silver tetraphenylborate (1-); $AgC_{24}H_{20}B;$ [14637-35-5] (2) Dimethylsulfoxide; $C_2H_6OS;$ [67-68-5]	Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1967</u> , <i>89</i> , 3703-12.		
VARIABLES:	PREPARED BY:		
One temperature: 25°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The solubility product of AgBPh ₄ in dimethylsulfoxide was reported as a product of ionic concentration at the ionic strength corresponding to the solubility:			
$pK_{s0} = 4.6 (K_{s0})$ ur	nits are mol ² dm^{-6}).		
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Not specified unambiguously: it	Dimethylsulfoxide (Crown Zellerbach		
could have been either potentiometric	. Corp.) was dried with Type 4A molecular sieves and fractionated		
photometry on a Unicam SP500 spec-	twice under a reduced pressure of		
trophotometer. Saturated solutions	dry nitrogen. Analar grade salts		
were prepared by shaking for 24 hours at 35°C and then for a further 24	were used as received.		
hours at 25°C.			
	POTMATER ERROR		
	None specified. A precision of +0.1		
	pK units is assumed by the compiler.		
	REFERENCES:		

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Silver

COMPONENTS:	ORIGINAL MEASUREMENTS:			
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium perchlorate; NaClO₄; [7601-89-0] (3) Sodium tetraphenylborate; 	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.			
NaC ₂₄ H ₂₀ B; [143-66-8] (4) Dimethylsulfoxide; C ₂ H ₆ OS; [67-68-5]				
VARIABLES:	PREPARED BY:			
One temperature: 25°C	Orest Popovych			
EXPERIMENTAL VALUES:				
The solubility (ion-activity) product of AgBPh ₄ in dimethylsulfoxide was determined in the presence of 0.01-0.005 mol dm ⁻³ NaBPh ₄ and reported as:				
$pK_{s0}^{\circ} = 5.1 \ (K_{s0}^{\circ})$	units are $mol^2 dm^{-6}$).			
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{1/2}/(I + (I)^{1/2}) - (1/3) I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 1.115 mol ^{-1/2} dm ^{3/2} .				
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Potentiometric tetration of 0.01 mol dm ⁻³ NaBPh ₄ with 0.01 mol dm ⁻³ AgClO ₄ . The ionic strength at the midpoint of the titration curve was used to calculate the activity coefficient.	Not stated.			
	ESTIMATED ERROR:			
	Nothing specified. A precision of ± 0.1 pK units is assumed by the compiler.			
	REFERENCES:			
Silver				
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COMPONENTS :	ORIGINAL MEASUREMENTS:			
<pre>(1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5]</pre>	Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem.1972, 76, 2024-34.			
(2) Sodium tetraphenylborate NaC ₂₄ H ₂₀ B; [143-66-8] (3) Dimethylsulfoxide; C ₂ H ₆ OS; [67-68-5]				
VARIABLES:	PREPARED BY:			
One temperature: 25°C	Orest Popovych			
EXPERIMENTAL VALUES:				
The solubility product of AgB reported as:	Ph_4 in dimethylsulfoxide was			
$pK_{s0}^{\circ} = 4.7_{5} (K_{s0}^{\circ})$) units are mol ² dm ⁻⁶).			
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Potentiometric determination of pa _{Ag} in a filtered saturated solution in the presence of NaBPh ₄ , as de- scribed for methanol (1). However, the reference cited by the authors (Kolthoff, I. M.; Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1971</u> , 93, 7104.) does not pertain to the methanol study.	Dimethylsulfoxide was purified by a literature method (2), as was NaBPh ₄ (Aldrich puriss. grade) (3). The preparation of AgBPh ₄ was not de- scribed, but most likely involved the metathesis of AgNO ₃ and NaBPh ₄ as in an earlier study (1).			
	ESTIMATED FREOR.			
	Nothing specified, except an accuracy of ± 0.2 pK units. A precision of ± 0.1 pK units is assumed by the compiler.			
	 (1) Kolthoff, I. M.; Chantooni, M. K. Jr. Anal. Chem. <u>1972</u>, 44, 194. (2) Kolthoff, I. M.; Reddy, T. B. Inorg. Chem. <u>1962</u>, 1, 189. (3) Popov, A. I.; Humphrey, R. J. J. Am. Chem. Soc. <u>1959</u>, 81, 2043. 			

COMPONENTS: (1) Silver tetraphenylborate (1-); $AgC_{24}H_{20}B$; [14637-35-5] (2) Dimethylsulfoxide: C.H.OS:	ORIGINAL MEASUREMENTS: Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u> , 76, 2024-34.		
(1) Silver tetraphenylborate (1-); $AgC_{24}H_{20}B$; [14637-35-5] (2) Dimethylsulfoxide: C.H.OS:	Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u> , 76, 2024-34.		
(2) Dimethylsulfoxide: C.H.OS:			
[67-68-5]			
VARIABLES:	PREPARED BY:		
One temperature: 25°C Orest Popovych			
EXPERIMENTAL VALUES:			
The solubility product of Ag reported as:	BPh ₄ in dimethylsulfoxide was		
pK [°] _{SO} = 4.7			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Conductometric determination on fil- tered saturated solutions using	Dimethylsulfoxide was purified by a literature method (2), as was NaBPh ₄ (Aldrich purise grade) (3) The		
Presumably the solubility C was cal-	preparation of AgBPh, was not de-		
$C = 10^{3} \kappa / \Lambda^{\infty}$, but this was not ex-	metathesis of $AgNO_3$ and $NaBPh_4$, as		
specified. The reported value of κ was 1.21 x 10 ⁻⁴ ohm ⁻¹ cm ⁻¹ .			
	ESTIMATED ERROR:		
	Precision of conductance data: ±2%.		
	REFERENCES; (1) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1961</u> , 83, 3927. (2) Kolthoff, I. M.; Reddy, T. B. Inorg. Chem. <u>1962</u> , 1, 189. (3) Popov, A. I.; Humphrey, R. J. Am. Chem. Soc. <u>1959</u> , 81, 2043		
	(4) Kolthoff, I. M.; Chantooni, M. K. Jr. Anal. Chem. <u>1972</u> , 44, 194.		

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COMPONENTS .	ORIGINAL MEASUREMENTS .				
(1) Silver tetraphenylborate (1-); $AgC_{24}H_{20}B;$ [14637-35-5] (2) Sodium perchlorate; NaClO ₄ ; [7601-89-0] (3) Sodium tetraphenylborate; NaC ₂₄ H ₂₀ B; [143-66-8] (4) Ethanol; C ₂ H ₆ O; [64-17-5]	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.				
VARIABLES :	PREPARED BY:				
One temperature: 25°C	Orest Popovych				
EXPERIMENTAL VALUES:					
The solubility (ion-activity) pr determined in the presence of 0.01-0.	coduct of $AgBPh_4$ in ethanol was 005 mol dm ⁻³ NaBPh ₄ and reported as:				
The mean ionic activity coefficient w in the form: $\log \gamma_{\pm} = -A [(I)^{1/2}/(I)^{1/2})$ ionic strength in mol dm ⁻³ and the va dm ^{3/2} . The solubility products and i infinite dilution by iteration, to all	vas calculated from the Davies equation $+ (I)^{1/2}) - (1/3)I]$, where I is the lue of <u>A</u> used was 2.956 mol ^{-1/2} onic strengths were "adjusted to .low for incomplete dissociation"				
AUXILIARY	INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:				
Potentionmetric titration of 0.01 mol dm ⁻³ NaBPh ₄ with 0.01 mol dm ⁻³ AgClO ₄ . The ionic strength at the midpoint of the titration curve was used to calculate the activity coefficient.	Not stated.				
	ESTIMATED ERROR: Nothing specified. A precision of ±0.1 pK units is assumed by the compiler. REFERENCES:				

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COMPONENTS: (1) Silver tetraphenyl-	ORIGINAL MEASUREMENTS:			
<pre>borate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium nitrate; NaNO₃ [7631-99-4] (3) Sodium tetraphenylborate; NaC₂₄H₂₀B; [143-66-8] (4) Formamide; CH₃NO; [75-12-7]</pre>	Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1967</u> , <i>89</i> , 3703-12.			
VARIABLES:	PREPARED BY:			
25°0				
one cemperature: 25 C	orest ropovych			
EXPERIMENTAL VALUES:				
The solubility product of AgBPh ₄ in formamide was reported as a product of ionic concentrations determined at ionic strengths in the range of 0.01-0.05 mol dm ⁻³ , maintained by NaBPh ₄ : $K_{SO}^{\circ} = 10.3$ (K_{SO}° units are in mol ² dm ⁻⁶).				
AUXILIARY	INFORMATION			
Potentiometric titration of 0.01 mol dm ⁻³ solution of NaBPh ₄ with AgNO ₃ using a silver indicator electrode and a silver-silver nitrate reference cell connected by a bridge of NEt ₄ picrate. A radiometer pH meter, Type PHM22r was used. Cell was thermo- statted, but limits of temperature	Formamide was dried with Type 4A molecular sieves and fractionated twice under a reduced pressure of dry nitrogen. The salts were of Analar grade and were used as received.			
CONTROL were not specified.				
The shave colubility product coome to				
comprise a combination of concen- tration (for the BPh4 ⁻ ion) and activity (for the Ag ⁺ ion). The validity of the reported value is therefore <u>doubtful</u> .	ESTIMATED ERROR: Nothing specified. A precision of ± 0.1 pK units is assumed by the compiler.			
	REFERENCES:			

Sil	ver .	165		
COMPONENTS:	ORIGINAL MEASUREMENTS:			
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Hexamethylphosphorotriamide; C₆H₁₈N₃OP; [680-31-9] 	Alexander, R.; Ko, E. C. F.: Mac, Y. C.; Parker, A. J. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1967</u> , <i>89</i> , 3703-12.			
VARIABLES:	PREPARED BY:			
One temperature: 25°C	Orest Popovych			
EXPERIMENTAL VALUES:				
The solubility product of AgBPh, was reported as a product of ionic co corresponding to the solubility:	in hexamethylphosphorotriamide oncentrations at the ionic strength			
pK _{s0} ≈ 4.7 (K _{s0} ur	tis are $mol^2 dm^{-6}$).			
	-			
AUXILIARY INFORMATION				
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Not specified unambiguously: it could have been either potentiometric titration with KI or UV-spectrophoto- metry on a Unicam SP500 spectrophoto- meter. Saturated solutions were prepared by shaking for 24 hours at 35°C and then for a further 24 hours at 25°C.	Hexamethylphosphorotriamide was dried with Type 4A molecular sieves and fractionated twice under a reduced pressure of dry nitrogen.	3		
	ESTIMATED ERROR: Nothing specified. A precision of ±0.1 pK units is assumed by the compiler.			
	REFERENCES :			

COMPONENTS :	EVALUATOR:
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14627-35-5] (2) Methanol; CH₄O; [67-56-1] 	Orest Popovych, Department of Chemistry, The City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. September 1979

CRITICAL EVALUATION:

Only two publications reported the solubility product of silver tetraphenylborate (AgBPh₄) in methanol, both at 298 K (1, 2). The formal (concentration) solubility product determined by Alexander et al. (1) from a potentiometric titration of BPh₄ with AgNO₃ using a silver electrode at ionic strength kept constant at 0.01 mol dm⁻³ was expressed as $pK_{s0} = 13.2$ (all K_{s0} units in this evaluation are mol² dm⁻⁶).

Kolthoff and Chantooni (2) employed both potentiometry in the presence of NaBPh₄ and chemical-exchange reactions in which either solid AgBr was equilibrated with a solution of NaBPh₄ or solid AgBPh₄ was equilibrated with a solution of NaBr to determine the pK_{SO}° of AgBPh₄. They obtained the same result by both methods: $pK_{SO}^{\circ} = 14.4 \pm 0.01$.

Despite the fact that the above result was obtained by two independent methods, one hesitates to designate it as better than <u>tentative</u>, because of the relatively poor precision of the determination. The corresponding solubility at 298 K, calculated simply as $(K_{SO}^{\circ})^2$ would be (6.3 ± 0.7) x 10^{-8} mol dm⁻³ (evaluator). From the results of the individual potentiometric experiments (see compilation), it is possible to calculate the $K_{SO}^{\circ} = (4.0 \pm 0.8) \times 10^{-15}$ and the corresponding solubility of (6.3 ± 0.6) x 10^{-8} mol dm⁻³ (compiler). The latter values of K_{SO}° and of the solubility are preferable to the extent that no error due to conversion from the pK value was involved. Nevertheless, it would seem that a relative precision of better than 10% could perhaps be achieved for the solubility in the future.

REFERENCES:

- Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 3703.
- 2. Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. 1972, 44, 194.

