INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION
COMMISSION ON SOLUBILITY DATA

SOLUBILITY DATA SERIES

Volume 40

HALIDES, OXYHALIDES AND SALTS OF HALOGEN COMPLEXES OF TITANIUM, ZIRCONIUM, HAFNIUM, VANADIUM, NIOBIUM AND TANTALUM

SOLUBILITY DATA SERIES

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY
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HALIDES, OXYHALIDES AND SALTS OF HALOGEN COMPLEXES OF TITANIUM, ZIRCONIUM, HAFNIUM, VANADIUM, NIOBIUM AND TANTALUM

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Note that the first page of each section above gives the system contents by formula.

FOREWORD

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

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

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of solubility data indeed existed, but they contained many errors, were in general uncritical, and were seriously out-of-date.

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

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

(i) A text which discusses the numerical solubility information which has been abstracted from the primary sources in the form of compilation sheets. The text concerns primarily the quality of the data, after consideration of the purity of the materials and their characterization, the experimental method used, the uncertainties in the experimental values, the reproducibility, the agreement with accepted test values, and, finally, the fitting of the data to suitable functions, along with statistical tests of the fitted data.

(ii) A set of recommended data, whenever possible, including weighted averages and estimated standard deviations. If applicable, one or more smoothing equations which have been computed or verified by the evaluator are also given.

(iii) A graphical plot of the recommended data, in the form of phase diagrams where appropriate.

The Compilation part consists of data sheets which summarize the experimental data from the primary literature. Here much effort is put into obtaining complete coverage; many good data have appeared in publications from the late nineteenth and early twentieth centuries, or in obscure journals. Data of demonstrably low precision are not compiled, but are mentioned in the Critical Evaluation. Similarly, graphical data, given the uncertainty of accurate conversion to numerical values, are compiled only where no better data are available. The documentation of data of low precision can serve to alert researchers to areas where more work is needed.

A typical data sheet contains the following information:

(i) list of components: names, formulas, Chemical Abstracts Registry Numbers;
(ii) primary source of the data;
(iii) experimental variables;
(iv) compiler's name;
(v) experimental values as they appear in the primary source, in modern units with explanations if appropriate;
(vi) experimental methods used;
(vii) apparatus and procedure used;
(viii) source and purity of materials used;
(ix) estimated error, either from the primary source or estimated by the compiler;
(x) references relevant to the generation of the data cited in the primary source.

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

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

January, 1989

J.W. Lorimer,
London, Canada

PREFACE

This volume presents solubility data of the halides, oxyhalides and halogen complexes of groups four and five metals of the periodic table, titanium, zirconium, hafnium, vanadium, niobium and tantalum. The literature for binary and multicomponent systems has been covered up to the end of 1986. There was a great effort to have the literature survey as complete as possible, however, the editors will be grateful to have any ommissions brought to their attention.

Except for the fluorides, the binary halides are predominantly covalent compounds highly susceptible to hydrolysis. No data on the solubility of the binary metal chlorides, bromides or iodides in water exists. The solubilities of these compounds in non-aqueous solvents are included. The oxyhalides and the salts of the halogen complexes solubilities are mainly studied in water and in aqueous solutions.

Phase diagrams are included for many of the multicomponent systems. For the simple eutonic systems phase diagrams were included only in the cases where no numerical data were reported in the origninal document, and the phase diagrams were the sole source of information.

Only those published results that report meaningful numerical data were considered for the volume. Papers that reported qualitative results with statements like "sparingly soluble", "insoluble", etc. were not considered. Papers in which the investigators failed to specify conditions such as temperature, equilibrium time, or methods of analysis were sometimes included. They were considered for the volume either if no other data were available for the system, or if the data were published in difficult to obtain older literature. The same criteria led the compiler to include estimates from a few graphically presented results.

The volume contains data on almost two hundred systems. Relatively few of the systems were studied over common ranges of temperature by more than one laboratory. Thus the opportunity to carry out evaluations is limited,and only sixteen systems are evaluated. When an evaluation was prepared the data were first compared by plotting them graphically to observe general agreement among the values from the various publications. Regression analysis was carried out in a few cases where the agreement among the various groups of investigators seemed to be good,using various polynomial functions. This was not done for systems where the data from different laboratories differed considerably and the reasons for the discrepancies were not clear.

The editors greatfully acknowledge advice and comments from members of the IUPAC Commission on Solubility Data, particullary the Chairman, Professor A. S. Kertes and the Coordinator for Solid/Liquid Systems, Dr. Mark Salomon. We thank Dr. Kurt Loening, Chemical Abstracts Service for providing Chemical Abstracts Regisry Numbers. We thank Ms. Laura Johnson and Ms. Carolyn Dowie for typing the final camera ready manuscript.

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

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1987, October

A check of *Chemical Abstracts* through 1988, June did not find any additional papers on the solubility of these systems.

1989, January

AVIEZER STEVAN KERTES

May 11, 1922 - July 8, 1988

Professor of Chemistry

The Hebrew University
of Jerusalem

THE SCIENTIFIC CAREER OF AVIEZER STEVAN KERTES: A PERSONAL APPRECIATION

Aviezer Stevan Kertes, known as Steve to his friends outside Israel, was a leading figure in the community of researchers on solvent extraction chemistry and the initiator and leader of the Solubility Data Project of IUPAC. He left us suddenly on July 8, 1988 at the age of sixty-six, in the midst of what were always hectic but highly efficient activities in his many fields of endeavor.

Steve Kertes was born in Szeged, Hungary, near the Yugoslav border, on May 11, 1922. This circumstance led to his fluency in both Hungarian and Serbian, to which languages he added in due course French, English and Hebrew. His scientific and technological education began at the University of Belgrade in Yugoslavia, where he obtained his M.S. degree in chemical technology in 1949. In this year he emigrated to Israel, where in Jerusalem he started and conducted his scientific career, except for a postdoctoral fellowship, periods of sabbatical leave and summer vacations spent at various institutes all over the world.

As a result of his training in chemical technology, Steve started his career at the laboratories of the Dead Sea Works, Ltd. which at that time were located in temporary accommodations in Jerusalem. It was also at this time that I first made his acquaintance, which slowly grew into a lasting friendship. In 1950 Steve quit that job and enrolled as a doctoral student at the Hebrew University of Jerusalem, under the supervision of the late Prof. Mordecai Max Bobtelsky. His Ph.D. thesis dealt with metal superphosphates and their complexes, and made extensive use of a solubility method. Later on, although Steve did not value his thesis greatly, he returned to the general problem of solubility with contributions of large scale and enormous impact. He obtained his doctoral degree in 1953, and continued for a time as an assistant in Prof. Bobtelsky's department.

The scientific career of Steve Kertes really took off once he accepted a postdoctoral fellowship with Prof. Michael Lederer at the Institut du Radium in Paris, where he stayed from 1955 to 1957. He learned there the use of radioactive tracers and came into contact with radiochemistry and nuclear technology, areas with which he maintained contact in later years. Steve's research in Paris concerned the use of paper chromatography for the study of metal complexes in aqueous organic - mineral acid solutions. When he was appointed a lecturer at the Hebrew University in Jerusalem in 1957 he continued this kind of research for some time with his first graduate student, Anna Beck.

Soon Steve decided that the key to the understanding of metal complexation in aqueous organic - mineral acid solutions was a deep knowledge of the physical chemistry of these solvent systems. He therefore started a series of studies with his wife, Vera, and graduate students Anna Beck, Jacob Elhanan-Habousha and Mordecai Halpern that dealt with these systems, in particular those in which the organic solvent was tri-*n*-butyl phosphate. This solvent, of prime importance in the reprocessing of spent nuclear fuel, was at that time under intensive study all over the world, but Steve found important aspects that became his domain, in particular the formation of three liquid phases in systems involving it. To be sure, this again is a solubility phenomenon, a subject that was not left alone by Steve throughout his career. Besides three-phase formation, Steve's team also studied the properties of extraction systems with tri-*n*-butyl phosphate and its degradation product, di-*n*-butyl phosphate, as applied to hydrochloric, hydrobromic, and perchloric acids, uranyl chloride and perrhenate salts. With these studies Steve joined the community of researchers dealing with solvent extraction, and he eventually became a leader in this community.

Extraction by means of these phosphate esters occupied Steve's attention during the late 1950's, but in the early 1960's he turned towards a new class of extractants: long-chain substituted ammonium salts. By 1962 a few publications with his students and coworkers Anna Beck, Jacob Elhanan-Habousha and Isaac Platzner concerned these extractants. At that time, I was doing radiochemical research at the Soreq Nuclear Research Center, and contact between Steve and myself was renewed, with far-reaching consequences.

In 1962 Steve went for his first sabbatical leave, which he spent at M.I.T. in Cambridge, Massachusetts with John W. Irvine, staying there till 1964. That was the time when Steve began to forge lasting friendships with a great number of colleagues whom he met at M.I.T. or elsewhere in the United States. These friendships later helped him to find collaborators for the Solubility Data Project and to find places to spend summer vacations where he could engage in scientific activities with others besides his students and colleagues in Jerusalem. His chemical research at M.I.T. concerned long-chain substituted ammonium salts in nonpolar organic diluents, a subject that continued to be in the center of his interest all through the 1960's.

The collaboration between Steve Kertes and myself crystallized in 1962 with a contract with John Wiley & Sons Ltd., then in London, to write a monograph on *Ion Exchange and Solvent Extraction of Metal Complexes*. This task took us more than four years, and it was not until February, 1967 that we could take out our wives for a dinner to celebrate having sent the completed manuscript to the publisher. These years were not easy for us. I was appointed in 1965 as a professor at the Hebrew University and became the head of the department at which Steve taught. There were periods of despair and tensions between us, but our satisfaction with the finished work - a book of 1050 pages published in 1969 - and with the impact it had on the scientific community overcame them all. Our names became household words in all the laboratories where ion exchange or solvent extraction were used to separate metal ions, and we received numerous invitations to lecture at conferences, symposia, universities and research institutes. Steve's contributions to our book were essential to its success and to the impact it had, so that my own career was much enhanced by this partnership with him. When Steve Kertes returned in 1964 from M.I.T. to his position in Jerusalem he dealt throughout the remaining 1960's and the early 1970's, together with his graduate students George Y. Markovits, Oscar Levy and Hilda Gutmann, with the behavior of long-chain substituted ammonium salts in organic solvents and in particular with their aggregation. A wide variety of physicochemical methods served for this purpose. X-rays were used for structure determination of the solid salts (in collaboration with Prof. I. Mayer) and studies of their infrared spectra established their hydrogen-bonding properties. The viscosity, conductivity, dielectric constant and in particular the vapor pressure, measured by a thermal osmometric method, helped to elucidate the aggregation of these substances in solution. A long series of publications reported on these studies.

Steve's diversity of interests were shown during another sabbatical leave in 1968/69 with Dr. Leonard Katzin at the Argonne National Laboratory in Argonne, Illinois, where he also collaborated with Dr. John Ferraro in studies of some chelate complexes. With another graduate student, Freddy Kassierer, he studied at that time the synergistic extraction with chelating extractants, and he also collaborated on this subject with Dr. Mendel Zangen of the Soreq Nuclear Research Center in Israel. The late 1960's and early 1970's constituted the peak of Steve's activities in the field of solvent extraction chemistry. He co-organized with me ISEC '68 (the 1968 International Solvent Extraction Conference) in Jerusalem and we co-edited its proceedings. At ISEC '74 in Lyon, France, he was elected to the international steering committee for these series of conferences, a position he held till 1986. His many contributions to this field were further recognized with a citation of merit at the ISEC '83 in Denver, Colorado, and finally, but alas posthumously, with the Carl Hanson medal at the recent ISEC '88 in Moscow.

The early 1970's were also an extremely fruitful period of Steve's research with his graduate students. Hilda Gutmann completed her work on the aggregation of long-chain substituted amines and their salts in nonpolar solvents, and she and Steve arrived at quite unconventional conclusions. These were that in these systems aggregation proceeded to yield a series of rather small oligomers, and that neither inverted micelles were formed, nor was the concept of critical micelle concentration valid for them. Fernanda Grauer and Liliane Tsimering measured, under Steve's supervision, the heats of mixing and dissolution of extractants in various diluents by means of precise calorimetry, and contributed thereby a new dimension to the thermodynamics of solvent extraction. Steve's summer-long stay in 1970 with Prof. Robert Guillaumont in his radiochemical laboratory of the University of Paris in Orsay brought him into contact with the field of molten salt chemistry. He then collaborated with Dr. Zangen at Soreq in the supervision of another graduate student, Judith David-Auslaender, studying extraction from molten salts with organic solvents. In another summer, 1977, at the City University of New York with Prof. Harmon Finston, Steve participated in work on the homogeneous liquid-liquid extraction of metal thenoyltrifluoroacetonates. Again, the diversity of Steve's interests and his ability to collaborate with others are hereby exemplified.

All through the 1970's publications appeared in the field of solvent extraction chemistry by Steve with his students and former students Markovits, Levy, Gutmann, Grauer and Tsimering. However, his main interest was diverted in the early 1970's in other directions. Two factors contributed mainly to this development. One arose from the work on the long-chain amines and the question of their micellization, the other from his election in 1967 to the Commission on Equilibrium Data of IUPAC (the International Union of Pure and Applied Chemistry), to deal initially with liquid-liquid distribution constants. The work on the aggregation and eventual micellization of the salts of long-chain substituted amines led naturally to Steve's interest in colloid chemistry, surface active substances, and microemulsions. The summer of 1973 that he spent in the Institute for Surface Chemistry in Stockholm and the subsequent sabbatical leave as a visiting professor during 1973/74 in McGill University in Montreal, Canada consolidated Steve's interaction with these fields that were up to then new to him. As a consequence he was able to act as a consultant in an industrial firm, Armac in Chicago, where he spent another sabbatical leave in 1979/80. The questions that he dealt with concerned soaps, that is, salts of long-chain carboxylic acids, in nonpolar or in aqueous-organic solvents. Other problems that he investigated concerned the formation of inverted micelles and microemulsions in systems involving polar solvents (short-chain alcohols), water, salts and nonpolar organic substances (solvents) that could be solubilized in such systems. Experimental studies on such systems were conducted in his laboratory by Lilian Tsimering (in collaboration with Prof. N. Garti of the Hebrew University) and a new graduate student, Wen-Chao Lai, in the late 1970's and early 1980's. Steve's stay in the summer of 1982 at Drexel University in Philadelphia was in this connection. His reputation in this field caused him to be nominated to the editorial boards of two scientific journals in the fields of colloid and surface chemistry, and to his chairing the 4th International Conference on Surface and Colloid Science in Jerusalem in 1981.

After election to IUPAC's Commission on Equilibrium Data in 1967, Steve started on projects of compilation and critical evaluation of equilibrium constants pertinent to solvent extraction together with Dr. Eytan Yanir and myself. He soon realized the importance of accurate data and their efficient transfer from the primary scientific literature to secondary and tertiary sources. He therefore found his way to CODATA (Committee on Data for Science and Technology), and became in 1972 a member and, since 1977, the chairman of the Israel National Committee for CODATA. This activity culminated in the organization by Steve of the 9th International CODATA Conference in Jerusalem in 1984, and his acting as its chairman. He continued with work for CODATA as a member of its task groups on the accessibility and dissemination of data and of education in the use of data. Within the IUPAC Commission on Equilibrium Data (Commission V.6) Steve sought for an activity that would fit his abilities and interests but would also have far-reaching consequences. He came to the conclusion that existing data on *solubilities*, which are fundamental not only to chemistry and chemical technology but also to many other branches of science and engineering, were in poor shape, being neither comprehensive nor particularly reliable. He therefore proposed to the Commission on Equilibrium Data of IUPAC that it should engage in a project of compilation and critical evaluation of solubility data. This proposal led to the creation within the commission in 1971 of a task group (consisting first of D.N. Hume, A.S. Kertes and F.J.C. Rossotti; later G.H. Nancollas replaced F.J.C. Rossotti). This task group examined the feasibility of such a project, and recommended that the Commission should undertake it under a subcommittee of Commission V.6. This was, indeed, authorized by IUPAC in 1973, and Subcommission V.6.1, under the chairmanship of Steve Kertes, was created.

The task of Subcommission V.6.1 was to formulate the scope of the project, establish the mechanism of the work of compilation and evaluation, define the format of the output, and find the means for its publication. Steve was the ideal person to handle both the organizational and scientific details of this task. His superb social qualifications permitted him to enlist hundreds of volunteers to work on the *Solubility Data Project*. He was very particular regarding who would be qualified to help. He wanted professional chemists who had experience in chemical research involving solubilities and had a stake in the accuracy of such data. Such people would naturally have interests in restricted areas of the whole field of solubility, and this meant that the project would have to be subdivided into many small sub-tasks. The overall picture would then be in the hands of topic editors and the editor-in-chief. Extended guidelines were prepared for compilers and evaluators, and sample compilations and evaluations were solicited from highly qualified colleagues. The scientific organization in topics and sub-topics was agreed on in many meetings, both at IUPAC General Assemblies and otherwise. In this connection, Steve stayed for a summer with Prof. Larry Clever at Emory University in Atlanta, Georgia. The onerous task of finding a publisher for the project fell to Steve, who travelled far and wide and had discussions with numerous potential publishers till one was found that finally took upon itself the financial risks (and eventual profits), Pergamon Press of Oxford, UK.

Thus, as in 1979 the first volumes of the *Solubility Data Project* were published, the time was ripe to remove the project from under the auspices of Commission V.6, and IUPAC authorized the creation of the new full-fledged Commission on Solubility, V.8, under the chairmanship of Steve Kertes. According to IUPAC's rules Steve had to relinquish this chairmanship after eight years, in 1987, and this retirement was celebrated at a memorable dinner at the Boston General Assembly of IUPAC. Steve retained the position of Editor-in-Chief, and within IUPAC's Analytical Chemistry Division Committee, to which he was elected in 1987, he continued to make Commission V.8 aware of his concerns and to provide it with advice. By now 40 volumes of the *Solubility Data Project* have been published, and more are in various stages of preparation, the project being viable and of lasting value and service to the chemical and other scientific communities.

Steve Kertes was also instrumental in calling into being a new series of international conferences, the *International Symposia on Solubility Phenomena*, the third of which took place in Guildford, UK after Steve's death. But while most of Steve's seemingly unlimited energy was channeled into organizational and editorial activities, he did not relinquish original scientific research in the field towards which most of his career was directed: *solvent extraction chemistry*. The opportunity for this arose from Steve's last sabbatical leave, which he spent with Prof. C. Judson King at the University of California in Berkeley in 1984/85, plus an additional summer in 1987. He supplemented Prof. King, who was busy with administrative duties, as the supervisor and counsellor of a number of graduate students. The team studied the solvent extraction of organic solutes from aqueous solutions, and two review articles by King and Kertes appeared in Steve's lifetime, one on the extraction of carboxylic acids and the other on the extraction of alcohols. The original research results will have to be published without Steve's very critical and painstaking evaluation. A further aspect of solvent extraction to which Steve returned in recent years was the behavior of tri-*n*-butyl phosphate as an extractant of acids, a subject that he studied experimentally some thirty years previously, and which was the subject of a volume that Steve co-edited a few years ago.

The very active career in science pursued by Steve Kertes, consisting of a harmonious mixture of teaching, original research in solvent extraction and surface chemistry, and organizational and editing activities, particularly in the field of solubilities, did not seem to affect Steve's health or diminish his energies. Despite quitting smoking a few years ago, he did suffer from shortness of breath, but otherwise did not appear to be approaching the age of retirement from his professorship at the Hebrew University or from his numerous other activities. He was full of plans for the near and far future, ranging from what he was going to do at the Catholic University of Leuven during his visit with Prof. Pierre Huyskens this past summer and his invited contributions to the ISEC '88 in Moscow and the 26th ICCC (International Conference on Coordination Chemistry) in Porto, Portugal, to his research with graduate students in Berkeley plus other old and new projects. These plans will never be realized now, and the scientific community of which he was such an active member will have to learn to do without him.

But it is not only projects that Steve's early demise leaves unfinished, nor not only colleagues that it leaves without a dedicated collaborator. Steve left Vera, his wife and lifelong companion and helper on voyages around the world, his daughter Tamar and son Amnon and their spouses and his two grandchildren in want of a devoted husband, father and grandfather. He left his very numerous friends on all continents the memory of a man of a charming and warm personality, who would always stand by them with advice and help if need be. Steve Kertes has left his mark not only on the fields of science in which he was active, but also on the minds and hearts of all of us, his friends.

Yizhak Marcus

Jerusalem, November, 1988

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INTRODUCTION TO THE SOLUBILITY OF SOLIDS IN LIQUIDS

Nature of the Project

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

Definitions

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

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

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

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

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

Quantities Used as Measures of Solubility

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

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

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

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

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

where m_s' is the mass of substance *s*. *Mass per cent* 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):

$$x_{s,B} = m_B / \sum_{s=1}^{c'} m_s = x_B / \sum_{s=1}^{c'} x_s \qquad [3]$$

$$w_{s,B} = m_B' / \sum_{s=1}^{c'} m_s' = w_B / \sum_{s=1}^{c'} w_s \qquad [3a]$$

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

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

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

where M_A is the molar mass of the solvent.

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

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

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

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

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

6. *Density*: $\rho = m/V \qquad \text{SI base units: kg m}^{-3} \qquad [6]$

7. *Relative density*: *d*; the ratio of the density of a mixture to the density of a reference substance under conditions which must be specified for both (1). The symbol $d_{t'}^{t}$ will be used for the density of a mixture at t°C, 1 bar divided by the density of water at t'°C, 1 bar. (In some cases 1 atm = 101.325 kPa is used instead of 1 bar = 100 kPa.)

8. *A note on nomenclature*. The above definitions use the nomenclature of the IUPAC *Green Book* (1), in which a solute is called *B* and a solvent *A* In compilations and evaluations, the first-named component (component 1) is the solute, and the second (component 2 for a two-component system) is the solvent. The reader should bear these distinctions in nomenclature in mind when comparing nomenclature and theoretical equations given in this Introduction with equations and nomenclature used on the evaluation and compilation sheets.

Thermodynamics of Solubility

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

Activity Coefficients (1)

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

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

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

$$\lim_{x_B \to 1} f_B = 1 \qquad [8]$$

(b) *Solutions*.

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

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

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

$$\gamma_B^{\infty} = 1 \qquad [10]$$

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

$$f_B = (1 + M_A\sum_s m_s)\gamma_B = [\rho + \sum_s(M_A - M_s)c_s]y_B/\rho^* \qquad [11]$$

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

$$y_B = \rho^* f_{x,B}[1 + \sum_s(M_s/M_A - 1)x_B]/\rho = \rho^*(1 + \sum_s M_s m_s)\gamma_B/\rho \qquad [13]$$

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

$$\gamma_B m_B = \gamma_\pm{}^\nu m_B{}^\nu Q^\nu \qquad [14]$$

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

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

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

$$x_+ = \nu_+x_B/[1 + \sum_s(\nu_s - 1)x_s]; \quad x_- = \nu_-x_B[1 + \sum_s(\nu_s - 1)x_s] \qquad [16]$$

where ν_s is the sum of the stoichiometric coefficients for the ions in a salt with mole fraction x_s. Note that the mole fraction of solvent is now

$$x_A{}' = (1 - \sum_s \nu_s x_s)/[1 + \sum_s(\nu_s - 1)x_s] \qquad [17]$$

so that

$$x_A{}' + \sum_s \nu_s x_s = 1 \qquad [18]$$

The relations among the various mean ionic activity coefficients are:

$$f_\pm = (1 + M_A\sum_s \nu_s ms)\gamma_\pm = [\rho + \sum_s(\nu_s M_A - M_s)c_s]y_\pm/\rho^* \qquad [19]$$

$$\gamma_\pm = \frac{(1 - \sum_s x_s)f_\pm}{1 + \sum_s(\nu_s - 1)x_s} = (\rho - \sum_s M_s c_s)y_\pm/\rho^* \qquad [20]$$

$$y_\pm = \frac{\rho^*[1 + \sum_s(M_s/M_A - 1)xs]f_\pm}{\rho[1 + \sum_s(\nu_s - 1)x_s]} = \rho^*(1 + \sum_s M_s m_s)\gamma_\pm/\rho \qquad [21]$$

(ii) *Solvent, A:*

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

$$\phi = (\mu_A{}^* - \mu_A)/RT\ M_A \sum_s m_s \qquad [22]$$

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

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

$$\phi_x = (\mu_A - \mu_A{}^*)/RT\ln x_A = \phi M_A \sum_s m_s/\ln(1 + M_A \sum_s m_s) \qquad [23]$$

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

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

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

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

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

$$\phi M_A\sum_s \nu_s m_s = -\ln(p/p_A{}^*) + (V^*_{m,A} - B_{AA})(p - p_A{}^*)/RT \qquad [25]$$

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

The Liquid Phase

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

$$\sum_{i=1}^{c} x_i'(S_i'dT - V_i'dp + d\mu_i') = 0 \qquad [26]$$

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

$$\sum_{i=1}^{c} x_i(S_i dT - V_i dp + d\mu_i') + \sum_{i=c+1}^{c'} x_i(S_i dT - V_i dp + d\mu_i) = 0 \qquad [27]$$

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

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

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

$$\sum_{i=1}^{c} x_i(d\mu_i')_{T,p} + \sum_{i=c+1}^{c'} x_i(d\mu_i)_{T,p} = 0 \qquad [29]$$

The resulting equation is:

$$RT\sum_{i=1}^{c} x_i'(d\ln a_i)_{T,p} = \sum_{i=1}^{c} x_i'(H_i - H_i')dT/T - \sum_{i=1}^{c} x_i'(V_i - V_i')dp \qquad [30]$$

where

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

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

Use of the equations

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

and

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

where superscript o indicates an arbitrary reference state gives:

$$RT\sum_{i=1}^{c} x_i'd\ln a_i = \sum_{i=1}^{c} x_i'(H_i^{o} - H_i')dT/T - \sum_{i=1}^{c} x_i'(V_i^{o} - V_i')dp \qquad [34]$$

where

$$d\ln a_i = (d\ln a_i)_{T,p} + (\partial\ln a_i/\partial T)_{x,p} + (\partial\ln a_i/\partial p)_{x,T} \qquad [35]$$

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

$$\sum_{i=1}^{c} x_i'H_i' = H_s^* \qquad \sum_{i=1}^{c} x_i'V_i' = V_s^* \qquad [36]$$

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

$$R\sum_{i=1}^{c} x_i'd\ln a_i = (H_s^* - \sum_{i=1}^{c} x_i'H_i^{o})d(1/T) - (V_s^* - \sum_{i=1}^{c} x_i'V_i^{o})dp/T \qquad [37]$$

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

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

(a) *Solubility as a function of temperature.*

Consider a binary solid compound 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 $c = 2$, $x_A{}' = n/(n + 1)$, $x_B{}' = 1/(n + 1)$, eqn [37] becomes:

$$d\ln(a_A{}^n a_B) = -\Delta H_{AB}{}^0 d(1/RT) \qquad [38]$$

where

$$\Delta H_{AB}{}^0 = nH_A + H_B - (n + 1)H_s{}^* \qquad [39]$$

is the molar enthalpy of melting and dissociation of pure solid A_nB to form A and B in their reference states. Integration between T and T_0, the melting point of the pure binary compound A_nB, gives:

$$\ln(a_A{}^n a_B) = \ln(a_A{}^n a_B)_{T=T_0} - \int_{T_0}^{T} \Delta H_{AB}{}^0 d(1/RT) \qquad [40]$$

(i) Non-electrolytes

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

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

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

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

where

$$G(T) = -\left\{\frac{\Delta H_{AB}{}^* - T^*\Delta C_p{}^*}{R}\right\}\left\{\frac{1}{T} - \frac{1}{T^*}\right\} + \frac{\Delta C_p{}^*}{R}\ln(T/T^*) - \frac{w}{R}\left\{\frac{x_A{}^2 + nx_B{}^2}{T} - \frac{n}{(n + 1)T^*}\right\} \qquad [43]$$

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

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

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

If the infinite dilution reference state is used, then:

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

and [39] becomes

$$\Delta H_{AB}{}^\infty = nH_A{}^* + H_B{}^\infty - (n + 1)H_s{}^* \qquad [46]$$

where $\Delta H_{AB}{}^\infty$ is the enthalpy of melting and dissociation of solid compound A_nB to the infinitely dilute reference state of solute B in solvent A; $H_A{}^*$ and $H_B{}^\infty$ are the partial molar enthalpies of the solute and solvent at infinite dilution. Clearly, the integral of eqn [32] will have the same form as eqn [35], with $\Delta H_{AB}{}^\infty$ replacing $\Delta H_{AB}{}^*$, $\Delta C_p{}^\infty$ replacing $\Delta C_p{}^*$, and $x_A{}^2 - 1$ replacing $x_A{}^2$ in the last term.

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

(ii) Electrolytes

(a) Mole fraction scale

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

$$\ln\left\{\frac{x_B{}^{\nu}(1 - x_B)^n}{[1 + (\nu - 1)x_B]^{n+\nu}}\right\} - \ln\left\{\frac{n^n}{(n + \nu)^{n+\nu}}\right\} + \ln\left\{\left[\frac{f_B}{f_B{}^*}\right]^{\nu}\left[\frac{f_A}{f_A{}^*}\right]^{n}\right\}$$

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

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

A similar equation (with $\nu = 2$ and without the heat capacity terms or activity coefficients) has been used to fit solubility data for some $MOH-H_2O$ systems, where M is an alkali metal (13); enthalpy values obtained agreed well with known values. The full equation has been deduced by another method in (14) and applied to MCl_2-H_2O systems in (14) and (15). For a summary of the use of equation [47] and similar equations, see (14).

(2) Molality scale

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

$$\nu\ln\left\{\frac{\gamma_{\pm}m_B}{\gamma_{\pm}{}^*m_B{}^*}\right\} - \nu(m_B/m_B{}^* - 1) - \nu\{m_B(\phi - 1)/m_B{}^* - \phi^* + 1\}$$

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

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

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

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

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

$$\mu_{A_nB}{}^* = \mu_{A_nB}(\mathrm{sln}) = n\mu_A + \mu_B \qquad [49]$$

$$= (n\mu_A{}^* + \nu_+\mu_+{}^{\infty} + \nu_-\mu_-{}^{\infty}) + nRT\ln f_Ax_A$$

$$+ \nu RT\ln(\gamma_{\pm}m_{\pm}Q)$$

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

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

$$= -RT\ln K_s$$

$$= -\nu RT \ln(Q\gamma_{\pm}m_B) \qquad [50]$$

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

$$\nu \ln\{m_B/m_B(0)\} = -\nu\ln\{\gamma_{\pm}/\gamma_{\pm}(0)\} - n \ln\{a_A/a_A(0)\} \qquad [51]$$

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

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

The Solid Phase

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

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

COMPILATIONS AND EVALUATIONS

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

Guide to the Compilations

The format used for the compilations is, for the most part, self-explanatory. The details presented below are those which are not found in the 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 (25) system and the choice of formula is governed by what is usual for most current users: i.e., IUPAC for inorganic compounds, and Hill system for organic compounds. Components are ordered according to:

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

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

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

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

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

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

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 and reporting errors are based on the papers by Ku and Eisenhart (27).

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

References. See the above description for Original Measurements.

Guide to the Evaluations

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

Components. See the description for the Compilations.

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

Critical Evaluation

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

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

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

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

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

(f) Units. While the original data may be reported in the units used by the investigators, the final recommended values are reported in S.I. units (1, 28) when the data can be accurately converted.

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September, 1986

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Table I-1

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

	mole fraction x_B =	mass fraction w_B =	molality m_B =	concentration c_B =
x_B	x_B	$\dfrac{M_B x_B}{M_A + \sum\limits_s (M_s - M_A) x_s}$	$\dfrac{x_B}{M_A(1 - \sum\limits_s x_s)}$	$\dfrac{\rho x_B}{M_A + \sum\limits_s (M_s - M_A) x_s}$
w_B	$\dfrac{w_B/M_B}{1/M_A + \sum\limits_s (1/M_s - 1/M_A) w_s}$	w_B	$\dfrac{w_B}{M_B(1 - \sum\limits_s w_s)}$	$\rho w_B/M_B$
m_B	$\dfrac{M_A m_B}{1 + M_A \sum\limits_s m_s}$	$\dfrac{M_B m_B}{1 + \sum\limits_s m_s M_s}$	m_B	$\dfrac{\rho m_B}{1 + \sum\limits_s M_s m_s}$
c_B	$\dfrac{M_A c_B}{\rho + \sum\limits_s (M_A - M_s) c_s}$	$M_B c_B/\rho$	$\dfrac{c_B}{\rho - \sum\limits_s M_s c_s}$	c_B

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

ACKNOWLEDGEMENTS

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Figure 1. Miscibility of titanium tetrachloride
with liquid sulfur dioxide. 39

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Figure 1. Solubility of niobium in hydrofluoric
acid solutions at 25 °C. 234
Figure 2. Portion of the niobium oxide-hydrofluoric
acid-water system at 25 °C. 234

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Figure 1. Solubility in the ZrF_4-HF-H_2O system. 64

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Figure 3. Solubility in the HF-NbF_5-H_2O system. 227

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Figure 3. Solubility in the TaF_5-H_2O system at 20 °C. 267

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Figure 1. Solubility isotherms in the ZrO_2-HCl-H_2O system 118

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Figure, page 2154. Acid free projection of the $ZrOCl_2$ $CaCl_2$-
HCl-H_2O isotherm at 25 C. 130

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Figure 1a-f. Solubilities at 25 °C in various systems.

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1c	199
1d	190
1e	201
1f	200

Figure 2b-d. Solubilities at 25 °C in various systems.

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2c	196
2d	197

Continued on the next page . . .

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Figures 2a and b. Solubility isotherms of $HfOCl_2$-HCl solutions at 0 (a) and 25 C (b). 189

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Figure 1. Acid free projection of the isotherm ($HfOCl_2$-$CaCl_2$-HCl-H_2O) at 25 °C. 195

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Figure 2. Phase diagram of the K_2NbOF_5-K_2TaF_7-H_2O system. 275

Figure 3. Salting out of K_2TaF_7 by K_2NboF_5. 283

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Figure 1. The HF-HfF_4-H_2O system (isotherm at 25 °C). 153

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Figure 1. Solubility in the HF-VO_2-H_2O system at 25 °C. 220

1. The solubility of titanium-containing substances.

COMPONENTS:

(1) Titanium(IV) fluoride; TiF_4; [7783-63-3]

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

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

ORIGINAL MEASUREMENTS:

Bamburov, V.G.; Demenev, N.V.; Polyakova, V.M.

Izv. Sib. Otd. Akad. Nauk SSSR 1962, *(4)*, 73-80.

VARIABLES:

T/K = 293
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions, t/°C = 20

KF		TiF_4		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
.211	.0369	.948	.0778	C
.652	.118	4.880	.417	B
.735	.131	2.825	.236	B
.830	.154	6.36	.553	A
1.050	.213	13.950	1.325	A
1.551	.272	.169	.0139	A
2.937	.521	.087	.00724	A
6.750	1.25	.052	.00450	D
11.020	2.13	.041	.00372	D

a. Calculated by compiler

b. A: $K_2TiF_6 \cdot H_2O$; B: $K_2TiF_6 \cdot 2H_2O$; C: $K_2TiF_6 \cdot 3H_2O$; D: K_2TiF_6
[23969-67-7] [107944-09-2] [107944-10-5] [16919-27-0]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. To a constant amount of TiF_4 solution, increasing amounts of KF and water were added to vary the TiF_4/KF mole ratio while keeping the total mass of the mixture at 100g. K determined gravimetrically as K_2SO_4, Ti colorimetrically, and F^- either titrimetrically with $Th(NO_3)_4$ against alizarine sulfonate or gravimetrically as CaF_2. The composition of the solid phases was deduced from the solubility isotherm.

SOURCE AND PURITY OF MATERIALS:

(1) A solution of TiF_4 prepared by reaction of TiO_2 with excess HF. Source and purity of chemicals not specified.

(2) KF, reagent grade, recrystallized twice from water.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 5 %.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Titanium fluoride; TiF_4; [7783-63-3] (2) (OC-6-11)-Uranium flouride; UF_6; [7783-81-5]	Nikolaev, N. S.; Sadikova, A. T. *At. Ener.* 1975, *39*, 338-43. *Sov. At. Energy (Engl. Transl.)* 1975, *39*, 338-43.
VARIABLES:	**PREPARED BY:**
T/K = 373	J. Hála

EXPERIMENTAL VALUES:

At 100°C the solubility of TiF_4 in UF_6 is reported to be 0.063 mol kg^{-1} (0.78 mass %).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility was determined in a Cu autoclave placed in a crucible furnace. Excess solid was equilibrated under constant mixing with 6 ml UF_6 for 30-40 h, and then allowed to stand for another 40 h which exceeded 3-4 times the time necessary to reach the equilibrium. After that the autoclave was rapidly cooled in liquid N. From the frozen sample, UF_6 was pumped off *in vacuo* at 80-90°C and Ti was determined in the residue. The method of analysis was not mentioned.

SOURCE AND PURITY OF MATERIALS:

The fluorides were prepared by the authors. No details were specified except for the fact that the products were strictly anhydrous.

ESTIMATED ERROR:

Temp: precision ± 5 K.
Soly: precision ± 5 %.

REFERENCES:

COMPONENTS:

(1) Ammonium hexafluorotitanate(IV); $(NH_4)_2TiF_6$; [16962-40-6]

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

ORIGINAL MEASUREMENTS:

Ginsberg, H.; Holder, G.

Z. Anorg. Allg. Chem. 1931, *201*, 193-206.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $(NH_4)_2TiF_6$ was reported to be 26 g/100 ml water (1.31 mol kg^{-1a}).

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2TiF_6$ was prepared from H_2TiF_6, NH_3, and NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 1.0 g/100 ml.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) (OC-6-11)-Diammonium hexafluorotitanate(2-); $(NH_4)_2TiF_6$; [16962-40-6] (2) Diammonium pentafluorooxoniobate; $(NH_4)_2NbOF_5$; [17871-12-4] (3) Hydrogen fluoride; HF; [7664-39-3] (4) Water; H_2O; [7732-18-5]	Skabichevskii, P. A. *Zh. Neorg. Khim.* <u>1966</u>, *11*, 675-7. *Russ. J. Inorg. Chem. (Engl.Transl.)* <u>1966</u>, *11*, 366-7.

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		HF^a	$(NH_4)_2NbOF_5$		$(NH_4)_2TiF_6$		Nature of Solid Phase^c
t/°C	*T*/K	mass%	mass%	m_2/mol kg^{-1} ^{b}	mass%	m_1/mol kg^{-1} ^{b}	
25	298	1.51	0	0	24.7	1.691	A
		1.48	4.0	0.230	22.0	1.532	
		1.44	7.8	0.463	20.5	1.474	
		1.39	11.7	0.714	18.6	1.375	
		1.35	15.3	0.964	17.2	1.313	
		1.29	20.5	1.347	14.8	1.179	
		1.26	24.0	1.625	13.2	1.083	
		1.20	28.4	2.009	11.5	0.986	
		1.13	33.2	2.494	10.2	0.929	
		1.13	34.5	2.596	9.0	0.821	
		1.02	42.0	3.488	6.8	0.685	
		0.96	45.8	4.066	6.3	0.678	
		0.87	51.5	5.022	4.9	0.579	
		0.79	56.2	6.066	4.4	0.576	
		0.75	59.6	6.740	2.8	0.384	A
		0.75	60.0	6.841	2.7	0.373	B
		0.73	63.0	7.383	0.71	0.101	
		0.73	63.5	7.398	0	0	B
50	323	1.36	0	0	32.2	2.448	A
		1.30	3.29	0.215	31.5	2.490	
		1.26	9.25	0.620	27.3	2.217	
		1.18	17.2	1.237	23.7	2.067	
		1.18	17.6	1.273	23.6	2.069	
		1.17	20.5	1.493	21.1	1.862	
		1.13	23.5	1.765	19.9	1.812	
		1.12	25.9	1.963	18.0	1.654	
		1.12	26.1	1.978	17.8	1.635	
		1.03	34.1	2.827	14.6	1.467	
		0.94	41.5	3.738	11.3	1.234	
		0.94	42.8	3.881	10.3	1.132	
		0.82	51.0	5.316	8.2	1.036	
		0.66	61.8	7.963	5.2	0.812	
		0.60	66.2	9.320	3.6	0.614	A
		0.59	67.0	9.521	3.3	0.573	B
		0.60	68.7	9.672	1.1	0.188	
		0.61	69.3	9.597	0	0	B

---

[a] The initial solvent was 2 mass% HF in water. Compiler calculated the actual HF concentration in the saturated solution which varied with increasing amount of salts dissolved.

[b] Calculated by compiler

[c] Solid phases: A: $(NH_4)_2TiF_6$; [16962-40-6]

B: $(NH_4)_2NbOF_5$; [17871-12-4]

Continued on the next page . . .

COMPONENTS:

(1) (OC-6-11)-Diammonium hexafluorotitanate(2-); $(NH_4)_2TiF_6$; [16962-40-6]
(2) Diammonium pentafluorooxoniobate; $(NH_4)_2NbOF_5$; [17871-12-4]
(3) Hydrogen fluoride; HF; [7664-39-3]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Skabichevskii, P. A.

Zh. Neorg. Khim. 1966, *11*, 675-7.

Russ. J. Inorg. Chem. (Engl. Transl.) 1966, *11*, 366-7.

VARIABLES:

T/K = 298, 323
Composition and HF molality

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. To prevent hydrolysis of the complex fluorides, the solubilities were determined in water containing 2 mass% HF. Equilibrium was attained within 3-4 h. Saturated solution and solid phases were analyzed for Ti and Nb spectrophotometrically. The samples were evaporated with H_2SO_4 to remove F^- and in the residue Ti and Nb were determined with H_2O_2 and SCN^- methods, respectively. Solid phases were also characterized by optical microscopy and the method of wet residues.

SOURCE AND PURITY OF MATERIALS:

Complex fluorides were prepared by evaporation of HF solutions of the corresponding metal oxide and NH_4F in the stoichiometric ratio. The salts were 3-times recrystallized. Analysis (mass%, found/calculated): $(NH_4)_2TiF_6$, Ti 24.19/24.20, NH_4 17.95/18.18; $(NH_4)_2NbOF_5$, Nb 38.78/38.72, NH_4 14.85/15.0. Source and purity of TiO_2, Nb_2O_5, and other chemicals used not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
The solubility error is not specified

REFERENCES:

COMPONENTS: (1) Ammonium hexafluorotitanate(IV); $(NH_4)_2TiF_6$; [16962-40-6] (2) Ethanol; C_2H_6O; [64-17-5]	**ORIGINAL MEASUREMENTS:** Ginsberg, H. *Z. Anorg. Allg. Chem.* 1932, *204*, 225-31.
VARIABLES: T/K = 294	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

The solubility at 21°C of $(NH_4)_2TiF_6$ was reported to be 0.004 g salt /100 cm^3 ethanol (0.00025 mol kg^{-1}[a]).

[a] Calculated by compiler by using the value of 0.799 g cm^{-3} for the density of 98% ethanol at 20°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2TiF_6$ prepared from H_2TiF_6, NH_3, and NH_4F according to ref 1.

(2) Ethanol, 98%. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 1 K.
The solubility error is not specified.

REFERENCES:

1. Ginsberg, H.; Holder, G. *Z. Anorg. Allg. Chem.* 1931, *201*, 193.

COMPONENTS:

(1) Lithium hexafluorotitanate(IV); Li_2TiF_6; [19193-50-1]

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

ORIGINAL MEASUREMENTS:

Ginsberg, H; Holder, G.

Z. Anorg. Allg. Chem. 1931, *201*, 193-206.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Li_2TiF_6 was reported to be 32 g/100 ml water (1.82 mol kg^{-1}[a]). The authors stated that this solubility value held only for freshly prepared salt. On aging, solubility decreased and an insoluble residue consisting of $TiO_2 \cdot xH_2O$ and LiF appeared.

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) $Li_2TiF_6 \cdot 2H_2O$ was prepared from H_2TiF_6 and Li_2CO_3. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: not specified
Soly: precision ± 0.5 g/100 ml.

REFERENCES:

COMPONENTS:

(1) Lithium hexafluorotitanate(IV); Li_2TiF_6; [19193-50-1]

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

ORIGINAL MEASUREMENTS:

Ginsberg, H.

Z. Anorg. Allg. Chem. 1932, *204*, 225-31.

VARIABLES:

T/K = 294

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 21° of Li_2TiF_6 was reported to be 48 g/100 ml water (2.73 mol kg^{-1a}). The author stated that the value 32 g/100 ml water given in an earlier paper (1) was erroneous since hydrolysis of the salt had been neglected.

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Li_2TiF_6 was prepared from H_2TiF_6 and Li_2CO_3 according to ref 1. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 1 K.
The solubility value is approximate (author).

REFERENCES:

1. Ginsberg, H.; Holder, G. *Z. Anorg. Allg. Chem.* 1931, *201*, 193.

COMPONENTS:

(1) Lithium hexafluorotitanate(IV); Li_2TiF_6; [19193-50-1]

(2) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Ginsberg, H.

Z. Anorg. Allg. Chem. 1932, *204*, 225-31.

VARIABLES:

$T/K = 294$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 21°C of Li_2TiF_6 was reported to be 0.030 g salt/100 cm^3 ethanol (0.00214 mol kg^{-1a}).

a Calculated by compiler by using the value of 0.799 gcm^{-3} for the density of 98% ethanol at 20°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Li_2TiF_6 prepared from Li_2CO_3 and H_2TiF_6 according to ref 1.

(2) Ethanol, 98%. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 1 K.
The solubility error is not specified.

REFERENCES:

1. Ginsberg, H.; Holder, G. *Z. Anorg. Allg. Chem.* 1931, *201*, 193.

COMPONENTS:

(1) Sodium hexafluorotitanate(IV); Na_2TiF_6; [17116-13-1]

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

ORIGINAL MEASUREMENTS:

Ginsberg, G.; Holder, G.

Z. Anorg. Allg. Chem. 1931, *201*, 193-206.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Na_2TiF_6 was reported to be 7 g/100 ml water (0.33 mol kg^{-1}[a]).

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Na_2TiF_6 was prepared from H_2TiF_6 and Na_2CO_3, and contained 1% water. Source and purity of chemicals not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Temp: precision ± 0.5 g/100 ml.

REFERENCES:

COMPONENTS:

(1) Sodium hexafluorotitanate(IV); Na_2TiF_6; [17116-13-1]

(2) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Ginsberg, H.

Z. Anorg. Allg. Chem. 1932, *204*, 225-31.

VARIABLES:

T/K = 294

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 21° of Na_2TiF_6 was reported to be 0.003 g salt/100cm^3 ethanol (0.00018 mol kg^{-1}[a]).

[a] Calculated by compiler by using the value of 0.799 g cm^{-3} for the density of 98% ethanol at 20°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Na_2TiF_6 prepared from H_2TiF_6 and Na_2CO_3 according to ref 1.

(2) Ethanol, 98%. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 1 K
The solubility error is not specified.

REFERENCES:

1. Ginsberg, H.; Holder, G. *Z. Anorg. Allg. Chem.* 1931, *201*, 193.

COMPONENTS:	EVALUATOR:
(1) (OC-6-11)-Dipotassium hexafluorotitanate(2-); K_2TiF_6; [16919-27-0] (2) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 611 37 Brno, Czechoslovakia October, 1984

CRITICAL EVALUATION:

The solubility of dipotassium hexafluorotitanate(2-) in water.

The solubility of K_2TiF_6 in water has been reported in four publications (ref 1-4). Marignac (ref 1) reports six values over the 273 to 293 K temperature interval. Weiss and Kaiser (ref 2) report values at temperatures of 293 and 371 K, and the others (ref 3 and 4) report a value at one temperature each. The Marignac (ref 1) data were published in a footnote with no experimental details or precision of measurement. However, the Marignac value at 293 K is identical to the 293 K value of Ginsberg and Holder (ref 3), and in good agreement with the value of Weiss and Kaiser (ref 2). All of the available data are summarized in Table 1. The molalities were calculated from the original solubility data.

Table 1. Tentative values of the solubility of K_2TiF_6 in water.

Temperature	Solubility		Reference
T/K	m_1/mol kg^{-1}	c_1/mol dm^{-3}	
273	0.0235	-	1
276	0.0269	-	1
279	0.0323	-	1
283	0.0379	-	1
287	0.0434	-	1
293	0.0534	-	1
	0.0534	-	3
	0.050	-	2
298	-	0.0595	4
371	0.445	-	2

REFERENCES:

1. Marignac, M. C.
   Ann. Chim. Phys. 1866, *8*[4], 5.
2. Weiss, L.; Kaiser, H.
   Z. Anorg. Allg. Chem. 1910, *65*, 345.
3. Ginsburg, H.; Holder, G.
   Z. Anorg. Allg. Chem. 1931, *201*, 193.
4. Schmitt, R. H.; Grove, E. L.; Brown, R. D.
   J. Am. Chem. Soc. 1960, *82*, 5292

COMPONENTS:

(1) Dipotassium (OC-6-11)-hexafluorotitanate(2-); K_2TiF_6; [16919-27-0]

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

ORIGINAL MEASUREMENTS:

Marignac, M. C.

Ann. Chim. Phys. 1866, *8*[*4*], 5-75.

VARIABLES:

$T/K = 273 - 293$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Temperature		K_2TiF_6	
$t/^{\circ}C$	T/K	Parts of Water Required to Dissolve 1 part of K_2TiF_6	$m_1/\text{mol kg}^{-1a}$
0	273	177	0.0235
3	276	155	0.0269
6	279	129	0.0323
10	283	110	0.0379
14	287	96	0.0434
20	293	78	0.0534

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

No details reported. (The data appeared in the original document in the footnote on p. 65.)

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorotitanate(IV)
K_2TiF_6; [16919-27-0]

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

ORIGINAL MEASUREMENTS:

Weiss, L.; Kaiser, H.

Z. Anorg. Chem. 1910, *65*, 345-402.

VARIABLES:

T/K = 293 and 371

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

Potassium Hexafluorotitanate (IV)

t/°C		w_1/g kg^{-1} a	m_1/mol kg^{-1} a
20	1 g in 78 ml H_2O	12.82	0.0534
98	1.1862 g in 11.1 ml H_2O	106.86	0.445
	1.3652 g in 12.8 ml H_2O	106.66	0.444

Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

To a flask containing a known amount of K_2TiF_6, water was gradually added until the salt dissolved completely. Measurements at 98° were carried out in a boiling water bath in a flask equipped with a reflux condenser. Solid phase was not examined.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TiF_6 containing 19.79% Ti was prepared by dissolving TiO_2 in HF (reagent grade, Kahlbaum). On addition of an excess of K_2CO_3 solution, K_2TiF_6 crystals were obtained. The solid was dried at 100°C. TiO_2 was prepared from Brazilian rutile by fusion with $KHSO_4$ and leaching the melt with water; it contained only traces of Fe.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorotitanate; K_2TiF_6; [16919-27-0]

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

ORIGINAL MEASUREMENTS:

Ginsberg, H.; Holder, G.

Z. Anorg. Allg. Chem. 1931, *201*, 193-206.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of K_2TiF_6 was reported to be 1.2 g/100 ml water (0.050 mol kg^{-1}[a]).

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 0.1 g/100 ml.

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorotitanate; K_2TiF_6; [16919-27-0]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298.15$

PREPARED BY:

J. Hala

EXPERIMENTAL VALUES:

The solubility of K_2TiF_6 at 25 °C in water is reported to be $c_1/\text{mol dm}^{-1} = 0.0595$.

The solubility is assumed to be the average of four measurements. Neither individual values nor a standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Two satd. solutions of K_2TiF_6 were prepared at 40 °C, another two below 20 °C. All solutions were brought to 25 °C with constant stirring. After attaining equilibrium, known volumes of the satd. solutions were evaporated to dryness at 70 °C, weighed, kept over P_2O_5 for several days and reweighed. All solutions were treated in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

K_2TiF_6 was prepd. by adding concd. soln. of reagent grade KCl to a soln. of H_2TiF_6. The salt was filtered, washed, and recrytallized several times. Pt or polyethylene containers and deionized water were used in all steps. Spectrographic analysis of K_2TiF_6 showed only traces of impurities. The H_2TiF_6 soln. was prepd. by dissolving very pure TiO_2, prepd. according to (ref 1), in excess HF.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K.
Soly: Nothing specified. See statement above.

REFERENCES:

1. Brauer, G. *Ann. Minnes.* 1859, *15*, 221.

COMPONENTS:

(1) Potassium hexafluorotitanate(IV); K_2TiF_6; [16919-27-0]

(2) Calcium nitrate; $Ca(NO_3)_2$; [10124-37-5]

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

ORIGINAL MEASUREMENTS:

Voitko, I. I.; Rozhenko, S.P.; Kvashenko, A.P.

**Ukr. Khim. Zh. (Russ. Ed.)* 1975, *41*, 754-6; *Sov. Prog. Chem. (Engl. Transl.)* 1975, *41*(7), 76-8.

VARIABLES:

$T/K = 293$

$c_2/\text{mol dm}^{-3} = 0.0127 - 1.018$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

$t/°C$	Initial Calcium Nitrate $c_2/\text{mol dm}^{-3}$	Saturated Solution Potassium Hexafluorotitanate(IV) $c_1/\text{mol dm}^{-3}$
20	0.0127	0.0577
	0.0254	0.0622
	0.0509	0.0650
	0.102	0.0735
	0.254	0.0945
	0.509	0.124
	1.018	0.148

Over the whole series the solid phase was composed of a mixture of K_2TiF_6 [16919-27-0], $K_2Ti(OH)_xF_{6-x}$, and CaF_2, [7789-75-5]. The increased solubility of K_2TiF_6 in $Ca(NO_3)_2$ solutions was ascribed to increasing acidity. Due to the hydrolytic equilibrium:

$$K_2TiF_6 + \frac{x}{2}\,Ca(NO_3)_2 + x\,H_2O \rightleftarrows K_2Ti(OH)_xF_{6-x} + \frac{x}{2}\,CaF_2 + x\,HNO_3$$

the pH of solutions decreased from 3.15 to 1.36 on going from 0.0127 to 1.018 mol dm^{-3} $Ca(NO_3)_2$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. After removal of F^- by evaporation with H_2SO_4 and leaching Ti with water, Ti was determined gravimetrically as TiO_2 via hydroxide or cupferrate. In the filtrate K was determined gravimetrically as K_2SO_4. Ca content not determined. Solid phases were identified by means of X-ray diffraction.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TiF_6, 99% purity, recrystallized in the presence of HF.

(2) $Ca(NO_3)_2$, reagent grade.

(3) Source and purity of water not specified.

ESTIMATED ERROR:

The temperature error is not specified.

Soly: Precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorotitanate(IV); K_2TiF_6; [16919-27-0]

(2) Strontium nitrate; $Sr(NO_3)_2$; [10042-76-9]

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

ORIGINAL MEASUREMENTS:

Voitko, I.I.; Rozhenko, S.P.; Kvashenko, A.P.

**Ukr. Khim. Zh. (Russ. Ed.)* 1975, *41*, 754-6; *Sov. Prog. Chem. (Engl. Transl.)* 1975, *41*(7), 76-8.

VARIABLES:

$T/K = 293$
$c_2/\text{mol dm}^{-3} = 0 - 2.84$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

$t/°C = 20$

Initial Strontium Nitrate	Composition of Saturated Solutions		Nature of Solid Phase[a]
	Strontium Nitrate	Potassium Hexafluorotitanate(IV)	
$c_2/\text{mol dm}^{-3}$	$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$	
0	0	0.0484	A+B+C
0.0121	0.0072	0.0513	
0.0242	0.0182	0.0528	
0.0484	0.0423	0.0588	
0.0968	0.0897	0.0660	
0.244	0.232	0.0865	
0.488	0.468	0.113	
0.977	0.836	0.118	
2.84	-	0.128	A+B+C+D

The increased solubility of K_2TiF_6 in $Sr(NO_3)_2$ solutions was ascribed to increasing acidity. Due to the hydrolytic equilibrium:

$$K_2TiF_6 + \frac{x}{2}\,Sr(NO_3)_2 + x\,H_2O \rightleftarrows K_2Ti(OH)_xF_{6-x} + \frac{x}{2}\,SrF_2 + x\,HNO_3$$

the pH of solutions decreased from 3.62 to 0.6 on going from 0.0121 to 2.84 mol dm^{-3} $Sr(NO_3)_2$.

[a] A: K_2TiF_6 [16919-27-0]; B: $K_2Ti(OH)_xF_{6-x}$; C: SrF_2 [7783-48-4]; D: unspecified phase X

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. After removal of F^- by evaporating with H_2SO_4 and leaching Ti with water, Ti was determined as TiO_2 via hydroxide or cupferrate. In the filtrate K was determined gravimetrically as K_2SO_4. Sr was determined gravimetrically as $SrSO_4$ in the residue remaining after leaching of Ti. Solid phases were identified by means of X-ray diffraction.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TiF_6, 99% purity, recrystallized in the presence of HF.

(2) $Sr(NO_3)_2$, reagent grade.

(3) Source and purity of water not specified.

ESTIMATED ERROR:

The temperature error is not specified. Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium hexafluorotitanate(IV); K_2TiF_6; [16919-27-0] (2) Ethanol; C_2H_6O; [64-17-5]	Ginsberg, H. *Z. Anorg. Allg. Chem.* 1932, *204*, 225-31.
VARIABLES:	**PREPARED BY:**
T/K = 294	J. Hála

EXPERIMENTAL VALUES:

The solubility at 21°C of K_2TiF_6 was reported to be 0.0045 g salt/100 cm^3 ethanol (0.000235 mol kg^{-1}[a]).

a Calculated by compiler by using the value of 0.799 g cm^{-3} for the density of 98% ethanol at 20°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Isothermal method used. No details were given.	(1) No details given for K_2TiF_6. (2) Ethanol, 98%.
	ESTIMATED ERROR:
	Temp: precision ± 1 K. The solubility error is not specified.
	REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Rubidium hexafluorotitanate; Rb_2TiF_6; [16962-41-7] (2) Water; H_2O; [7732-18-5]	Ginsberg, H.; Holder, G. *Z. Anorg. Allg. Chem.* 1931, *201*, 193-206.
VARIABLES:	**PREPARED BY:**
T/K = 298	J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Rb_2TiF_6 was reported to be 0.8 g/100 ml water (0.024 mol kg^{-1a}).

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2TiF_6 was prepared from Rb_2CO_3 (Kahlbaum) and H_2TiF_6. Source and purity of the latter not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 0.1 g/100 ml.

REFERENCES:

COMPONENTS:

(1) Rubidium hexafluorotitanate; Rb_2TiF_6; [16962-41-7]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Rb_2TiF_6 at 25°C is reported to be 0.0248 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Two saturated solutions of Rb_2TiF_6 were prepared at 40°, another two below 20°. All solutions were brought to equilibrium at 25° with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70°, weighed, kept over P_2O_5 for several days, and reweighed. All solutions were treated in polyethylene ware.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K.
The solubility error is not specified. The solubility value reported is a result of 4 independent measurements (individual values not reported).

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2TiF_6 was prepared by adding concentrated solution of RbF to a solution of H_2TiF_6. The salt was filtered, washed, and recrystallized several times. Pt or polyethylene containers and deionized water were used in all steps. Spectrographic analysis of Rb_2TiF_6 showed only minor traces of impurities. The H_2TiF_6 solution was prepared by dissolving very pure TiO_2, prepared according to ref (1), in excess HF.

(2) Deionized water was used.

REFERENCES:

1. Brauer, G. *Ann. Minnes.* 1859, *15*, 221.

COMPONENTS:

(1) Cesium hexafluorotitanate(IV); Cs_2TiF_6; [16919-28-1]

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

ORIGINAL MEASUREMENTS:

Ginsberg, H.; Holder, G.

Z. Anorg. Allg. Chem. 1931, *201*, 193-206.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Cs_2TiF_6 was reported to be 2.5 g/100 ml water (0.0585 mol kg^{-1a}).

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2TiF_6 was prepared from Cs_2CO_3 and H_2TiF_6. Source and purity of chemicals not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 0.1 g/100 ml.

REFERENCES:

COMPONENTS:

(1) Cesium hexafluorotitanate; Cs_2TiF_6; [16919-28-1]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Cs_2TiF_6 at 25° is reported to be 0.0551 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Two saturated solutions of Cs_2TiF_6 were prepared at 40°, another two below 20°. All solutions were brought to equilibrium at 25° with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70°, weighed, kept over P_2O_5 for several days, and reweighed. All solutions were treated in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2TiF_6 was prepared by adding concentrated solution of an unspecified Cs halide to a solution of H_2TiF_6. The salt was filtered, washed, and recrystallized several times. Pt or polyethylene containers and deionized water were used in all steps. Spectrographic analysis of Cs_2TiF_6 showed only minor traces of impurities. The H_2TiF_6 solution was prepared by dissolving very pure TiO_2, prepared according to ref (1), in excess HF.

(2) Deionized water was used.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K.
The solubility error is not specified. The solubility value reported is a result of 4 independent measurements (individual values not reported).

REFERENCES:

1. Brauer, G. *Ann. Minnes.* 1859, *15*, 221.

COMPONENTS:

(1) Cesium hexafluorotitanate(IV); Cs_2TiF_6; [16919-28-1]

(2) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Ginsberg, H.

Z. Anorg. Allg. Chem. 1932, *204*, 225-31.

VARIABLES:

T/K = 294

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 21°C of Cs_2TiF_6 was reported to be 0.002 g salt/100 cm^3 ethanol (0.000058 mol kg^{-1}[a]).

a Calculated by compiler by using the value of 0.799 g cm^{-3} for the density of 98% ethanol at 20°C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. No details were given.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2TiF_6 prepared from H_2TiF_6 and Cs_2CO_3 according to ref 1.