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COMPONENTS: (1) Silver tetraphenyl-	ORIGINAL MEASUREMENTS:
borate $(1-)$; AgC ₂₄ H ₂₀ B; [14637-35-5]	
(2) Sodium nitrate; NaNO ₃ ; [7621.00.4]	Alexander, R.; Ko, E. C. F.; Mac,
(3) Sodium tetraphenylborate:	Soc. 1967. 89. 3703-12.
$NaC_{2}H_{2}B; [143-66-8]$,,
(4) Methanol; CH40; [67-56-1]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES.	
The solubility product of AgBPh	4 in methanol was reported as a
range of 0.01-0.005 mol dm ⁻³ maintain	mined at ionic strengths in the ed by NaBPh. :
$pK_{s0} = 13.2 (K_{s0})$	units are mol ² dm ⁻⁶).
30 50	
	-
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Potentionethic tituetion of 0.01	For the numification method for
$mol dm^{-3}$ solution of NaBPh with	methanol the reader was referred
AgNO, using a silver indicator	to a literature source (1).
electrode and a silver-silver nitrate	The salts were of Analar grade and
reference cell connected by a bridge	were used as received.
of NEt, picrate. A radiometer pH	
Meter, Type PHM22r was used. Cell	
temperature control were not	
specified.	
}	
	ESTIMATED ERROR:
	None specified. A precision of
	± 0.1 pK units is assumed by the
Į	compiler.
	REFERENCES:
	E. C. F., Mac. Y. C.: Parker.
]	A. J. J. Am. Chem. Soc. 1966.
	88, 1911.
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ORIGINAL MEASUREMENTS:			
Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u> , 44, 194-5.			
PREPARED BY:			
Orest Bereuveh			
orest ropovych			
oduct of AgBPh4 in methanol was			
inits are $mol^2 dm^{-6}$).			
cal-exchange experiments described			
Ż AgBPh. (s) + NaBr			
[RPb 7]			
was measured.			
[Br]			
for using a literature value for the dissociation constant, K ^d = 0.10 (2) (presumably in units of mol dm ⁻³). Activity coefficients y were cal- culated from the partially extended Debye-Hückel equation, using the following values for the ion-size parameters: BPh ₄ 1.2 nm, Br ⁻ -0.3 nm, Na ⁺ -0.4 nm. The solubility product of AgBPh ₄ was determined also from potentio- metric measurements in NaBPh ₄ solutions saturated with AgBPh ₄ , employing			
AUXILIARY INFORMATION			
<pre>SOURCE AND PURITY OF MATERIALS: Methanol was Matheson Spectroquality distilled once over Mg turnings (H₂O content 0.01% by Karl Fischer). NaBr was Mallinckrodt AR Grade, recrystal- lized from water. NaBPh₄ was Aldrich puriss. product, recrystallized by a literature method (3). AgBPh₄ was prepared by metathesis of AgNO3 and 2% excess of NaBPh₄. The product was washed well with methanol, dried <u>in</u> <u>vacuo</u> at 50°C for 3 hrs., all pre- parations and storage being in the dark. AgBr was prepared and handled analogously. ESTIMATED ERROR: Precision ±0.1 pK units Accuracy ±0.2 pK units Temperature control: ±1°C REFERENCES: (1) Buckley, P.; Hartley, H. <i>Phil. Mag.</i> <u>1929</u>, <i>8</i>, 320. (2) Jervis, R.; Muir, D.; Butler, J.; Gordon, A. J. Am. Chem. Soc. <u>1953</u>, 75, 2855. (3) Popov, A. I.; Humphrey, R. J. Am. <i>Chem. Soc.</i> <u>1959</u>, <i>81</i>, 2043.</pre>			

			Silver		•		169
COMPONENTS:			ORI	GINAL	MEASUR	EMENTS:	
<pre>(1) Silver AgC₂₄H₂ (2) Sodium NaC₂₄H₂ (3) Sodium (4) Methano</pre>	tetraphen $_{0}$ B; [1462 tetraphen $_{0}$ B; [143- bromide; 1; CH ₄ O;	ylborate (1- 27-35-5] sylborate; 66-8] NaBr; [7647- [67-56-1]	-); -15-6]	olthof r. Ana	f, I. I I. Cher	M.; Chantoon: m. <u>1972</u> , 44,	1, М. К., 194-5.
EXPERIMENTAL	VALUES:	(continued	1)			<u></u>	
a silver in electrode i are mol ² dm	a silver indicator electrode and a 0.01 mol dm^{-3} AgNO ₃ /Ag reference electrode in methanol. It was reported as $pK_{SO}^{\circ} = 14.4 \pm 0.1$ (K_{SO}° units are mol ² dm^{-6}). Below are the results of individual experiments.					ce units	
		Exchange	Experime	nts			
(All concen	trations	are in mol o equilibi	lm ⁻³ . The ium conce	quant ntrati	ities ons).	in brackets a	are
Initial	10 ⁴ [NaBr]	10 ⁴ [Br ⁻] 10) ² [BPh4 ⁻]	y _{BPh} ,	y _{Br} -	K [°] ₅₀ (AgBPh ₄)	pK_{s0}°
C _{NaBPh4}						K _{s0} (AgBr)	(
or C _{NaBr}							
		NaBPh ₄ -	- AgBr				
0.0030 0.0186	0.37 1.0	7.0 1.3 ₇	0.86 ₀ 1.7 ₁	0.78 0.74	0.72 0.62	12 15	14.4 14.3
		NaBr + A	gBr				
0.0113 0.0226	0.77 2.25	12.7 27. ₂	1.00 1.99	0.77 0.72	0.70 0.60	8.7 8.8	14.5 14.5
		Potentic	metric Ex	perime	nts		
(All concen	trations	and activiti	es are in	units	of mo	1 dm ⁻³)	
10 ³ C _{NaBPh4}	E, mV	10 ¹² a _{Ag} +	y _{BPh4} -	K	° (AgBl s0	Ph ₄) x 10 ¹⁵ /r	$nol^2 dm^{-6}$
1.57 3.92 9.80	-540 -552 -586	2.5 1.6 0.43	0.88 0.83 0.78		3. 5. 3.	5 2 3	
The authors report only an average value of pK_{s0}° . This compiler calculates from the above data $K_{s0}^{\circ} = (4.0 \pm 0.8) \times 10^{-15} \text{ mol}^2 \text{ dm}^{-6}$. Neglecting activity corrections, the solubility is (6.3 ± 0.6) x 10^{-8} mol dm ⁻³ (compiler).							

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170 Sil	Silver			
COMPONENTS:	ORIGINAL MEASUREMENTS:			
 (1) Silver tetraphenylborate (1-); AgC₂₄H₂₀B; [14637-35-5] (2) Sodium perchlorate; NaClO₄; [7601-89-0] (3) Sodium tetraphenylborate; NaC₂₄H₂₀B; [143-66-8] (4) N-Methyl-2-pyrrolidinone; C=HoNO: [872-50-4] 	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.			
VARIABLES:	PREPARED BY:			
One temperature: 25°C	Orest Popovych			
EXPERIMENTAL VALUES:				
The solubility (ion-activity) property pyrrolidinone was determined in the pyrrolidinone reported as:	coduct of AgBPh ₄ in N-methyl-2- presence of 0.01-0.005 mol dm ⁻³			
$pK_{s0}^{\circ} = 4.9 \ (K_{s0}^{\circ} \ u)$	nits are mol ² dm ⁻⁶).			
The mean ionic acticity coefficient $\gamma_{\pm} = -A$ [equation in the form: log $\gamma_{\pm} = -A$ [I is the ionic strength in mol dm ⁻³ ; mol ^{-1/2} dm ^{3/2} .	was calculated from the Davies $(I)^{1/2}/(1 + (I)^{1/2}) - (1/3)I]$, where and the value of <u>A</u> used was 2.004			
AUXILIARY	INFORMATION			
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:			
Potentionmetric titration of 0.01 mol dm ⁻³ NaBPh ₄ with 0.01 mol dm ⁻³ AgClO ₄ . The ionic strength at the midpoint of the titration curve was used to calculate the activity coefficient.	Not stated.			
	ESTIMATED ERROR: Nothing specified. A precision of ±0.1 pK units is assumed by the compiler.			
	KEFERENCES:			

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COMPONENTS: (1) Silver tetraphenylborate (1-); $AgC_{24}H_{20}B;$ [14637-35-5] (2) Sodium perchlorate; NaClO ₄ ; [7601-89-0] (3) Sodium tetraphenylborate; $NaC_{24}H_{20}B;$ [143-66-8] (4) Nitromethane; $CH_3NO_2;$ [75-52-5]	ORIGINAL MEASUREMENTS: Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) product of AgBPh ₄ in nitromethane was determined in the presence of 0.01-0.005 mol dm^{-3} NaBPh ₄ and reported as:	
$pK_{s0}^{\circ} = 15.6 (K_{s0}^{\circ})$	units are mol ² dm ⁻⁶).
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{1/2}/(I + (I)^{1/2}) - (I/3) I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 1.479 mol ^{-1/2} dm ^{3/2} .	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Potentiometric tetration of 0.01 mol dm ⁻³ NaBPh ₄ with 0.01 mol dm ⁻³ AgClO ₄ . The ionic strength at the midpoint of the titration curve was used to calculate the activity coefficient.	Not stated.
	ESTIMATED ERROR: Nothing specified. A precision of ±0.1 pK units is assumed by the compiler. REFERENCES:

Silver

COMPONENTS: (1) Silver tetraphenyl-	ORIGINAL MEASUREMENTS:
borate (1-); $AgC_{24}H_{20}B$; [14637-35-5]	
(2) Sodium perchlorate; NaClO ₄ ;	Alexander, R.; Parker, A. J.; Sharp,
[/601-89-0]	J. H.; Waghorne, W. E. J. Am. Chem.
(3) Sodium tetraphenyiborate;	<i>500</i> . <u>1972</u> , <i>94</i> , 1148-58.
(4) Propagedio1-1.2-carbonate (pro-	
pylene carbonate); C ₁ H _c O ₂ ;	
[108-32-7]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EVPERTMENTAL VALUES.	
The solubility (ion-activity) pr was determined in the presence of 0.0 as:	oduct of AgBPh4 in propylene carbonate)1-0.005 mol dm ⁻³ NaBPh4 and reported
$pK_{S0}^{\circ} = 12.8 \ (K_{S0}^{\circ})$	units are $mol^2 dm^{-6}$).
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{1/2}/(1 + (I)^{1/2}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 0.661 mol ^{-1/2} dm ^{3/2} .	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS:	
Potentiometric titration of 0.01 mol dm^{-3} NaBPh ₄ with 0.01 mol dm^{-3} AgClO ₄ . The ionic strength at the midpoint of the titration curve was	Not stated.
used to calculate the activity coefficient.	
	ESTIMATED ERROR: Nothing specified. A precision of ± 0.1 pK units is assumed by the compiler.
	REFERENCES:

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COMPONENTS: (1) Silver tetraphenylborate (1-); $AgC_{24}H_{20}B$; [14637-35-5] (2) Sodium perchlorate; NaClO ₄ ; [7601-89-0] (3) Sodium tetraphenylborate; NaC ₂₄ H ₂₀ B; [143-66-8] (4) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]	ORIGINAL MEASUREMENTS: Alexander, R.; Parker, A. J.; Sharp, J. H. Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.
VARIABLES: One temperature: 25°C	PREPARED BY: Orest Popovych
EXPERIMENTAL VALUES: The solubility (ion-activity) pr determined in the presence of $0.01-0.0$ $pK_{S0}^{\circ} = 13.1$ (K_{S0}° ur The mean ionic activity coefficient we equation in the form: $\log \gamma_{\pm} = -A$ [$(\frac{1}{2} \text{ is the ionic strength in mol } dm^{-3} \text{ are mol}^{-1/2} dm^{3/2}$. The solubility product to infinite dilution by iteration, to	roduct of AgBPh4 in acetone was .005 mol dm ⁻³ NaBPh ₄ and reported as: mits are mol ² dm ⁻⁶). was calculated from the Davies $(1)^{1/2}/(1 + (1)^{1/2}) - (1/3)I]$, where and the value of <u>A</u> used was 3.760 ets and ionic strengths were "adjusted to allow for incomplete dissociation"

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;
Potentiometric titration of 0.01 mol	
dm ⁻⁵ NaBPh ₄ with 0.01 mol dm ⁻⁵	Not stated.
AgClo ₄ . The ionic strength at the	
used to coloulate the activity	
coefficient	
cocriticient.	
	ESTIMATED ERROR:
	Nothing specified. A precision
	of ± 0.1 pK units is assumed by the
	compiler.
	REFERENCES:
	[

COMPONENTS:	EVALUATOR:
(1) Silver tetraphenylborate $(1-)$; AgC ₂₄ H ₂₀ B; [14637-35-5]	Orest Popovych, Department of Chemistry, The City University of New York, Brooklyn College,
(2) Tetrahydrothiophene-1,1-dioxide (sulfolane, tetramethylene sul- fone); C ₄ H ₈ O ₂ S; [126-33-0]	Brooklyn, N. Y. 11210, U. S. A. September 1979

The solubility product of silver tetraphenylborate (AgBPh₄) in sulfolane at 303 K was reported twice from the same laboratory (1, 2). The first determination employed UV-spectrophotometry, obtaining a formal (concentration) solubility product expressed as $pK_{SO} = 9.5 \pm 0.1$ (here all K_{SO} values have units of mol² dm⁻⁶). In the second publication (2) the determination was based on a potentiometric titration of $BPh_4^$ with Ag⁺ using a silver electrode, coupled with a calculation of activity coefficients from the Davies equation (see compilation). The new result was $pK_{SO}^{\circ} = 10.2$. Unfortunately, neither study mentioned the nature of temperature control and the second study did not specify how saturation was ascertained. The solubility itself might be best calculated from the concentration pK_{s0} of 9.5, because it is at least free of uncertainty with respect to the activity correction. Taking simply the square root of the K_{s0}, we obtain for the solubility: (1.8 ± 0.2) x 10⁻⁵ mol dm⁻³ as the tentative value.

REFERENCES:

- 1.
- Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. 2. J. Am. Chem. Soc. 1972, 94, 1148.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Silver tetraphenylborate(1-); AgC₂₄H₂₀B; [14637-35-5]</pre>	Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.
<pre>(2) Tetrahydrothiophene-1,1-dioxide (sulfolane); C₄H₈O₂S; [126-33-0]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 30°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubility product of ${\tt AgBPh}_{\mu}$ in sulfolane was reported as:	
$pK_{s0}^{\circ} = 9.5$	(K_{s0}° units are mol ² dm ⁻⁶).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions	The purification of materials has
saturated under nitrogen, using a	been described in the literature
Saturated solutions were prepared	
by shaking for 24 hours at 35°C	
30°C.	
	ESTIMATED ERROR:
	Absolute precision was estimated to be ±0.1 pK units.
	REFERENCES :
	(1) Clare, B. W.; Cook, D.; Ko, E. C.
	J. Am. Chem. Soc. 1966.88. 1911.
	(2) Alexander, R.; Ko, E. C. F.; Mac,
	<i>L. U.; Parker, A. J. J. Am. Chem.</i> Soc. 1967, 89, 3703.
	(3) Parker, A. J. J. Chem. Soc. A

COMPONENTS: (1) Silver tetraphenylborate	ORIGINAL MEASUREMENTS:
(2) Sodium perchlorate; NaClO ₄ ;	Alexander, R.; Parker, A. J.; Sharp,
[7601-89-0]	J. H.; Waghorne, W. E. J. Am. Chem.
NaC ₂₄ H ₂₀ B; $[143-66-8]$	<i>500</i> , <u>1972</u> , <i>3</i> , 1140-50.
(4) Tetrahydrothiophene-1,1-dioxide	
$(sufforme); C_4H_8O_2S; [126-33-0]$	
VARIABLES:	PREPARED BY:
One temperature: 30°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) pr determined in the presence of 0.01-0.0	roduct of AgBPh ₄ in sulfolane was DO5 mol dm ⁻³ NaBPh ₄ and reported as:
$pK_{s0}^{\circ} = 10.2 \ (K_{s0}^{\circ})$	units are mol ² dm ⁻⁶).
The mean ionic activity coefficient we in the form: log $\gamma_{\pm} = -A [(I)^{\frac{1}{2}}/(1 + I)^{\frac{1}{2}})$ ionic strength in mol dm ⁻³ and the value of the strength in mol dm ⁻³ and the value of the strength in mol dm ⁻³ and stre	as calculated from the Davies equation $(I)^{\frac{1}{2}}$ - $(1/3)I$, where <u>I</u> is the lue of <u>A</u> used was 1.244 mol ^{-1/2} dm ^{3/2} .
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Potentiometric titration of 0.01 mol dm ⁻³ NaBPh ₄ with 0.01 mol dm ⁻³ AgClO ₄ . The ionic strength at the midpoint of the titration curve was used to calculate the activity coefficient	Not stated.
	ESTIMATED ERROR: Not specified. A precision of ±0.1 pK units is assumed by the compiler.
	REFERENCES:
	1

COMPONENTS:	EVALUATOR:
<pre>(1) Thallium(I) tetraphenylborate</pre>	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A. December 1979

The solubility of thallium(I) tetraphenylborate (TlBPh₄) at 298 K was reported as 5.29×10^{-5} mol dm⁻³ in pure water (1) and as 1.1×10^{-5} mol dm⁻³ in a THAM buffer solution (2). Both were determined by uv-spectrophotometry, but the molar absorption coefficients in the first study were characteristic of acetonitrile (not aqueous) solutions. (For a discussion of the consequences, see the critical evaluation for KBPh₄ in aqueous systems). In the second study, the molar absorption coefficients were not specified.