(2) Ethanol, 98%. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 1 K

The solubility error is not specified.

REFERENCES:

1. Ginsberg, H.; Holder, G. *Z. Anorg. Allg. Chem.* 1931, *201*, 193.

COMPONENTS:

(1) Titanium(II) chloride; $TiCl_2$;
[10049-06-6]
(2) Sodium bromide; NaBr; [7647-15-6]
(3) Sodium amalgam; $NaHg_x$
(4) Ammonia; NH_3; [7664-41-7]

ORIGINAL MEASUREMENTS

Oshiba, T.

Kogyo Kagaku Zasshi 1959, *62*, 985-92.

EXPERIMENTAL VALUES

Composition of Saturated Solutions

	NaBr		Ti	$TiCl_2$	
t/°C	g/100g NH_3	m_2/mol kg^{-1} [a]	g/100g NH_3	g/100g NH_3 [b]	m_1/mol kg^{-1} [a]
5	47.35	4.60	1.07	2.66	.224
	50.13	4.87	1.17	2.91	.245
	49.45	4.81	1.19	2.95	.248
15	50.14	4.87	1.36	3.37	.284
	49.06	4.77	1.31	3.26	.274
	50.20	4.88	1.28	3.18	.268
25	7.73	.751	.12	.31	.0261
	7.36	.715	.10	.25	.0210
	7.63	.742	.12	.30	.0252
	15.86	1.54	.33	.82	.0690
	16.05	1.56	.19	.47	.0396
	28.78	2.80	.85	2.10	.177
	29.17	2.83	.80	1.99	.167
	31.30	3.04	.98	2.44	.205
	32.17	3.13	.78	1.94	.163
	42.84	4.163	1.36	3.38	.284
	42.86	4.165	1.33	3.31	.279
	48.25	4.69	1.41	3.64	.306
	51.21	4.98	.94	2.35	.198
	58.71	5.71	1.22	3.02	.254
	58.18	5.65	1.12	2.77	.233
	71.00	6.90	.93	2.33	.196
	68.97	6.70	.93	2.32	.195
	78.75	7.65	1.00	2.48	.209
	78.44	7.62	.93	2.32	.195
	76.53	7.43	.99	2.45	.206
	85.24	8.28	1.19	2.96	.249
	84.88	8.25	1.20	2.98	.251
	87.91	8.54	1.18	2.93	.247
	119.70	11.63	.70	1.75	.147
	121.30	11.79	.71	1.78	.150
	123.20	11.97	.72	1.79	.151

$TiCl_xBr_{(2-x)}\cdot 4NH_3$ was assumed to be the equilibrium solid phase

a Calculated by compiler (J.H.)

b It was estimated that the following displacement reaction takes place in solution:

$$TiCl_2 + n\ NaBr \rightleftarrows TiCl_xBr_{(2-x)} + (2-x)NaCl + (n-2+x)NaBr$$

Continued on the next page. . .

COMPONENTS:

(1) Titanium(II) chloride; $TiCl_2$; [10049-06-6]
(2) Sodium bromide; NaBr; [7647-15-6]
(3) Sodium amalgam; $NaHg_x$
(4) Ammonia; NH_3; [7664-41-7]

ORIGINAL MEASUREMENTS:

Oshiba, T.

Kogyo Kagaku Zasshi 1959, *62*, 985-92.

VARIABLES:

T/K = 278-298
m_2/mol kg^{-1} = 0.715-5.71

PREPARED BY:

T. Oshiba and J. Hála

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A glass pressure vessel, in which sedimentation, decantation, and filtration of the $TiCl_2$ ammoniate could be done, was used. A small glass ampoule with $TiCl_4$, 0.2-0.3% Na amalgam containing excess Na, and NaBr was introduced into the vessel; the latter was evacuated and shaken vigorously to crush the ampoule, and then shaken slowly until all $TiCl_4$ was reduced, as indicated by no further increase in temperature. Then NH_3 gas was introduced at ordinary pressure until formation of the ammoniate was completed. The vessel was cooled, liquid NH_3 distilled into it, and the vessel kept in a thermostat for some hours with occasional shaking. Finally a portion of the saturated solution was poured out through an auxiliary glass tube with glass filter into another cooled vessel, and weighed. NH_3 was allowed to evaporate at room temp. and its content was obtained from loss of weight. The residue was analyzed for other components by standard methods.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_4$ distilled in the presence of Cu powder.
(2) NaBr, reagent grade, was dried at 500-600°C and treated with a solution of Na in NH_3 to remove traces of water.
(3) Na-amalgam was prepared either by electrolysis of aqueous solution of NaCl or NaOH, or by direct reaction of Na metal with Hg.
(4) NH_3 distilled in the presence of metallic Na.

ESTIMATED ERROR:

Temp: precision ± 0.5 K
Soly: precision ± 5 %.

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Titanium(III) chloride; $TiCl_3$; [7705-07-9] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Morozov, I.S.; Toptygina, G.M. **Zh. Neorg. Khim.* <u>1957</u>, *2*, 1629-38; *J. Inorg. Chem. (USSR)* <u>1957</u>, *2(7)*, 286-300.

EXPERIMENTAL VALUES:

The solubility of $TiCl_3$ in aqueous HCl at 0°C

HCl		$TiCl_3$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
2.98	1.27	32.90	3.33
4.11	1.75	31.60	3.19
4.32	1.84	31.15	3.13
7.25	3.07	27.90	2.79
8.79	3.73	26.65	2.68
10.40	4.36	24.20	2.40
12.75	5.31	21.45	2.11
14.80	6.08	18.40	1.79
18.30	7.55	15.20	1.48
19.70	8.18	14.25	1.40
25.90	10.66	7.47	0.727
32.20	13.70	3.32	.334
34.40	15.06	2.96	.306
36.70	16.53	2.41	.257
37.45	17.16	2.59	.280
40.60	19.68	2.81	.322
42.10	21.26	3.60	.428
42.90	21.90	3.39	.409
42.95	22.23	4.07	.498
43.00[b]	22.12	3.7	.450
45.14	22.57	0	0

The solid phase was $TiCl_3 \cdot 6H_2O$ throughout the whole HCl concentration range. The increase in solubility at HCl concentrations above 37 mass% was ascribed to the formation of anionic complexes in the solution, e.g. $H_2[TiCl_5]$.

a. Calculated by compiler

b. Eutonic point

Continued on next page...

COMPONENTS:

(1) Titanium(III) chloride; $TiCl_3$; [7705-07-9]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I.S.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1957, *2*, 1629-38; *J. Inorg. Chem. (USSR)* 1957, *2(7)*, 286-300.

VARIABLES:

T/K = 273
m_2/mol kg^{-1} = 1.27-22.57

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. HCl solutions containing excess solid were mixed for 6 h. Solutions containing more than 37 mass% HCl were prepared from dilute solution by saturating them with HCl gas. The solutions were analyzed for Ti(III) and Cl^- content but the methods used were not given. The composition of the solid phase was determined from chemical analysis and graphically by Schreinemakers' method. Also determined were partial pressures of HCl over $TiCl_3$ solutions in HCl at 0°C.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_3 \cdot 6H_2O$ was prepared by precipitation from HCl solution of $TiCl_3$. The product was stored in argon atmosphere over concentrated H_2SO_4 or KOH. Source and purity of $TiCl_3$ and HCl not specified.

ESTIMATED ERROR:

Temp: precision ± 0.2 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Titanium(III) chloride; $TiCl_3$; [7705-07-9]

(2) Ammonium chloride; NH_4Cl; [12125-02-9]

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

ORIGINAL MEASUREMENTS:

Morozov, I.S.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1960, *5*, 1637-8; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 794-5.

VARIABLES:

T/K = 273
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions, *t*/°C = 0

NH_4Cl		$TiCl_3$		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0	0	36.00	3.65	A
2.13	0.614	34.20	3.482	A
3.50	1.027	33.98	3.523	A
4.68[c]	1.401	34.03	3.599	A+B
5.01	1.425	30.47	3.06	B
5.91	1.613	26.85	2.59	B
6.16	1.552	21.02	1.87	B
8.25	2.01	16.64	1.44	B
14.15	3.35	8.38	0.701	B
22.9	5.55	0	0	B

a Calculated by compiler

b A: $TiCl_3 \cdot 6H_2O$; [19114-57-9] B: NH_4Cl; [12125-02-9]

c Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 6 h under argon atmosphere. Cl^- was determined by Volhard's method, NH_4^+ by Kjeldahl's method, and Ti^{3+} titrimetrically with $KMnO_4$. Compositions of the solid phases were determined graphically by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_3 \cdot 6H_2O$ dried in argon atmosphere, its source and purity not specified.

(2) NH_4Cl, reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.05 K
The temperature error is not specified.

REFERENCES:

COMPONENTS:

(1) Titanium(III) chloride; $TiCl_3$; [7705-07-9]

(2) Sodium bromide; NaBr; [7647-15-6]

(3) Ammonia; NH_3; [7664-41-7]

ORIGINAL MEASUREMENTS

Oshiba, T.

Kogyo Kagaku Zasshi <u>1959</u>, *62*, 985-92.

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	NaBr		Ti	$TiCl_3$	
t/°C	g/100g NH_3	m_2/mol kg^{-1a}	g/100g NH_3	g/100g NH_3^b	m_1/mol kg^{-1a}
5	47.63	4.63	1.18	3.78	.245
	46.70	4.54	1.52	4.86	.315
15	46.15	4.48	.84	2.72	.176
	45.73	4.44	.85	2.73	.177
	46.21	4.49	.81	2.61	.169
25	7.45	.724	.08	.28	.0182
	6.73	.654	.07	.24	.0156
	7.37	.716	.07	.23	.0149
	16.02	1.56	.14	.45	.0292
	15.63	1.52	.13	.44	.0285
	15.90	1.55	.14	.46	.0298
	22.27	2.164	.29	.93	.0603
	22.20	2.157	.32	1.04	.0674
	31.14	3.03	.42	1.36	.0882
	33.07	3.21	.42	1.35	.0875
	31.65	3.08	.40	1.30	.0843
	40.95	3.98	.86	2.76	.179
	41.07	3.99	.86	2.78	.180
	40.56	3.94	.80	2.58	.167
	52.79	5.13	1.19	3.83	.248
	53.05	5.16	1.21	3.87	.251
	52.81	5.13	1.12	3.59	.233
	46.64	4.53	1.22	3.91	.253
	57.69	5.61	1.21	3.88	.252
	53.87	5.23	1.20	3.84	.249
	49.87	4.85	1.17	3.76	.244
	85.22	8.28	1.33	4.29	.278
	85.35	8.29	1.37	4.42	.287
	86.22	8.38	1.37	4.42	.287
	119.57	11.62	1.36	4.38	.284
	119.58	11.62	1.36	4.38	.284

$TiCl_xBr_{(3-x)} \cdot 6NH_3$ was assumed to be the equilibrium solid phase

a Calculated by compiler (J.H.)

b It was estimated that the following displacement reaction takes place in solution:

$$TiCl_3 + n\ NaBr \rightleftarrows TiCl_xBr_{(3-x)} + (3-x)NaCl + (n-3+x)NaBr$$

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COMPONENTS:

(1) Titanium(III) chloride; $TiCl_3$; [7705-07-9]

(2) Sodium bromide; NaBr; [7647-15-6]

(3) Ammonia; NH_3; [7664-41-7]

ORIGINAL MEASUREMENTS:

Oshiba, T.

Kogyo Kagaku Zasshi 1959, *62*, 985-92.

VARIABLES:

T/K = 278-298

m_2/mol kg^{-1} = 0.654-11.62

PREPARED BY:

T. Oshiba and J. Hála

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A glass pressure vessel in which sedimentation, decantation, and filtration of the $TiCl_3$ ammoniate could be done, was used. The vessel with $TiCl_3$ and liquid NH_3 was kept in a thermostat for some hours with occasional shaking. Finally a portion of the saturated solution was poured out through an auxiliary glass tube with glass filter into another cooled vessel, and weighed. NH_3 was allowed to evaporate at room temp. and its content was obtained from loss of weight. The residue was analyzed for the remaining components by standard methods.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_3$ was prepared by reduction of $TiCl_4$ with Ti metal at about 600°. $TiCl_4$ was purified by distillation in the presence of Cu powder.

(2) NaBr, reagent grade, was dried at 500-600°C and treated with a solution of Na in NH_3 to remove traces of water.

(3) NH_3 was distilled in the presence of metallic Na.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.

Soly: precision ± 5 %.

REFERENCES:

COMPONENTS:

(1) Titanium (IV) chloride; $TiCl_4$; [7550-45-0]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Toptygina, G.M.; Morozov, I.S.

**Zh. Neorg. Khim.* 1961, *6*, 1685-92; *Russ. J. Inorg. Chem. (Engl. Transl)* 1961, *6*, 861-4.

VARIABLES:

T/K = 273, 293

m_2/mol kg^{-1} = 0.773 - 5.45

PREPARED BY:

J. Hala

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	HCl		TiO_2(soly)	$TiCl_4$(soly)		Nature of the Solid Phase
t/°C	mass%	m_2/mol kg^{-1a}	mass%	mass%^{a}	m_1/mol kg^{-1a}	
20	2.74	0.773	0.018	0.0427	0.00232	$TiO_2 \cdot nH_2O$
	4.69	1.35	.050	.119	.00659	
	5.61	1.63	.055	.130	.00727	
	6.72	1.98	.125	.297	.0168	
	10.32	3.17	.200	.475	.0281	
	12.04	3.78	.250	.594	.0358	
	14.12	4.59	.601	1.427	.0891	
	16.20	5.45	.930	2.208	.143	
0	36.74		30.28	71.89	bc	$H_2Ti(OH)_3Cl_3$
	37.07		28.61	67.93	bc	
	37.49		27.62	65.58	bc	
	38.17		27.10	64.34	bc	
	40.12		23.73	56.34	b	
	41.74		23.64	56.13	b	
	42.59		24.73	58.72	bc	
	44.01		24.85	59.00	bc	

a. Calculated by compiler

b. The mol kg^{-1} values referred to H_2O as the solvent could not be calculated since the water content in these solutions is very low and for most data points the experimental data are inconsistent (see footnote c).

c. The sum (mass% $TiCl_4$ + mass% HCl)>100.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: Isothermal method used. Measurements started with supersaturated solutions of $TiCl_4$ in ice-cooled HCl. For HCl concentrations above 36 mass%, solutions were mixed for several weeks to allow for precipitation of the equilibrium solid phase, and kept in thermostat for several days. Mixtures containing less than 16 mass% HCl were prepared from the supersaturated $TiCl_4$ solution by diluting it with water or dilute HCl. Since at 0°C, equilibrium state in these solutions could not be reached even after 2 months, solubility determinations at less than 16 mass% were done at 20°C. At 26-36 mass%, HCl, viscosity of the solutions was so high that the solid phase settled neither after several weeks standing nor after centrifuging at 3500 rpm. therefore the system could not be studied within this HCl concentration range. At HCl concentrations around 25% gels were obtained. Ti was determined gravimetrically as TiO_2 or colorimetrically with H_2O_2, Cl^- determined by Volhard's method. Solid phases were characterized by chemical analysis and microscopy.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.

Soly: precision ± 5 %.

COMPONENTS:

(1) Titanium(IV) chloride; $TiCl_4$; [7550-45-0]

(2) Ammonium chloride; NH_4Cl; [12125-02-9]

(3) Ammonia; NH_3; [7664-41-7]

ORIGINAL MEASUREMENTS:

Oshiba, T.

Kogyo Kagaku Zasshi 1959, *62*, 985-92.

VARIABLES:

T/K = 298

PREPARED BY:

T. Oshiba and J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

Ammonium Chloride		Titanium(IV) Chloride	
g/100g NH_3	m_2/mol kg^{-1a}	g/100 g NH_3	m_1/mol kg^{-1a}
14.412	2.69	0.523	0.0276
24.086	4.50	0.650	0.0343
37.010	6.92	0.833	0.0439
40.582	7.59	1.003	0.0529
52.239	9.77	1.423	0.0750
60.622	11.33	1.185	0.0625

$TiCl_4 \cdot xNH_4Cl \cdot 6NH_3$ was assumed to be the equilibrium solid phase.

a. Calculated by compiler (J.H.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A glass pressure vessel, in which sedimentation, decantation, and filtration of $TiCl_4$ ammonate could be done, was used. A small glass ampoule with $TiCl_4$ and NH_4Cl was introduced into the vessel; the latter was evacuated and shaken vigorously to crush the ampoule. Then NH_3 gas was introduced at ordinary pressure until the formation of the ammonate was completed. The vessel was then cooled, liquid NH_3 distilled into it, and the vessel was kept in a thermostat for some hours with occasional shaking until equilibrium was attained. Finally a portion of the saturated solution was poured out through an auxilliary glass tube with glass filter into another cooled vessel, and weighed. NH_3 was allowed to evaporate at room temp. and its content was obtained from loss of weight. The residue was analyzed for remaining components by standard methods.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_4$ purified by distillation with Cu powder.
(2) NH_4Cl reagent grade, sublimed at 100-200°C at reduced pressure.
(3) NH_3 distilled in the presence of metallic Na.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: precision ± 5 %.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Titanium(IV) chloride; $TiCl_4$; [7550-45-0] (2) Sodium chloride; NaCl; [7647-14-5] (3) Ammonia; NH_3; [7664-41-7]	Oshiba, T. *Kogyo Kagaku Zasshi* 1959, *62*, 985-92.
VARIABLES:	**PREPARED BY:**
T/K = 298 Composition	T. Oshiba and J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

Sodium Chloride		Titanium(IV) Chloride	
g/100 g NH_3	m_2/mol kg^{-1a}	g/100 g NH_3	m_1/mol kg^{-1a}
2.40	0.411	0.082	0.00432
5.39	0.922	0.141	0.00743
7.44	1.273	0.123	0.00648
7.46	1.276	0.124	0.00654

$TiCl_4 \cdot xNaCl \cdot 6NH_3$ was assumed to be the equilibrium solid phase.

a. Calculated by compiler (J.H.)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A glass pressure vessel, in which sedimentation, decantation, and filtration of $TiCl_4$ ammonate could be done, was used. A small glass ampoule with $TiCl_4$ and NaCl was introduced into the vessel; the latter was evacuated and shaken vigorously to crush the ampoule. Then NH_3 gas was introduced at ordinary pressure until the formation of the ammonate was completed. The vessel was then cooled, liquid NH_3 distilled into it, and the vessel was kept in a thermostat for some hours with occasional shaking until equilibrium was attained. Finally a portion of the saturated solution was poured out through an auxilliary glass tube with glass filter into another cooled vessel, and weighed. NH_3 was allowed to evaporate at room temp. and its content was obtained from loss of weight. The residue was analyzed for remaining components by standard methods.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_4$ purified by distillation with Cu powder.

(2) NaCl, reagent grade.

(3) NH_3 distilled in the presence of metallic Na.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: precision ± 5 %.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Titanium(IV) chloride; $TiCl_4$; [7550-45-0] (2) Sodium bromide; NaBr; [7647-15-6] (3) Ammonia; NH_3; [7664-41-7]	Oshiba, T. *Kogyo Kagaku Zasshi* 1959, *62*, 985-92.

EXPERIMENTAL VALUES

Composition of Saturated Solutions

	Sodium Bromide		Titanium	Titanium(IV) chloride	
t/°C	g/100g NH_3	m_2/mol kg^{-1}[a]	g/100g NH_3	g/100g NH_3[b]	m_1/mol kg^{-1}[a]
5	48.66	4.73	1.32	5.26	0.277
	49.06	4.77	1.36	5.40	0.285
15.5	45.23	4.40	1.23	4.89	0.258
	44.85	4.36	1.16	4.60	0.242
	45.31	4.40	1.21	4.81	0.254
25	8.35	0.811	0.04	0.18	0.00949
	8.50	0.826	0.03	0.14	0.00738
	8.48	0.824	0.03	0.15	0.00790
	15.67	1.52	0.13	0.51	0.02688
	15.83	1.54	0.14	0.58	0.03057
	18.99	1.85	0.18	0.72	0.03795
	21.06	2.05	0.34	1.24	0.06536
	21.28	2.07	0.27	1.20	0.06325
	30.47	2.96	0.67	2.68	0.141
	30.00	2.92	0.65	2.58	0.136
	40.18	3.90	0.99	3.93	0.207
	40.34	3.92	1.00	3.96	0.209
	49.56	4.82	1.30	5.17	0.273
	48.37	4.70	1.33	5.30	0.279
	49.50	4.81	1.30	5.16	0.272
	50.19	4.88	1.28	5.10	0.269
	56.59	5.50	1.29	5.13	0.270
	58.67	5.70	1.31	5.22	0.275
	63.15	6.14	1.30	5.18	0.273
	70.62	6.86	1.31	5.19	0.274
	63.86	6.21	1.45	5.77	0.304
	68.50	6.66	1.75	6.94	0.366
	67.34	6.54	2.29	9.07	0.478
	65.22	6.34	1.96	7.79	0.411
	77.18	7.50	1.80	7.14	0.376
	76.10	7.40	1.75	6.94	0.366
	76.93	7.48	1.75	6.94	0.366
	102.91	10.00	1.01	4.03	0.212
	107.50	10.45	1.00	3.98	0.210
	105.99	10.30	1.00	3.98	0.210

$TiCl_4 \cdot xNaBr \cdot 6NH_3$ was assumed to be the equilibrium solid phase.

[a] Calculated by compiler (J.H.)

[b] Analysis showed that the following displacement reaction takes place in solution:

$$TiCl_4 + n\ NaBr \rightleftarrows TiCl_4Br_{4-x} + (4-x)NaCl + (n-4+x)NaBr.$$

With increasing NaBr concentration, x gradually diminished and NaCl precipitated. The values g $TiCl_4$/100g NH_3 were calculated by the author assuming that only $TiCl_4$ existed in solution.

Continued on the next page...

COMPONENTS:

(1) Titanium(IV) chloride; $TiCl_4$; [7550-45-0]

(2) Sodium bromide; NaBr; [7647-15-6]

(3) Ammonia; NH_3; [7664-41-7]

ORIGINAL MEASUREMENTS:

Oshiba, T.

Kogyo Kagaku Zasshi <u>1959</u>, *62*, 985-92.

VARIABLES:

T/K = 278-298
Composition

PREPARED BY:

T. Oshiba and J. Hála

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

A glass pressure vessel, in which sedimentation, decantation, and filtration of $TiCl_4$ ammonate could be done, was used. A small glass ampoule with $TiCl_4$ and NaBr was introduced into the vessel; the latter was evacuated and shaken vigorously to crush the ampoule. Then NH_3 gas was introduced at ordinary pressure until the formation of the ammonate was completed. The vessel was then cooled, liquid NH_3 distilled into it, and the vessel was kept in a thermostat for some hours with occasional shaking until equilibrium was attained. Finally a portion of the saturated solution was poured out through an auxilliary glass tube with glass filter into another cooled vessel, and weighed. NH_3 was allowed to evaporate at room temp. and its content was obtained from loss of weight. The residue was analyzed for remaining components by standard methods.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_4$ distilled in the presence of Cu powder.

(2) NaBr, reagent grade, was dried at 500-600°C and treated with a solution of Na in NH_3 to remove traces of moisture.

(3) NH_3 distilled in the presence of metallic Na.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: precision ± 5 %.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Titanium(IV) chloride; $TiCl_4$; [7750-45-0] (2) Sulfur dioxide; SO_2; [7446-09-5]	Bond, P.A.; Stephens, W.R. *J. Am. Chem. Soc.* <u>1929</u>; *51*, 2910-22.

EXPERIMENTAL VALUES

Critical Temperature	Composition of Saturated Solutions			
	$TiCl_4$ $TiCl_4$-rich Phase		$TiCl_4$ SO_2-rich Phase	
t/°C	mass%	m_1/mol kg^{-1} [a]	mass%	m_1/mol kg^{-1} [a]
-42	96.31	137.5	-	-
-36.1	-	-	6.44	0.363
-33.7	94.95	99.1	-	-
-31.4	-	-	7.05	0.400
-27.9	-	-	8.23	0.473
-23.7	-	-	9.53	0.555
-16.8	-	-	12.26	0.736
-13.7	90.65	51.1	-	-
-12.2	-	-	14.44	0.889
-11.2	-	-	15.02	0.931
- 6.3	88.66	41.2	-	-
- 3.3	-	-	19.92	1.31
- 1.5	-	-	21.09	1.41
- 0.3	85.35	30.7	-	-
+ 0.1	85.16	30.2	-	-
1.5	-	-	23.56	1.62
3.5	-	-	26.17	1.87
4.0	82.43	24.7	-	-
6.5	-	-	30.47	2.31
6.8	79.35	20.3	-	-
8.3	-	-	33.87	2.70
9.6	-	-	37.67	3.18
10.2	73.26	14.44	-	-
11.0	-	-	43.69	4.09
11.5	68.08	11.24	48.20	4.90
11.8	65.40	9.96	52.82	5.90
11.9	61.80	8.53	56.23	6.77
12.0 [b]	60.46	8.06	58.05	7.29

[a] Calculated by compiler

[b] A third value, 58.40 mass% $TiCl_4$, also given.

Continued on next page...

COMPONENTS:

(1) Titanium(IV) chloride;
$TiCl_4$; [7750-45-0]

(2) Sulfur dioxide; SO_2; [7446-09-5]

ORIGINAL MEASUREMENTS:

Bond, P.A.; Stephens, W.R.

J. Am. Chem Soc. 1929, *51*, 2910-22.

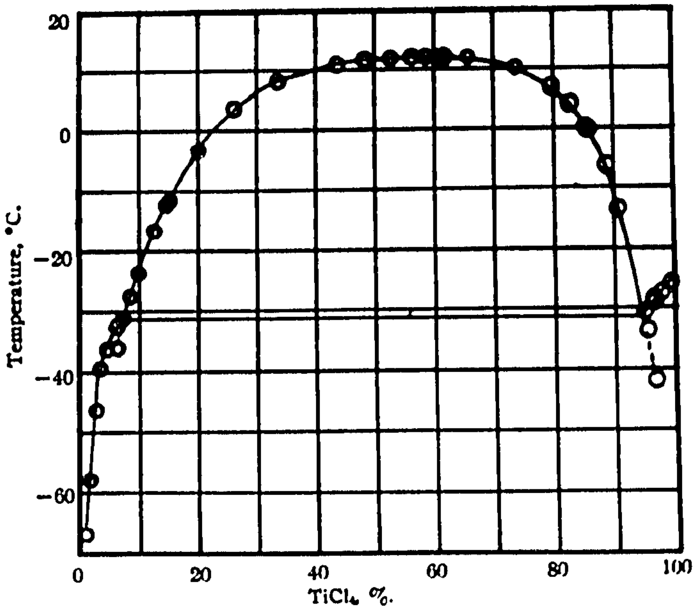
VARIABLES:

T/K = 231-285

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$TiCl_4$ was distilled into glass tubes in a dry atmosphere; the tubes were sealed off and weighed. The tube was then opened and the procedure was repeated with SO_2. The apparatus used for filling the tubes was that described by Bond and Beach (ref 1). The tubes were rotated in a thermostated bath, and the critical temp. was determined visually.

SOURCE AND PURITY OF MATERIALS:

(1) $TiCl_4$, distilled fractionally 8 times on a 30" long column. The lemon-yellow product was allowed to stand over Hg for several days and then distilled first from Hg and then repeatedly from metallic Na to obtain colorless product with b.p. 136.1°C at 752 mm Hg pressure.

(2) SO_2 purified by passing through H_2SO_4 and $NaHSO_3$ solution, dried with $CaCl_2$ and P_2O_5.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 %
(compiler).

REFERENCES:

1. Bond, P.A.; Beach, H.T. *J. Am. Chem. Soc.* 1926, *48*, 348.

COMPONENTS:

(1) Titanium dichloride oxide or dichlorooxotitanium; $TiOCl_2$; [13780-39-7]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

VARIABLES:

T/K = 253, 293, 409

ORIGINAL MEASUREMENTS:

Zavaritskaya, T. A.; Pustovalova, S.S. *Tsvetn. Met. (Moscow)* (Non-Ferrous Metals) 1958, No. 10, 50-3.

Delarova, N. I.; Zavaritskaya, T. A.; Zevakin, I.A.; Tsechovolskaya, Z. I. *Izv. Akad. Nauk SSSR, Otd. Tekh.Nauk, Metall. Topl.* 1960, No. 4, 33-8.

Zavaritskaya, T. A.; Zevakin, I. A. *Tr. Vses. Nauchuo-Issled. Proektn. Inst. Alyum., Magnievoi Elektrodnoi Prom-st.* 1961, No. 47, 85-90.

EXPERIMENTAL VALUES:

PREPARED BY:

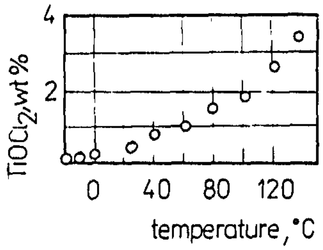
J. Hála

Composition of the saturated solutions.

Temperature		$TiOCl_2$	
$t/{}^{\circ}C$	T/K	mass %	m_1/mol kg^{-1} [a]
-20	253	0.17	0.0126
20	293	0.43	0.0320
136	409	3.5	0.27

[a] Calculated by compiler.

Other values were presented in graphical form only. See right.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $TiOCl_2$ was stirred with $TiCl_4$ for at least 10 h in a thermostated bath. The equilibrium saturated solutions were transfered into a sampling vessel, weighed, $TiCl_4$ removed by vacuum distillation at 30-40 °C, and the residue was vacuum dried and weighed.

In some cases the saturated solutions were analyzed for $TiOCl_2$ content spectroscopically from the IR absorption at 1356 cm^{-1} . Preliminary experiments confirmed that $TiOCl_2$ did not change on prolonged refluxing in $TiCl_4$. A pronounced tendency of $TiOCl_2$ to form supersaturated solutions in $TiCl_4$ was mentioned.

SOURCE AND PURITY OF MATERIALS:

(1) $TiOCl_2$ was prepared by partial hydrolysis of $TiCl_4$. The $TiCl_4$ was removed from the reaction mixture by vacuum distillation, and the product was vacuum dried. Its density was ρ/g cm^{-3} = 2.46-2.49, and molecular weight, as determined ebulioscopically, varied within the range 132-137; calculated 134.8.

ESTIMATED ERROR:

Temp: precision ± 1 K.
Soly: precision ± 3-7 %.

REFERENCES:

COMPONENTS:

(1) Titanium dichloride oxide; $TiOCl_2$; [13780-39-7]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Ehrlich, P.; Engel, W.

Z. Anorg. Allg. Chem. 1962, *317*, 21-4.

VARIABLES:

$T/K = 298 - 403$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.[a]

Temperature		$TiOCl_2$		
$t/^{\circ}C$	T/K	mass %	mol %	m_1/mol kg^{-1} [b]
25	298	2.5	3.5	0.190
50	323	3.2	4.4	0.245
75	348	4.0	5.6	0.309
100	373	5.1	7.0	0.399
110	383	5.1	7.0	0.399
120	393	5.3	7.3	0.415
130	403	5.6	7.6_5	0.440

[a] Because of the method used (see below) all solutions contained identical concentration of $AsCl_3$. Based on quantities of $TiCl_4$ and As_2O_3 used in the measurements, and the density of $TiCl_4$ = 1.726 g cm^{-3} (ref 1), the compiler calculated the concentration of $AsCl_3$ to be approximately 0.12 mol kg^{-1}.

[b] Calculated by compiler for the ($TiCl_4$ + $AsCl_3$) solvent.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturated solutions of $TiOCl_2$ in $TiCl_4$ were prepared by reacting As_2O_3 with excess $TiCl_4$ in a 3-neck flask equipped with a condenser, stirrer, and a rubber stopper through which samples for analysis could be withdrawn. 150cm $TiCl_4$ was distilled onto 3 g As_2O_3 in the flask and $TiOCl_2$ precipitated out as a pale yellow solid via the reaction

$$As_2O_3 + 3\ TiCl_4 \rightarrow TiOCl_2 + 2\ AsCl_3.$$

$AsCl_3$ produced, which is miscible with $TiCl_4$, was not separated from the mixture and consequently all solutions contained identical concentration of $AsCl_3$ corresponding to the amount of As_2O_3 used. The slurry was stirred for 2-3 h at each temperature after which pressure was applied through the condenser to withdraw a 10 cm^3 sample of the saturated solution with a pipette equipped with a glass filter. All procedures were carried out with exclusion of air moisture. The samples were added dropwise to ice-cooled H_2SO_4 solution, and Ti was determined by titration with Fe(III) against KSCN indicator after reduction to Ti(III) in Jones reductor. Cl was determined by titration with $AgNO_3$, and As by titration with $NaBrO_3$. From the concentrations of Ti, Cl, and As the content of oxygen in the saturated solution was obtained by difference, and used to calculate the solubility of $TiOCl_2$. The equilibrium solid phase was confirmed by chemical analysis to be $TiOCl_2$.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

REFERENCES:

1. Kaye, G. W. C.; Leby, T. H. *Tables of Physical and Chemical Constants*, 14th Ed., 1978, p. 166, Longman, London.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:

(1) Ammonium pentachlorotitanate(III); $(NH_4)_2TiCl_5$; [100656-75-5]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I. S.; Toptygina, G. M.; Lipatova, N. P.

Zh. Neorg. Khim. 1961, *6*, 2528-35.

Russ. J. Inorg. Chem. (Engl. Transl.) 1961, *6*, 1279-82.

VARIABLES:

$T/K = 273$

$m_2/\text{mol kg}^{-1} = 10.49 - 22.48$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions at $0^{\circ}C$

HCl		$TiCl_3$		NH_4Cl		Nature of the Solid Phases[b]
mass%	$m_2/\text{mol kg}^{-1}$ [a]	mass%	$m/\text{mol kg}^{-1}$ [a]	mass%	$m/\text{mol kg}^{-1}$ [a]	
25.92	10.49	4.240	0.406	2.07	0.571	A + B
30.76	14.82	7.640	0.870	4.68	1.537	A + B
30.88	14.19	5.690	0.618	3.76	1.178	A + C
35.61	16.47	3.416	0.373	1.67	0.526	A + C
36.25	16.98	2.350	0.260	2.84	0.907	A + C
37.37	17.32	2.030	0.222	1.41	0.445	A + C
39.41	18.81	1.880	0.212	1.24	0.403	C
39.80	18.69	1.060	0.118	0.73	0.234	C
40.59	19.34	1.090	0.123	0.75	0.244	C
41.58	20.07	0.941	0.107	0.65	0.214	C
44.37	22.43	0.814	0.0973	0.57	0.196	C
44.53	22.48	0.674	0.0804	0.46	0.158	C

[a] Calculated by compiler.

[b] A: NH_4Cl, [12125-02-9]; B: $TiCl_3.6H_2O$, [19114-57-9];
C: $(NH_4)_2TiCl_5.H_2O$, [107944-12-7]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess of either $(NH_4)_2TiCl_5.H_2O$ or a mixture of NH_4Cl and $TiCl_3.6H_2O$ was equilibrated with HCl solutions of the desired concentration at 0° in argon atmosphere for 6-8 h. Solutions with high HCl concentrations were prepared by saturating the solutions with HCl gas at 0°. In the samples of the saturated solutions and the solid phases Ti(III) was determined by titration with $KMnO_4$ after reacting the sample with excess $KFe(SO_4)_2$, Cl^- by Volhard method, and NH_4^+ by Kjeldahl method. To check for the presence of Ti(IV), the total Ti content was determined gravimetrically as TiO_2. HCl concentration was determined as the difference of total Cl and the Cl content combined with Ti(III) and NH_4^+. Solid phases were also characterized by microscopic analysis and the method of wet residues.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2TiCl_5.H_2O$ was prepared by precipitation from a solution of $TiCl_3$ and NH_4Cl (reagent grade) in concentrated HCl at 0° by saturating the solution with HCl gas. The crystals were dried in a stream of Ar + HCl gases. Analysis, mass% (found/calculated): NH_4 12.86/12.92, Ti 17.20/17.15, Cl 63.58/63.49, H_2O -/6.44. $TiCl_3.6H_2O$ used was prepared by dissolving Ti metal, obtained by iodide method, in concentrated HCl, and saturating the solution with HCl gas at 0°. The crystals were dried in a stream of Ar + HCl gases.

ESTIMATED ERROR:

Temperature was kept within the range of $0 - 0.5^{\circ}C$.

The solubility error is not specified.

COMPONENTS:

(1) Dipotassium pentachlorotitanate(2-); K_2TiCl_5; [12200-03-2].

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I. S.; Toptygina, G. M.; Lipatova, N. P.

Zh. Neorg. Khim. 1961, *6*, 2528-35.

Russ. J. Inorg. Chem. (Engl.Transl.) 1961, *6*, 1279-82.

VARIABLES:

$T/K = 273$

$m_2/\text{mol kg}^{-1} = 12.82 - 22.69$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions at 0°C

HCl		$TiCl_3$		KCl		Nature of the Solid Phases[b]
mass%	$m_2/\text{mol kg}^{-1}$ [a]	mass%	$m/\text{mol kg}^{-1}$ [a]	mass%	$m/\text{mol kg}^{-1}$ [a]	
30.76	12.82	2.260	0.223	1.17	0.238	A
35.33	16.19	3.601	0.390	1.20	0.269	A
35.52	16.27	3.436	0.372	1.16	0.260	A
35.91	16.60	3.560	0.389	1.20	0.271	A + B
38.83	18.67	2.840	0.323	1.30	0.306	A + B
42.06	21.01	1.809	0.214	1.23	0.301	A + B
42.28	21.16	1.764	0.209	1.15	0.281	A + B
42.69	21.51	1.753	0.209	1.12	0.276	A + B
42.87	21.67	1.702	0.203	1.16	0.287	A + B
43.93	22.69	1.501	0.183	1.46	0.369	B

[a] Calculated by the compiler.

[b] Solid phases: A: KCl; [7447-40-7]

B: $K_2TiCl_5 \cdot H_2O$; [23969-67-7]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess of either $K_2TiCl_5.H_2O$ or a mixture of KCl and $TiCl_3.6H_2O$ was equilibrated with HCl solutions of the desired concentration at 0° in argon atmosphere for 6-8 h. Solutions with high HCl concentrations were prepared by saturating the solutions with HCl gas at 0°. In the samples of the saturated solutions and the solid phases Ti(III) was determined by titration with $KMnO_4$ after reacting the sample with excess $KFe(SO_4)_2$, Cl^- by Volhard method, and K^+ gravimetrically as K_2SO_4. To check for the presence of Ti(IV), the total Ti content was determined gravimetrically as TiO_2. HCl concentration was obtained as the difference of total Cl and the Cl content combined with Ti(III) and K^+. Solid phases were also characterized by microscopic analysis and the method of wet residues.

SOURCE AND PURITY OF MATERIALS:

(1) Attempts at preparation of pure $K_2TiCl_5.H_2O$ by precipitation from a solution of $TiCl_3.6H_2O$ and KCl (reagent grade) in concentrated HCl at 0° by gaseous HCl failed. The product always contained variable amount of KCl and was used as such. $TiCl_3.6H_2O$ used was prepared by dissolving Ti metal, obtained by iodide method, in concentrated HCl and saturating the solution with HCl gas at 0°. The crystals were dried in a stream of Ar+HCl gases.

ESTIMATED ERROR:

Temperature was kept within the range of 0 - 0.5°C.

The solubility error is not specified.

COMPONENTS:

(1) Rubidium pentachlorotitanate(III): Rb_2TiCl_5; [100656-87-9]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I. S.; Toptygina, G. M.; Lipatova, N. P.

Zh. Neorg. Khim. 1961, *6*, 2528-35.

Russ. J. Inorg. Chem. (Engl. Transl.) 1961, *6*, 1279-82.

VARIABLES:

$T/K = 273$

$m_2/\text{mol kg}^{-1} = 9.71 - 22.30$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions at 0°C

HCl		$TiCl_3$		RbCl		Nature of the Solid Phases[b]
mass%	m_2/mol kg^{-1} [a]	mass%	m/mol kg^{-1} [a]	mass%	m/mol kg^{-1} [a]	
21.76	9.709	8.061	0.850	8.71	1.172	A + B
24.60	10.55	4.498	0.456	6.96	0.900	
27.90[c]	11.81	3.598[c]	0.360	3.69[c]	0.471	
29.85	12.39	1.847	0.181	2.24	0.280	
30.26	12.59	1.629	0.160	2.19	0.275	
30.42	12.78	1.686	0.167	2.60	0.329	B
30.91	13.07	1.660	0.166	2.59	0.330	
32.59	13.88	1.176	0.118	1.84	0.236	
33.92	14.57	0.865	0.0878	1.36	0.176	
34.87	15.26	0.960	0.0993	1.50	0.198	
37.68	16.88	0.429	0.0454	0.67	0.0905	
37.72	16.92	0.439	0.0465	0.69	0.0933	
38.74	17.70	0.470	0.0507	0.75	0.103	
41.38	19.56	0.227	0.0254	0.36	0.0513	
42.38	20.41	0.261	0.0297	0.41	0.0595	
42.64	20.64	0.270	0.0309	0.42	0.0613	
44.54	22.30	0.265	0.0314	0.42	0.0634	

[a] Calculated by compiler.

[b] A: RbCl, [7791-11-9] B: $Rb_2TiCl_5.H_2O$; [107944-13-8]

[c] Two identical measurements with different compositions of the corresponding solid phases given in the original document.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $Rb_2TiCl_5.H_2O$ was equilibrated with HCl solutions of the desired concentration in argon atmosphere for 6-8 h. Solutions with high HCl concentrations were prepared by saturating the solutions with HCl gas at 0°. In the samples of the saturated solutions and the solid phases Ti(III) was determined by titration with $KMnO_4$ after reacting the sample with excess $KFe(SO_4)_2$, Cl^- by Volhard method, Rb gravimetrically as Rb_2SO_4 after removal of Ti by precipitation with NH_4OH. To check for the presence of Ti(IV), total Ti content was determined gravimetrically as TiO_2. HCl concentration was obtained as the difference of total Cl and the Cl combined with Ti(III) and Rb(I). Solid phases were also characterized by microscopic analysis and the method of wet residues.

SOURCE AND PURITY OF MATERIALS:

(1) $Rb_2TiCl_5.H_2O$ was prepared by precipitation from a solution of $TiCl_3$ and RbCl (reagent grade) in concentrated HCl at 0° by saturating the solution with HCl gas. The crystals were dried in a stream of Ar+ HCl gases. Analysis, in mass% (found/calculated) Rb 39.87/41.28, Ti 11.76/11.57, Cl 43.72/42.81, H_2O 4.51/4.34. $TiCl_3.6H_2O$ used was prepared by dissolving Ti metal, obtained by iodide method, in concentrated HCl, and saturating the solution with HCl gas at 0°. The crystals were dried in a stream of Ar+ HCl gases.

ESTIMATED ERROR:

Temperature was kept constant within the range of 0 - 0.5°C.
Solubility error is not specified.

COMPONENTS:

(1) Cesium pentachlorotitanate(III); Cs_2TiCl_5; [100656-77-7]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morosov, I. S.; Toptygina, G. M.; Lipatova, N. P.

Zh. Neorg. Khim. 1961, *6*, 2528-35.

Russ. J. Inorg. Chem. (Engl. Transl.) 1961, *6*, 1279-82.

VARIABLES:

$T/K = 273$
$m_2/\text{mol kg}^{-1} = 3.355 - 21.93$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions at 0°C

HCl		$TiCl_3$		CsCl		Nature of the Solid Phases[b]
mass%	m_2/mol kg^{-1} [a]	mass%	m/mol kg^{-1} [a]	mass%	m/mol kg^{-1} [a]	
6.24[c]	3.355	15.456[c]	1.964	27.30[c]	3.18	A + B
19.80	8.229	4.740	0.466	9.47	0.852	A + B
20.33	8.602	4.960	0.496	9.89	0.906	B + C
25.81	10.95	3.040	0.305	6.52	0.599	B + C
25.81	10.82	2.880	0.285	5.88	0.534	B + C
27.07	11.60	2.760	0.279	6.15	0.571	B + C
28.96	12.14	2.040	0.202	3.58	0.325	B + C
29.84[c]	12.93	2.222[c]	0.228	4.66[c]	0.437	C
31.14	13.49	1.749	0.179	3.79	0.356	
33.06	14.40	1.166	0.120	2.54	0.239	
34.18	15.06	1.053	0.110	2.50	0.238	
35.04	15.55	0.988	0.104	2.16	0.208	
35.51	15.78	0.868	0.0912	1.90	0.183	
36.11	16.21	0.876	0.0929	1.91	0.186	
41.00	19.62	0.473	0.0535	1.22	0.126	
41.17	19.76_2	0.473	0.0537	1.22	0.127	
41.32	19.76_5	0.423	0.0478	0.92	0.0953	
43.93	21.93	0.354	0.0418	0.77	0.0832	

[a] Calculated by compiler.

[b] A: CsCl, [7647-17-8]; B: $TiCl_3.6H_2O$; [19114-57-9] C: $Cs_2TiCl_5.H_2O$, [107944-14-9]

[c] Two identical measurements given in the original document with different compositions of the corresponding solid phases.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $Cs_2TiCl_5.H_2O$ was equilibrated with HCl solutions of the desired concentration in argon atmosphere for 6-8 h. Solutions with high HCl concentrations were prepared by saturating the solutions with HCl gas at 0°. In the samples of the saturated solutions and the solid phases Ti(III) was determined by titration with $KMnO_4$ after reacting the sample with excess $KFe(SO_4)_2$, Cl^- by Volhard method, Cs gravimetrically as Cs_2SO_4 after removal of Ti by precipitation with NH_4OH. To check for the presence of Ti(IV), total Ti content was determined gravimetrically as TiO_2. HCl concentration was obtained as the difference of total Cl and the Cl combined with Ti(III) and Cs(I). Solid phases were also characterized by microscopic analysis and the method of wet residues.

SOURCE AND PURITY OF MATERIALS:

(1) $Cs_2TiCl_5.H_2O$ was prepared by precipitation from a solution of $TiCl_3$ and CsCl (reagent grade) in concentrated HCl at 0° by saturating the solution with HCl gas. The crystals were dried in a stream of Ar+ HCl gases. Analysis, in mass% (found/calculated): Cs 52.32/52.22, Ti 9.49/9.41, Cl 35.56/34.83, H_2O 3.60/3.54. $TiCl_3.6H_2O$ used was prepared by dissolving Ti metal, obtained by iodide method, in concentrated HCl and saturating the solution with HCl gas at 0°. The crystals were dried in a stream of Ar+ HCl gases.

ESTIMATED ERROR:

Temperature was kept constant within the range of 0 - 0.5°C.
Solubility error is not specified.

COMPONENTS:

(1) Ammonium hexachlorotitanate(IV); $(NH_4)_2TiCl_6$; [21439-26-9]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I.S.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1960, *5*, 2518-29; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 1218-24.

VARIABLES:

T/K = 273
m_2/mol kg^{-1} = 7.91-22.30

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 0°C

HCl		TiO_2	$TiOCl_2$	$TiCl_4$	NH_4Cl	$(NH_4)_2TiCl_6$		Nature of the Solid Phase[b]
mass %	m_2/mol kg^{-1} [a]	mass %	mass %	mass %	mass %	mass %	m_1/mol kg^{-1} [a]	
17.53	7.91	5.834	9.842	-	3.79	21.66	1.20	A
17.82	9.21	7.840	13.226	-	3.80	29.11	1.85	A+B
21.78	10.15	5.218	8.803	-	5.29	19.38	1.11	A+B
22.80	9.92	3.810	6.428	-	5.16	14.15	0.756	B
27.44	11.23	1.499	2.529	-	3.53	5.57	.280	B
28.23	11.59	1.337	2.256	-	2.75	4.96	.250	B
30.80	13.17	1.359	2.293	-	2.02	5.05	.265	B
31.15	13.14	1.033	1.743	-	1.80	3.84	.199	B
32.99	13.94	0.563	0.949	-	2.40	2.09	.109	B
35.08	15.05	0.269	.454	-	1.82	1.00	.0527	B
35.23	16.07	1.254	-	2.981	0.861	4.66	.261	C
36.32	16.14	.524	-	1.246	.702	1.95	.106	C
37.47	16.87	.436	-	1.032	.584	1.62	.0896	C
38.43	17.49	.352	-	0.837	.471	1.31	.0733	C
39.13	17.91	.257	-	.611	.266	0.954	.0537	C
40.27	18.72	.199	-	.474	.228	.738	.0422	C
44.70	22.30	.086	-	.204	.118	.319	.0196	C

a. Calculated by compiler. The values mass % $(NH_4)_2TiCl_6$ were calculated from mass % TiO_2. Similar calculations from mass % NH_4Cl yielded higher results.

b. A: NH_4Cl; [12125-02-9] B: $3NH_4Cl\cdot 2TiOCl_2\cdot 4H_2O$ C: $(NH_4)_2TiCl_6$; [21439-26-9].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for several hours. Solutions containing more than 37% HCl were prepared by saturating with HCl gas. Ti was determined gravimetrically as TiO_2 or colorimetrically at low Ti concentrations, Cl^- determined by Volhard's method. No method given for NH_4^+ determination. HCl content found by difference. Solid phases were identified by microscopy and chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2TiCl_6\cdot H_2O$ was prepared by mixing stoichiometric amounts of NH_4Cl and $TiCl_4$ in a solution of HCl through which was passed a stream of HCl gas. The product was stored over concentrated H_2SO_4. Source and purity of chemicals not specified.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Ammonium hexachlorotitanate(IV); $(NH_4)_2TiCl_6$; [21439-26-9]
(2) Ammonium chloride; NH_4Cl; [12125-02-9]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Seidel, W.; Fischer, W.

Z. Anorg. Allg. Chem. 1941, *247*, 367-83.

VARIABLES:

$T/K = 273$
$c_2/\text{mol dm}^{-3} = 0.0275\text{-}0.734$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Ammonium Chloride		Solubility[b]	
		Titanium	Ammonium Hexachlorotitanate (IV)
g/100ml soln	c_2/mol dm^{-3} [a]	mg/100 ml soln	10^3 c_1/mol dm^{-3} [a]
0.15	0.0275	65	13.6
0.52	0.0954	8.2	1.71
1.0	0.184	2.9	0.605
2.0	0.367	1.4	0.292
3.0	0.551	0.75	0.157
4.0	0.734	0.5	0.0104

[a] Calculated by compiler.

[b] Nature of solid phase not specified.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. NH_4Cl solutions in concentrated HCl were saturated with HCl gas at 0°C and equilibrated with excess $(NH_4)_2TiCl_6$ for 1 h. Ti determined gravimetrically as TiO_2 via hydroxide; NH_4Cl concentration in saturated solutions was obtained as the sum of initial NH_4Cl amount and the NH_4^+ content of the dissolved $(NH_4)_2TiCl_6$. HCl concentration not specified.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2TiCl_6$ prepared by saturation with HCl gas of a solution of $TiCl_4$ and NH_4Cl in approx. 6 mol dm^{-3} HCl. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Soly: precision ± 2-5 % (compiler).
The temperature error is not specified.

REFERENCES:

COMPONENTS:

(1) Potassium hexachlorotitanate(IV); K_2TiCl_6; [16918-46-0]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I.S.; Toptygina, G.M.

**Zh. Neorg. Khim.* <u>1960</u>, *5*, 2518-29; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1960</u>, *5*, 1218-24.

VARIABLES:

T/K = 273
m_2/mol kg^{-1} = 15.93 - 21.71

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 0°C

HCl		TiO_2	$TiCl_4$	KCl	K_2TiCl_6		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1} [a]	mass%	mass%	mass%	mass%	m_1/mol kg^{-1}[a]	
19.36	15.93	11.156	26.527	1.356	47.31	4.19	A+B
25.00	16.78	8.061	19.161	1.825	34.18	2.47	A+B
26.08	15.76	6.738	16.016	1.428	28.57	1.86	A+B
35.51	16.86	1.590	3.779	1.052	6.74	.344	A+B
41.80	19.98	0.195	0.461	0.372	0.827	.0425	A+B
42.61	20.50	.092	.219	.172	.390	.0202	B
44.06	21.71	.064	.152	.119	.271	.0144	B

a. Calculated by compiler. The values mass% K_2TiCl_6 were calculated from mass% TiO_2. Similar calculations from mass% KCl showed that both sets of results agreed only for high HCl concentrations where the equilibrium solid phase was K_2TiCl_6.

b. A: KCl [7447-40-7]; B: K_2TiCl_6 [16918-46-0]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for 3-4 h. Solutions containing > 37% HCl were prepared by saturating with HCl gas. Ti was determined gravimetrically as TiO_2 or, at low Ti concentrations, colorimetrically. K was determined gravimetrically as $KClO_4$ or K_2SO_4, Cl^- determined by Volhard's method. Solid phases were identified by microscopy and chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $K_2TiCl_6 \cdot H_2O$ was prepared by passing HCl gas through a solution of $TiCl_4$ in HCl which was in contact with stoichiometric amount of KCl. The product was stored over concentrated H_2SO_4. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Rubidium hexachlorotitanate(IV); Rb_2TiCl_6; [16902-24-2]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I.S.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1960, *5*, 2518-29; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 1218-24.

VARIABLES:

T/K = 273
m_2/mol kg^{-1} = 9.07-21.99

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 0°C

HCl		TiO_2	$TiOCl_2$	$TiCl_4$	RbCl	Rb_2TiCl_6		Nature of the Solid Phase^b
mass %	m_2/mol kg^{-1a}	mass %	mass %	mass %	mass %	mass %	m_1/mol kg^{-1a}	
14.79	9.07	7.501	12.654	-	12.30	40.51	2.10	A+B
16.19	8.20	5.49	9.261	-	12.43	29.65	1.27	A+B
21.39	9.65	3.302	5.571	-	9.50	17.84	0.680	B
21.67	10.05	3.55	5.989	-	10.34	19.17	.751	B
24.84	10.60	2.016	3.401	-	6.00	10.89	.393	B
28.19	11.90	1.266	2.136	-	3.87	6.84	.244	B
29.90	12.63	0.956	1.612	-	3.00	5.16	.184	B
30.35	12.36	.430	-	0.672	1.40	2.32	.0798	C
30.92	12.78	.503	-	1.196	1.51	2.72	.0950	C
35.52	15.12	.013	-	0.031	0.04	0.0702	.00252	C
36.25	15.60	.010	-	.024	0.030	.540	.00196	C
42.29	20.10	.003	-	.007	.009	.0162	.000651	C
44.50	21.99	.002	-	.005	.006	.0108	.000451	C

a. Calculated by compiler. The values mass % Rb_2TiCl_6 were calculated from mass % TiO_2. Similar calculations from mass % RbCl showed that both sets of results agreed only for high HCl concentrations where the equilibrium solid phase was Rb_2TiCl_6.

b. A: RbCl [7791-11-9]; B: $Rb_2TiOCl_4 \cdot H_2O$ [24419-03-2];
C: Rb_2TiCl_6 [16902-24-2].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for 3-4 h (solid phase Rb_2TiCl_6) or several weeks (solid phase $Rb_2TiOCl_4 \cdot H_2O$). Solutions containing more than 37% HCl were prepared by saturating with HCl gas. Ti was determined gravimetrically as TiO_2 or colorimetrically at low Ti concentrations, Rb determined gravimetrically as $RbClO_4$, or Rb_2SO_4, and Cl^- determined by Volhard's method. HCl content found by difference. Solid phases were identified by microscopy and chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2TiCl_6 was prepared by saturating a solution of $TiCl_4$ and RbCl in HCl with HCl gas. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.5 K
Soly: precision ± 2-5 %.
(compiler).

REFERENCES:

COMPONENTS:

(1) Cesium hexachlorotitanate(IV); Cs_2TiCl_6; [16919-28-1]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Morozov, I.S.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1960, *5*, 2518-29; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 1218-24.

VARIABLES:

$T/K = 273$
$m_2/\mathrm{mol\ kg^{-1}} = 4.03\text{-}22.04$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 0°C

HCl		TiO_2	$TiCl_4$	CsCl	Cs_2TiCl_6		Nature of the Solid Phase
mass%	$m_2/\mathrm{mol\ kg^{-1}}$ a	mass%	mass%	mass%	mass%	$m_1/\mathrm{mol\ kg^{-1}}$ a	
10.59	4.03	4.150	7.001	17.49	27.34	0.721	$Cs_2TiOCl_4 \cdot H_2O$
13.13	5.53	3.303	5.572	13.92	21.76	.635	
16.77	6.94	2.508	4.231	10.58	16.52	.473	
25.20	9.89	0.746	1.258	3.14	4.91	.133	
25.45	9.96	.677	1.143	2.85	4.46	.121	
25.54	10.04	.714	1.242	3.00	4.70	.128	
26.16	10.25	.586	0.988	2.47	3.86	.105	
26.72	10.52	.548	.924	2.31	3.61	.0984	
27.72	11.00	.480	.810	2.02	3.16	.0868	
27.92	11.08	.449	.757	1.89	2.96	.0813	
28.33	11.30	.441	.744	1.86	2.91	.0804	
29.30	11.70	.302	.718	1.27	1.99	.0550	Cs_2TiCl_6 [16919-28-1]
30.05	12.04	.226	.537	0.95	1.49	.0413	
31.70	12.93	.159	.378	.67	1.05	.0297	
32.20	13.17	.109	.259	.46	0.718	.0203	
33.85	14.10	.044	.105	.18	.290	.00836	
34.78	14.69	.042	.100	.18	.277	.00810	
35.20	14.95	.035	.083	.15	.231	.00680	
39.97	18.28	.010	.024	.04	.0659	.00209	
44.20	21.75	.010	.024	.04	.0659	.00225	
44.53	22.04	.009	.021	.04	.0593	.00203	

a Calculated by compiler. The values mass% Cs_2TiCl_6 were calculated from mass% TiO_2. Similar calculations from mass% CsCl yielded higher results.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for 3-4 h (solid phase Cs_2TiCl_6) or several weeks (solid phase $Cs_2TiOCl_4 \cdot H_2O$.) Solutions containing more than 37% HCl were prepared by saturating with HCl gas. Ti was determined gravimetrically as TiO_2 or colorimetrically at low Ti concentrations, Cs determined gravimetrically as $CsClO_4$ or Cs_2SO_4, and Cl^- determined by Volhard's method. HCl content found by difference. Solid phases were identified by microscopy and chemical analysis.

Note: $Cs_2TiOCl_4 \cdot H_2O$; [24419-02-1]

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2TiCl_6 was prepared by saturating a solution of $TiCl_4$ and CsCl in HCl with HCl gas. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.5 K
Soly: precision ± 2-5 %.
(compiler).

REFERENCES:

COMPONENTS:

(1) Titanium(IV) bromide; $TiBr_4$; [7789-68-6]

(2) Ethanol; C_2H_6O; [64-17-5]

ORIGINAL MEASUREMENTS:

Olsen, J.C.; Ryan, E.P.

J. Am. Chem. Soc. 1932, *54*, 2215-8.

VARIABLES:

$T/K = 293$

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Solubility of Titanium(IV) Bromide, $t/°C = 20$

Reported value	m_1/mol kg^{-1a}	c_1/mol dm^{-3b}
287 g/100 cm^3 C_2H_5OH	9.89	4.89

a Calculated by compilers by using the value of 0.7894 g cm^{-3} for the density of ethanol at 20°C

b Calculated by compilers by using the value of 2.29 g cm^{-3} for the density of the saturated solution reported in the original document

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$TiBr_4$ was distilled in a stream of dry CO_2 into a small flask and the solvent was added. The flask was allowed to stand overnight and then shaken 2 hr at 20°C. A portion of the supernatant liquid was weighed and analyzed for Br^- content. The method of analysis not mentioned.

SOURCE AND PURITY OF MATERIALS:

(1) $TiBr_4$ was prepared by bromination of a mixture of TiO_2 and either C or TiC, or by reacting $TiCl_4$ with HBr. $TiBr_4$ was then twice distilled under dry CO_2, and the fraction b. at 228°C was collected. Source and purity of chemicals not specified.

(2) Absolute ethanol

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Titanium(IV) bromide; $TiBr_4$; [7789-68-6]

(2) Diethyl ether; $C_4H_{10}O$; [60-29-7]

ORIGINAL MEASUREMENTS:

Olsen, J.C.; Ryan, E.P.

J. Am. Chem. Soc. 1932, *54*, 2215-8.

VARIABLES:

T/K = 293

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

The solubility of $TiBr_4$ at 20°C is reported to be 3.6 g/100 cm^3 diethyl ether (0.137 mol kg^{-1}). [a]

[a] Calculated by compilers by using the value of 0.7135 g cm^{-3} for the density of diethyl ether at 20°C

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$TiBr_4$ was distilled in a stream of dry CO_2 into a small flask and the solvent was added. The flask was allowed to stand overnight and then shaken 2 hr at 20°C. A portion of the supernatant liquid was weighed and analyzed for Br^- content. The method of analysis not mentioned.

SOURCE AND PURITY OF MATERIALS:

(1) $TiBr_4$ was prepared by bromination of a mixture of TiO_2 and either C or TiC, or by reacting $TiCl_4$ with HBr. $TiBr_4$ was then twice distilled under dry CO_2, and the fraction b. at 228°C was collected. Chemicals not specified.

(2) Absolute diethyl ether

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Titanium bromide; $TiBr_4$; [7789-68-6]

(2) Trichloromethane (chloroform); $CHCl_3$; [67-66-3]

ORIGINAL MEASUREMENTS:

Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G.

Vestn. Mosk. Univ., Ser. 2: Khim. 1963, *18* (1), 38-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $TiBr_4$ at 25°C to be approximately 42 mass% (1.97 mol kg^{-1}). Based on spectrophotometric measurements the authors assumed the existence of a molecular complex $TiBr_4 \cdot CHCl_3$ in the saturated solution.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $TiBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to TiO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $TiBr_4$ was prepared by bromination of a mixture of TiO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 230°C. Analysis (mass%, found/calculated): Ti 13.08-13.11/13.04, Br 87.00-87.18/86.96.