Because the ionic strength of the THAM buffer in the second study is not known, it is impossible to estimate the corresponding solubility at zero ionic strength. However, it is clear that the latter value should be lower than 1.1 x 10^{-5} mol dm⁻³, which makes for an even greater discrepancy between the two literature data. Thus, the <u>solubility of</u> <u>5.29 x 10^{-5} mol dm⁻³</u> reported by Pflaum and Howick (1) must be evaluated as highly <u>tentative</u>.

REFERNECES:

Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u>, 28, 1542.
 McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u>, 38, 136.

178 Thalli	um(l)
COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Thallium(I) tetraphenylborate (1-); TlC₂₄H₂₀B; [14637-31-1]</pre>	Pflaum, R. T.; Howick, L. C. Anal. Chem. <u>1956</u> , 28, 1542-4.
(2) Water; H ₂ O; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of TlBPh4 in water was	reported as 5.29 x 10^{-5} mol dm ⁻³ .
METHOD/APPAKATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Ultraviolet spectrophotometry. For	See compilation for KBPh ₄ in water
KBPh ₄ in water based on the same	was prepared by metathesis of T1C1
reference.	and NaBPh ₄ and recrystallized from
	an aceconterite-water mixture.
	ESTIMATED EREOR.
	Nothing is specified, but the
	precision is likely to be ±1%
	(compiler).
	REFERENCES:

ORIGINAL MEASUREMENTS:

 (1) Thallium(I) tetraphenylborate (1-); TIC₂₄H₂₀B; [14637-31-1] (2) Tris(hydroxymethyl)aminoethane; C₄H₁₁NO₃; [77-86-1] (3) Acetic acid; C₂H₄O₂: [64-19-7] (4) Water; H₂O; [7732-18-5] 	McClure, J. E.; Rechnitz, G. A. Anal. Chem. <u>1966</u> , 38, 136-9.
VARIABLES:	PREPARED BY:
One temperature: 24.8°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of thallium(I) to tris(hydroxymethyl)aminomethane (THA)	etraphenylborate (TlBPh ₄) in aqueous M) at pH 5.1 was reported as:
1.1 x 10 ⁻⁵ mo.	1 dm ⁻³ .
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: UV-spectrophotometry according to the procedure of Howick and Pflaum •(1). No other details.	<pre>SOURCE AND PURITY OF MATERIALS: The buffer solution consisted of 0.1 mol dm⁻³ THAM and 0.01 mol dm⁻³ acetic acid, adjusted to pH 5.1 with G. F. Smith reagent-grade HClO₄. The source of BPh₄ was a solution of Ca(BPh₄) in THAM prepared from Fisher Scientific reagent-grade NaBPh₄ by the procedure of Rechnitz et al. (2) and standardized by poten- tiometric titration with KCl and RbCl. Tl⁺ solutions were prepared by dis- solving Tl₂CO₃ (A. D. Mackay, Inc.) in HClO₄. ESTIMATED ERROR: Not stated. Temperature: ±0.3°C REFERENCES: (1) Howick, L. C.; Pflaum, R. T. Anal. Chim. Acta 1958, 19, 342. (2) Rechnitz, G. A.; Katz, S. A.; Zamochnick, S. B. Anal. Chem. 1963, 35, 1322.</pre>

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COMPONENTS:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Thallium(I) tetraphenylborate (1-); TlC₂₄H₂₀B; [14637-31-1]</pre>	Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u> , 76, 2024-34.
<pre>(2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product of TlBPh4 reported as:	in N,N-dimethylformamide was
$pK_{s0}^{\circ} = 4.5 (K_{s0}^{\circ} un)$	its are mol ² dm ⁻⁶).
The above value was derived from the saturated solution $\kappa = 3.80 \times 10^{-4}$ oh coefficient calculated from the Gugge	electrolytic conductivity of the m ⁻¹ cm ⁻¹ and a mean molar activity nheim equation (not shown).
AUXILIARY	
METHOD/APPARATUS/PROCEDURE: Electrolytic conductance of the	SOURCE AND PURITY OF MATERIALS: N,N-Dimethylformamide was purified
saturated solution, using apparatus previously described (1). The	by a literature method (3). $T1BPh_4$ was prepared as described in the
authors state the precision of the	compilation for dimethysulfoxide.
for the λ^{∞} of T1 ⁺ employed in the	
calculation was taken from the literature (2) and if the average	
value from the above source was used,	
it was 91.1 S cm ² mol ⁻¹ . The λ^{-1} for the BPh ₀ ⁻ ion was estimated from the	
Walden rule using the known (unspecified) value in acetonitrile	
Presumably, the solubility <u>C</u> was	ESTIMATED ERROR:
$C = 1000\kappa/\Lambda^{\infty}$, but this is not ex-	Nothing specified.
plained in the text and the actual solubility is not reported.	
COMMENTS, Halden's rule to known	REFERENCES: (1) Kolthoff, I. M.;
to be unreliable. The use of	Bruckenstein, S.; Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1961</u> , 83,
limiting conductivities for solutions of the order of 10^{-2} mol dm ⁻³ is	3927.
questionable. The method of	J. Phys. Chem. 1970, 74, 963.
specified.	(3) Kolthoff, I. M.; Chantooni, M. K., Jr.; Smagowski, H. Anal. Chem.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Thallium(I) tetraphenylborate (1-); $TIC_{24}H_{20}B$; [14637-31-1] (2) Dimethylsulfoxide; $C_{2}H_{2}OS$;	Kolthoff, I. M.; Chantooni, M. K., Jr. <i>J. Phys. Chem.</i> <u>1972</u> , 76, 2024-34.
[67-68-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility of TlBPh4 in dime	thylsulfoxide was reported as:
$C = 4.9 \times 10^{-2} \text{ mol}$. dm ⁻³ .
After determining that the above salt was completely dissociated (based on conductance data), the authors calculated the mean ionic activity coefficients from the Guggenheim equation (not shown) and reported the solubility product of TlBPh4 in dimethylsulfoxide as:	
$pK_{S0}^{\circ} = 2.9 \ (K_{S0}^{\circ} \ ur$	tts are mol ² dm ⁻⁶).
	INFORMATION
METHOD/APPARATUS/PROCEDURE: Electrolytic conductance of the saturated solution, using previously described apparatus (1). The elec- trolytic conductivity of the saturated solution at 25°C was re- ported as 11.5 x 10 ⁻⁴ ohm ⁻¹ cm ⁻¹ , with a precision of $\pm 2\%$. Values of Λ^{∞} in dimethylsulfoxide were estimated from those in acetonitrile using Walden's rule. Presumably, the solubility <u>C</u> was calculated from the relationship C = $1000\kappa/\Lambda^{\infty}$, where	SOURCE AND PURITY OF MATERIALS: Dimethylsulfoxide was thoroughly purified by a literature method (2). Sodium tetraphenylborate (Aldrich puriss. grade) was purified by the method of Popov and Humphrey (3). TlBPh ₄ was prepared by metathesis of TlNO ₃ with NaBPh ₄ .
K is the electrolytic conductivity.	ESTIMATED ERROR:
COMMENTS:	Nothing specified.
Walden's rule is notoriously unre- liable. In addition, errors are incurred by employing limiting conductivities at concentrations as high as the reported solubility value. The method of ascertaining saturation was not specified.	REFERENCES: (1) Kolthoff, I. M.; Bruckenstein, S.; Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1961</u> , 83, 3927. (2) Kolthoff, I. M.; Reddy, T. B. Inorg. Chem. <u>1962</u> , 1, 189. (3) Popov, A. I.; Humphrey, R. J. Am. Chem. Soc. <u>1959</u> , 81, 2043.

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COMPONENTS:	EVALUATOR:
<pre>(1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈ H₄₀ BAs; [15627-12-0] (2) Water; H₂0; [7732-18-5]</pre>	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
	November 1979

All three reasonable estimates of the solubility of tetraphenylarsonium tetraphenylborate (Ph_4 As BPh_4) in water come from Parker's laboratory (1-3) and all were determined at 298 K. The first two were reported as formal (concentration) solubility products (in the units of mol² dm⁻⁶) expressed in the form $pK_{s0} = 16.7$ (1) and 17.2 (2), respectively. The latter value corresponds to a solubility of 2.5 x 10⁻⁹ mol dm⁻³, but the authors' estimate of precision is ±0.5 pK units, which means that the solubility could range anywhere from 4.5 x 10⁻⁹ mol dm⁻³ to 1.4 x 10⁻⁹ mol dm⁻³. Although the spectral region in which the saturated solutions were analyzed was not specified, the uv-determination of the solubility must have been carried out in the non-specific shortwavelength region of the near-uv spectrum, where absorption is high, but where the tetraphenyl species cannot be distinguished from other aromatics, including decomposition products. On the other hand, in the region of 260-275 nm, where tetraphenyl compounds show characteristic spectra, the molar absorption coefficients are of the order of 10³ dm³ (cm mol)⁻¹, which renders impossible a uv-analysis of 10⁻⁹ mol dm⁻³ solutions. The need to analyze in the non-specific region of the spectrum may be responsible for the low precision of the reported solubility product.

Subsequently, Cox and Parker (3) expressed their preference for the determination of the solubility product by chemical-exchange experiments, between a solution of $AgNO_3$ and solid Ph_4As BPh_4 and a solution of Ph_4As NO_3 and solid $AgBPh_4$. The resulting value of $pK_{SO} = 17.4$ (K_{SO} units are mol² dm⁻⁶) is difficult to assess as to precision. For one thing, it is based on the literature value for the pK_{SO} of $AgBPh_4$ which itself is subject to an error of the order of 0.1 pK units (4). Furthermore, Cox and Parker did not mention whether or not any corrections were introduced for the activity coefficients of Ag^+ and Ph_4As^+ ions in their computation. Therefore, the K_{SO} of Ph_4As BPh_4 is likely to be partially based on activity and partially on concentration. Since the precision in the pK_{SO} can be no better than ± 0.2 pK units, the solubility of Ph_4As BPh_4 in water calculated as (K_{SO})⁴ could range from about 2.5 x 10⁻⁹ mol dm⁻³ to 1.6 x 10⁻⁹ mol dm⁻³. The nominal solubility value of 2.0 x 10⁻⁹ mol dm⁻³

In view of the results in all three studies by Parker et al. (1-3), the K_{SO} value of 5.0 x 10^{-9} mol² dm⁻⁶ reported by Cole and Pflaum (5) must be of the wrong order of magnitude. Since the authors did specify uvanalysis at 264 nm and 271 nm, it would appear that what they observed was absorption due to decomposition products and possibly, the starting materials.

References:

Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 5549.
 Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313.
 Cox, B. G.; Parker, A. J. J. Am. Chem. Soc. <u>1972</u>, 94, 3674.
 Kolthoff, I. M.; Chantooni, M. K., Jr. Anal. Chem. <u>1972</u>, 44, 194.
 Cole, J. J.; Pflaum, R. T. Proc. Iowa Acad. Sciences <u>1964</u>, 71, 145.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. J. Am. Chem. Soc. 1967, 89, 5549-51.
(2) Water; H ₂ 0; [7732-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubilit was reported as:	y product of $Ph_4As BPh_4$ in water
pK _{s0} = 16.7 (K _{s0} un	its are $mol^2 dm^{-6}$).
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AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.
,	
	ESTIMATED ERROR:
	None specified.
	DEPENDENCIE .
	REFERENCES:

Tetraphenylarsonium

COMPONENTS :	ORIGINAL MEASUREMENTS:
 (1) Tetraphenylarsonium tetra- phenylborate (1-); C₄₈H₄₀BAs; [15627-12-0] (2) Water; H₂0; [7732-18-5] 	Parker, A. J.; Alexander, R. • J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.
WADTADI 200 +	DEBARED BY.
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubilit was reported as: pK _{SO} = 17.2 (K _{SO} u	y product of Ph ₄ As BPh ₄ in water nits are mol ² dm ⁻⁶).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen, using a Unicam SP500 spectrophotometer. Saturated solutions were prepared by shaking for 24 hours at 35°C and then for a further 24 hours at 25°C.	The purification of materials has been described in the literature (1-3).
	ESTIMATED ERROR:
	Absolute precision was estimated to be ± 0.5 pK units.
	 REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1966</u>, 88, 1911. (2) Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 3703. (3) Parker, A. J. J. Am. Chem. Soc. A <u>1966</u>, 220.

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tetraphenylborate (1-): C. H. BAS:	ORIGINAL MEASUREMENTS:
[15627-12-0]	Cox, B. G.; Parker, A. J.
(2) Silver nitrate; AgNO ₃ ; [7761-88-8]	J Am Cham Sea 1972 04 3674-5
(3) Tetraphenylarsonium nitrate;	<i>a. Am. chem. 500.</i> <u>1972</u> , 94, 5074-5.
$C_{24H_{2}0AsN03}$; [6727-90-8]	
(4) water; H_20 ; [//32-18-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility product of Ph4As BPh4	in water was reported in the form:
$pK_{s0} = 17.4 (K_{s0})$	units are $mol^2 dm^{-6}$).
The above value was obtained from me	asurements on the equilibrium:
$Ph_4As BPh_4 (s) + AgNC$	/ ₃ ← Ph ₄ As NO ₃ + AgBPh ₄ (s)
which is governed by the relationshi	p:
$pK_{s0}(Ph_4As BPh_4) = -1$	og [($Ph_{\mu}As^{+}$)/(Ag^{+})] + PK_{eO} (AgBPh.)
The value of $p_{KSO}(AgbFn_4) = 1/.2$ was	taken from the literature (1).
AUXILIARY	INFORMATION
METHOD / APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
Fifty cm ³ of 0.01 mol dm ⁻³ AgNO ₂	
were equilibrated with 1 g of ³	Not stated.
AgBPh ₄ as seed and 50 cm ³ of 0.01	
mol dm ⁻³ Ph ₄ As NO ₃ were equilibrated	
with i g of AgBPh ₄ containing a trace of Ph ₄ As BPh ₄ as seed, all in	
CO_2 -free water under nitrogen and in	
light-proof vessels. The solutions	
absorption and for Ph ₄ As ⁺ by UV	
spectrophotometry at 265 nm.	
	ESTIMATED ERROR:
(
	Not specified.
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	KEFEKENGES:
	(1) Kolthoff, I. M.; Chantooni, M. K.
	Jr. Anal. Chem. <u>1972</u> , 44, 194.

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186	Tetraphenylarsonium	
COMPON	VENTS:	ORIGINAL MEASUREMENTS:
(1)	Tetraphenylarsonium tetraphenylborate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	Cole, J. J.; Pflaum, R. T. Proc. Iowa Acad. Sciences <u>1964</u> , 71, 145-150.
(2)	Water; H ₂ O; [7732-18-5]	
VARIA	BLES:	PREPARED BY:
One	temperature: 25.0°C	Orest Popovych
EXPER	IMENTAL VALUES:	
The	authors reported the solubility o	f Ph ₄ As BPh4 in water at 25°C as:
C = dm ⁻¹ corr	4.99 x 10^{-4} g/100 cm ³ and the cor ⁶ . Apparently K _{SO} was calculated rection.	responding $K_{s}O$ as 5.0 x 10^{-9} mol^2 as C^2 , i.e., there was no activity
}		
<u> </u>		ΙΝΕΩΡΜΑΤΙΩΝ
METHO UV s pho pre bati when with	DD/APPARATUS/PROCEDURE: spectrophotometry at 264 and 271 using a Cary Model 14 spectro- tometer. Saturated solutions pared in a constant-temperature h and equilibration was assumed n successive analyzes agreed to hin ±0.5%.	SOURCE AND PURITY OF MATERIALS; Ph ₄ AsCl (G. Frederick Smith Chemical Co.) and NaBPh ₄ were reacted to form the Ph ₄ As BPh ₄ , which was recrystal- lized from acetone-water.
		ESTIMATED ERROR:
		Precision of ±0.5% (authors). Temperature control: ±0.1°C
		REFERENCES:

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COMPONENTS:	EVALUATOR:
<pre>(1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Orest Popovych, Department.of Chemistry, City University of New York, Brooklyn College, Brooklyn N. Y. 11210 H. C. A
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]	November 1979

All four literature values pertaining to the solubility of tetraphenylarsonium tetraphenylborate ($Ph_4As BPh_4$) in acetonitrile were determined at 298 K by Parker and his associates (1-4). All data were reported as pK_{s0} values where the K_{s0} units were mol² dm⁻⁶. The first datum, $pK_{s0} = 5.2$ (1) was reported with a paucity of experimental detail, except that is was a concentration solubility product determined by uvspectrophotometry. It was superceded by another concentration solubility product, expressed as $pK_{s0} = 5.7$ with the precision stated as ± 0.1 pK units (2). Since the experimental details were somewhat better defined in this second article, the above value may serve as the basis for calculating the solubility as $(K_{s0})^2 = (1.4 \pm 0.2) \times 10^{-3} \text{ mol dm}^{-3}$. Considering that the solubility value is precise to only one decimal and that no mention is made in the article of ascertaining saturation, this datum must be considered as only tentative.

The two later data are less reliable as sources of the solubility value. The thermodynamic ion-activity product reported as $pK_{SO}^{s} = 5.8$ (3) contained an activity coefficient calculated from the Davies equation (see compilation), but the break-down between the solubility and the activity coefficient was not shown. Finally, Cox and Parker (4) expressed preference for determining the solubility product of Ph4As BPh4 from chemical-exchange experiments, rather than by direct uv-spectrophotometry (see compilation). Unfortunately, it is not clear whether activity coefficients were used in the calculation of the solubility product, so that the reported $pK_{s0} = 6.0$ may be a concentration or an activity product and therefore not suitable for the calculation of the solubility value. The precision of the last pK_{sO} value cannot be better than ±0.2 pK units, considering that it is based on a literature value of the pK_{s0} (AgBPh_u) which itself is precise to only ±0.1 pK units.

References:

- 1.
- Alexander, R; Parker. A. J. J. Am. Chem Soc. <u>1967</u>, 89, 5549. Parker, A. J.; Alexander, R. J. Am. Chem Soc. <u>1968</u>, 90, 3313 2. <u>1968, 90,</u> 3313.
- 3. Alexander, R.; Parker, A. J. Sharp, J. H.; Waghorne, W. E. J. Am. Chem Soc. <u>1972</u>, 94, 1148. Cox, B. G.; Parker, A. J. J. Am. Chem. Soc. <u>1972</u>, 94, 3674.
- 4.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. <i>J. Am. Chem. Soc.</i> <u>1967</u> , 89, 5549-51.
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubi acetonitrile was reported as:	lity product of $Ph_4As BPh_4$ in
pK _{s0} = 5,2 (K _{s0} uni	ts are mol ² dm ⁻⁶).
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.
	ESTIMATED ERROR:
	None specified.
	REFERENCES:

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 COMPONENTS: (1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈H₄₀BAs; [15627-12-0] (2) Acetonitrile; C₂H₃N; [75-05-8] ORIGINAL MEASUREMENTS: Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3. 	
 (1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈H₄₀BAs; [15627-12-0] (2) Acetonitrile; C₂H₃N; [75-05-8] Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3. 	
(2) Acetonitrile; $C_{2}H_{3}N$; [75-05-8]	313-9.
TREFARED DI:	
One temperature:25°C Orest Popovych	
EXPERIMENTAL VALUES:	
The formal (concentration) solubility product of $Ph_4As BPh_4$ in acetonitrile was reported as:	
$pK_{s0} = 5.7 (K_{s0} \text{ units are mol}^2 \text{ dm}^{-6})$	
AUXILIARY INFORMATION	
METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions The purification of materials	has
saturated under nitrogen, using a Unicam SP500 spectrophotometer. Saturated solutions were prepared by shaking for 24 hours at 35°C and	ire
then for a further 24 hours at 25°C.	
POTTWINTE TERO	
ESTIMATED ERROR:	ed to
ESTIMATED ERROR: Absolute precision was estimat be ±0.1 pK units.	
ESTIMATED ERROR: Absolute precision was estimat be ±0.1 pK units. REFERENCES.	
ESTIMATED ERROR: Absolute precision was estimat be ±0.1 pK units. REFERENCES: (1) Clare, B. W.; Cook, D.; Ko	E. C.
ESTIMATED ERROR: Absolute precision was estimate be ±0.1 pK units. REFERENCES: (1) Clare, B. W.; Cook, D.; Ko F.; Mac, Y. C.; Parker, A. J. J. Am. Char. Cook. 1066 (20) 100	E. C.
ESTIMATED ERROR: Absolute precision was estimate be ±0.1 pK units. REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1966</u> , 88, 193 (2) Alexander, R.; Ko, E. C. F.	E. C.
ESTIMATED ERROR: Absolute precision was estimate be ±0.1 pK units. REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. 1966, 88, 193 (2) Alexander, R.; Ko, E. C. F. Y. C.; Parker, A. J. J. Am. Che 1967 80 2702	E. C. ; Mac, ; <i>Mac</i> ,

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenylborate (1-); C₄₀H₄₈As; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) product of $Ph_4As BPh_4$ in acetonitrile was reported as:	
$pK_{s0}^{\circ} = 5.8$ (1)	K_{s0}° units are mol ² dm ⁻⁶).
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^2/(1 + (I)^2) - (1/3)I]$, where I is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was $1.543 \text{ mol}^{-1/2} \text{ dm}^{3/2}$.	
AUXILIARY	INFORMATION
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS.
Probably UV spectrophotometry. No	Not stated.
other details.	
	ESTIMATED ERROR:
	Not specified.
	REFERENCES :



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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Abraham, M. H.; Danil de Manor, A. F. <i>J. Chem. Soc. Faraday Trans. 1 <u>1976</u>, 72, 955-62.</i>	
<pre>(2) 1,1-Dichloroethane; C₂H₄Cl₂; [75-34-3]</pre>		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:	· · · · · · · · · · · · · · · · · · ·	
The authors reported the solubility of $Ph_{4}AsBPh_{4}$ in 1,1-dichloroethane as: 2.70 x 10 ⁻⁴ mol dm ⁻³ . Using an estimated association constant of 3.60 x 10 ³ mol ⁻¹ dm ³ and an ion-size parameter of $a = 0.66$ nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained for the standard Gibbs free energy of solution: $\Delta G_{S0}^{\circ} = 10.51$ kcal mol ⁻¹ = 43.99 kJ mol ⁻¹ (compiler). The solubility (ion-activity) product of $Ph_{4}AsBPh_{4}$ can be calculated from the relationship $\Delta G_{S}^{\circ} = -RT$ ln K_{S0}° , yielding $pK_{S0}^{\circ} = 7.705$, where K_{S0}° units are mol ² dm ⁻⁶ (compiler).		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. The source and purification of Ph ₄ AsBPh ₄ were not specified.	
	ESTIMATED ERROR:	
	Precision of 0.1 kcal mol ⁻¹ in ΔG_{S}° .	
-	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C48H40BAS; [15627-12-0]</pre>	Abraham, M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.
<pre>(2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The authors reported the solubility of Ph_4AsBPh_4 in 1,2-dichloro- ethane as: 4.99 x 10 ⁻³ mol dm ⁻³ . Using an estimated association constant of 6.00 x 10 ² mol ⁻¹ dm ³ and an ion-size parameter of $a = 0.66$ nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained the standard Gibbs free energy of solution:	
$\Delta G_{S}^{\circ} = 7.90 \text{ kcal mol}^{-1} =$	33.1 kJ mol ⁻¹ (compiler).
The solubility (ion-activity) product	of PhhAsBPhh can be calculated from
the solubility (ion-activity) product of Pn_4ASBPn_4 can be calculated from the relationship: $\Delta G_s^\circ = -RT$ in K_{s0}° , yielding $pK_{s0}^\circ = 5.792$, where K_{s0}° units are mol ² dm ⁻⁶ (compiler).	
	-
AUXILIARY	INFORMATION
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. The source and purification of Ph ₄ AsBPh ₄ were not specified.
	ESTIMATED ERROR:
	Precision of 0,1 kcal mol∽l in ∆Gg,
	REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Tetraphenylarsonium	Orest Popovych, Department of
tetraphenylborate (1-);	Chemistry, City University of
C ₄₈ H ₄₀ BAs; [15627-12-0]	New York, Brooklyn College,
(2) N,N-Dimethylacetamide; C ₄ H ₉ NO;	Brooklyn, N. Y. 11210, U. S. A.
[127-19-5]	November 1979

All three available data on the solubility of tetraphenylarsonium tetraphenylborate (Ph4As BPh4) in N,N-dimethylacetamide come from the laboratory of Parker and his associates (1-3). All were determined by uv-spectrophotometry at 298 K. The first two data were concentration solubility products (in mol² dm⁻⁶) reported in the form $pK_{SO} = 3.4$ (1) and 3.7 (2), respectively. Since the latter was obtained under conditions that were better defined in the article, with a specified precision of ± 0.1 pK units, it represents the best available quantity from which the solubility can be estimated. Thus, if the solubility is taken simply as $(K_{SO})^{\frac{1}{2}}$, we obtain for it (1.4 ± 0.2) x 10^{-2} mol dm⁻³. It should be considered as a <u>tentative</u> value. The thermodynamic solubility product determined subsequently and expressed as $pK_{s0}^{\circ} = 4.0$ (3) is based on an activity coefficient calculated from the Davies equation (see compilation), but unfortunately the solubility itself was not specified in that study.

References:

- 1.
- Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 5549. Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313. 2. 3. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E.
- J. Am. Chem. Soc. <u>1972</u>, 94, 1148.