(2) Trichloromethane (chloroform) (source and purity not specified) was purified and dried by standrad methods.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Titanium bromide; $TiBr_4$; [7789-68-6] (2) Tetrachloromethane; CCl_4; [56-23-5]	Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G. *Vestn. Mosk. Univ., Ser. 2: Khim.* 1963, *18* (1), 38-9.
VARIABLES:	**PREPARED BY:**
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $TiBr_4$ at 25°C to be approximately 30 mass% (1.17 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $TiBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to TiO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $TiBr_4$ was prepared by bromination of a mixture of TiO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 230°C. Analysis (mass%, found/calculated): Ti 13.08-13.11/13.04, Br 87.00-87.18/86.96.

(2) Tetrachloromethane (source and purity not specified) was purified and dried by standard methods.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:

(1) Titanium bromide; $TiBr_4$; [7789-68-6]

(2) 1,2-Dichloroethane; $C_2H_4Cl_2$; [107-06-2]

ORIGINAL MEASUREMENTS:

Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G.

Vestn. Mosk. Univ., Ser. 2: Khim. <u>1963</u>, *18* (1), 38-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $TiBr_4$ at 25°C to be approximately 31 mass% (1.22 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $TiBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to TiO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $TiBr_4$ was prepared by bromination of a mixture of TiO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 230°C. Analysis (mass%, found/calculated): Ti 13.08-13.11/13.04, Br 87.00-87.18/86.96.

(2) 1,2-Dichloroethane (source and purity not specified) was purified and dried by standard methods.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Titanium(IV) bromide; $TiBr_4$; [7789-68-6] (2) Sulfur dioxide; SO_2; [7446-09-5]	Bond, P.A.; Crone, E.B. *J. Am. Chem. Soc.* 1934, *56*, 2028-31.

EXPERIMENTAL VALUES

Composition of Saturated Solutions

Critical Temperature t/°C	$TiBr_4$ $TiBr_4$-rich phase mass%	$TiBr_4$-rich phase m_1/mol kg^{-1}[a]	$TiBr_4$ SO_2-rich phase mass%	SO_2-rich phase m_1/mol kg^{-1}[a]
16.0	-	-	6.36	0.185
18.8	-	-	7.05	0.206
22.0	-	-	7.45	0.219
23.5	97.03	88.9	-	-
29.0	-	-	8.94	0.267
31.6	-	-	9.20	0.276
33.8	-	-	9.88	0.298
34.5	95.95	64.5	-	-
36.1	-	-	10.66	0.325
40.3	-	-	11.47	0.352
44.0	-	-	12.52	0.389
45.3	95.14	53.2	-	-
50.8	-	-	15.92	0.515
53.4	94.10	43.4	-	-
57.8	93.20	37.3	-	-
61.2	-	-	19.24	0.648
64.7	-	-	21.06	0.726
67.6	91.96	31.1	-	-
70.8	-	-	24.22	0.870
72.0	91.43	29.0	-	-
74.9	-	-	26.28	.970
79.9	-	-	29.33	1.13
81.4	88.73	21.4	-	-
83.3	-	-	32.46	1.31
84.5	88.05	20.0	-	-
87.6	-	-	36.46	1.56
92.6	84.23	14.5	-	-
94.1	-	-	42.28	1.99
97.8	80.82	11.5	-	-
98.9	-	-	48.58	2.57
100.4	-	-	51.61	2.90
100.8	78.54	9.96	52.24	2.98
101.4	-	-	53.18	3.09
102.4	-	-	57.20	3.64
102.9	74.90	8.12	-	-
103.0	-	-	60.63	4.19
103.2	73.57	7.57	-	-
103.3	71.97	6.99	63.78	4.79
103.5	71.08	6.69	-	-
103.7	70.05	6.36	-	-
103.8[bc]	68.87	6.02	64.53	4.95

[a] Calculated by compiler

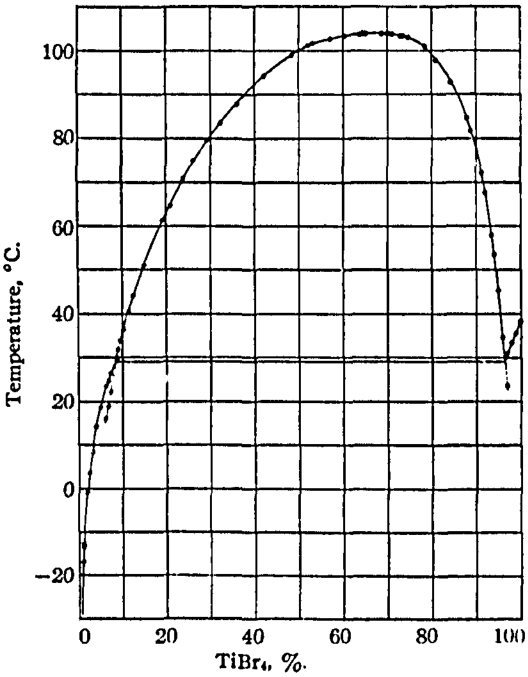
[b] A third value, 65.22 wt % $TiBr_4$, was also given.

[c] Critical temperature [376·95K; compare with the calculated value 377.65K (ref 3)].

Continued on the next page...

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Titanium(IV) bromide; $TiBr_4$; [7789-68-6] (2) Sulfur dioxide; SO_2; [7446-09-5]	Bond, P.A.; Crone, E.B. *J. Am. Chem. Soc.* 1934, *56*, 2028-31.
VARIABLES:	**PREPARED BY:**
$T/K = 289-377$	J. Hála

EXPERIMENTAL VALUES:



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

$TiBr_4$ was distilled into glass tubes in a dry atmosphere; the tubes were sealed off and weighed. The tubes were then opened and the procedure repeated with SO_2. The apparatus used for filling the tubes was that described by Bond and Beach (ref 1). The tubes were rotated in a thermostated bath, and the critical temp. was determined visually.

SOURCE AND PURITY OF MATERIALS:

(1) $TiBr_4$ was prepared by reacting $TiCl_4$ (Kahlbaum) with HBr or by bromination of a mixture of TiO_2+ C at red heat. The product was fractionally distilled 6 times, melted, HBr removed by a stream of dry air, and the product 3 times recrystallized. B.p. 230°C (751 mm Hg), m.p. 38.2°C.

(2) SO_2 purified by passing through concentrated H_2SO_4, $CaCl_2$ and P_2O_5.

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, from ref 2).

Soly: precision ± 1-2 % (compiler).

REFERENCES:

1. Bond, P.A.; Beach, H.T. *J. Am. Chem. Soc.* 1926, *48*, 348.
2. Bond, P.A.; Stephens, W.R. *J. Am. Chem. Soc.* 1929, *51*, 2910.
3. Vnuk, F. *J. Chem. Soc., Faraday Trans. 2*, 1981, *77*, 1045.

COMPONENTS:

(1) Titanium(IV) iodide; TiI_4; [7720-83-4]

(2) Benzene; C_6H_6; [71-43-2]

ORIGINAL MEASUREMENTS:

Krichevskii, I.R.; Ivanovskii, G.F.; Safronov, E.K.

**Zh. Fiz. Khim.* 1965, *39*, 2684; *Russ. J. Phys. Chem. (Engl. Transl.)* 1965, *39*, 1436.

VARIABLES:

T/K = 292-351

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Titanium(IV) Iodide	
t/°C	mol fraction	m_1/mol kg^{-1a}
19.0	0.0041	0.0527
31.2	0.0077	0.0993
39.2	0.0103	0.133
50.1	0.0151	0.196
60.3	0.0209	0.273
70.9	0.0302	0.399
78.0	0.0393	0.524

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. An apparatus consisting of 2 ampoules, one of which contained TiI_4 and C_6H_6, was shaken, excess TiI_4 allowed to settle, and the saturated solution transferred in to the empty ampoule which was then cooled by liquid N. In a dry box the ampoule was attached to a vacuum line, benzene was condensed in a trap cooled with liquid N and weighed. TiI_4 was weighed as the residue in the ampoule.

SOURCE AND PURITY OF MATERIALS:

(1) TiI_4 prepared by direct synthesis from Ti and I_2, and sublimed in vacuo. Source and purity of chemicals not specified.

ESTIMATED ERROR:

The temperature error is not specified.

Soly: precision ± 1-2 % (compiler).

REFERENCES:

2. The solubility of zirconium-containing substances.

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

ORIGINAL MEASUREMENTS:

Jache, A.W.; Cady, G.H.

J. Phys. Chem. 1952, *56*, 1106-9.

VARIABLES:

T/K = 250-285

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

t/°C	Zirconium(IV) fluoride g ZrF_4/100 g HF	 m_1/mol kg^{-1}[a]
12.4	0.009	0.00054
- 8.3	0.015	0.00090
-23.1	0.023	0.00138

Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Liquid HF was mixed with excess ZrF_4 in polyethylene bottles for several days. Before mixing diluted F_2 was bubbled through the solution for 1 h to remove traces of water. Samples for analysis were taken into a teflon sampling bottle by using a hypodermic needle with a teflon adapter. The sample was weighed and evaporated to dryness in a Pt crucible. The residue, ZrF_4, was dried at 110° and weighed. The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) ZrF_4 was prepared from HF and Zr(IV) nitrate. The purity and source of the latter were not specified.

(2) HF was prepared according to Simons (ref 1) by absorbing commercial HF in molted KHF_2. Traces of water and other impurities were removed by electrolysis, and HF was then distilled from the mixture through a Cu cooler and stored in polyethylene bottles.

ESTIMATED ERROR:

The temperature error is not specified.
The solubility error is ±0.002 g ZrF_4/100 g HF (precision).

REFERENCES:

1. Simons, J.H. *Inorganic Synthesis*, Vol. 1, McGraw-Hill Book Comp., Inc., New York, 1939, p. 134.

COMPONENTS:	EVALUATOR:
(1) Zirconium fluoride; ZrF_4; [7783-64-4] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61137 Brno, Czechoslovakia June 1985

CRITICAL EVALUATION:

The solubility of zirconium fluoride in aqueous hydrogen fluoride.

Of the three documents which report solubility measurements of ZrF_4 as a function of HF concentration those of Hevesy and Wagner (ref 1) and Nikolaev et al. (ref 2) at 298 K can be compared. In the third paper the solubility at 0.5°C is reported (ref 3). Even a brief inspection of the molal (m_1/mol kg^{-1}) data in the compilations shows that the data of Hevesy and Wagner (1) and Nikolaev et al. (ref 2) differ greatly, those of (ref 1) being much higher especially for low HF concentration. Only the value of 3.62 mol ZrF_4/kg for 18.76 mol HF/kg (ref 1) seems to approach the solubility isotherm of Nikolaev et al. (ref 2). The reason for this discrepancy is not clear. It should be noted that the same solid was used for the solubility measurements in both studies, i.e. $ZrF_4 \cdot 3H_2O$, although Hevesy and Wagner (ref 1) gave the older formula for it ($ZrOF_2 \cdot H_2F_2 \cdot 2H_2O$) (ref 4). The sharp decrease of ZrF_4 solubility at high HF concentrations (ref 2) is in agreement with the solubility of ZrF_4 in nonaqueous HF (ref 5), i.e. 0.00054 mol kg^{-1} at 285.6K.

Due to the lack of agreement in the published data the evaluator cannot recommend any data. For tentative values the evaluator suggests the data of Nikolaev et al. (ref 2) for 298 K to be used (see the compilation for numerical data).

REFERENCES:

(1) von Hevesy, G.; Wagner, O. H. *Z. Anorg. Allgem. Chem.* 1930, *191*, 194.
(2) Nikolaev, N. S.; Buslaev, Yu. A.; Gustyakova, M. P. *Zh. Neorg. Khim.* 1962, *7*, 1685.
(3) Tananaev, I. V.; Nikolaev, N. S.; Buslaev, Yu. A. *Zh. Neorg. Khim.* 1956, *1*, 274.
(4) Buslaev, Yu. A.; Nikolaev, N. S. *Dokl. Akad. Nauk SSSR* 1960, *135*, 1385.
(5) Jache, A. W.; Cady, G. H. *J. Phys. Chem.* 1952, *56*, 1106.

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

von Hevesy, G.; Wagner, O.H.

Z. Anorg. Allg. Chem. 1930, *191*, 194-200.

VARIABLES:

T/K = 298

c_2/mol dm^{-3} = 0 - 20.09

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

HF		Solubility, 25°C [c]			Density of Saturated Solutions
		ZrO_2	ZrF_4		
c_2/mol dm^{-3}	m_2/mol kg^{-1} [a]	g dm^{-3}	c_1/mol dm^{-3}	m_1/mol kg^{-1} [a]	g cm^{-3}
0	0	406.3	3.300	3.52	1.488
0	0	410.7	3.332	3.57	1.490
1.06	1.24	502.2	4.078	4.76	1.559
1.06	1.16	496.5	4.030	4.41	1.608
6.03	7.39	571.8	4.639	5.69	1.712
6.03	7.40	571.7	4.639	5.69	1.711
10.05	13.60	548.5	4.455	6.03	1.685
10.05	13.52	549.6	4.459	6.00	1.690
15.05	21.63	444.3	3.608	5.19	1.600
20.09 [b]	31.55	288.3	2.340	3.67	1.430

[a] Calculated by compiler by using the authors' density values

[b] The authors report poor reproducibility at this HF concentration; the reported solubility is the mean value of 6 determinations ranging from 267.2 to 328.3 g ZrO_2/dm^3 (the other 4 values not reported).

[c] Solid phase believed to be $ZrOF_2 \cdot H_2F_2 \cdot 2H_2O$ (see below).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess solid was shaken for unspecified period of time with aqueous HF. Method of analysis not specified. The composition of solid phases was not reported.

SOURCE AND PURITY OF MATERIALS:

(1) The solid used for measurements was prepared by dissolving ZrO_2 in aqueous HF. The composition of the solid obtained by crystallization from 5-20 mol HF/dm^3 was constant, and according to Chauvenet (ref 1) who obtained a compound with identical composition, was written as $ZrOF_2 \cdot H_2F_2 \cdot 2H_2O$.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Chauvenet, E. *C.R. Hebd. Seances Acad. Sci.* 1916, *164*, 727.

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS

Tananaev, I.V.; Nikolaev, N.S.; Buslaev, Yu.A.

**Zh. Neorg. Khim.* 1956, *1*, 274-81.

J. Inorg. Chem. USSR (Engl. Transl.) 1956, *1* (2), 88-95.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 0.5°C

HF	ZrO_2	ZrF_4[a]		Nature of the Solid Phase[b]
mass%	mass%	mass%	m_1/mol kg^{-1}	
2.21	3.14	4.26	0.272	A
2.80	4.37	5.93	.386	A
3.95	6.19	8.40	.573	A
5.84	7.92	10.75	.771	B
6.01	8.35	11.33	.820	B
6.79	8.30	11.26	.822	B
10.10	13.05	17.71	1.47	B
12.34	15.41	20.91	1.87	B
16.06	19.73	26.77	2.80	B
18.97	23.21	31.50	3.80	B
22.43	26.42	35.85	5.14	B
25.42	29.11	39.50	6.73	B
30.00	32.37	43.92	10.07	B
31.63	31.95	43.36	10.37	C
32.81	30.41	41.27	9.52	C
33.98	24.71	33.53	6.17	C
34.37	19.83	26.90	4.15	C
35.61	12.58	17.07	2.16	C
36.85	10.68	14.49	1.77	C
38.41	9.73	13.20	1.63	C
39.92	7.27	9.87	1.175	C
39.67	4.87	6.61	0.736	C
40.41	4.25	5.77	.641	C
44.14	2.35	3.19	.362	C
44.42	1.52	2.06	.230	C
46.15	1.05	1.42	.159	C
54.11	0.091	0.123	.0161	C
60.35	.048	.0651	.00983	C
70.12	.017	.0231	.00463	C
79.31	.016	.0217	.00628	C
82.05	.015	.0204	.00680	C
84.35	.015	.0204	.00780	C
85.81	.015	.0204	.00861	C
92.59	.0104	.0141	.0114	D
96.47	.0109	.0148	.0251	D
99.98	.0107	.0145	(8.67)[c]	D

a. Calculated by compilers

b. A: $ZrOF_2 \cdot 2HF$

B: $ZrF_4 \cdot 3H_2O$; [14517-16-9]

C: $H_2ZrF_6 \cdot H_2O$; [107944-15-0]

D: ZrF_4; [7783-64-4]

c. Unreasonably high value resulting from the low water content in this solution.

Continued on the next page...

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Nikolaev, N.S.; Buslaev, Yu.A.

* *Zh. Neorg. Khim.* <u>1956</u>, *1*, 274-81. *J. Inorg. Chem. USSR (Engl. Transl.)* <u>1956</u>, *1* (2), 88-95

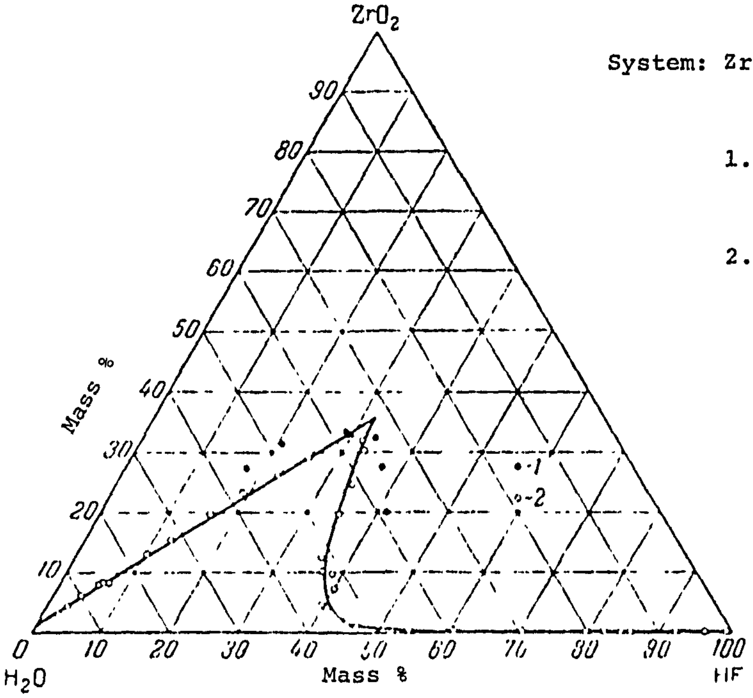
VARIABLES:

T/K = 274
HF/mass% = 2.21-99.98

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:



System: ZrO_2 + HF + H_2O

273.7 K

1. von Hevesy and Wagner (ref 1) results
2. Authors' results

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess ZrF_4 was shaken with aqueous HF for 3 h. in bottles made of fluoroplast-4. Samples of solutions were taken by means of a Pt pipette. F^- in solutions containing Zr was determined alkalimetrically against phenolphthalein whereby free HF and 3/4 of F bound to Zr were titrated. Total F^- content was determined titrimetrically in such a way that excess alkali and $CaCl_2$ were added, and alkali excess was back-titrated with acid. Zr was determined gravimetrically as ZrO_2 after removal of F^- with H_2SO_4. Solid phases were identified by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) ZrF_4 was prepared from $ZrCl_4$ or $ZrOCl_2 \cdot 8H_2O$ and liquid HF. Source and purity of starting materials not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % ZrF_4;
precision ± 5 % HF.

REFERENCES:

1. von Hevesy, G.; Wagner, O. H. *Z. Anorg. Allgem.* <u>1960</u>, *191*, 194.

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS

Nikolaev, N.S.; Buslaev, Yu.A. Gustyakova, M.P.

*_Zh. Neorg. Khim._ 1962, _7_, 1685-92; _Russ. J. Inorg. Chem. (Engl. Transl.)_ 1962, _7_, 869-73.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 25°C

HF	ZrO_2	ZrF_4[a]		Nature of the Solid Phase[b]
mass%	mass%	mass%	m_1/mol kg^{-1}	
0.51	1.58	2.14	0.131	A
2.04	2.97	4.03	.257	A
3.86	5.50	7.46	.503	A
7.26	10.09	13.69	1.04	A
8.50	10.92	14.82	1.16	B
10.14	12.79	17.36	1.43	B
13.50	17.04	23.12	2.18	B
15.07	18.95	25.72	2.60	B
17.35	21.59	29.30	3.28	B
22.01	25.62	34.77	4.81	B
23.70	28.60	38.81	6.19	B
27.78	32.48	44.02	9.34	B
29.28	35.03	47.54	12.26	B
29.83	34.15	46.34	11.63	C
30.51	33.68	45.71	11.50	C
32.23	32.93	44.69	11.58	C
31.72	32.47	44.06	10.88	C
32.84	31.92	43.32	10.87	C
33.43	31.97	43.38	11.19	C
33.79	32.06	43.51	11.46	C+D
33.56	29.32	39.79	8.93	D
33.23	26.98	36.61	7.26	D
33.14	22.08	29.96	4.86	D
35.05	19.47	26.42	4.10	D
35.61	18.86	25.59	3.94	D
35.60	18.31	24.85	3.76	D
36.20	16.32	22.15	3.18	D
37.62	13.58	18.43	2.51	D
38.95	9.68	13.13	1.64	D
41.01	7.18	9.74	1.18	D
42.44	5.30	7.19	.855	D
44.17	3.69	5.01	.590	D
48.44	1.07	1.45	.173	D
50.08	.574	.779	.0948	D
52.57	.236	.320	.0406	D
54.55	.221	.300	.0397	D
58.78	.077	.105	.0152	D
69.98	.035	.0475	.00948	D
70.49	.034	.0461	.00936	D

a Calculated by compilers

b A: $Zr_4(OH)_6F_{10}\cdot3H_2O$; [108151-18-4]

B: $ZrF_4\cdot3H_2O$; [14517-16-9]

C: $HZrF_5\cdot4H_2O$; [18129-16-3]

D: $H_2ZrF_6\cdot2H_2O$; [107944-16-1]

Continued on the next page...

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N.S.; Buslaev, Yu.A.; Gustyakova, M.P.

**Zh. Neorg. Khim.* <u>1962</u>, *7*, 1685-92; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1962</u>, *7*, 869-73.

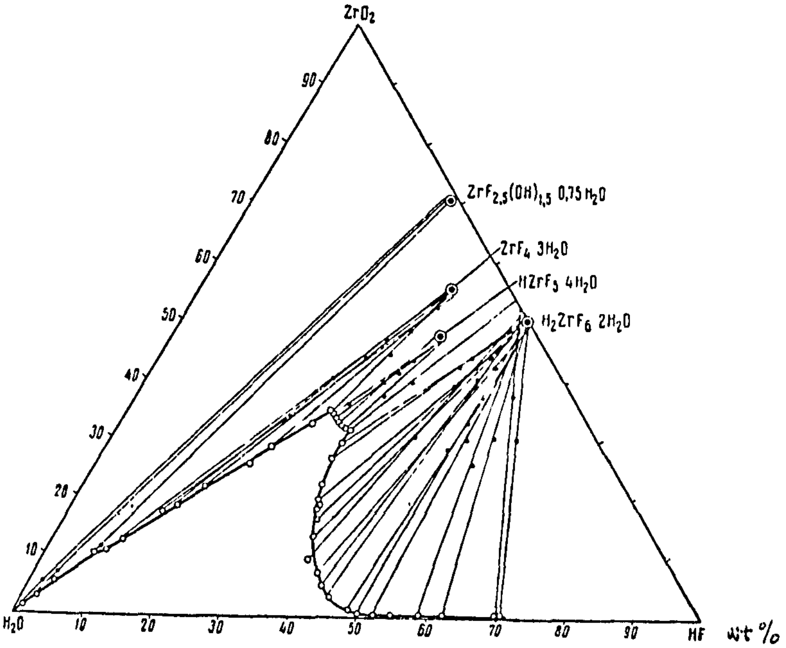
VARIABLES:

$T/K = 298$
HF/mass% = 0.51-70.49

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess ZrF_4 was shaken with aqueous HF for 3 h. in bottles made of fluoroplast-4. Samples of solutions were taken by means of a Pt pipette. F^- was determined alkalimetrically against phenolphtalein whereby free HF and 3/4 of F bound to Zr were titrated. Total F^- content was determined titrimetrically in such a way that excess alkali and $CaCl_2$ were added, and alkali was back-titrated with acid. Zr was determined gravimetrically as ZrO_2 after removal of F^- with H_2SO_4. Solid phases were identified by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) The solid used for measurement was $ZrF_4 \cdot 3H_2O$. Its source and purity were not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 (compiler, fro ref 1). Soly: Precision ± 1-2 % ZrF_4; ± 5 % HF (compiler).

REFERENCES:

1. Tananaev, I.V.; Buslaev, Yu.A. Nikolaev, N.S. *Zh. Neorg. Khim.* <u>1956</u>, *1*, 274; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1956</u>, *1*(2), 88-95.

COMPONENTS:

(1) Zirconium fluoride; ZrF_4; [7783-64-4]

(2) Nitrogen oxide; N_2O_4; [10544-72-6]

(3) Hydrogen fluoride;HF; [7664-39-3]

ORIGINAL MEASUREMENTS:

Tarnero, M.

Rapport CEA-R 3205, 1967, 77 pp. [Centre D'etudes Nucleaires DeFontenay-aux-Roses, France]

Chem. Abstr. 1969, *70*, 23527m.

VARIABLES:

$T/K = 295, 333$

$m_2/\text{mol\%} = 0 - 14.3$ at 295 K

$0 - 14.1$ at 333 K

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions.

Temperature		N_2O_4	Zr	ZrF_4[a]
t/ C	T/K	mol%	mg / 100 g solution	g / 100 g solution
22	295	0	5	0.0092
		3.1	185	0.339
		7.7	170	0.312
		11.5	165	0.302
		14.3	135	0.247
60	333	0	18	0.0330
		2.8	264	0.484
		5.3	625	0.146
		9.1	510	0.935
		11.5	318	0.583
		14.1	213	0.390

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. The N_2O_4-HF solutions were prepared in a vacuum line made of monel, Kel-F, and teflon parts. It contained 2 Kel-F burettes connected to reservoirs with freshly distilled solvents. From the burettes the solvents were introduced onto excess ZrF_4 in a Kel-F dissolution vessel by applying N gas pressure under cooling. The mixtures were then brought to the desired temperature and agitated with a magnetic stirrer in a thermostated glycol bath for 1000-1300 min, although equilibrium results were obtained after 360 min. After another 360-400 min standing, an aliquot of the saturated solution was withdrawn, evaporated to dryness and Zr determined gravimetrically in the residue. (The formula of Zr compound weighed not reported.) Solid phases were not investigated.

SOURCE AND PURITY OF MATERIALS:

(1) ZrF_4, purity 99.5%, source not specified.

(2) N_2O_4 was prepared either by dehydration of HNO_3 with P_2O_5 and decomposition of the N_2O_5 obtained at 260°, or by thermal decomposition of $Pb(NO_3)_2$. Occasionally, a 99.5% product of Societé L'Air Liquide was also used. It was distilled over a column of P_2O_5 to obtain the anhydrous product (white when solid).

(3) HF of high purity (Societé Ugine) was distilled before use to yield a product with specific conductivity of $(2-9)\times10^{-3}$ $\Omega^{-1}cm^{-1}$ at -15°. The conductivity was reported to increase slightly on storing in Monel containers.

ESTIMATED ERROR:

Error in composition of the solvent: ±5% (the accuracy with which the Kel-F burettes could be operated.)

Temperature and solubility error were not reported.

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4] (2) Nitric acid; HNO_3; [7697-37-2] (3) Water; H_2O; [7732-18-5]	Chapman, A.G.; Slansky, C.M. *USAEC*, Report IDO-14442 (1958). *Chem. Abstr.* 1958, *52*, 17904b.

EXPERIMENTAL VALUES

Solubility at

Zirconium(IV) fluoride

HNO_3 [b] c_2/mol dm^{-3}	0°C g dm^{-3}	0°C c_1/mol dm^{-3} [a]	25°C g dm^{-3}	25°C c_1/mol dm^{-3} [a]	40°C g dm^{-3}	40°C c_1/mol dm^{-3} [a]
1	83.95	0.502	132.7	0.793	200.4	1.20
2	50.55	0.302	88.47	0.529^A	142.6	0.853
4	23.47	0.140	41.53	0.248	70.4	0.421
6	12.64	0.0756	25.27^A	0.151	37.9	0.227
8	7.58^A	0.0453	17.15	0.102	20.8	0.124
10	5.69	0.0340	8.67	0.0518	9.93	0.0593
12	2.71	0.0162	4.97	0.0297	6.32^B	0.0378
16	0.54	0.0032	1.72	0.0103	2.35	0.0140

HNO_3 [b] c_2/mol dm^{-3}	50°C g dm^{-3}	50°C c_1/mol dm^{-3} [a]	55°C g dm^{-3}	55°C c_1/mol dm^{-3} [a]	60°C g dm^{-3}	60°C c_1/mol dm^{-3} [a]
1	262^C	1.57	290	1.73	297	1.78
2	189.5^C	1.13	216	1.29	248	1.48
4	110.1^B	0.658	110.1	0.658	108	0.646
6	45.1	0.270	47.8	0.286	$-^B$	-
8	23.5^B	0.141	23.5	0.140	26.2	0.157
10	12.64	0.0756	12.64	0.0756	14.4	0.0861
12	6.95	0.0416	8.12	0.0456	9.45	0.0565
16	3.43	0.0205	3.43	0.0205	3.43	0.0205

HNO_3 [b] c_2/mol dm^{-3}	70°C g dm^{-3}	70°C c_1/mol dm^{-3} [a]	80°C g dm^{-3}	80°C c_1/mol dm^{-3} [a]
1	294	1.76	291	1.74
2	243	1.45	239	1.43
4	111	0.664	113	0.678
6	53.5	0.319	58.7	0.351
8	28.9	0.173	31.6	0.189
10	17.1	0.102	18.96	0.113
12	10.2	0.0610	11.7	0.0700
16	4.06	0.0243	4.78	0.0286

[a] Calculated by compiler

Solid phases: A: $ZrF_4 \cdot 3H_2O$ [14517-16-9] B: $ZrF_4 \cdot H_2O$ [14596-11-3] C: $ZrOF_2 \cdot HF \cdot H_2O$ (approximately)

[b] Initial HNO_3 concentration.

Continued on the next page...

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Nitric acid; HNO_3; [7697-37-2]

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

ORIGINAL MEASUREMENTS:

Chapman, A.G.; Slansky, C.M.

USAEC, Report IDO-14442 (1958).

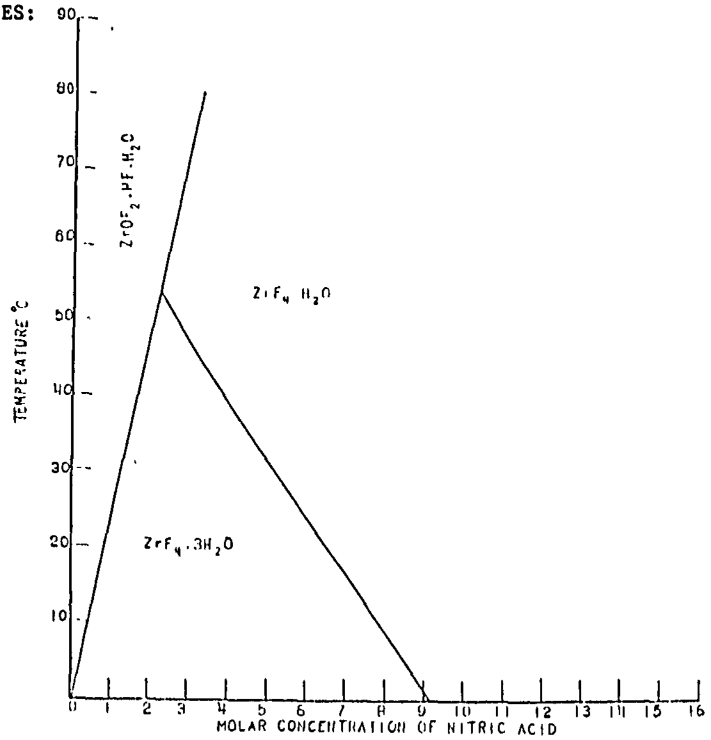
VARIABLES:

$T/K = 273-353$
$c_2/\text{mol dm}^{-3} = 1-16$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $ZrF_4 \cdot H_2O$ was equilibrated with aqueous HNO_3 solutions. Equilibrium was attained very slowly at low HNO_3 concentrations and temperatures. A measured volume of the saturated solution was evaporated to dryness in a Pt dish. The residue was ignited first for several hours at 500-550°C, then at 1000°C, and ZrO_2 was weighed. Solid phases were identified by X-ray diffraction.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrF_4 \cdot H_2O$ was prepared by dissolution of reactor grade Zr metal in a mixture of concentrated HNO_3 and 48% HF, both analytical grade. The reaction was carried out in a teflon vessel equipped with a polyethylene reflux condenser. After complete dissolution of Zr the mixture was digested for 0.5 h, filtered, the crystals washed with acetone, and either air or oven dried.

ESTIMATED ERROR:

Temp: precision ± 1 K.
Soly: precision ± 5 %

REFERENCES:

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Sodium fluoride; NaF; [7681-49-4]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 590-3.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

Sodium Fluoride		Zirconium(IV) Fluoride		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0.104	0.0259	4.29	0.268	A
0.12	0.030	4.00	0.249	A
0.21	0.051	1.56	0.0950	B
0.32	0.077	1.02	0.0618	B
0.465	0.111	0.054	0.00325	C
0.815	0.196	0.046	0.00277	C
1.18	0.284	0.046	0.00278	C
2.36	0.576	0.034	0.00208	D
3.37	0.831	0.016	0.00099	D
3.85	0.954	0.016	0.00099	D
4.04	1.00	0.016	0.0010	D

a. Calculated by compilers

b. A: $NaZrF_5 \cdot H_2O$; [20982-58-5] B: Na_2ZrF_6 [16925-26-1]
C: $Na_5Zr_2F_{13}$; [12022-20-7] D: Na_3ZrF_7; [17442-98-7].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Overnight mixing was carried out in teflon bottles. The systems were prepared either by mixing ZrF_4 and NaF solutions or by dissolving sodium fluorozirconates in NaF solutions. Zr was detd. gravimetrically as ZrO_2 after the removal of F^- by evaporation with H_2SO_4. Na determined gravimetrically as Na_2SO_4 after the precipitation of Zr hydroxide. Solid phases were identified by Schreinemakers' method and by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of starting materials and of water not specified.

(2) NaF reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 - 2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

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

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

ORIGINAL MEASUREMENTS:

Bamburov, V.G.; Demenev, N.V.; Polyakova, V.M.

Izv. Sib. Otd. Akad. Nauk SSSR 1962, (5), *70-5.*

VARIABLES:

T/K = 293
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 20°C

Potassium Fluoride		Zirconium(IV) Fluoride		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0.315	0.0578	5.940	0.379	A
0.630	0.112	2.600	0.161	A
0.642	0.114	2.250	0.139	B+A
0.786	0.139	1.565	0.0955	B
1.700	0.299	0.306	0.0187	B
2.300	0.406	0.262	0.0161	B+C
4.665	0.843	0.100	0.00628	C
7.520	1.400	0.065	0.00421	C
9.060	1.715	0.025	0.00164	C

a Calculated by compiler

b A: $KZrF_5$; [13782-18-8]

B: K_2ZrF_6; [16923-95-8]

C: K_3ZrF_7; [17442-97-6]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. The solutions were prepared so that water and increasing amounts of KF were added to a constant amount of $ZrF_4 \cdot 3H_2O$ while keeping the total weight of the mixture at 100 g. K was determined gravimetrically as K_2SO_4, F^- determined titrimetrically with $Th(NO_3)_4$ against alizarine sulfonate as indicator, or gravimetrically as CaF_2. No method was given for Zr determination. The composition of solid phases was deduced from the solubility isotherm.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrF_4 \cdot 3H_2O$ was prepared by dissolving ZrO_2 in HF and subsequent evaporation. Source and purity of starting materials and of water not specified.

(2) KF, reagent grade, recrystallized twice from water.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Rubidium fluoride; RbF; [13446-74-7]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 590-3.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

Rubidium Fluoride		Zirconium(IV) Fluoride		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0.61	0.060	1.39	0.0848	A
0.74	0.073	1.63	0.0998	A
1.8	0.178	1.66	0.103	A
3.05	0.310	2.65	0.168	A+B
3.54	0.358	1.7	0.11	B
4.99	0.512	1.65	0.1006	B
6.41	0.666	1.52	0.0987	B
7.65	0.805	1.42	0.0934	B
10.58	1.14	0.58	0.039	B
12.65	1.40	0.93	0.064	B
19.11	2.30	1.36	0.102	B+C
21.9	2.72	1.02	0.0791	C
25.9	3.37	0.6	0.05	C
29.64	4.05	0.36	0.031	C

a Calculated by compiler

b A: $RbZrF_5 \cdot H_2O$, [20982-60-9]; B: Rb_2ZrF_6, [16962-10-0]; C: Rb_3ZrF_7, [20449-70-1].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Overnight mixing was carried out in teflon bottles. The systems were prepared either by mixing ZrF_4 and RbF solutions or by dissolving rubidium fluorozirconates in RbF solutions. Zr was detd. gravimetrically as ZrO_2 after the removal of F^- by evaporation with H_2SO_4. Rb determined gravimetrically as Rb_2SO_4 after the precipitation of Zr hydroxide. Solid phases were identified by Schreinemakers' method and by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of starting materials and of water not specified.

(2) RbF reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 - 2 %

REFERENCES:

COMPONENTS:

(1) Zirconium(IV) fluoride; ZrF_4; [7783-64-4]

(2) Cesium fluoride; CsF; [13400-13-0]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* <u>1966</u>, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1966</u>, *11*, 590-3.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

Cesium Fluoride		Zirconium(IV) Fluoride		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	
1.33	0.0922	3.68	0.232	A
2.50	.174	3.16	.200	A
3.82	.270	3.20	.206	A+B
5.30	.382	3.50	.230	B
6.44	.464	2.20	.144	B
8.87	.646	0.77	.0510	B
12.93	.983	0.52	.0359	B
17.18	1.37	0.40	.0290	B
21.90	1.85	0.36	.0277	B
27.61	2.51	0.30	.0249	B
42.79	4.92	0.20	.0210	B
65.45	12.47	0.11	.0191	B

a Calculated by compilers

b A: $CsZrF_5 \cdot H_2O$; [20982-59-6]

B: Cs_2ZrF_6; [16919-30-5]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Overnight stirring was carried out in teflon bottles immersed in a water thermostat. The systems were prepared either by mixing ZrF_4 and CsF solutions or by dissolving Cs fluorozirconates in CsF solutions. Equilibrium was established within 8-10 hours as determined by successive analysis. Zr was detd. gravimetrically as ZrO_2 after the removal of F^- by evaporation with H_2SO_4. Cs determined gravimetrically as Cs_2SO_4 after the precipitation of Zr hydroxide. Solid phases were identified by Schreinemakers' method and by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of starting materials and of water not specified. Analysis of ZrF_4:
Found: Zr 54.33, F 45.04
Calcd: Zr 54.55, F 45.45

(2) CsF prepared from Cs_2CO_3 and bidistilled HF.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 %

REFERENCES:

COMPONENTS:

(1) Ammonium pentafluorozirconate(IV); NH_4ZrF_5; [13859-62-6]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N.S.; Buslaev, Yu.A.; Gustyakova, M.P.

**Zh. Neorg. Khim.* 1965, *10*, 2577-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1401-2.

VARIABLES:

$T/K = 293$

$m_2/\text{mol kg}^{-1} = 0\text{-}11.35$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of NH_4ZrF_5 in aqueous HF at 20°C

Hydrogen Fluoride		Ammonium Pentafluorozirconate(IV)	
mass %	$m_2/\text{mol kg}^{-1}$ [a]	mass %	$m_1/\text{mol kg}^{-1}$ [a]
0	0	10.16	0.551
0.22	0.123	10.95	0.600
0.39	0.220	11.15	0.643
1.63	0.965	13.92	0.803
2.13	1.30	16.23	0.969
3.39	2.21	20.04	1.275
3.45	2.26	20.27	1.295
4.43	3.03	22.58	1.507
5.55	3.83	22.06	1.485
6.10	4.25	22.14	1.503
8.04	5.68	21.20	1.460
14.70	11.35	20.54	1.545

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for several days. Zr was determined gravimetrically as ZrO_2 after removal of HF with H_2SO_4. HF determined by potentiometric titration with alkali in the presence of KF (ref 1). The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) NH_4ZrF_5 was prepared from $ZrF_4 \cdot 3H_2O$ by heating it with water and a stoichiometric amount of NH_4F. NH_4ZrF_5 crystallized on cooling. Source and purity of chemicals not given except for the Hf content (0.05%) of $ZrF_4 \cdot 3H_2O$.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 % NH_4ZrF_5;
precision ± 2 % HF.

REFERENCES:

1. Nikolaev, N.S.; Buslaev, Yu.A.

Zh. Neorg. Khim. 1959, *4*, 543; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, *4*, 246-9.

COMPONENTS:

(1) Sodium pentafluorozirconate(IV); $NaZrF_5$; [13871-10-8]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 590-3.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $NaZrF_5 \cdot H_2O$ [20982-58-5] was reported as 0.37 mass %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $NaZrF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after the removal of F^- by evaporation with H_2SO_4. Na determined gravimetrically as Na_2SO_4 after the precipitation of Zr hydroxide. $NaZrF_5 \cdot H_2O$ dissolves congruently, and can be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) $NaZrF_5 \cdot H_2O$ prepared by equilibrating ZrF_4 with solutions containing 0.10-0.12 mass % NaF. Under these conditions $NaZrF_5 \cdot H_2O$ is obtained as the equilibrium solid phase, as follows from the measurement of the ZrF_4-NaF-H_2O system studied in the same document. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified; NaF was reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium pentafluorozirconate-(IV); $KZrF_5$; [13782-18-8] (2) Water; H_2O; [7732-18-5]	Bamburov, V.C.; Demenev, N.V.; Polyakova, V.M. *Izv. Sib. Otd. Akad. Nauk SSSR* 1962, (5), 70-5.
VARIABLES:	**PREPARED BY:**
T/K = 293	J. Hála

EXPERIMENTAL VALUES:

The solubility at 20°C of $KZrF_5$ is reported as 0.94 mass% (0.0421 mol kg^{-1a}).

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $KZrF_5$ were shaken until equilibrium was reached. K was determined gravimetrically as K_2SO_4, F^- determined titrimetrically with $Th(NO_3)_4$ against alizarine sulfonate as indicator, or gravimetrically as CaF_2. No method was mentioned for Zr determination.

SOURCE AND PURITY OF MATERIALS:

(1) $KZrF_5$ was prepared by equilibrating $ZrF_4 \cdot 3H_2O$ with solutions containing >0.63 wt% KF. Under these conditions $KZrF_5$ is obtained as the equilibrium solid phase, as follows from the study of the ZrF_4-KF-H_2O system carried out in the same document. KF, reagent grade. $ZrF_4 \cdot 3H_2O$ prepared by dissolving ZrO_2 in HF and subsequent evaporation. Source and purity of starting materials not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Potassium pentafluorozirconate(IV)
$KZrF_5$; [13782-18-8]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khem.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. Engl. Transl.)* 1966, *11*, 590-3.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $KZrF_5 \cdot H_2O$ [20982-57-4] was reported as 1.13 mass %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $KZrF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after the removal of F^- with H_2SO_4. K determined gravimetrically as K_2SO_4 after precipitation of Zr hydroxide. $KZrF_5 \cdot H_2O$ dissolves congruently and can be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) $KZrF_5 \cdot H_2O$ prepared by equilibrating ZrF_4 with solutions containing such an amount of KF as to yield $KZrF_5 \cdot H_2O$ as the equilibrium solid phase. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified; KF was reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Potassium pentafluorozirconate(IV); $KZrF_5$; [13782-18-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N.S.; Buslaev, Yu.A.; Gustyakova, M.P.

**Zh. Neorg. Khim.* 1965, *10*, 2577-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1401-2.

VARIABLES:

$T/K = 293$
$m_2/\text{mol kg}^{-1} = 0\text{-}21.82$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $KZrF_5$ in aqueous HF at 20°C

Hydrogen Fluoride		Potassium Pentafluorozirconate(IV)[b]	
mass %	$m_2/\text{mol kg}^{-1}$ [a]	mass %	$m_1/\text{mol kg}^{-1}$ [a]
0	0	2.05	0.093
1.41	0.758	5.58	.266
1.50	0.810	5.92	.284
2.67	1.49	7.70	.381
3.02	1.71	8.65	.435
4.09	2.39	10.37	.538
5.74	3.51	12.49	.678
7.67	4.78	12.09	.669
15.45	10.68	12.21	.749
25.98	21.82	14.50	1.08

[a] Calculated by compiler

[b] It is unclear whether the calculations of mass% are based upon $KZrF_5$ [13782-18-8] or $KZrF_5 \cdot H_2O$ [20982-57-4]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for several days. Zr was determined gravimetrically as ZrO_2 after removal of HF with H_2SO_4. HF determined by potentiometric titration with alkali in the presence of KF (ref 1). The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) $KZrF_5 \cdot H_2O$ was prepared from $ZrF_4 \cdot 3H_2O$ by heating it with water and a stoichiometric amount of KF. $KZrF_5 \cdot H_2O$ crystallized on cooling. Source and purity of chemicals not given except for the Hf content (0.05%) of $ZrF_4 \cdot 3H_2O$.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 % $KZrF_5$.
Conc: precision ± 2 % HF.

REFERENCES:

1. Nikolaev, N.S.; Buslaev, Yu.A. *Zh. Neorg. Khim.* 1959, *4*, 543; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, *4*, 246-9.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Rubidium pentafluorozirconate(IV); $RbZrF_5$; [13782-19-9] (2) Water; H_2O; [7732-18-5]	Tananaev, I.V.; Guzeeva, L.S. **Zh. Neorg. Khim.* <u>1966</u>, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1966</u>, *11*, 590-3.
VARIABLES:	PREPARED BY:
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $RbZrF_5 \cdot H_2O$ [20982-60-9] is reported as 2.48 mass %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Isothermal method used. Solutions containing excess $RbZrF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after removal of F^- by evaporation with H_2SO_4. Rb determined gravimetrically as Rb_2SO_4 after the precipitation of Zr hydroxide. $RbZrF_5 \cdot H_2O$ dissolves congruently, and can be recrystallized from water.	(1) $RbZrF_5 \cdot H_2O$ prepared by equilibrating ZrF_4 with solutions containing less than 1.8 mass% RbF. Under these conditions $RbZrF_5 \cdot H_2O$ is obtained as the equilibrium solid phase, as follows from the measurement of the ZrF_4-NaF-H_2O system studied in the same document. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified, RbF was reagent grade.
	ESTIMATED ERROR:
	Temp: precision ± 0.1 K. Soly: precision ± 1-2 % (compiler).

COMPONENTS: (1) Cesium pentafluorozirconate(IV); $CsZrF_5$; [13782-20-2] (2) Water; H_2O; [7732-18-5]	**ORIGINAL MEASUREMENTS:** Tananaev, I.V.; Guzeeva, L.S. **Zh. Neorg. Khim.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966; *11*, 590-3.
VARIABLES: $T/K = 298$	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $CsZrF_5 \cdot H_2O$ [20982-59-6] is reported as 3.58 mass %.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $CsZrF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after removal of F^- by evaporation with H_2SO_4. Cs determined gravimetrically as Cs_2SO_4 after the precipitation of Zr hydroxide. $CsZrF_5 \cdot H_2O$ dissolves congruently, and can be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) $CsZrF_5 \cdot H_2O$ prepared by equilibrating ZrF_4 with solutions containing less than 2.50 mass % CsF. Under these conditions $CsZrF_5 \cdot H_2O$ is obtained as the equilibrium solid phase, as follows from the measurement of the ZrF_4-CsF-H_2O system studied in the same document. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified, CsF was prepared from Cs_2CO_3 and twice distilled HF.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

COMPONENTS:

(1) Ammonium hexafluorozirconate(IV); $(NH_4)_2ZrF_6$; [16919-31-6]

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

ORIGINAL MEASUREMENTS:

1. von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74.
2. von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk Selsk.* 1925, *6*, 1-149.

VARIABLES:

T/K = 273-363

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

t/°C	Ammonium Hexafluorozirconate(IV) c_1/mol dm^{-3}	ρ/g cm^{-3}
0	0.611	-
20	1.050	1.154
45	1.842	-
90	2.96	-

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Zr was determined gravimetrically as ZrO_2 after evaporation with H_2SO_4 and ignition of the residue of an aliquot from the saturated solution. The authors do not report on the composition of the solid phase.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2ZrF_6$ was prepared by dissolution of ZrO_2 in concentrated HF, and by adding a stoichiometric amount of NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K ($T \leq 293$).
precision ± 0.1 K ($T > 293$).
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Ammonium hexafluorozirconate(IV); $(NH_4)_2ZrF_6$; [16919-31-6]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N.S.; Buslaev, Yu.A.; Gustyakova, M.P.

**Zh. Neorg. Khim.* 1965, *10*, 2577-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1401-2.

VARIABLES:

$T/K = 293$
$m_2/\text{mol kg}^{-1} = 0\text{-}25.82$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions, $t/°C = 20$

Hydrogen Fluoride		Ammonium Hexafluorozirconate(IV)	
mass %	$m_2/\text{mol kg}^{-1a}$	mass %	$m_1/\text{mol kg}^{-1a}$
0	0	23.71	1.277
5.85	3.92	19.48	1.072
20.30	16.67	18.84	1.272
27.56	25.82	19.09	1.471

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for several days. Zr was determined gravimetrically as ZrO_2 after removal of HF with H_2SO_4. HF determined by potentiometric titration with alkali in the presence of KF (ref 1). The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2ZrF_6$ was prepared from $ZrF_4 \cdot 3H_2O$ by heating it with water and a stoichiometric amount of NH_4F. $(NH_4)_2ZrF_6$ crystallized on cooling. Source and purity of chemicals not given except for the Hf content (0.05%) of $ZrF_4 \cdot 3H_2O$.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 % $(NH_4)_2ZrF_6$.
Conc: precision ± 2 % HF.

REFERENCES:

1. Nikolaev, N.S.; Buslaev, Yu.A. *Zh. Neorg. Khim.* 1959, *4*, 543; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, *4* 246-9.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Sodium hexafluorozirconate(IV); Na_2ZrF_6; [16925-26-1] (2) Water; H_2O; [7732-18-5]	Tananaev, I.V.; Guzeeva, L.S. **Zh. Neorg. Khim.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 590-3.
VARIABLES:	**PREPARED BY:**
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Na_2ZrF_6 is reported as 0.58 g/100 g water ($0.0231 \text{ mol kg}^{-1}$ [a])

a. Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Na_2ZrF_6 were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after removal of F^- by evaporation with H_2SO_4. Na determined gravimetrically as Na_2SO_4 after the precipitation of Zr hydroxide. Na_2ZrF_6 dissolves congruently, and can be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) Na_2ZrF_6 was prepared by equilibrating ZrF_4 with solutions containing 0.21-0.32 mass % NaF. Under these conditions Na_2ZrF_6 is obtained as the equilibrium solid phase, as follows from the measurement of the ZrF_4-NaF-H_2O system studied in the same document. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified; NaF was reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

COMPONENTS:	EVALUATOR:
(1) (OC-6-11)-Dipotassium hexafluorozirconate(2-); K_2ZrF_6; [16923-95-8] (2) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia September 1985

CRITICAL EVALUATION:

An evaluation of the solubility of K_2ZrF_6 in water.

Seven literature sources of the solubility of K_2ZrF_6 in H_2O are available (ref 1 - 7). Of these the results of six are compared in Figure 1. The data of Egerev and Pogorelyi (ref 5, 6) and Missenden (ref 2) present the solubilities over wide temperature ranges. At 10 °C the two data sets agree exactly, but at the higher temperatures they differ considerably,the data of Egerev and Pogorelyi (ref 5) being much higher. Egerev and Pogorelyi (ref 5) state that insufficiently pure K_2ZrF_6 was used in the older studies (ref 1, 2). This statement should be taken as only an assumption since Missenden (ref 2) reported on neither the analytical method nor the purity of the K_2ZrF_6 used. It is possible that the preparations of K_2ZrF_6 used in these studies may have been contaminated with some isomorphous hafnium salt.

At 0 °C (273.15 K) the two available experimental values (ref 1, 5) agree within 10 %. At 10 °C (283.15 K) the values from papers (ref 2, 5) agree exactly at a value of 0.043 mol kg^{-1}. The value of Marden (ref 1) for 20 °C is obviously in error. Egerev and Pogorelyi report two sets of data (ref 5, 6). The later data (ref 6) are consistently 2.5 - 4.2 % higher than the data reported only a couple of month earlier (ref 5). Only two of the values from ref 6 are shown in the figure. The single value of Schmitt *et al.* (ref 3) at 25 °C (298.15 K) (0.0812 mol dm^{-3}) appears to fit the overall pattern well, but it cannot be compared directly because it is in a different unit than the other data. Tananaev and Guzeeva (ref 7) carried out a detailed study of the ZrF_4 + KF + H_2O system. They report solubility values of K_2ZrF_6 under conditions that K_2ZrF_6 is the equilibrium solid that follow closely the values reported by Egerev and Pogorelyi (ref 5, 6).

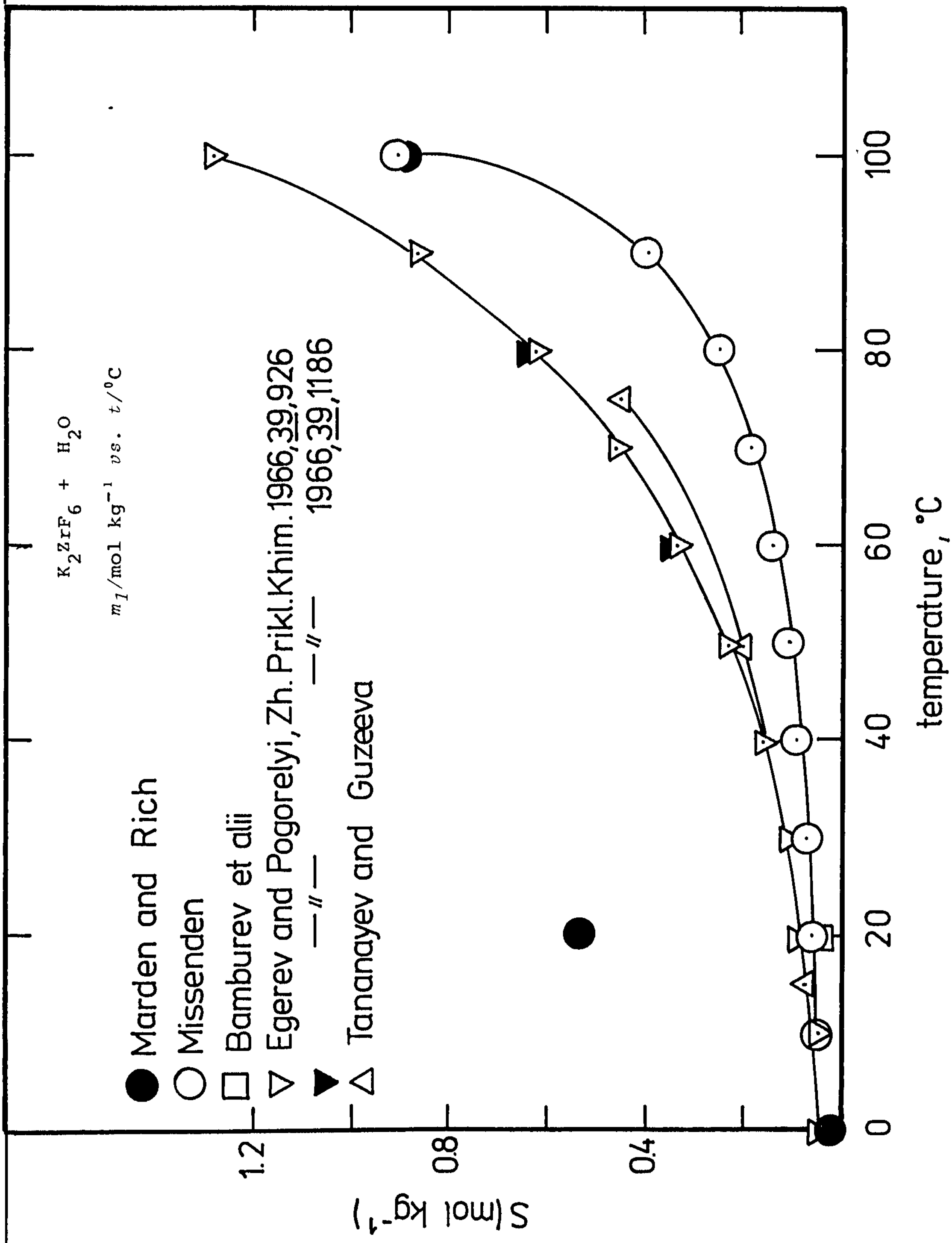
Tentative values: Due to the lack of agreement in the published data, the evaluator cannot recommend any data. For tentative values, the evaluator suggests the data of Egerev and Pogorelyi (ref 5) be used (see the compilation for numerical values).

REFERENCES:

1. Marden, J. W.
   J. Ind. Eng. Chem. 1920, *12*, 651.
2. Missenden, J.
   Chem. News 1922, *124*, 326.
3. Schmitt, R. H.; Grove, E. L.; Brown, R. D.
   J. Am. Chem. Soc. 1960, *82*, 5292.
4. Bamburov, V. G.; Demenev, N. V.; Polyakova, V. M.
   Izv. Sibirsk. Otdel. Akad. Nauk SSSR 1962, No. 5, 70.
5. Egerev, O. I.; Pogorelyi, A. D.
   Zh. Prikl. Khim. 1966, *39*, 926.
6. Egerev, O. I.; Pogorelyi, A. D.
   Zh. Prikl. Khim. 1966, *39*, 1186.
7. Tananaev, I. V.; Guzeeva, L. S.
   Zh. Neorg. Khim. 1966, *11*, 1096.

COMPONENTS:	EVALUATOR:
(1) (OC-6-11)-dipotassium hexafluorozirconate(2-); K_2ZrF_6; [16923-95-8] (2) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia September 1985

CRITICAL EVALUATION:



COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium hexafluorozirconate(IV) K_2ZrF_6; [16923-95-8] (2) Water; H_2O; [7732-18-5]	Marden, J.W.; Rich, M.N. *J. Ind. Eng. Chem.* 1920, *12*, 651-6.
VARIABLES:	**PREPARED BY:**
T/K = 273-373	J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

t/°C	Potassium Hexafluorozirconate(IV)	
	g/100 g water	m_1/mol kg^{-1} [a]
0	0.78	0.0275
20	15.0	0.529
100	25.0	0.882

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used but no details were given. Methods of analysis and equilibrium solid phases were not reported.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrF_6 was prepared by dissolution of ZrO_2 (98% purity) in HF and neutralizing the solution with K_2CO_3 (C.P.) until a slight excess of acid remained. Pb vessels were used. After cooling, K_2ZrF_6 crystals were seperated and 3x recrystallized from water. Purity of K_2ZrF_6 was estimated to be greater than 99.99%. Source and purity of water and HF not specified.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorozirconate(IV); K_2ZrF_6; [16923-95-8]

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

ORIGINAL MEASUREMENTS:

Missenden, J.

Chem. News J. Ind. Sci. 1922, *124*, 326-7.

VARIABLES:

T/K = 283-373

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Potassium Hexafluorozirconate(IV)	
t/°C	g/100 g water	m_1/mol kg^{-1}[a]
10	1.22	0.0430
20	1.55	0.0547
30	1.92	0.0677
40	2.37	0.0836
50	2.94	0.104
60	3.81	0.134
70	5.06	0.179
80	6.90	0.243
90	11.11	0.392
100	25.53	0.901

[a] Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Apparently isothermal method was used but no details were given. Methods of analysis and equilibrium solid phases not reported.

SOURCE AND PURITY OF MATERIALS:

(1) Although two methods for the preparation of K_2ZrF_6 were mentioned, i.e. dissolution of $ZrF_4 \cdot 3H_2O$ in KF solution, and fusion of zircon ($ZrSiO_4$) with KHF_2, it was not specified which one was used for the solubility measurements.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) (OC-6-11)-Dipotassium hexafluorozirconate(2-); K_2ZrF_6; [16923-95-8]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of K_2ZrF_6 at 25 °C is reported to be c_1/mol dm^{-3} = 0.0812. The value is the average of four measurements, but neither the individual values or standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Two saturated solutions of K_2ZrF_6 were prepared at 40 °C and another two were prepared at 20 °C. All solutions were brought to equilibrium at 25 °C with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70 °C, weighed, kept over P_2O_5 for several days and reweighed. All work was carried out in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrF_6 was prepared by adding a concentrated solution of reagent grade KCl to a solution of H_2ZrF_6. The salt was filtered, washed, and recrytallized several times. Either Pt or polyethylene containers and deionized water were used in all steps.

SOURCE AND PURITY OF MATERIALS:(continued)

The H_2ZrF_6 solution was prepared by dissolving ZrO_2 (source not specified) in excess HF. The ZrO_2 was not purified since its chief impurity, Hf, was removed by the recrystallization of the K_2ZrF_6. Spectrographic analysis of the K_2ZrF_6 showed only minor traces of impurities. The Hf content was not reported.

(2) Deionized water was used.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K.
The solubility error is not specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium hexafluorozirconate(IV); K_2ZrF_6; [16923-95-8] (2) Water; H_2O; [7732-18-5]	Bamburov, V.G.; Demenev, N.V.; Polyakova, V.M. *Izv. Sib. Otd. Akad. Nauk SSSR* 1962, *5*, 70-5.
VARIABLES:	**PREPARED BY:**
$T/\mathrm{K} = 293$	J. Hála

EXPERIMENTAL VALUES:

The solubility at 20°C of K_2ZrF_6 is reported as 1.48 mass %

(0.0530 mol kg^{-1} [a]).