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Tetraphenylarsonium	Alexander, R.; Parker, A. J.	
C ₄₈ H ₄₀ BAs; [15627-12-0]	J. Am. Chem. Soc. <u>1967</u> , 89, 5549-5	1.
(2) N,N-Dimethylacetamide; C ₄ H ₉ NO; [127-19-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The formal (concentration) solubil: N,N-dimethylacetamide was reported	ity product of $Ph_4As BPh_4$ in as:	
$pK_{s0} = 3.4 (K_{s0} uni)$	ts are mol ² dm^{-6}).	
AUXILIAR	Y INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.	
	ESTIMATED ERROR:	
	None specified.	
	REFERENCES:	

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COMPONENTS:	ORIGINAL MEASUREMENTS:
 (1) Tetraphenylarsonium tetra- phenylborate (1-); C₄₈H₄₀BAs; [15627-12-0] (2) N,N-Dimethylacetamide; C₄H₀NO; 	Parker, A. J.; Alexander, R. <i>J. Am. Chem. Soc.</i> <u>1968</u> , <i>90</i> , 3313-9.
[127-19-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubility product of Ph ₄ As BPh ₄ in N,N-dimethylacetamide was reported as: pK _{SO} = 3.7 (K _{SO} units are mol ² dm ⁻⁶).	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen, using a Unicam SP500 spectrophotometer. Saturated solutions were prepared by shaking for 24 hours at 35°C and then for a further 24 hours at 25°C.	The purification of materials has been described in the literature (1-3).
	ESTIMATED ERROR: Absolute precision was estimated to be ±0.1 pK units.
	REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1966</u> , 88, 1911. (2) Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> , 89, 3703. (3) Parker, A. J. J. Chem. Soc. A. <u>1966</u> , 220.
COMPONENTS:	ORIGINAL MEASUREMENTS:
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<pre>(1) Tetraphenylarsonium tetra- phenylborate (1-); C₄₈ H₄₀ BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.
(2) N,N-Dimethylacetamide; C ₄ H ₉ NO; [127-19-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) produc N,N-dimethylacetamide was reported a	t of Ph ₄ As BPh ₄ in as:
$pK_{S0}^{\circ} = 4.0 \ (K_{S0}^{\circ} \text{ units})$	s are mol2 dm-6).
The mean ionic activity coefficient equation in the form; log $\gamma_{\pm} = -A$ [<u>I</u> is the ionic strength in mol dm ⁻³ mol ^{-1/2} dm ^{3/2} .	was calculated from the Davies $(I)^{\frac{5}{2}}/(1 + (I)^{\frac{5}{2}}) - (1/3)I]$, where and the value of <u>A</u> used was 1.551
AUXILIARY	INFORMATION
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR: Not specified.
	REFERENCES

COMPONENTS:		EVALUATOR:
(1)	Tetraphenylarsonium tetraphenylborate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College,
(2)	N,N-Dimethylformamide; C ₃ H ₇ NO; [68-12-2]	Brooklyn, N. Y. 11210, U. S. A. November, 1979

Three of the four available literature data pertaining to the solubility of tetraphenylarsonium tetraphenylborate (Ph $_4$ As BPh $_4$) in N,N-dimethylformamide were determined at 298 K by uv-spectrophotometry in the laboratory of Parker and his associates (1-3). The first two data were concentration solubility products (in mol² dm⁻⁶) reported in the form $pK_{g0} = 3.7 (1,2)$, showing agreement to one decimal in the logarithm between the two studies. If we take the solubility as being equal to $(K_{s0})^2$ and accept the authors' estimate of the precision as ± 0.1 pK units (2), the solubility value becomes (1.4 \pm 0.2) x 10^{-2} mol dm⁻³. The above value is probably the best estimate of the solubility we have to date, but it should be considered as no better than tentative.

The thermodynamic solubility product reported subsequently as pK_{s0}° = 4.9 (3) is not a reliable source of the solubility value because it contains an appreciable activity correction calculated via the Davies equation (see compilation). Unfortunately, the solubility was not specified separately in the last study (3).

The pK_{SO}^{*} value of 3.9 reported by Kolthoff and Chantooni (4) on the basis of measurements of electrolytic conductance would seem less reliable for two reasons. Firstly, the values of molar conductances for the $Ph_{\mu}As$ and $BPh_{i_{\mu}}^{-}$ ions required for the calculation (see compilations) were not known in N,N-dimethylformamide and had to be estimated from those in acetonitrile via Walden's rule. The latter can lead to very serious errors, however. Secondly, at the 10^{-2} mol dm⁻³ concentration levels, additional errors result from the use of limiting molar conductances. These objections pertain to the evaluation of the value of the solubility product. To derive the solubility from it, one would have to know the form of the Guggenheim equation used to calculate the activity coefficient, which was not specified by the authors.

References:

- 1. Alexander, R.; Parker, A. J. J. Am. Chem. Soc. 1967, 89, 5549.
- Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. 2.
- 3.
- J. Am. Chem. Soc. <u>1972</u>, 94, 1148. Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024. 4.

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COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> ,89, 5549-51.
<pre>(2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES: The formal (concent	ration) solubility product of
Ph ₄ As BPh ₄ in N,N-dimethylformamide	was reported as:
$pK_{s0} = 3.7 (K_{s0} ur)$	its are mol ² dm ⁻⁶).
	-
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE: SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.
	PETIMATED EDDOD.
	None specified.
	REFERENCES :

CONDONENTE	OPTCINAL MEACHDEMENTS .
 (1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0] (2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2] 	Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubility ylformamide was reported as:	product of Ph ₄ As BPh ₄ in N,N-dimeth-
$pK_{s0} = 3.7 (K_{s0} u)$	nits are mol ² dm^{-6}).
AUXILIARY	INFORMATION
	CONDER AND DUDITY OF MATERIALS
UV spectrophotometry on solutions saturated under nitrogen, using a Unicam SP500 spectrophotometer. Saturated solutions were prepared by shaking for 24 hours at 35°C and then for a further 24 hours at 25°C.	The purification of materials has been described in the literature (1-3).
	ESTIMATED ERROR:
	Absolute precision was estimated to be \pm 0.1 pK units.
	 REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. 1966, 88, 1911. (2) Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker. A. J. J. Am. Chem. Soc. 1967, 89, 3703. (3) Parker, A. J. J. Chem. Soc. A 1966, 220.

Tetraphenylarsonium

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.
<pre>(2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) product formamide was reported as:	of Ph ₄ As BPh ₄ in N,N-dimethy1-
$pK_{s0}^{\circ} = 4.9 \ (K_{s0}^{\circ} \ units a)$	re $mol^2 dm^{-6}$).
The mean ionic activity coefficient we equation in the form: $\log \gamma_{\pm} = -A$ [(<u>I</u> is the ionic strength in mol dm ⁻³ and mol ^{-1/2} dm ^{3/2} .	Tas calculated from the Davies $I \frac{1}{2}/(1 + (I)\frac{1}{2}) - (1/3)I]$, where nd the value of <u>A</u> used was 1.551
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Kolthoff, I. S.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u> , 76, 2024-34.	
<pre>(2) N,N-Dimethylformamide; C₃H₇NO; [68-12-2]</pre>		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The authors report tetraphenylarsonium tetraphenylborate	only the solubility product of (Ph4As BPh4):	
$pK_{s0}^{\circ} = 3.9 (K_{s0}^{\circ})$ has unit	s of $mol^2 dm^{-6}$).	
The above value was derived from the electrolytic conductivity of the saturated solution $\kappa = 5.00 \times 10^{-4}$ ohm ⁻¹ cm ⁻¹ and a mean molar activity coefficient calculated from the Guggenheim equation (not shown).		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Electrolytic conductance of the saturated solution, using conduc- tance apparatus previously described (1). The authors state the precision of their conductance data as $\pm 2\%$. The values of λ^{∞} for the BPh ₄ and the Ph ₄ As ⁺ ion required for the cal- culation of the solubility were esti- mated from those in acetonitrile and the Walden rule. Presumably the solubility C was obtained using the relationship $C = 1000 \text{ sc/} \Lambda^{\infty}$	N,N-Dimethylformamide was purified by a literature method (2). Ph ₄ As BPh ₄ was prepared by the method of Popov and Humphrey (3).	
but this is not explained and the	ESTIMATED ERROR:	
actual C is not reported.	None specified.	
	 REFERENCES: (1) Kolthoff, I. M.; Bruckenstein, S. Chantooni, M. K., Jr. J. Am. Chem. Soc. <u>1961</u>, 83, 3927. (2) Kolthoff, I. M.; Chantooni, M. K., Jr.; Smagowski, H. Anal. Chem. <u>1970</u>, 42, 1622. (3) Popov, A. I.; Humphrey, R., J. Am. Chem. Soc. 1959, 81, 2043. 	

COMPONENTS:	EVALUATOR:
 (1) Tetraphenylarsonium tetraphenyl- borate (1-); C48H40BAs; [15627-12-0] (0) Diamital 1, 15, 11, 2, 10, 00, 10 	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
(2) Dimethylsulfoxide C_2H_6OS ; [67-68-5]	November 1979

All four literature data pertaining to the solubility of tetraphenylarsonium tetraphenylborate (Ph₄As BPh₄) in dimethylsulfoxide are solubility products in units of mol² dm⁻⁶, reported in the form of pK_{s0} (or pK_{s0}). All were determined at 298 K. The first two data were concentration solubility products determined by uv-spectrophotometry by Alexander and Parker and reported as $pK_{s0} = 3.3$ (1) and 3.6 (2), respectively. The second value was obtained under experimental conditions that were better described in the article and was accompanoed \overline{by} a stated precision of ±0.1 pK units. Consequently, it may represent the best source for the solubility value, which calculated as $(K_{\rm SO})^{\frac{1}{2}}$ is (1.6 ± 0.2) x 10⁻² mol dm⁻³ (evaluator) and should be regarded as the tentative value.

The thermodynamic solubility product reported subsequently as pKe 3.6 (3) was based on an activity coefficient calculated from the Davies equation (see compilation), but the break-down between the solubility and the activity correction was not shown. Considering the relatively high ionic concentration involved, the thermodynamic solubility product is not a good datum for the calculation of the solubility.

The only independent check on the above data from another laboratory comes from Kolthoff and Chantooni (4). Unfortunately, their value expressed as $pK_{s0}^{\circ} = 4.3$ is subject to too many sources of error to be reliable. Here the solubility was calculated from electrolytic conductivity κ , presumably using the relationship Solubility = $1000\kappa/\Lambda^{\infty}$, where Λ^∞ is the limiting molar conductivity of the electrolyte. However, the limiting molar conductivity in dimethylsulfoxide was not known and had to be estimated from the Walden's rule, which is a highly unsatisfactory procedure. Furthermore, limiting molar conductivities are not anywhere near applicable to electrolyte solutions at concentrations of the order of 10^{-2} mol dm⁻³.

References:

1. 4	Alexander,	R.;	Parker,	Α.	J.	J.	Am.	Chem.	Soc.	1967,	89,	554	9
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- Parker, A. J.; Alexander, R. J. Am. Chem. Soc. 1968, 90, 3313. 2.
- з. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E.
- J. Am. Chem. Soc. <u>1972</u>, 94, 1148. Kolthoff, I. M.; Chantooni, M. K., Jr. J. Phys. Chem. <u>1972</u>, 76, 2024. 4.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tetraphenylarsonium tetraphenyl- borate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	Alexander, R.; Parker, A. J. <i>J. Am. Chem. Soc</i> . <u>1967</u> , 89, 5549-51.
<pre>(2) Dimethylsulfoxide; C₂H₆OS; [67-68-5]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
	•
EXPERIMENTAL VALUES:	
The formal (concentration) so in dimethylsulfoxide was reported as: pK _{SO} = 3.3 (R	olubility product of Ph ₄ As BPh ₄ C _{SO} units are mol ² dm ⁻⁶).
AUXILIARY	INFORMATION
METHOD / APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.
	ESTIMATED ERROR:
	None specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.
<pre>(2) Dimethylsulfoxide; C₂H₆OS; [67-68-5]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solut dimethylsulfoxide was reported as:	pility product of $Ph_4As BPh_4$ in

 $pK_{s0} = 3.6 (K_{s0} \text{ units are mol}^2 dm^{-6}).$

AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
UV spectrophotometry on solutions saturated under nitrogen, using a Unicam SP500 spectrophotometer. Saturated solutions were prepared by shaking for 24 hours at 35°C and	The purification of materials has been described in the literature (1-3).		
then for a further 24 hours at 25°C.	ESTIMATED ERROR:		
	Absolute precision was estimated to be ± 0.1 pK units.		
	 REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem Soc. <u>1966</u>, 88, 1911. (2) Alexander, R.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 3703. (3) Parker, A. J. J. Chem. Soc. A <u>1966</u>, 220. 		

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1976</u> , <i>94</i> , 1148-58.	
(2) Dimethylsulfoxide; C ₂ H ₆ OS; [67-68-5]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility (ion-activity) sulfoxide was reported as:	product of Ph_4As BPh_4 in dimethyl-	
$pK_{s0}^{\circ} = 3.6 \ (K_{s0}^{\circ})$	$_0$ units are mol ² dm ⁻⁶).	
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A[(1)^{\frac{1}{2}}/(1 + (1)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 1.115 mol ^{-1/2} dm ^{3/2} .		
AUXILIARY	INFORMATION	
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:	
Probably UV spectrophotometry. No	Not stated.	
other details.		
	ESTIMATED EDDOD.	
1	LOTIFICIED ERROR:	
	Not specified.	
	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C48H40BAS; [156-27-12-0]</pre>	Kolthoff, I. M.; Chantooni, M. K.,Jr. J. Phys. Chem. <u>1972</u> , 76, 2024-34.	
<pre>(2) Dimethylsulfoxide; C₂H₆OS; [67-68-5]</pre>		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The authors report only the solubility product of tetraphenyl-arsonium tetraphenylborate $(Ph_4As BPh_4)$:		
$pK_{SO}^{\circ} = 4.3 \ (K_{SO}^{\circ} has units of mol^2 dm^{-6}).$		
The above value was derived from the electrolytic conductivity of the saturated solution $\kappa = 1.43 \times 10^{-4}$ ohm ⁻¹ cm ⁻¹ and a mean molar activity coefficient calculated from the Guggenheim equation (not shown).		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;	
Electrolytic conductance. Identical to that described on the compilation for Ph ₄ As BPh ₄ in N,N-dimethyl- formamide based on the same reference as this compilation.	Dimethylsulfoxide was purified by a literature method (1). Ph ₄ As BPh ₄ was prepared by the method of Popov and Humphrey (2).	
	ESTIMATED ERROR:	
	None specified.	
	REFERENCES :	
	 (1) Kolthoff, I. M.; Reddy, T. B. <i>Inorg. Chem.</i> <u>1962</u>, <i>1</i>, 189. (2) Popov, A. I.; Humphrey, R. <i>J. Am. Chem. Soc.</i> <u>1959</u>, <i>81</i>, 2043. 	