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess K_2ZrF_6 were shaken until equilibrium was reached. K was determined gravimetrically as K_2SO_4, F^- determined titrimetrically with $Th(NO_3)_4$ against alizarine sulfonate as indicator, or gravimetrically as CaF_2. No method was mentioned for Zr determination.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrF_6 was prepared by equilibrating $ZrF_4\cdot 3H_2O$ with solutions containing 0.78-1.7 mass % KF. Under these conditions K_2ZrF_6 is obtained as the equilibrium solid phase, as follows from the study of the ZrF_4-KF-H_2O system carried out in the same document. KF, reagent grade. $ZrF_4\cdot 3H_2O$ prepared by dissolving ZrO_2 in HF and subsequent evaporation. Source and purity of materials not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorozirconate(IV); K_2ZrF_6; [16923-95-8]

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

ORIGINAL MEASUREMENTS:

Egerev, O.I.; Pogorelyi, A.D.

**Zh. Prikl. Khim. (Leningrad)* 1966, *39*, 926-8; *J. Appl. Chem. USSR (Engl. Transl.)* 1966, *39*, 866-7.

VARIABLES:

T/K = 273-373

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

T/K	Potassium Hexafluorozirconate(IV) g/100 g H_2O	m_1/mol kg^{-1}
273.16	0.936	0.03304
283.16	1.219	0.04302
293.16	1.822	0.0643
303.16	2.776	0.09796
313.16	4.222	0.14896
323.16	6.349	0.22400
333.16	9.336	0.32939
343.16	12.853	0.45349
353.16	17.404	0.61406
363.16	24.42	0.86169
373.16	36.2	1.27819

Least squares treatment of the data yielded for the temperature dependency of K_2ZrF_6 solubility the following equation:

$$\log S = -(1709.1/T) + 3.6387$$ (author's equation).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Each measurement was repeated 2-6 times. Samples of saturated solutions were taken by means of a pipette heated to the corresponding temperature. The samples were weighed, evaporated, and the residue dried at 105°C and weighed. The authors do not report on the equilibrium solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrF_6 was prepared from Zr metal obtained by thermal decomposition of ZrI_4. Zr contained less than 0.1% Hf and 10^{-2}% Si, Fe, Al, and Ti. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The arithmetic mean solubility varied from 0.07 to 2.35% depending on the number of determinations.

REFERENCES:

COMPONENTS:

(1) (OC-6-11)-Dipotassium hexafluorozirconate(2-); K_2ZrF_6; [16923-95-8]

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

ORIGINAL MEASUREMENTS:

Egerev, O. I.; Pogorelyi, A. D.

**Zh. Prikl. Khim.* 1966, *39*, 1186-7.

J. Appl. Chem. USSR (Engl.Transl.) 1966, *39*, 1110-1.

VARIABLES:

T/K = 293 - 353

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		K_2ZrF_6	
$t/^\circ C$	T/K	g/100 g H_2O	m_1/mol kg^{-1}[a]
20[b]	293	1.8695	0.0660
40	313	4.3739	0.154
60	333	9.6620	0.341
80	353	18.1614	0.641

[a] Calculated by compiler

[b] The document states 30° for this measurement which is obviously a misprint. The solubility value reported is very close to that for 20° in the authors' previous work (ref 1) and also other measurements such as separation factors related to this temperature are reported for 20° rather than for 30°.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Nothing is specified but presumably the same method as in the authors' previous work (ref 1) was used. After isothermal equilibration (time not specified) of excess K_2ZrF_6 with water, samples of saturated solutions were withdrawn using a pipette preheated to the corresponding temperature, evaporated, and the residue was dried at 105° and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) Presumably, as in the authors' previous work, K_2ZrF_6 was prepared from Zr metal obtained by thermal decomposition of ZrI_4. It contained 0.1% Hf and 10^{-4}% Si, Fe, Al, and Ti.

ESTIMATED ERROR:

REFERENCES:

1. Egerev, O. I.; Pogorelyi, A. D. *Zh. Prikl. Khim.* 1966, *39*, 926.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium hexafluorozirconate(IV); K_2ZrF_6; [16923-95-8] (2) Water; H_2O; [7732-18-5]	Tananaev, I.V.; Guzeeva, L.S. **Zh. Neorg. Khim.* <u>1966</u>, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1966</u>, *11*, 590-3.
VARIABLES:	**PREPARED BY:**
T/K = 298-348	J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Potassium Hexafluorozirconate(IV)	
t/°C	g/100 g water	m_1/mol kg^{-1} [a]
25	2.16	0.0762
50	5.85	0.206
75	12.60	0.445

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess K_2ZrF_6 were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after removal of F^- by evaporation with H_2SO_4. K determined gravimetrically as K_2SO_4 after the precipitation of Zr hydroxide. K_2ZrF_6 dissolved congruently, and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrF_6 was prepared by equilibrating ZrF_4 with solutions containing such an amount of KF as to yield K_2ZrF_6 as the equilibrium solid phase. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified; KF was reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorozirconate(IV); K_2ZrF_6; [16923-95-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

1. von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74.
2. von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.

VARIABLES:

T/K = 293
c_2/mol dm^{-3} = 0.125-5.89

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of K_2ZrF_6 in aqueous HF at 20°C

Hydrogen Fluoride c_2/mol dm^{-3}	Potassium Hexafluorozirconate(IV) c_1/mol dm^{-3}
0.125	0.0655
5.89	0.1297

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Zr was determined gravimetrically as ZrO_2 but no details were reported. The authors do not report on the composition of solid phases.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.

The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorozirconate(IV); K_2ZrF_6; [16923-95-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N.S.; Buslaev, Yu.A.; Gustyakova, M.P.

**Zh. Neorg. Khim.* 1965, *10*, 2577-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1401-2.

VARIABLES:

$T/K = 293$
$m_2/\text{mol kg}^{-1} = 0.0868\text{-}31.24$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of K_2ZrF_6 in aqueous HF at 20°C

Hydrogen Fluoride		Potassium Hexafluorozirconate(IV)	
mass %	$m_2/\text{mol kg}^{-1\,a}$	mass %	$m_1/\text{mol kg}^{-1\,a}$
0.17	0.0868	1.91	0.0688
3.85	2.05	2.39	.0899
8.41	4.75	3.06	.122
11.84	7.03	4.02	.169
15.65	9.96	5.77	.259
25.96	19.74	8.35	.448
33.87	31.24	11.94	.777

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for several days. Zr was determined gravimetrically as ZrO_2 after removal of HF with H_2SO_4. HF determined by potentiometric titration with alkali in the presence of KF (ref 1). The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrF_6 was prepared from $ZrF_4 \cdot 3H_2O$ by heating it with water and a stoichiometric amount of KF. K_2ZrF_6 crystallized on cooling. Source and purity of chemicals not given except for the Hf content (0.05%) of $ZrF_4 \cdot 3H_2O$.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 % K_2ZrF_6.
Conc: precision ± 2 % HF.

REFERENCES:

1. Nikolaev, N.S.; Buslaev Yu.A. *Zh. Neorg. Khim.* 1959, *4*, 543; *Russ J. Inorg. Chem. (Engl. Transl.)* 1959, *4*, 246-9.

COMPONENTS:

(1) (OC-6-11)-Dirubidium hexafluorozirconate(2-); Rb_2ZrF_6; [16962-10-0]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Rb_2ZrF_6 at 25°C is reported to be $c_1/\text{mol dm}^{-3} = 0.0848$. The value is the average of four measurements, but neither the individual values or standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Two saturated solutions of Rb_2ZrF_6 were prepared at 40°C and another two were prepared at 20°C. All solutions were brought to equilibrium at 25°C with constant stirring. After attaining equilibrium known volumes of the saturated solutions were evaporated to dryness at 70°C, weighed, kept over P_2O_5 for several days and reweighed. All work was carried out in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2ZrF_6 was prepared by adding concentrated solution of RbF to a solution of H_2ZrF_6. The salt was filtered, washed, and recrystallized several times. Either Pt or polyethylene containers and deionized water were used in all steps.

The H_2ZrF_6 solution was prepared by dissolving ZrO_2 (source not specified) in excess HF.

SOURCE AND PURITY OF MATERIALS: (continued)

The ZrO_2 was not purified since its chief impurity, Hf, was removed by the recrystallization of the Rb_2ZrF_6.

Spectrographic analysis of the Rb_2ZrF_6 showed only minor traces of impurities. The Hf content was not reported.

(2) Deionized water was used.

ESTIMATED ERROR: Temp: accuracy ± 0.005 K. (NBS calibration).

The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Rubidium hexafluorozirconate(IV); Rb_2ZrF_6; [16962-10-0]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* <u>1966</u>, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1966</u>, *11*, 590-3.

VARIABLES:

T/K = 298-348

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Rubidium Hexafluorozirconate(IV)	
t/°C	g/100 g water	m_1/mol kg^{-1a}
25	4.16	0.111
50	9.92	0.264
75	18.16	0.483

[a] Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Rb_2ZrF_6 were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after removal of F^- by evaporation with H_2SO_4. Rb determined gravimetrically as $RbSO_4$ after the precipitation of Zr hydroxide. Rb_2ZrF_6 dissolves congruently, and can be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2ZrF_6 was prepared by equilibrating ZrF_4 with solutions containing 3.54-12.65 mass % RbF. Under these conditions Rb_2ZrF_6 is obtained as the equilibrium solid phase, as follows from the measurement of the ZrF_4-RbF-H_2O system studied in the same document. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified; RbF was reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

COMPONENTS:

(1) Cesium hexafluorozirconate;
Cs_2ZrF_6; [16919-30-5]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.;
Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Cs_2ZrF_6 at 25°C is reported to be $c_1/\text{mol dm}^{-3} = 0.112$. The value is the average of four measurements, but neither the individual values or standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Two saturated solutions of Cs_2ZrF_6 were prepared at 40°C and another two were prepared at 20°C. All solutions were brought to equilibrium at 25°C with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70°C, weighed, kept over P_2O_5 for several days and reweighed. All work was carried out in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2ZrF_6 was prepared by adding concentrated solution of an unspecified Cs halide to a solution of H_2ZrF_6.

The salt was filtered, washed, and recrystallized several times. Either Pt or polyethylene containers and deionized water were used in all steps.

SOURCE AND PURITY OF MATERIALS:

The H_2ZrF_6 solution was prepared by dissolving ZrO_2 (source not specified) in excess HF. The ZrO_2 was not purified since its chief impurity, Hf, was removed by the recrystallization of the Cs_2ZrF_6.

Spectrographic analysis of the Cs_2ZrF_6 showed only minor traces of impurities. The Hf content was not reported.

(2) Deionized water was used.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K.
(NBS calibration).

The solubility error is not specified.

COMPONENTS:

(1) Cesium hexafluorozirconate(IV); Cs_2ZrF_6; [16919-30-5]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1096-1102; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 590-3.

VARIABLES:

T/K = 298-348

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

t/°C	Cesium Hexafluorozirconate(IV)	
	g/100 g water	m_1/mol kg^{-1a}
25	6.45	0.137
50	14.38	0.305
75	25.60	0.542

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Cs_2ZrF_6 were shaken overnight in teflon bottles. Zr was determined gravimetrically as ZrO_2 after removal of F^- by evaporation with H_2SO_4. Cs determined gravimetrically as Cs_2SO_4 after the precipitation of Zr hydroxide. Cs_2ZrF_6 dissolves congruently, and can be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2ZrF_6 was prepared by equilibrating ZrF_4 with solutions containing more than 5.30 mass % CsF. Under these conditions Cs_2ZrF_6 is obtained as the equilibrium solid phase, as follows from the measurement of the ZrF_4-CsF-H_2O system studied in the same document. ZrF_4 was prepared by reacting $ZrOCl_2 \cdot 8H_2O$ with liquid HF and heating the product to 300-400°C. Source and purity of $ZrOCl_2 \cdot 8H_2O$ and HF not specified, CsF prepared from Cs_2CO_3 and twice distilled HF.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

COMPONENTS:	EVALUATOR:
(1) Triammonium heptafluorozirconate(3-); $(NH_4)_3ZrF_7$; [17250-81-6] (2) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia June 1985

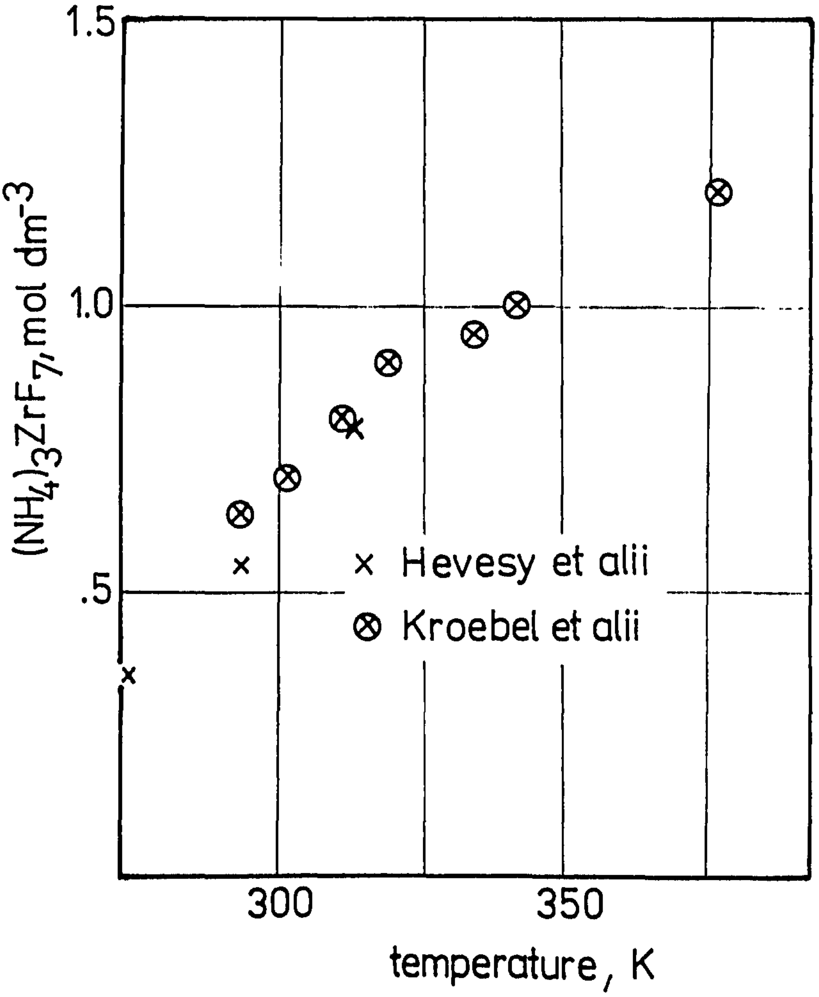
CRITICAL EVALUATION:

An evaluation of the solubility of $(NH_4)_3ZrF_7$ in water.

Two laboratories report the solubility of $(NH_4)_3ZrF_7$ in water as a function of temperature. Hevesy *et al.* (ref 1) report three values between 273 and 313 K by an isothermal method, and Kroebel *et al.* (ref 2) report a number of values between 294 and 377 K by observation of the crytallization temperature. The solubility values from the two sources are compared in the Figure. There is good agreement near 313 K, but at 293 K the Kroebel *et al.* value is much higher than the Hevesy *et al.* value.

Hevesy *et al.* (ref 1) used good control of temperature along with a precise gravimetric analysis. Kroebel *et al.* (ref 2) observed the crystallization temperatures with an uncertainty of ± 2 K. Thus the evaluator prefers the Hevesy *et al.* data as tentative values over the 273 to 313 K temperature range, and the data of Kroebel *et al.* for the higher temperatures.

REFERENCES: 1. von Hevesy, G.; Christiansen, J. A.; Berglund, V. *Z. Anorg. Allgem. Chem.* 1925, *144*, 69.
2. Kroebel, R.; Eschrich, H.; Pivato, J. M.; Hansen, P. *Eur. Co. Chem. Process. Irradiat. Fuels ETR* 1978, *259*, 44pp.



COMPONENTS:

(1) Ammonium heptafluorozirconate(IV); $(NH_4)_3ZrF_7$; [17250-81-6]

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

ORIGINAL MEASUREMENTS:

1. von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74.
2. von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.

VARIABLES:

T/K = 273-313

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Ammonium Heptafluorozirconate(IV)	
t/°C	c_1/mol dm^{-3}	ρ/g cm^{-3}
0	0.360	-
20	0.551	1.086
40	0.788	-

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Zr was determined gravimetrically as ZrO_2 after evaporation with H_2SO_4 and ignition of the residue of an aliquot from the saturated solution. The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_3ZrF_7$ was prepared by dissolution of ZrO_2 in concentrated HF, and by adding an excess of NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 (T=273,293K).
precision ± 0.1 (T= 313 K).
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Ammonium heptafluorozirconate(IV); $(NH_4)_3ZrF_7$; [17250-81-6]

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

ORIGINAL MEASUREMENTS:

Kroebel, R.; Eschrich, R.; Pivato, J.M.; Hansen, P.

Eur. Co Chem. Process. Irradiat. Fuels [*Eurochemic Tech. Rep.*] *ETR* 1978, *ETR 259*, 44 pp; *Chem. Abstr.* 1979, *91*, 98625j.

VARIABLES:

$T/K = 294\text{-}377$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Ammonium Heptafluorozirconate(IV)
$t/°C$	$c_1/\text{mol dm}^{-3}$
21	0.64
28	0.70
38	0.80
46	0.90
61	0.95
69	1.0
104	1.2

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities were obtained from crystallization temperatures. Dry solid was shaken with an appropriate NH_4F solution in a thermostat until it dissolved completely. It was then allowed to crystallize, and the temperature of crystallization was read. Several cycles of dissolution and crystallization were repeated, and temperature values averaged. The authors did not report on the composition of the equilibrium solid phases.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temp: precision ± 2 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Triammonium heptafluorozirconate(3-); $(NH_4)_3ZrF_7$; [17250-81-6] (2) Ammonium fluoride; NH_4F; [12125-01-8] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia June 1985

CRITICAL EVALUATION:

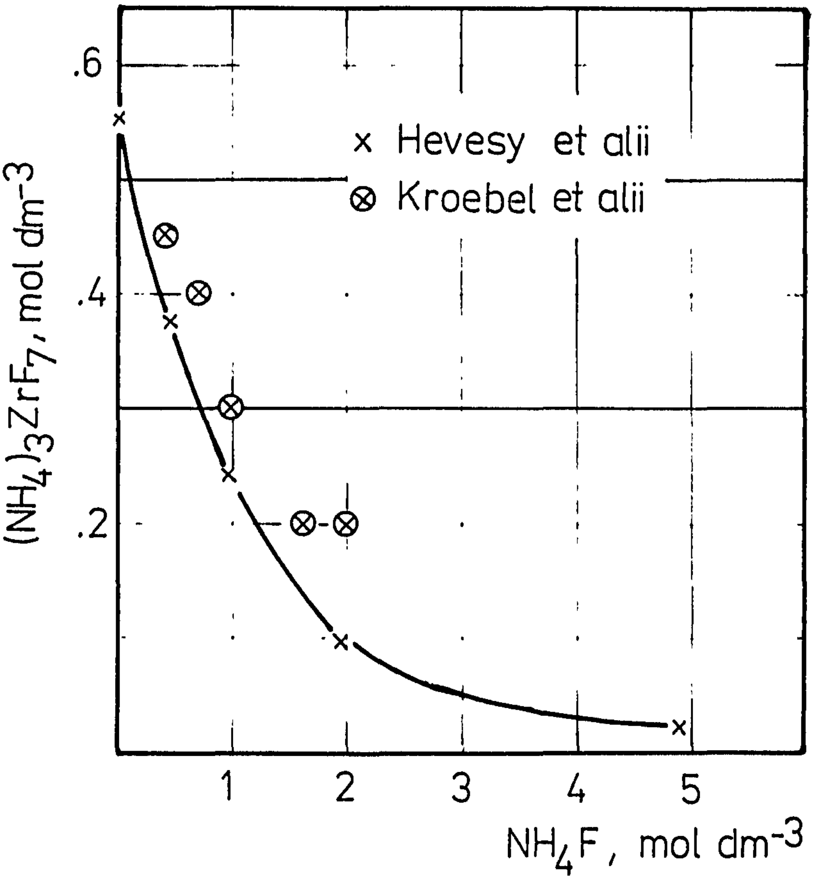
An evaluation of the solubility of $(NH_4)_3ZrF_7$ in aqueous ammonium fluoride solutions.

Two laboratories report the solubility of $(NH_4)_3ZrF_7$ as a function of ammonium fluoride concentration in aqueous solution. Hevesy *et al.* (ref 1) report values at 293 K for solutions up to 9.72 mol dm^{-3} NH_4F. Kroebel *et al.* (ref 2) report solubility values at 294, 314, and 337 K for solutions up to 4.5 mol dm^{-3} NH_4F. The solubility values at 293/294 K from the two groups are compared in the Figure. The agreement is not good, the solubility values differ by a factor of 2 in 2.0 mol dm^{-3} NH_4F. The values of Kroebel *et al.* are higher than those of Hevesy *et al.* at all NH4F concentrations and tend to level off at a constant value above 2.0 mol dm^{-3} NH_4F at this and the other temperatures.

Hevesy *et al.* (ref 1) used good temperature control (± 0.01 - 0.1 K) along with a precise gravimetric analysis. Kroebel *et al.* (ref 2) observed crystallization temperatures with an uncertainty of ± 2 K. The evaluator prefers the use of Hevesy *et al.* data as the tentative values at 293 K. Hevesy *et al.* identified the solid phase as $(NH_4)_3ZrF_7$.

REFERENCES:

1. von Hevesy, G.; Christiansen, J. A.; Berglund, V. *Z. Anorg. Allgem. Chem.* 1925, *144*, 69.
2. Kroebel, R.; Eschrich, H.; Pivato, J. M.; Hansen, P. *Eur. Co. Chem. Process. Irradiat. Fuels [Eurochemic Tech. Rep.]* 1978, *ETR 259*, 44 pp.; *Chem. Abstr.* 1979, *91*, 98625j.



COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Ammonium heptafluorozirconate(IV); $(NH_4)_3ZrF_7$; [17250-81-6] (2) Ammonium fluoride; NH_4F; [12125-01-8] (3) Water; H_2O; [7732-18-5]	1. von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74. 2. von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.
VARIABLES:	PREPARED BY:
T/K = 293 c_2/mol dm^{-3} - 0.002-9.721	J. Hála

EXPERIMENTAL VALUES:

Solubility of $(NH_4)_3ZrF_7$ in aqueous NH_4F at 20°C

Ammonium Fluoride	Ammonium Heptafluorozirconate(IV)		Nature of Solid Phase[a]
c_2/mol dm^{-3}	c_1/mol dm^{-3}	ρ/g cm^{-3}	
0.002	0.551	1.086	A
0.462	0.375	-	A
0.966	0.242	-	A
1.941	0.0972	-	A
4.872	0.0226	1.068	A
9.721	0.01716	1.105	A

[a] A: $(NH_4)_3ZrF_7$, [17250-81-6]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Zr was determined gravimetrically as ZrO_2 after evaporation with H_2SO_4 and ignition of the residue of an aliquot from the saturated solution. NH_4^+ concentration determined by Kjeldahl's method. The composition of the solid phase was determined by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_3ZrF_7$ was prepared by dissolution of ZrO_2 in concentrated HF, and by adding an excess of NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Ammonium Heptafluorozirconate(IV); $(NH_4)_3ZrF_7$; [17250-81-6]

(2) Ammonium fluoride; NH_4F; [12125-01-8]

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

ORIGINAL MEASUREMENTS:

Kroebel, R.; Eschrich, H.; Pivato, J.M.; Hansen, P.

Eur. Co. Chem. Process. Irradiat. Fuels [*Eurochemic Tech. Rep.*] 1978, *ETR 259*, 44 pp.

VARIABLES:

T/K = 294-337
c_2/mol dm^{-3} = 0.40-4.5

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $(NH_4)_3ZrF_7$ in aqueous NH_4F at 21, 41, and 64°C

	Ammonium Fluoride	Ammonium Heptafluorozirconate(IV)
t/°C	c_2/mol dm^{-3}	c_1/mol dm^{-3}
21	0.40	0.50
	0.70	0.40
	1.0	0.30
	1.60	0.20
	2.0	0.20
41	0.8	0.60
	1.2	0.50
	1.4	0.45
	2.0	0.35
	3.15	0.20
64	0.6	0.85
	1.4	0.65
	2.0	0.50
	2.5	0.40
	3.8	0.30
	4.5	0.20

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities were obtained from crystallization temperatures. Dry solid was shaken with an appropriate NH_4F solution in a thermostat until it dissolved completely. It was then allowed to crystallize, and the temperature of crystallization was read. Several cycles of dissolution and crystallization were repeated, and the temperature values averaged. The authors did not report on the composition of the equilibrium solid phase.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temp: precision ± 2 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:	**ORIGINAL MEASUREMENTS:**
(1) Ammonium heptafluorozirconate(IV); $(NH_4)_3ZrF_7$; [17250-81-6] (2) Ammonium nitrate; NH_4NO_3; [6484-52-2] (3) Water; H_2O; [7732-18-5]	Kroebel, R.; Eschrich, H.; Pivato, J.M.; Hansen, P. *Eur. Co. Chem. Process. Irradiat. Fuels* [*Eurochemic Tech. Rep.*] *ETR* 1978, *ETR 259*, 44 pp.
VARIABLES:	**PREPARED BY:**
$T/K = 296\text{-}316$ $c_2/\text{mol dm}^{-3} = 0.4\text{-}0.8$	J. Hála

EXPERIMENTAL VALUES:

Solubility of $(NH_4)_3ZrF_7$ in aqueous NH_4NO_3 at 23 and 43°C

	Ammonium Nitrate	Ammonium Heptafluorozirconate(IV)
$t/°C$	$c_2/\text{mol dm}^{-3}$	$c_1/\text{mol dm}^{-3}$
23	0.4	0.50
43	0.8	0.60

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	**SOURCE AND PURITY OF MATERIALS:**
Solubilities were obtained from crystallization temperatures. Dry solid was shaken with an appropriate NH_4F solution in a thermostat until it dissolved completely. It was then allowed to crystallize, and the temperature of crystallization was read. Several cycles of dissolution and crystallization were repeated, and the temperature values averaged. The authors did not report on the composition of the equilibrium solid phase.	Nothing specified.
	ESTIMATED ERROR:
	Temp: precision ± 2 K. The solubility error is not specified.
	REFERENCES:

COMPONENTS:

(1) Potassium heptafluorozirconate(IV) K_3ZrF_7; [17442-97-6]

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

ORIGINAL MEASUREMENTS:

Bamburov, V.G.; Demenev, N.V.; Polyakova, V.M.

Izv. Sib. Otd. Akad. Nauk SSSR, 1962, *(5)*, 70-5.

VARIABLES:

T/K = 293

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 20°C of K_3ZrF_7 is reported as 1.31 mass % (0.0389 mol kg^{-1} [a]).

[a] Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess K_3ZrF_7 were shaken until equilibrium was reached. K was determined gravimetrically as K_2SO_4, F^- determined titrimetrically with $Th(NO_3)_4$ against alizarine sulfonate as indicator, or gravimetrically as CaF_2. No method was mentioned for Zr determination.

SOURCE AND PURITY OF MATERIALS:

(1) K_3ZrF_7 was prepared by equilibrating $ZrF_4 \cdot 3H_2O$ with solutions containing >4.66 mass % KF. Under these conditions K_3ZrF_7 is obtained as the equilibrium solid phase, as follows from the study of the ZrF_4-KF-H_2O system carried out in the same document. KF, reagent grade. $ZrF_4 \cdot 3H_2O$ prepared by dissolving ZrO_2 in HF and subsequent evaporation. Source and purity not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Zirconium(IV) chloride; $ZrCl_4$; [10026-11-6]

(2) Chloroacetic acid; $C_2H_3ClO_2$; [79-11-8]

ORIGINAL MEASUREMENTS:

Malhotra, K.C.; Sud, R.G.

J. Inorg. Nucl. Chem. 1974, *36*, 3767-72.

VARIABLES:

T/K = 367

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of $ZrCl_4$ at 93.5°C was reported to be 4.62g/100g $C_2H_3ClO_2$ (0.198 mol kg^{-1}[a]).

a Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. $ClCH_2COOH$ was placed in a dried ampoule containing a sufficient amount of $ZrCl_4$. The ampoule was sealed and shaken for 24 h. The ampoule was then broken, the contents filtered quickly through sintered glass in dry atmosphere, and a sample of known weight was taken. Method for Zr determination not specified.

SOURCE AND PURITY OF MATERIALS:

(1) Source and purity of $ZrCl_4$ not specified.

(2) $ClCH_2COOH$, B.D.H., purified by distillation under reduced pressure and recrystallization from benzene.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.

The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Zirconium(IV) chloride; $ZrCl_4$; [10026-11-6]
(2) Acetonitrile; C_2H_3N; [75-05-8]
(3) Bis(3-methylbutyl) ether, or *isoamyl ether*; $C_{10}H_{22}O$; [544-01-4]

ORIGINAL MEASUREMENTS:

Larsen, E.M.; Trevorrow, L.E.

J. Inorg. Nucl. Chem., 1956, *2*, 254-9.

VARIABLES:

T/K = 298
Solvent composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Experimental data were given in graphical form as the phase diagram for the $ZrCl_4/CH_3CN$/isoamyl ether system at 25°C*. The solubility line AB represents the solubility of the solid phase in liquid mixtures of varying composition. The solid phase existing in equilibrium with the solutions along the entire ABC line was $ZrCl_4 \cdot 2CH_3CN$. Numerical data were given for the following points of the diagram:

Point	CH_3CN mass%	Isoamyl ether mass%	$ZrCl_4$ mass%
A	6	92.4	1.6
B	66	19	15
C	81.9±0.8	-	18.1±0.8
D	-	94.5±0.9	5.50±0.9

* See diagram on the next page

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility of $ZrCl_4$ in CH_3CN/isoamyl ether mixtures was obtained from the ternary $ZrCl_4/CH_3CN$/isoamyl ether phase diagram at 25°C. To prepare the 3-component mixtures, $ZrCl_4$ was sublimed *in vacuo* into a cell fitted with serum-bottle caps at sidearms; the cell was brought to atm. pressure by admission of dry air, transferred to a paraffin oil-sealed stirrer assembly, thermostated, and the solvents added through the bottle caps with hypodermic syringes. The location of points A and B on the phase diagram was determined by the interaction of the solubility line with the liquid-liquid curves. The CH_3CN-rich side of the binodal curve was constructed from clear and cloud points obtained by alternately titrating with each solvent. The points on the ether-rich side were obtained by titrating with a solution of $ZrCl_4$ in CH_3CN of a

Continued on the next page. .