ORIGINAL MEASUREMENTS:		
Alexander, R.; Parker, A. J. Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.		
PREPARED BY:		
Orost Popowych		
orest ropovych		
<u></u>		
The solubility (ion-activity) product of Ph_4As BPh_4 in ethanol was reported as:		
nits are $mol^2 dm^{-6}$).		
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{\frac{1}{2}}/(1 + (I)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 2.956 mol ^{-1/2} dm ^{3/2} . The solubility products and ionic strengths were "adjusted to infinite dilution by iteration, to allow for incomplete dissociation"		
AUXILIARY INFORMATION		
SOURCE AND PURITY OF MATERIALS:		
Not stated.		
ESTIMATED ERROR:		
Not specified.		
REFERENCES:		

COMPONENTS:	EVALUATOR:
(1) Tetraphenylarsonium tetraphenylborate (1-); C _{4.8} H _{4.0} BAs; [15627-12-0]	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College.
(2) Formamide; CH ₃ NO; [75-12-7]	Brooklyn, N. Y. 11210, U. S. A. November 1979

All three available data on the solubility of tetraphenylarsonium tetraphenylborate (Ph_LAs BPh_L) in formamide were determined at 298 K by uv-spectrophotometry in the laboratory of Parker and his associates (1-3). The first two data were concentration solubility products (in mol² dm⁻⁶) reported in the form $pK_{SO} = 8.3$ (1) and 8.9 (2), respectively. Since the latter was obtained under experimental conditions that were better defined in the article, with a specified precision of ± 0.1 pK units, it is the best available datum from which the solubility can be estimated as $(K_{s0})^{\frac{1}{2}}$. We obtain for the solubility (3.6 ± 0.4) x 10⁻⁵ mol dm⁻³ as a <u>tentative</u> value. Subsequently, the thermodynamic solubility product of Ph₄As BPh₄ in formamide was reported in the form $pK_{s0}^{s} = 8.8$ (3). However, the solubility itself was not reported in the last study.

References:

- Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>, 89, 5549. Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. 1.
- 2.
- 3.
- J. Am. Chem. Soc. 1972, 94, 1148.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetra- phenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> , 89, 5549-51.	
(2) Formamide; CH ₃ NO; [75-12-7]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The formal (concentration) solubility product of Ph_4As BPh ₄ in formamide was reported as:		
$pK_{s0} = 8.3 (K_{s0} units a)$	re mol ² dm ⁻⁶).	
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.	
	ESTIMATED ERROR:	
	None specified.	
	REFERENCES	
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COMPONENTS:	ORIGINAL MEASUREMENTS:
 Tetraphenylarsonium tetraphenyl- borate (1-); C₁₀H₁₀BAs; 	Parker, A. J.; Alexander, R. J. Am. Chem. Soc. 1968, 90, 3313-9.
[15627-12-0] 48 40	<u> </u>
(2) Formamide; CH ₃ NO; [75-12-7]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	.
The formal (concentration) solubilit was reported as:	y product of $Ph_4As BPh_4$ in formamide
$pK_{s0} = 8.9 (K_{s0} units)$	are $mol^2 dm^{-6}$).
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen, using a Unicam SP500 spectrophotometer.	The purification of materials has been described in the literature (1-3).
by shaking for 24 hours at 35°C and	
then for a further 24 hours at 25°C.	
	Absolute precision was estimated
	to be ± 0.1 pK units.
	REFERENCES: (1) Clare, B. W.; Cook, D.;
	Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1966</u> , 88, 1911. (2) Alexander, R.; Ko, E. C. F.; Mac, Y. C. Parker, A. J. J. C. K.
	Soc. <u>1967</u> , 89, 3703. (3) Parker, A. J. J. Chem. Soc. A <u>1966</u> , 220.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Tetraphenylarsonium tetra- phenylborate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	Alexander, R.; Parker, A. J.; Sharp, J. S.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.	
(2) Formamide; CH ₃ NO; [75-12-7]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
one temperature. 25 6	orest ropovych	
EXPERIMENTAL VALUES:		
The solubility (ion-activity) product of $Ph_4As BPh_4$ in formamide was reported as:		
$pK_{s0}^{\circ} = 8.8 \ (K_{s0}^{\circ} \ unit$	s are mol ² dm ⁻⁶).	
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{\frac{1}{2}}/(1 + (I)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 0.309 mol ^{-1/2} dm ^{3/2} .		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Probably HV spectrophotometry.	Not stated.	
No other details.	Not Stated.	
	ESTIMATED ERROR:	
	Not specified.	
	REFERENCES :	
1		

COMPONENTS:	EVALUATOR:
<pre>(1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
(2) Hexamethylphosphorotriamide; C ₆ H ₁₈ N ₃ OP; [680-31-9]	November 1979

All three available data on the solubility of tetraphenylarsonium tetraphenylborate (PhuAs BPhu) in hexamethylphosphorotriamide were determined at 298 K by uv-spectrophotometry in the laboratory of Parker and his associates (1-3). The first two data were concentration solubility products (in mol² dm⁻⁶) reported in the form $pK_{SO} = 3.1$ (1) and 3.7 (2), respectively. Since the latter was obtained under experimental conditions that were better defined in the article, with a specified precision of ± 0.1 pK units, it represents the best available quantity from which the solubility can be estimated. If we calculate the solubility simply as $(K_{\rm SO})^{\frac{1}{2}}$, we obtain (1.4 ± 0.2) x 10^{-2} mol dm⁻³. It should be considered as a tentative value. The thermodynamic solubility product reported subsequently as $pK_{SO}^{\circ} = 3.7$ (3), which was calculated using an activity coefficient derived from the Davies equation (see compilation), has, surprisingly, the same numerical value as the earlier formal solubility product. Unless this is an error, it would imply that the thermodynamic solubility product was based on a new (revised) solubility value. The latter, unfortunately, was not reported.

References:

Alexander, R; Parker, A. J. J. Am. Chem. Soc. 1967, 89, 5549. 1.

- Parker, A. J.; Alexander, R. J. Am. Chem. Soc. 1968, 90, 3313. Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem Soc. 1972, 94, 1148. 2. 3.

COMPONENTS:	ORIGINAL MEASUREMENTS:	
(1) Tetraphenylarsonium tetraphenyl-	Alexander, R.; Parker, A. J.	
borate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	J. Am. Chem. Soc. <u>1967</u> , 89,5549-51.	
(2) Hexamethylphosphorotriamide;		
C ₆ H ₁₈ N ₃ OP; [680-31-9]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The formal (concentration) solubility product of Ph ₄ As BPh ₄ in hexamethylphosphorotriamide was reported as:		
$pK_{s0} = 3.1 (K_{s0} \text{ units are mol}^2 \text{ dm}^{-6}).$		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.	
	ESTIMATED ERROR:	
	None specified.	
	REFERENCES	

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tetraphenylarsonium tetra- phenylborate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.
(2) Hexamethylphosphorotriamide; C ₆ H ₁₈ N ₃ OP; [680-31-9]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	······
The formal (concentration) solubine hexamethylphosphorotriamide was r	llity product of Ph ₄ As BPh ₄ in reported as:
рК _{SO} = 3.7 (К _{SO}	units are mol ² dm ^{-b}).
AUXILI	ARY INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions saturated under nitrogen, using a Unicam SP500 spectrophotometer. Saturated solutions were prepared by shaking for 24 hours at 35°C a then for a further 24 hours at 25	The purification of materials has been described in the literature (1-3). and 5°C.
	ESTIMATED ERROR: Absolute precision was estimated to be ±0.1 pK units.
	REFERENCES: (1) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1966</u> , 88, 1911. (2) Alexander, R.; Ko, E. C. F., Mac, Y. C.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u> , 89, 3703. (3) Parker, A. J. J. Chem. Soc. A. <u>1966</u> , 220.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetra- phenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.
<pre>(2) Hexamethylphosphorotriamide; C₆H₁₈N₃OP; [680-31-9]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) product of Ph ₄ As BPh ₄ in hexamethylphosphorotriamide was reported as:	
$pK_{s0}^{\circ} = 3.7 \ (K_{s0}^{\circ} \text{ units are mol}^2 \ dm^{-6}).$	
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{\frac{1}{2}}/(1 + (I)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 2.201 mol ^{-1/2} dm ^{3/2} .	
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AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS;
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
	REFERENCES:

COMPONENTS:	EVALUATOR:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
(2) Methanol; CH ₄ 0; [67-56-1]	November 1979

All three determinations of the solubility of tetraphenylarsonium tetraphenylborate (Ph $_4$ As BPh $_4$) in methanol were reported from the laboratory of Parker and his associates (1-3). All results were obtained at 298 K by uv-spectrophotometry. The first two data were reported to be concentration solubility products, expressed as $pK_{s0} = 8.5$ (1) and 9.0 (2), respectively. However, the 9.0 value was obtained under somewhat better defined experimental conditions and had a specified precision of ± 0.1 pK units. Taking the solubility as $(K_{s0})^{\frac{1}{2}} = (10^{-9})^{\frac{1}{2}}$, we obtain for it the value (3.2 \pm 0.4) x 10^{-5} mol dm⁻³. Considering that temperature control was not specified and the estimate is good to only two significant figures, the above value cannot be considered as better than tentative.

The third datum was a thermodynamic solubility product for which the activity coefficient was calculated from the Davies equation shown in the compilation; it was expressed as $pK_{SO}^{\circ} = 9.0$ (3). Unfortunately, the value of the solubility itself was not specified in the last study.

References:

- Alexander, R.; Parker, A. J. J. Am. Chem. Soc. <u>1967</u>,89, 5549.
 Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>,90, 3313.
 Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u>, 94, 1148.

COMPONENTS :	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. <i>J. Am.</i> <i>Chem. Soc.</i> <u>1967</u> , 89, 5549-51.	
(2) Methanol; CH ₄ 0; [67-56-1]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The formal (concentration) solubility product of $Ph_{\mu}As BPh_{\mu}$ in methanol was reported as:		
$pK_{s0} = 8.5 (K_{s0} \text{ units are mol}^2 \text{ dm}^{-6}).$		
AUXILIARY INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
UV spectrophotometry on solutions saturated under nitrogen. No other details.	Not stated.	
	ESTIMATED ERROR:	
	None specified.	
	REFERENCES:	

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetra- phenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u> , 90, 3313-9.
(2) Methanol; CH ₄ O; [67-56-1]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The formal (concentration) solubility product of $Ph_{\mu}As BPh_{\mu}$ in methanol was reported as:	
$pK_{s0} = 9.0 (K_{s0} unit)$	s are mol ² dm ^{-6}).
	•
AUXILIARI	
METHOD /APPARATUS / PROCEDURE :	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions	The purification of materials has
saturated under nitrogen, using a	been described in the literature
Saturated solutions were prepared	
by shaking for 24 hours at 35°C and	
then for a further 24 hours at 25°C.	
	ESTIMATED ERROR:
	Absolute precision was estimated to
	be ±0.1 pK units.
	REFERENCES:(1) Clare, B. W.: Cook, D.:
Į	Ko, E. C. F.; Mac, Y. C.; Parker, A.
	[J. J. Am. Chem. Soc. <u>1966</u> , 88, 1911.
1	Y. C.; Parker, A. J. J. Am. Chem.
	soc. <u>1967</u> , 89, 3703.
	(3) Parker, A. J. J. Chem. Soc. A <u>1966</u> , 220.

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COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> ,1148-58.	
(2) Methanol; CH ₄ 0; [67-56-1]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES:		
The solubility (ion-activity) product of $Ph_4As BPh_4$ in methanol was reported as:		
$pK_{s0}^{\circ} = 9.0 \ (K_{s0}^{\circ} \ unit)$	s are $mol^2 dm^{-6}$).	
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(1)^{\frac{1}{2}}/(1 + (1)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 1.900 mol ^{-1/2} dm ^{3/2} .		
`		
AUXILIARY	INFORMATION	
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:	
Probably UV spectrophotometry. No other details.	Not stated.	
	ESTIMATED ERROR: Not specified.	
	REFERENCES :	

Tetraphenylarsonium . 221	
COMPONENTS: (1) Tetraphenylarsonium tetraphenyl- borate (1-); C ₄₈ H ₄₀ BAs; [15627-12-0]	ORIGINAL MEASUREMENTS: Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.
<pre>(2) 1-Methyl-2-pyrrolidinone (N-Methyl-2-pyrrolidone); C₅H₉NO; [872-50-4]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) 2-pyrrolidone was reported as:	product of Ph ₄ As BPh ₄ in N-methyl-
$pK_{s0}^{\circ} = 3.3$ (2)	K_{s0}° units are mol ² dm ⁻⁶).
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A[(I)^{\frac{1}{2}}/(1 + (I)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 2.004 mol ^{-1/2} dm ^{3/2} .	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. Sharp; J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.
(2) Nitromethane; CH ₃ NO ₂ ; [75-52-5]	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) pr was reported as:	oduct of Ph_4As BPh ₄ in nitromethane
рК _{\$0} = 5.7 (К	$_{s0}^{\circ}$ units are mol ² dm ⁻⁶).
The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{\frac{1}{2}}/(1 + (I)^{\frac{1}{2}}) - (1/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 1.479 mol ^{-1/2} dm ^{3/2} .	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J. Sharp; J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> <i>Soc.</i> <u>1972</u> , <i>94</i> , 1148-58.
<pre>(2) Propanedio1-1,2-carbonate (propylene carbonate); C₄H₆O₃; [108-32-7]</pre>	
VARIABLES:	PREPARED BY:
One temperature: 25°C	Orest Popovych
EXPERIMENTAL VALUES:	

The solubility (ion-activity) product of ${\rm Ph}_4{\rm As}~{\rm BPh}_4$ in propylene carbonate was reported as:

 $pK_{SO}^{\circ} = 4.6 \ (K_{SO}^{\circ} \ units \ are \ mol^2 \ dm^{-6}).$

The mean ionic activity coefficient was calculated from the Davies equation in the form: $\log \gamma_{\pm} = -A [(I)^{\frac{1}{2}}/(1 + (I)^{\frac{1}{2}} - (1/3)I]$, where I is the ionic strength in mol dm⁻³ and the value of <u>A</u> used was 0.661 mol^{-1/2} dm^{3/2}.

AUXILIARY	INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
-	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:	
<pre>(1) Tetraphenylarsonium tetraphenyl- borate (1-); C48H40BAs; [15627-12-0]</pre>	Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. <i>J. Am. Chem.</i> Soc. <u>1972</u> , 94, 1148-58.	
(2) 2-Propanone (acetone); C ₃ H ₆ O; [67-64-1]		
VARIABLES:	PREPARED BY:	
One temperature: 25°C	Orest Popovych	
EXPERIMENTAL VALUES: The solubility (ion-activity) product of $Ph_4As BPh_4$ in acetone was reported as: $pK_{SO}^{\circ} = 8.0 (K_{SO}^{\circ} units are mol^2 dm^{-6}).$		
The mean ionic activity coefficient v equation in the form: $\log \gamma_{\pm} = -A$ [is the ionic strength in mol dm ⁻³ and mol ^{-1/2} dm ^{3/2} . The solubility produc to infinite dilution by iteration, to	was calculated from the Davies (I) $\frac{1}{2}/(1 + (I)\frac{1}{2}) - (1/3)I]$, where <u>I</u> d the value of <u>A</u> used was 3.760 cts and ionic strengths were "adjusted o allow for incomplete dissociation"	

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
	REFERENCES :

COMPONENTS:	EVALUATOR:
<pre>(1) Tetraphenylarsonium tetraphenylborate (1-); C₄₈H₄₀BAs; [15627-12-0]</pre>	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College, Brooklyn, N. Y. 11210, U. S. A.
(2) Tetrahydrothiophene-1,1-dioxide (sulfolane, tetramethylene sulfone); C ₄ H ₈ O ₂ S; [126-33-0]	November 1979

There are two data pertaining to the solubility of tetraphenylarsonium tetraphenylborate (Ph₄AsBPh₄) in sulfolane, both determined in Parker's laboratory at 303 K (1,2). It is the first datum, the concentration solu-bility product in mol² dm⁻⁶, expressed as $pK_{s0} = 5.0$, that provides us with the most reliable means of calculating the solubility. Taking the solubility as $(K_{s0})^{\frac{1}{2}}$ and using the precision of ± 0.1 pK units as estimated by the authors, we obtain: $(3.2 \pm 0.4) \times 10^{-3} \text{ mol dm}^{-3}$. Considering the lack of information on the temperature control and the fact that the solubility estimate has only two significant figures, the above value can be considered no better than tentative.

The thermodynamic solubility product reported later as $pK_{SO}^{\circ} = 5.2$ (2) is less reliable for calculating the solubility, as the degree of the activity correction incorporated in it is not readily known.

<u>References</u>:

Parker, A. J.; Alexander, R. J. Am. Chem. Soc. <u>1968</u>, 90, 3313.
 Alexander, R.; Parker, A. J.; Sharp, J. H. Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u>, 94, 1148.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tetraphenylarsonium tetraphenyl-	
borate $(1-)$; $C_{48}H_{40}BAs$;	Parker, A. J.; Alexander, R.
[13027=12=0]	J. Am. Chem. Soc. <u>1968</u> ,90, 3313-9.
(2) Tetrahydrothiophene-1,1-dioxide	
(sulfolane, tetramethylene	
$[1, 1, 1]$ surrower; $C_4 H_8 O_2 S$; $[126 - 33 - 0]$	
VARIABLES:	PREPARED BY:
one cemperature: 30 C	Orest Popových
EXPERIMENTAL VALUES:	
The formal (concentration) solubility	product of Ph ₄ As BPh ₄ in sulfolane
was reported as:	
$nK_{-0} = 5.0 (K_{-1})$	$1 \text{ ts are } mol^2 \text{ dm}^{-6}$
	its are not um).
{	
}	
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
UV spectrophotometry on solutions	The purification of materials has
saturated under nitrogen, using a	been described in the literature
Unicam SP500 spectrophotometer.	(1-3).
by shaking for 24 hours at 35°C and	
then for a further 24 hours at 30°C.	
	ESTIMATED ERROR:
	Absolute precision was estimated
	to be ± 0.1 pK units.
	REFERENCES: 1) Class B The State
1	Ko. E. C. F.: Mac. Y. C.: Parker
	J. J. Am. Chem. Soc. 1966, 88, 1911.
	2) Alexander, R.; Ko, E. C. F.; Mac,
	Y. C.; Parker, A. J. J. Am. Chem.
	Soc. 1967, 89, 3703. 3) Parker, A. J. J. Chem. Soc. A
	1966, 220,

<pre>COMPONENTS: (1) Tetraphenylarsonium tetraphenyl- borate (1-); C₄₈H₄₀BAs; [15627-12-0] (2) Tetrahydrothiophene-1,1-dioxide (sulfolane, tetramethylene</pre>	ORIGINAL MEASUREMENTS: Alexander, R.; Parker, A. J.; Sharp, J. H.; Waghorne, W. E. J. Am. Chem. Soc. <u>1972</u> , 94, 1148-58.
sulfone); C ₄ H ₈ O ₂ S; [126-33-0]	
VARIABLES:	PREPARED BY:
One temperature: 30°C	Orest Popovych
EXPERIMENTAL VALUES:	
The solubility (ion-activity) product reported as:	of Ph ₄ As BPh ₄ in sulfolane was
$pK_{s0}^{\circ} = 5.2 \ (K_{s0}^{\circ} \ units)$	are $mol^2 dm^{-6}$).
The mean ionic activity coefficient was, calculated from the Davies equation in the form: log $\gamma_{\pm} = -A [(I)^2/(I + (I)^2) - (I/3)I]$, where <u>I</u> is the ionic strength in mol dm ⁻³ and the value of <u>A</u> used was 1.244 mol ^{-1/2} dm ^{3/2} .	
	-
AUXILIARY	INFORMATION
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Probably UV spectrophotometry. No other details.	Not stated.
	ESTIMATED ERROR:
	Not specified.
	REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Tetraphenylphosphonium tetra- phenylborate (1-); ChoHueBP: [15525-15-2]	Orest Popovych, Department of Chemistry, City University of New York, Brooklyn College,
(2) Water: H_0 (7732-18-5]	Brooklyn, N. Y. 11210, U. S. A.
(2) water; n_20 ; $(7752-10-5)$	December 1979

The very low solubility of tetraphenylphosphonium tetraphenylborate $(Ph_{4}P \ BPh_{4})$ in water would render its direct determination unreliable, and it has never been reported. However, its solubility (ion-activity) product in water was evaluated indirectly (1) using the experimentally determined solubility product of Ph_4P BPh_4 in acetonitrile and the transfer activity coefficient of Ph_4P BPh_4 in acetonitrile calculated from those of other electrolytes. Under the circumstances, the calculated pK_{SO}^{\circ} of Ph_4P BPh_4 in water and the solubility value derived from it represent data worthy of evaluation and application.

The above calculation made use of the fact that the transfer activity coefficient of Ph_4P BPh₄ in acetonitrile (i.e., for the transfer from water to acetonitrile) is related to the solubility products in the two solvents as follows:

 $\log_{m} \gamma_{\perp}^{2} = pK_{S0}^{\circ} \text{ (acetonitrile)} - pK_{S0}^{\circ} \text{ (water)}$ (1)

where log γ_{\pm}^{2} is the transfer activity coefficient, which in this evaluation ^mis expressed on the weight basis (molal scale), as are the ion-activity products K_{S0}° . Since the pK_{S0}° for $Ph_{4}P$ BPh₄ in acetonitrile was reported as 5.68 ± 0.05 (1) (see compilation), the corresponding pK_{S0}° in water could be calculated from Equation 1 if the value of log ${}_{m}\gamma_{\pm}^{2}$ were known. The latter was calculated from the relationship:

 $\log_{m}\gamma_{\pm}^{2}(Ph_{\mu}P BPh_{\mu}) = \log_{m}\gamma_{\pm}^{2}(Ph_{\mu}P Pi) + \log_{m}\gamma_{\pm}^{2}(KBPh_{\mu}) - \log_{m}\gamma_{\pm}^{2}(KPi)$ (2)

Substituting into Equation 2 the corresponding experimentally determined values (1), where Pi is the picrate ion, we obtain:

 $\log_{m} \gamma_{\pm}^{2} (Ph_{4}P BPh_{4}) = (-6.15 \pm 0.04) + (-4.68 \pm 0.04) - (0.62 \pm 0.04) \\ = -11.45 \pm 0.07.$

Consequently, from Equation 1:

 $pK_{s0}^{\circ}(water) = (5.68 \pm 0.05) - (-11.45 \pm 0.07) = 17.13 \pm 0.09.$

The solubility of Ph₄P BPh₄ in water taken simply as $(K_{s0}^{\circ})^{\frac{1}{2}}$ is therefore: (2.7 ± 0.3) x 10⁻⁹ mol kg⁻¹. Of course, the solubility value would be the same in units of mol dm⁻³ as well. This values of the solubility and the solubility product should be considered <u>tentative</u>.

REFERENCES:

(1) Popovych, O; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u>, 44, 811.

COMPONENTS:	ORIGINAL MEASUREMENTS:
<pre>(1) Tetraphenylphosphonium tetra- phenylborate (1-); C₄₈H₄₀BP; [15525-15-2]</pre>	Popovych, O.; Gibofsky, A.; Berne, D. H. Anal. Chem. <u>1972</u> , 44, 811-7.
(2) Acetonitrile; C ₂ H ₃ N; [75-05-8]	
VARIABLES:	PREPARED BY:
One temperature: 25.00°C	Orest Popovych

EXPERIMENTAL VALUES:

The solubility (ion-activity) product of tetraphenylphosphonium tetraphenylborate (Ph_4P BPh_4) in acetonitrile was reported as:

 $pK_{s0}^{\circ} = 5.68 \ (K_{s0}^{\circ} \text{ units are mol}^2 \ kg^{-2}).$

The mean molar activity coefficient was calculated using the relationship:

$$-\log y_{\pm} = \frac{1.64 \ C^{\frac{1}{2}}}{1 + 0.485 \ ac^{\frac{1}{2}}}$$

where C was the solubility in mol dm⁻³ and a, the mean ion-size parameter. Although the article states that an ion size of 0.5 nm was adopted for the tetraphenyl ions, this is an error. According to the calculations in the research notebook of A. Gibofsky (1), the magnitude of a used in the calculations was 0.82 nm. The actual values for the solubility and the activity coefficient were not published, but they were 1.262 x 10^{-3} mol dm⁻³ and $y_{\pm} = 0.889$, respectively (1). The resulting pK^{*}_{SO} = 5.90 (K_{SO} units of mol² dm⁻⁶). The published value of pK^{*}_{SO} = 5.68 was calculated from the above using the density of acetonitrile, 0.777 g cm⁻³.

AUXILIARY INFORMATION				
Ultraviolet spectrophotometry using a Cary Model 14 spectrophotometer. Saturation achieved by shaking the salt suspension for 2 weeks in water- jacketed flasks. Solutions filtered and analyzed at 266 and 274 nm. All solutions and containers were deaerated.	SOURCE AND PURITY OF MATERIALS: Acetonitrile (Matheson, spectro- quality) was refluxed for 24 hrs over CaH ₂ and fractionally distilled. Ph ₄ P BPh ₄ was prepared from the chloride (Alfa Inorganics, Inc.) and NaBPh ₄ (Fisher, 99.7%). It was re- crystallized three times from 3:1 acetone-water and dried <u>in vacuo</u> at 80°C. ESTIMATED ERROR: Precision ±10% in K ^o _{SO} (authors) Temperature control: ±0.01°C			
	REFERENCES: 1. Gibofsky, A., Unpublished research, Brooklyn College, 1969.			

230 retraphenyip	nosphonium		
COMPONENTS:	ORIGINAL MEASUREMENTS:		
<pre>(1) Tetraphenylphosphonium tetra- phenylborate (1-); C₄₈H₄₀BP; [15525-15-2]</pre>	Abraham. M. H.; Danil de Namor, A. F. J. Chem. Soc. Faraday Trans. 1 <u>1976</u> , 72, 955-62.		
(2) 1,1-Dichloroethane; C ₂ H ₄ Cl ₂ ; [75-34-3]			
VARIABLES:	PREPARED BY:		
One temperature: 25°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The authors reported the solubility of $Ph_{4}P BPh_{4}$ in 1,1-dichloroethane as: 3.22 x 10 ⁻⁴ mol dm ⁻³ . Using an estimated association constant of 3.60 x 10 ³ mol ⁻¹ dm ³ and an ion-size parameter of a = 0.66 nm with which to calculate the mean ionic activity coefficient from the extended Debye-Huckel equation, they obtained for the standard Gibbs free energy of solution: $\Delta G_{9}^{\circ} = 10.36 \text{ kcal mol}^{-1}$ = 43.37 kJ mol ⁻¹ (compiler). The solubility (ion-activity) of Ph ₄ P BPh ₄ can be calculated from the relationship: $\Delta G_{9}^{\circ} = -RT \ln K_{50}^{\circ}$, yielding $pK_{50}^{\circ} = 7.595$, where K_{50}° units are mol ² dm ⁻⁶ (compiler).			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:		
Evaporation and weighing. Saturated solutions prepared by shaking the suspensions for several days at 25°C. No solvate was detected. Method of temperature control was not . specified.	The solvent was shaken with anhydrous K_2CO_3 , passed through a column of basic activated alumina into distil- lation flask and fractionated under N_2 through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Source and purification of Ph ₄ P BPh ₄ were not specified.		
	Precision of 0.1 kcal mol ⁻¹ in ΔG_g° .		
	REFERENCES :		

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COMPONENTS:	ORIGINAL MEASUREMENTS:		
<pre>(1) Tetraphenylphosphonium tetra- phenylborate (1-); C₄₈H₄₀BP; [15525-15-2]</pre>	Abraham, M. H.; Danil de Namor, A. F. <i>J. Chem. Soc. Faraday Trans. 1</i> <u>1976</u> , 72, 955-62.		
<pre>(2) 1,2-Dichloroethane; C₂H₄Cl₂; [107-06-2]</pre>			
VARIABLES:	PREPARED BY:		
One temperature: 25°C	Orest Popovych		
EXPERIMENTAL VALUES:			
The authors reported the solubility of $Ph_{4}P BPh_{4}$ in 1,2-dichloroethane as: 4.87 x 10^{-3} mol dm ⁻³ . Using an estimated association constant of 6.00 x 10^{2} mol ⁻¹ dm ³ and an ion-size parameter of $a^{\circ} = 0.66$ nm with which to calculate the mean ionic activity coefficient from the extended Debye-Hückel equation, they obtained for the standard Gibbs free energy of solution: $\Delta G_{s}^{\circ} = 7.91$ kcal mol ⁻¹ - 33.1 kJ mol ⁻¹ (compiler). The solubility (ion-activity) product of $Ph_{4}P$ BPh ₄ can be calculated from the relationship: $\Delta G_{s}^{\circ} = -RT$ in K_{s0}° , yielding $pK_{s0}^{\circ} = 5.799$, where K_{s0}° units are mol ² dm ⁻⁶ (compiler).			
AUXILIARY	INFORMATION		
METHOD/APPARATUS/PROCEDURE: Evaporation and weighing. Saturated solutions prepared by shaking the suspensions prepared for several days at 25°C. No solvate was detected. Method of temperature control was not specified.	SOURCE AND PURITY OF MATERIALS: The solvent was shaken with anhydrous K ₂ CO ₃ , passed through a column of basic activated alumina into distil- lation flask and fractionated under N through a 3-foot column. At least 10% of distillate was rejected, the rest collected over freshly activated molecular sieve. Source and purifi- cation of Ph ₄ P BPh ₄ were not specified. ESTIMATED ERROR: Precision of 0,1 kcal mol ⁻¹ in ΔG ^o _S . REFERENCES:		

SYSTEM INDEX

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Underlined page numbers refer to evaluation text and those not underlined to compiled tables. All compounds, except tetraphenylborates are listed as in Chemical Abstract indexes. For example, toluene is listed as benzene, methyl-, and dimethylsulfoxide is listed as methane, sulfinylbis-. The second and subsequent components of ternary and multicomponent systems are given as molecular formulae rather than chemical name. In this volume only tetraphenylborates are listed under their IUPAC name.

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                                                                              25, 26
                    + KC_{24}H_{20}B + C_{2}H_{6}O + H_{2}O
                    + KC_{24}H_{20}B + NaOH + CH_{4}O + H_{2}O
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                    + RbC_{24}H_{20}B + C_{2}H_{6}O
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                                                                                    1
                    + water
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                    + AgC_{24}H_{20}B + NaC_{24}H_{20}B + C_{2}H_{3}N
                    + AgC_{24}H_{20}B + NaC_{24}H_{20}B + CH_{3}NO
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                    + AgC_{24}H_{20}B + NaC_{24}H_{20}B + CH_{4}O
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                                                                                  155
                    + AgC_{24}H_{20}B + NaC_{24}H_{20}B + C_{3}H_{7}NO
                    + AgC_{24}H_{20}B + NaC_{24}H_{20}B + H_{2}O
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2-Propanol	+ tris(a-phenanthroline)ruthenium(II)-	
a rropanoa	tetraphenvlborate (1-)	128
	$+ AqC_{2}H_{20}B + C_{7}H_{8} + H_{2}O$	147, 148
	$+ C_{33}H_{62}BN + C_7H_8 + H_2O$	86
2-Propanone	+ potassium tetraphenylborate (1-)	40-41, 42
-	+ tetraphenylarsonium tetraphenylborate	224
	+ tris(o-phenanthroline)ruthenium(II)-	
	tetraphenylborate (1-)	135, 136
	+ $AgC_{24}H_{20}B$ + $NaClO_4$ + $NaC_{24}H_{20}B$	173
	$+ C_{24}H_{24}BN + H_{2}O$	/9
	+ $CSC_{24}H_{20}B$ + H_{20}	15 16
	+ $KC_{24}H_{20}B$ + H_{20}	21 22 23 T2, T0
	$+ N_2 C_4 R_2 O_5 + R_2 O_5$	$\frac{21}{4}, 22, 23$
	$+ \text{ RbC}_{24}\text{H}_{20}\text{B} + \text{H}_{20}$	48
iso-Propul alcoh	1. see 2-propanol	-20
iso-Propyl ether	see propane, 2.2'-oxybis-	
Propylammonium te	etraphenvlborate (1-)	
	+ water	96
Propylene carbona	ate, see 1,3-dioxolan-2-one, 4-methyl-	
Pyridinium tetra	phenylborate (1-)	
-	+ water	97
2-Pyrrolidinone,	l-methyl-	. -
	+ ammonium tetraphenylborate (1-)	80
	+ potassium tetraphenylborate (1-)	39
	+ sodium tetraphenylborate (1-)	5

2-Pyrrolidinone,	<pre>1-methyl- + tetrabutylammonium tetraphenylborate (1-) + tetraphenylarsonium tetraphenylborate (1-) + thallium(I) tetraphenylborate (1-) + AgC₂₄H₂₀B + NaClO₄ + NaC₂₄H₂₀B</pre>) 2: 11 1	02 21 80 70
R			
Rubidium tetraph S	enylborate + acetonitrile + ethane, 1,2-dichloro- + water + $C_3H_6O + H_2O$ + $C_4H_{11}NO_3 + C_2H_4O_2 + H_2O$ + LiCl + C_2H_6O	<u>43</u> , 44-	49 50 46 47 51
Silver nitrate	+ $C_{48}H_{40}BAs + C_{24}H_{20}AsNO_{3} + C_{2}H_{3}N$	1:	91
Silver tetraphen	+ $C_{48}H_{40}BAs + C_{24}H_{20}AsNO_3 + H_2O$	18	85
Silver Letraphen	+ acetonitrile + formamide, N,N-dimethyl- + methane, sulfinylbis- + methanol + phosphoric triamide, hexamethyl- + thisphore totrabudges l l-dioxide	<u>14</u> <u>159</u> , 159, 16 <u>1</u> 174 1/	49 54 62 66 65
	+ water	$\frac{1}{1}$	40
	+ $C_{3}H_{8}O$ + $C_{7}H_{6}$ + $H_{2}O$ + $C_{4}H_{11}NO_{3}$ + $C_{2}H_{4}O_{2}$ + $H_{2}O$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{2}H_{3}N$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{2}H_{6}OS$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{2}H_{6}O$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{3}H_{6}O$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{3}H_{6}O$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{3}H_{7}NO$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{5}H_{9}NO$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{5}H_{9}NO$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{4}H_{8}O_{2}S$ + $NaClO_{4}$ + $NaC_{2}H_{2}OB$ + $C_{4}H_{8}O_{2}S$ + $NaC_{2}H_{2}OB$ + $C_{2}H_{3}N$ + $NaC_{2}H_{2}OB$ + $C_{2}H_{0}OB$	147, 14 17 19 10 10 10 11 11 11 11 11 11	46 71 51 60 63 73 172 156 176 152
	+ $NaC_{24}H_{20}B$ + H_{20} + $NaC_{24}H_{20}B$ + H_{20}	141, 1	142
	+ $NaC_{24}H_{20}B$ + $NaBr$ + CH_4O + $NaC_{24}H_{20}B$ + NaI + H_{2O} + $NaNO_3$ + $NaC_{24}H_{20}B$ + CH_3NO + $NaNO_3$ + $NaC_{24}H_{20}B$ + $C_{2}H_3N$ + $NaNO_3$ + $NaC_{24}H_{20}B$ + $C_{2}H_3N$ + $NaNO_3$ + $NaC_{24}H_{20}B$ + $C_{3}H_7NO$ + $NaNO_3$ + $NaC_{24}H_{20}B$ + $C_{4}H_9NO$ + $NaNO_3$ + $NaC_{24}H_{20}B$ + H_{2O}	168, 1 144, 14 16 16 16 16 16 16 16 16 16 16 16 16 16	45 64 67 50 55 53 43
Sodium bromide Sodium hydroxide	+ $AgC_{24}H_{20}B$ + $NaC_{24}H_{20}B$ + $CH_{4}O$ + $C_{33}H_{62}BN$ + $H_{2}O$ + $C_{40}H_{56}BN$ + $H_{2}O$ + $CsC_{24}H_{20}B$ + LiCl + $CH_{4}O$ + $H_{2}O$	168, 16 8 9 61, 6	69 84 98 62
Sodium iodide Sodium nitrate, s Sodium perchloros Sodium sulfate, s Sodium tetraphen	+ $KC_{24}H_{20}B$ + LiCl + CH ₄ O + H ₂ O + $AgC_{24}H_{20}B$ + $NaC_{24}H_{20}B$ + H ₂ O see nitric acid, sodium salt ate, see perchloric acid, sodium salt see sulfuric acid, sodium salt vlborate (1-)	27-2 144-14	29 45
_ .	+ 1-propanol + 2-pyrrolidinone, 1-methyl-		6 5
	+ water + $AgC_{24}H_{20}B + C_{2}H_{3}N$ + $AgC_{24}H_{20}B + NaClO_4 + C_2H_3N$ + $AgC_{24}H_{20}B + C_2H_6OS$ + $AgC_{24}H_{20}B + C_3H_7NO$	15 15 16	3 52 51 51 57

.

Sodium tetraphenylborate (1-) + $AgC_{24}H_{20}B + H_{20}$ + $AgC_{24}H_{20}B + NaBr + CH_{40}$ + $AgC_{24}H_{20}B + NaClO_{4} + C_{2}H_{6}OS$ + $AgC_{24}H_{20}B + NaClO_{4} + C_{2}H_{6}O$ + $AgC_{24}H_{20}B + NaClO_{4} + C_{3}H_{6}O$ + $AgC_{24}H_{20}B + NaClO_{4} + C_{3}H_{7}NO$ + $AgC_{24}H_{20}B + NaClO_{4} + C_{4}H_{8}O_{2}S$ + $AgC_{24}H_{20}B + NaClO_{4} + C_{5}H_{9}NO$ + $AgC_{24}H_{20}B + NaNO_{3} + CH_{3}NO$ + $AgC_{24}H_{20}B + NaNO_{3} + CH_{4}O$ + $AgC_{24}H_{20}B + NaNO_{3} + CH_{4}O$ + $AgC_{24}H_{20}B + NaNO_{3} + C_{4}H_{9}NO$ + $AgC_{24}H_{20}B + NaNO_{3} + H_{2}O$ + $C_{3}H_{6}O + H_{2}O$ Sulfolane, see thiophene, tetrahydro-, 1,1-dioxide Sulfuric acid, sodium salt + $C_{24}H_{20}B + H_{2}O$ + $KC_{24}H_{20}B + H_{2}O$	141, 142168, 169171160163173156176170172144-145169167155153143476, 7755, 5617, 18	
т		
Tetrabutylammonium tetraphenylborate (1-) + ethane, 1,1-dichloro- + ethane, 1,2-dichloro- + methanol + 2-pyrrolidinone, 1-methyl- + NaOH + H ₂ O	99 100 101 102 98	
Tetraethylammonium tetraphenylborate (1-) + ethane, l,l-dichloro- + ethane, l,2-dichloro- + l-propanol	103 104 105	
Tetrahydrofuran, see butane, epoxy- Tetrahydrothiophene, 1,1-dioxide, see thiophene, tetrahydro-,		
Tetramethylammonium tetraphenylborate (1-) + ethane, 1,1-dichloro- + ethane, 1,2-dichloro- + 1-propanol + water	109 110 111	
2,2,4,4-Tetramethy1-3-pentanone, see 3-pentanone, 2,2,4,4-tetramethy1-	<u>100</u> / 10// 100	
Tetraphenylarsonium nitrate, see arsonium, tetraphenyl-, Tetraphenylarsonium tetraphenylborate (1-) + acetamide, N,N-dimethyl- + acetonitrile + ethane, 1,1-dichloro-	nitrate <u>194</u> , 195-197 <u>187</u> , 188-190 <u>192</u>	
+ ethane, 1,2-dichloro- + ethanol + formamide + formamide, N,N-dimethyl- + methane, nitro-	193 208 209, 210-212 <u>198</u> , 199-202 222	
<pre>+ methane, sulfinylbis- + methanol + phosphoric triamide, hexamethyl- + thiophene, tetrahydro-, l,l-dioxide + l,3-dioxolan-2-one, 4-methyl- + 2-propanone + 2-propanone</pre>	$\begin{array}{c} 203, & 204-207\\ \hline 217, & 218-220\\ \hline 213, & 214-216\\ \hline 225, & 226, & 227\\ \hline & & & & \\ 223\\ \hline & & & & & \\ 224\\ \hline & & & & & \\ 221\end{array}$	
$\begin{array}{r} + 2 - pyrrolldinone, 1 - metnyl - \\ + water \\ + AgNO_3 + C_{24}H_{20}AsNO_3 + H_{20} \\ + AgNO_3 + C_{24}H_{20}AsNO_3 + C_{2}H_{3}N \\ \end{array}$ Tetraphenylphosphonium tetraphenylborate (1-)	221 183, 184, 186 185 191	
+ acetonitrile + ethane, 1,1-dichloro- + ethane, 1,2-dichloro- + water	229 230 231 <u>228</u>	

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Tetrapropylammonium tetraphenylborate (1-)
                   + ethane, 1,1-dichloro-
                                                                            112
                                                                            113
                   + ethane, 1,2-dichloro-
                   + 1-propanol
                                                                            114
Thallium(I) tetraphenylborate (1-)
                                                                            181
                   + methane, sulfinylbis-
                   + formamide, N,N-dimethyl-
+ C_4H_{11}NO_3 + C_2H_4O_2 + H_2O
                                                                            180
                                                                            179
                                                                      177, 178
                   + water
Thiophene, tetrahydro-, 1,1-dioxide
                   + tetraphenylarsonium
                                                               <u>225</u>, 226, 227
                         tetraphenylborate (1-)
                   + silver tetraphenylborate (1-)
                                                                      174, 175
                                                                            176
                   + AgC_{24}H_{20}B + NaClO_4 + NaC_{24}H_{20}B
Toluene, see benzene, methyl-
Trichloromethane, see methane, trichloro-
Trimethylammonium tetraphenylborate (1-)
                                                                            115
                   + water
Tris(0-phenanthroline)ruthenium(II) tetraphenylborate (1-)
                   + acetic acid, butyl ester
+ acetic acid, ethyl ester
                                                                            120
                                                                            127
                                                                            133
                   + acetic acid, 2-methylpropyl ester
                                                                            137
                   + acetic acid, propyl ester
                                                                            117
                   + benzenemethanol
                   + benzene, chloro-
                                                                            121
                                                                            138
                   + butane, epoxy-
                   + ethane, 1,2-dichloro-
                                                                            124
                   + ethane, 1,1'-oxybis(2-chloro-
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                   + ethanol
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                   + methane, trichloro-
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                   + methanol
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                   + propane, 2,2'-oxybis-
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                   + 2-propanol
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                   + 2-propanone
                   + 3-pentanone, 2,2,4,4-tetramethyl-
                                                                            139
Tris (hydroxymethyl) aminomethane,
                   see 1,3-propanediol, 2-amino-2-(hydroxymethyl)-
U
                                                                             30
                  + KC_{24}H_{20}B + H_{2}O
Ilrea
W
Water, see under other components
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