SOURCE AND PURITY OF MATERIALS:

(1) $ZrCl_4$ was prepared by passing Cl_2 gas over a mixture of ZrO_2 (containing 58 ppm Hf) and charcoal at 600°C, and purified by first subliming in an atmosphere of H_2 and then resubliming several times *in vacuo*. It was kept in sealed ampoules.
(2) CH_3CN was was dried over P_2O_5 and distilled (n_D^{25} = 1.3418).

Continued on the next page. . .

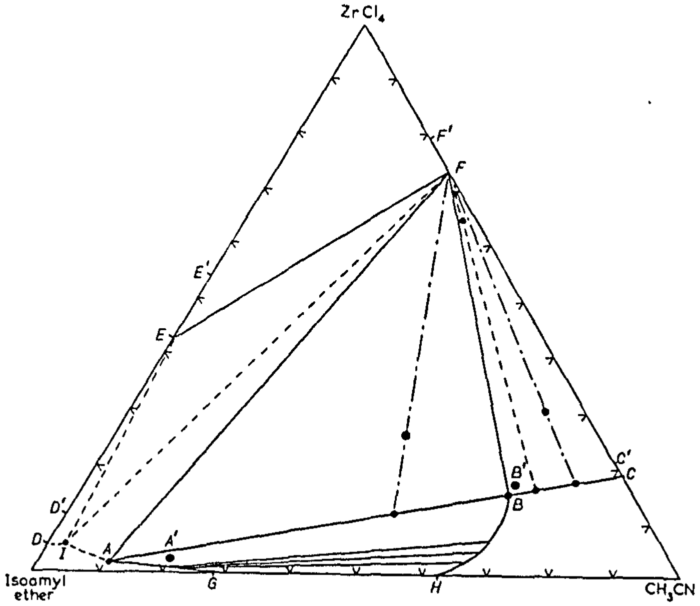
ESTIMATED ERROR:

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zirconium(IV) chloride; $ZrCl_4$; [10026-11-6] (2) Acetonitrile; C_2H_3N; [75-05-8] (3) Bis(3-methylbutyl) ether, or *isoamyl ether*; $C_{10}H_{22}O$; [544-01-4]	Larsen, E.M.; Trevorrow, L.E. *J. Inorg. Nucl. Chem.* 1956, *2*, 254-9.
VARIABLES: T/K = 298 Solvent composition	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

The ternary systems with $ZrCl_4$ and with $HfCl_4$ are similar. Only the complete $ZrCl_4$ system is shown. The corresponding $HfCl_4$ points are indicated by the primed letters.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Continued from preceding page. . . homogeneous ether-rich solvent mixture until the 2-liquid phase region was reached. The points on the line representing equilibrium between the solid phase and the mixed solvent were determined by adding various solvent mixtures to $ZrCl_4$ until the solid phase disappeared. The composition of the equilibrium solid phase was obtained by the method of wet residues. Zr in liquid or solid samples was determined by adding the samples to an excess of water, distilling off the solvent with steam, and precipitating hydrated Zr oxide with NH_3 solution. To determine N in the solid phases, samples were dissolved in glacial acetic acid and N determined by the Kjeldahl method. The ether was obtained by difference.	Continued from preceding page. . . (3) Isoamyl ether was purified from peroxides, dried with $CaCl_2$ and Na ribbon, and distilled (n_D^{25} = 1.4059). Atmospheric moisture was excluded during distillation of the solvents. **ESTIMATED ERROR:** **REFERENCES:**

COMPONENTS:

(1) Zirconium(IV) chloride; $ZrCl_4$; [10026-11-6]

(2) Sulfur dioxide; SO_2; [7446-09-5]

ORIGINAL MEASUREMENTS:

Bond, P.A.; Stephens, W.R.

J. Am. Chem. Soc. 1929, *51*, 2910-22.

VARIABLES:

T/K = 273-293

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	SO_2	Zirconium(IV) chloride		
t/°C	g	g	mole %	m_1/mol kg^{-1a}
0	5.3286	0.2742	1.39	0.218
0	5.2905	0.2667	1.37	
10	5.8132	0.4247	1.95	0.317
10	6.4758	0.4815	2.00	
20	5.8122	0.5649	2.60	0.413
20	4.1985	0.4011	2.57	

a Average values calculated by compilers

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. A monel metal bomb with two chambers connected with a needle valve was used. In the upper compartment $ZrCl_4$ and SO_2 were equilibrated for 12-14 h. A sample of the saturated solution was taken through the needle valve into the lower compartment. After cleaning the upper compartment the bomb was weighed, the needle valve loosened and SO_2 from the sample allowed to vaporize in a dessicator under a current of dry air. The residue was washed out and analyzed for Zr by the phosphate method (ref 1). Samples of the solid at or below -10°C analyzed as $ZrCl_4 \cdot SO_2$.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$ repeatedly recrystallized, was ignited to ZrO_2 and chlorinated to $ZrCl_4$. Source and purity of starting material not specified.

(2) SO_2, commercial grade, purified by passing it through concentrated H_2SO_4 and Na bisulfite solution, and dried by means of $CaCl_2$ and P_2O_5.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 1-2 %.

REFERENCES:

1. Lundell, G.E.F.; Knowles, H.B. *J. Am. Chem. Soc.* 1919, *41*, 1801.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

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

ORIGINAL MEASUREMENTS:

Komissarova, L.N.; Plyushchev, V.E.; Kremenskaya, I.N.

**Zh. Neorg. Khim.* 1960, *5*, 586-92; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1960, *5*, 281-4.

VARIABLES:

T/K = 271-378

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

t/°C	$ZrOCl_2$ mass%	m_1/mol kg^{-1a}
-2	34.11	2.90
0	34.30	2.94
5	34.71	2.99
10	35.26	3.06
15	36.15	3.21
20	36.69	3.25
25	37.07	3.30
30	37.65	3.38
35	38.55	3.52
40	38.69	3.54
45	38.98	3.59
50	39.95	3.73
55	41.83	4.04
60	45.34	4.66
65	51.17	5.88
70	60.02	8.43
70.5	60.74	8.69
72	57.72	7.66
75	53.24	6.39
80	49.90	5.59
85	48.32	5.24
90	47.64	5.10
95	47.15	5.01
100	46.66	4.91
105	46.58	4.89

a. Calculated by compiler

Up to 72° the solid phase is zirconium dichloride oxide octahydrate, $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]. Above 72°, due to partial hydrolysis of Zr(IV), the solid phase contained less Cl^- than would correspond to $ZrOCl_2 \cdot 8H_2O$. The decrease in solubility above 72° was accordingly explained by lower solubility of the hydrolyzed species.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 24 h (2 h were necessary to reach equilibrium). Up to 50°, samples for analysis were taken by means of a pipette with a thermostated jacket. Above 50° samples were sucked into a weighed glass tube. Zr was determined gravimetrically as ZrO_2, Cl^- gravimetrically as AgCl.

SOURCE AND PURITY OF MATERIALS:

(1) Specpure $ZrOCl_2 \cdot 8H_2O$ was purified by ion-exchange chromatography to reduce Hf content to < 0.01%, and then 5-times recrystallized from 6 mol dm^{-3} HCl.

(2) Source and purity of water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.05 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Zirconium chloride oxide or dichlorooxozirconium; $ZrOCl_2$; [7699-43-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia June 1985

CRITICAL EVALUATION:

An evaluation of the solubility of $ZrOCl_2$ in aqueous hydrogen chloride solutions.

Although four literature sources (ref 1-4) on the $ZrOCl_2$ + HCl + H_2O system are available their data are not strictly comparable. The work of Hevesy (ref 1) gives the solubility in mol dm^{-3} at 20 °C whereas the other three sources give the solubility in mol kg^{-1}. Of the later three, the data of Schmid (ref 2) cannot be used for comparison because the equilibrium concentration of HCl was not given. Schmid's results are based on a solution that was initially 37% HCl. He used the solid $ZrOCl_2 \cdot 8H_2O$ and, as he mentions himself, he did not take into account the dilution of the system by the dissolved water of crystallization.

In comparing the data published by Goroshchenko and Spasibenko (ref 3) for 0, 30, 50 and 70 °C and by Kamaeva *et al.* (ref 4) at 25 °C the regions for low and high HCl concentration should be considered separately. The data of Kamaeva *et al.* (ref 4) for 25 °C are compared with the 30 °C data of Goroshchenko and Spasibenko (ref 3) in Figure 1. At low HCl concentrations the two data sets differ considerably. The most obvious reason for the difference is that Goroshchenko and Spasibenko started with solid hydrated ZrO_2 rather than $ZrOCl_2$. A comparison of the data at high acidities is not possible because of the difference in temperature used by the two laboratories. Another discrepancy is that although Goroshchenko and Spasibenko clearly show that the solubility increases with temperature, the data of Kamaeva *et al.* at 25 °C are higher than the Goroshchenko *et al.* data at 30 °C. A possible reason for the difference may be in the method of determination of the equilibrium HCl concentration. Kamaeva *et al.* used titration with alkali in hot solutions while the other workers (ref 3) did not mention the analytical method used.

The features in which the papers (ref 1, 3, 4) agree is the increase of $ZrOCl_2$ solubility in the high acidity range. This is caused by anionic chloro-complexes of Zr(IV).

Tentative values: Due to the lack of agreement among the published data, the evaluator cannot recommend any data. For tentative values, the evaluator suggests the 298 K data of Kamaeva *et al.* (ref 4) and the 293 K data of Hevesy (ref 1) be used for the mol kg^{-1} and mol dm^{-3} scales, respectively (see the compilations for the numerical values).

REFERENCES:

1. von Hevesy, G.
   Kgl. Danske Videnskab. Selskab. 1925, *6*, No. 7
2. Schmid, P.
   Z. Anorg. Allgem. Chem. 1927, *167*, 369.
3. Goroshchenko, Ya. G.; Spasibenko, T. P.
   Zh. Neorg. Khim. 1962, *7*, 1159.
4. Kamaeva, I. G.; Melnik, V. V.; Serebrennikov, V. V.
   Zh. Neorg. Khim. 1968, *13*, 1974.

COMPONENTS:

(1) Zirconium chloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

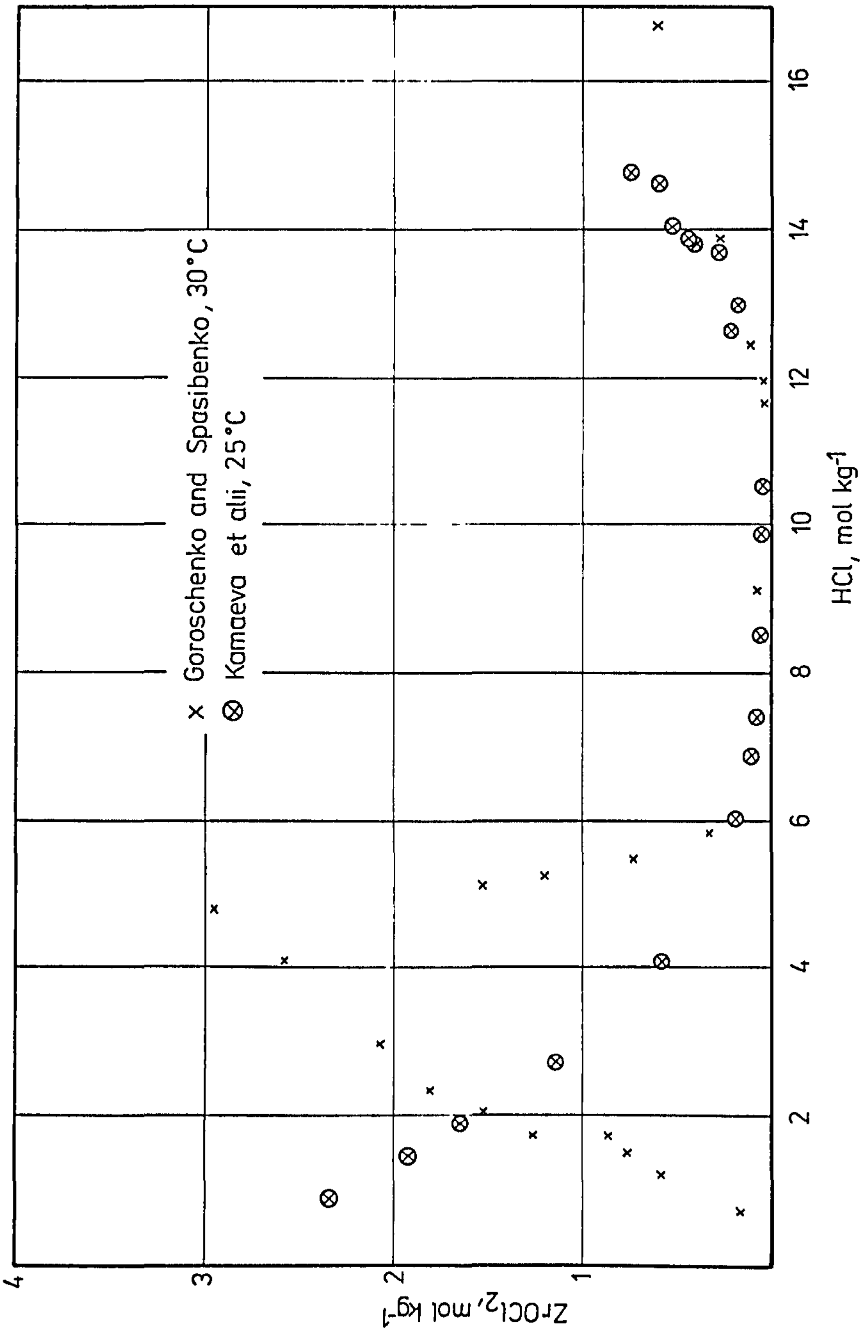
(3) Water; H_2O; [7732-18-5]

EVALUATOR:

J. Hála
Department of Inorganic Chemistry
J. E. Purkyne University
61 137 Brno, Czechoslovakia

June 1985

CRITICAL EVALUATION:



COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

von Hevesy, G.

Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk. 1925, *6*, 1-149.

VARIABLES:

$T/K = 293$
$c_2/\text{mol dm}^{-3} = 0.2\text{-}11.61$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $ZrOCl_2$ in aqueous HCl at 20°C

HCl $c_2/\text{mol dm}^{-3}$	$ZrOCl_2$ $c_1/\text{mol dm}^{-3}$
0.2	2.91
1.47	2.14
3.72	0.832
4.97	0.329
5.81	0.157
6.35	0.1037
8.72	0.0547
10.14	0.00988
10.94	0.205
11.61	0.334

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. The solid used for the solubility measurements was $ZrOCl_2 \cdot 3H_2O$. Zr was determined gravimetrically as ZrO_2 after evaporation of the samples with H_2SO_4. Total Cl^- content determined by Volhard's method; HCl concentration found by difference. The author does not report on the composition of solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) ZrO_2 containing 0.4% HfO_2 was converted to $ZrOCl_2 \cdot 8H_2O$ which was heated in a stream of HCl to yield $ZrOCl_2 \cdot 3H_2O$.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Schmid, P.

Z. Anorg. Allg. Chem. 1927, *167*, 369-84.

VARIABLES:

T/K = 273-341
HCl /mass % = 30.3-33.4

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $ZrOCl_2$ in aqueous HCl between 0 and 68°C

	$ZrOCl_2 \cdot 8H_2O$	$ZrOCl_2$		HCl	
t/°C	mass%	mass%[a]	m_1/mol kg^{-1}[a]	mass%[b]	m_2/mol kg^{-1}[a]
0	2.72	1.50	0.129	33.4	14.07
10	3.15	1.74	.150	33.1	13.93
20	4.51	2.49	.216	32.9	13.97
30	6.42	3.55	.308	31.8	13.49
40	9.67	5.35	.476	31.6	13.75
50	14.19	7.84	.712	30.3	13.43
60	20.45	11.30	-	-	-
68	23.85	13.18	1.325	31.0	15.22

a. Calculated by compiler

b. Calculated by author

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Zr determined gravimetrically as ZrO_2. The author does not report on the composition of the solid phases. Dissolution of $ZrOCl_2 \cdot 8H_2O$ was carried out in 37.05 (mass)% HCl. Due to the dilution of HCl with crystal water from the dissolved salt the equilibrium HCl concentration was not constant (see Experimental Values).

SOURCE AND PURITY OF MATERIALS:

Not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 1-2 %

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	Goroshchenko, Ya. G.; Spasibenko, T. P. **Zh. Neorg. Khim.* <u>1962</u>, *7*, *1159-68*; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1962</u>, *7*, 595-9.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 0°C

HCl	ZrO_2	$ZrOCl_2$^{a}		Nature of the Solid Phase^b
mass%	mass%	mass%	m_1/mol kg^{-1}	
1.87	0.86	1.24	.0718	A
3.26	1.44	2.08	.123	A
5.11	4.29	6.20	.392	A
7.09	6.45	9.32	.626	A
8.73	8.37	12.09	.856	A
9.59	10.61	15.34	1.15	A
11.13	12.35	17.85	1.41	A
12.50	14.45	20.89	1.76	A
13.00	18.25	26.38	2.44	A
14.00	19.21	27.77	2.68	A
14.48	23.60	34.12	3.73	A
14.99	14.41	20.83	1.82	A+B
15.57	5.32	7.69	.565	B
18.73	1.75	2.53	.180	B
21.24	.81	1.71	.125	B
23.95	.61	.882	.0659	B
26.90	.31	.448	.0346	B
28.34	.29	.419	.0330	B
30.14	.41	.593	.0477	B+C
32.67	.78	1.13	.0944	C
33.95	.83	1.20	.104	C
37.14	2.24	3.24	.305	C
39.53	2.97	4.29	.429	C

Composition of Saturated Solutions at 30°C

				Nature of the Solid Phase^b
2.56	1.96	2.83	.168	A
4.21	6.66	9.62	.627	A
5.17	8.64	12.49	.852	A
5.85	9.41	13.60	.948	A
5.93	13.19	19.07	1.43	A
7.00	15.95	23.05	1.85	A
7.81	18.23	26.35	2.25	A
9.75	20.31	29.36	2.71	A
13.00	24.10	34.84	3.75	A
14.82	26.69	38.58	4.55	A+B
15.73	16.05	23.20	2.13	B
16.06	12.98	18.76	1.62	B
16.59	8.23	11.90	.934	B
17.51	3.92	5.67	.414	B
21.46	1.20	1.73	.126	B
24.92	.96	1.39	.106	B
29.81	.55	.795	.0643	B
30.32	.61	.882	.0720	B
31.20	.53	.766	.0632	B+C
33.58	3.42	4.94	.451	C
37.90	6.87	9.93	1.07	C

Continued on the next page. . .

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS

Goroshchenko,Ya.G.; Spasibenko, T.P.

Zh. Neorg. Khim. 1962, *7*, 1159-68; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1962, *7*, 595-9.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 50°C

HCl mass%	ZrO_2 mass%	$ZrOCl_2$[a] mass%	$ZrOCl_2$[a] m_1/mol kg^{-1}	Nature of the Solid Phase[b]
2.21	2.63	3.80	.227	A
3.08	5.69	8.22	.521	A
3.91	8.87	12.82	.864	A
5.32	12.19	17.62	1.27	A
5.63	15.03	21.73	1.68	A
7.82	19.98	28.88	2.56	A
8.03	20.11	29.07	2.64	A
11.24	24.47	35.37	3.72	A
12.11	26.93	38.93	4.46	A
13.86	27.13	39.22	4.69	A
14.75	30.15	43.58	5.87	A+B
16.01	22.19	32.08	3.47	B
16.89	16.11	23.29	2.19	B
17.82	12.61	18.23	1.60	B
18.52	6.45	9.32	.725	B
20.26	3.08	4.45	.332	B
25.17	1.32	1.91	.147	B
26.40	1.71	2.47	.195	B
30.57	3.96	5.72	.504	B
32.60	6.83	9.87	.963	B
33.57	8.29	11.98	1.04	B

Composition of Saturated Solutions at 75°C

				Nature of the Solid Phase[b]
1.57	2.28	3.30	.195	A
2.67	8.64	12.49	.826	A
3.98	14.83	21.44	1.61	A
4.31	14.97	21.64	1.64	A
5.53	19.38	28.02	2.37	A
7.44	24.59	35.55	3.50	A
9.39	30.79	44.51	5.42	A
12.87	30.61	44.25	5.79	A
12.90	31.42	45.42	6.12	A+B
16.74	33.14	47.91	7.61	B
17.98	22.03	31.85	3.56	B
20.63	11.34	16.39	1.46	B
21.86	5.64	8.15	.654	B
26.50	4.26	6.16	.514	B
27.90	5.40	7.81	.681	B
29.56	6.92	10.00	.929	B
30.21	8.12	11.74	1.14	B

a. Calculated by compiler

b. A: $ZrO_2 \cdot xH_2O$

B: $ZrOCl_2 \cdot 8H_2O$; [13520-92-8]

C: $ZrOCl_2 \cdot 3H_2O$; [66905-82-6]

Continued on the next page...

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Goroshchenko,Ya.G.; Spasibenko, T.P.

**Zh. Neorg. Khim.* 1962, *7*, 1159-68; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1962, *7*, 595-9.

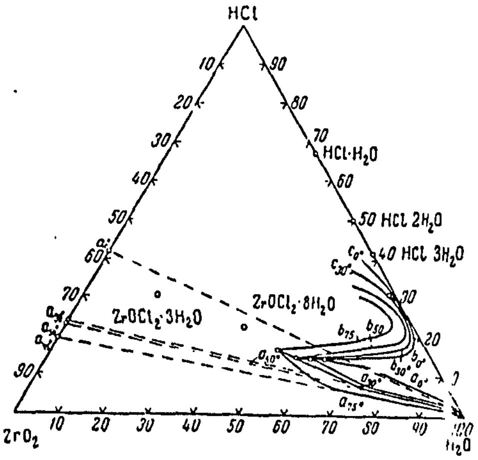
VARIABLES:

$T/K = 273-348$
HCl/mass% = 1.57-39.53

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



A and a: $ZrO_2 \cdot xH_2O$

B and b: $ZrOCl_2 \cdot 8H_2O$

C and c: $ZrOCl_2 \cdot 3H_2O$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid, either Zr hydroxide or $ZrOCl_2$, were mixed for 3 hours-8 days. Equilibrium was slow in the regions of hydrolysis and $ZrOCl_2 \cdot 8H_2O$ crystallization. In the range of high HCl concentrations the systems were prepared by saturating aqueous solutions of $ZrOCl_2$ with gaseous HCl. Analytical methods not given. Solid phases were identified by microscopy, chemical analysis, and Schreinemakers' method.

ESTIMATED ERROR

Temp: precision ± 0.1 K.
The solubility error cannot be estimated since the methods of analysis were not given.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$ prepared from tech. grade ZrO_2 and purified from Hf by ferrocyanide method and by cyclohexanone extraction. After recrystallization from aqueous HCl its Hf content was less than 0.02%. Zr hydroxide was prepared by passing a $ZrOCl_2$ solution through an anion exchange resin in OH^- form to remove free HCl. Neutral $ZrOCl_2$ solution was then mixed with anion exchange resin, and Zr hydroxide was obtained by hydrolysis. It was washed with water and dried at 100°. The product contained 44.46% ZrO_2 3.67% HCl and 51.87% H_2O.

(2) Source and purity of HCl not specified.

(3) Distilled water.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Kamaeva, I.G.; Melnik, L.A.; Serebrennikov, V.V.

**Zh. Neorg. Khim.* 1968, *13*, 1974-80; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 1026-9.

VARIABLES:

T/K = 298
m_2/mol kg^{-1} = 0-18.06

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES: Solubility of $ZrOCl_2$ in aqueous HCl at 25 C

HCl mass%	HCl m_2/mol kg^{-1a}	$ZrOCl_2$ mass%	$ZrOCl_2$ m_1/mol kg^{-1a}	Nature of the Solid Phase^b
0	0	39.69	3.69	A
3.21	1.30	29.35	2.44	A
5.01	1.98	25.51	2.06	A
6.50	2.51	22.59	1.79	A
9.03	3.34	16.85	1.28	A
12.93	4.62	9.37	.686	A
18.09	6.31	3.27	.233	A
20.06	7.05	1.91	.137	A
21.32	7.58	1.50	.109	A
23.72	8.65	1.07	.0798	A
26.47	10.01	1.03	.0797	A
27.78	10.67	0.80	.0629	A
31.54	13.38	3.79	.329	A
32.17	13.62	3.06	.265	B
33.28	14.72	4.71	.426	B
33.50	15.32	6.54	.612	B
33.58	15.45	6.83	.643	B
33.62	15.60	7.29	.693	B
33.92	16.19	8.61	.841	B
34.78	17.42	10.50	1.08	B
35.01	18.06	11.82	1.25	B

a. Calculated by compilers

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8] B: $ZrOCl_2 \cdot 2HCl \cdot 10\ H_2O$ ($H_2ZrOCl_4 \cdot 10H_2O$)

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used as described previously. Solutions containing excess solid were mechanically mixed, and equilibrium was assumed to be reached in 8 days by analogy to previous results (ref 1). Zr determined by compolexometric titration using Xylenol Orange as an indicator. HCl determined by titration with NaOH against Methyl Orange in heated solutions. Solid phases were identified by the method of Schreinemakers and by microscopy.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, twice recrystallized from aqueous HCl.

(2) HCl prepared from cp grade NaCl and H_2SO_4.

(3) Distilled water was used.

ESTIMATED ERROR:

Temp: precision ± 0.05 K.
Soly: precision ± 1-2 %.

REFERENCES:

1. Kamaeva, I.G.; Serebrennikov, V.V. *Zh. Neorg. Khim.* 1963, *8*, 2151; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1963, *8*, 1124.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Ammonium chloride; NH_4Cl; [12125-02-9]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol. 1967, *10*, 255-8.

VARIABLES:

T/K = 298
m_2/mol kg^{-1} = 0-7.31

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions				Nature of the Solid Phase^b
NH_4Cl		$ZrOCl_2$		
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	
0	0	37.60	3.38	A
3.20	0.966	34.90	3.17	A
5.68	1.74	33.20	3.05	A
6.70	2.08	32.96	3.07	B
7.64	2.35	31.55	2.91	B
8.66	2.62	29.57	2.69	B
10.80	3.18	25.75	2.28	B
12.14	3.51	23.22	2.02	B
13.16	3.77	21.59	1.86	B
16.10	4.53	17.50	1.48	B
20.12	5.49	11.35	0.930	B
23.89	6.32	5.43	0.431	B
28.12	7.31	0	0	C

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: solid solution of $ZrOCl_2$ in NH_4Cl; C: NH_4Cl [12125-02-9]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 10-12 h. Total Cl^- content determined by Volhard's method; Zr determined gravimetrically as ZrO_2. NH_4Cl concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3} HCl.

(2) NH_4Cl, reagent grade, recrystallized from water.

(3) Source and purity of water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Trimethylammonium chloride; $(CH_3)_3NHCl$; [593-81-7]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1970, *15*, 2572-3; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1970, *15*, 1333.

VARIABLES:

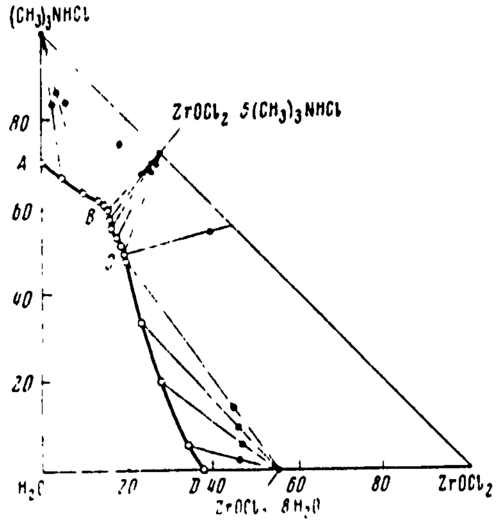
T/K = 298
Composition

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

The authors report numerical values for only two saturated solutions, at the eutonic points. The remaining solubility data were presented graphically.



Composition at the Eutonic Points

$(CH_3)_3NHCl$		$ZrOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
60.30	27.61	16.85	4.140
51.50	18.68	19.65	3.824

a. Calculated by compilers

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Equilibrium solid phases were studies by X-ray diffraction, thermal analysis, crystal-optical analysis, and infrared spectroscopy. No other details were given, but the isothermal method was probably used as in earlier work (ref 1).

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temp: precision 0.1 K (ref 1).
Soly: precision 1-2 % (compiler, ref 1).

REFERENCES:

1. Barskaya, I.B.; Morozov, I.S. *Zh. Neorg. Khim.* 1968, *13*, 1408; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, (For details see the compilations for this paper.)

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Zinc Chloride; $ZnCl_2$; [7646-85-7]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.; Efimushkhina, L.I.

**Zh. Prikl. Khim. (Leningrad)* 1977, *50*, 1233-7; *J. Appl. Chem. USSR (Engl. Transl.)* 1977, *50*, 1188-91.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions					
$ZnCl_2$ mass%	m_2/mol kg^{-1} a	$ZrOCl_2$ mass%	m_1/mol kg^{-1} a	Density g cm^{-3}	Nature of the Solid Phase^b
-	-	37.70	3.40	1.492	A
4.80	0.586	35.11	3.28	1.555	A
13.92	1.98	34.52	3.76	1.685	A
20.03	3.12	32.82	3.91	1.755	A
25.17	4.33	32.17	4.23	1.775	A
29.16	5.53	32.13	4.66	1.805	A
32.20	6.57	31.85	4.97	1.9000	A+B
34.49	6.71	27.81	4.14	1.891	B
38.45	7.23	22.55	3.25	1.854	B
42.98	8.15	18.32	2.66	1.876	B
47.97	9.14	13.51	1.97	1.904	B
54.86	11.16	9.08	1.41	1.950	B
58.93	12.55	6.60	1.075	2.025	B
62.27	13.52	3.93	0.653	2.085	B
63.73	14.15	3.21	0.545	2.150	B
64.50	14.79	3.50	0.614	2.205	B
71.20	21.59	4.60	1.067	2.285	B
74.87	28.66	5.96	1.745	2.350	B+C
75.28	28.50	5.34	1.547	2.307	C
75.25	27.93	4.98	1.414	2.255	C
74.50	23.65	2.38	0.578	2.050	C
76.95	24.50	-	-	2.066	C

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $ZrOCl_2 \cdot ZnCl_2 \cdot 6.5H_2O$ (to which the structure of $[Zr_4(OH)_8(H_2O)_{20}][ZnCl_4]_4 \cdot 2H_2O$ was ascribed); C: $ZnCl_2$ [7646-85-7]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 15-30 h. Zr and Zn were determined titrimetrically with EDTA, total Cl^- content determined by Volhard's method. Solid phases were identified by Schreinemakers' method. Viscosities and electrical conductivities also reported for the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) Not specified. Presumably $ZrOCl_2 \cdot 8H_2O$ was reagent grade and recrystallized from 6 mol dm^{-3} HCl as in the authors' earlier work (ref 1).

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, from ref 1).
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Belyaev, I.N.; Lobas, L.M. *Zh. Neorg. Khim.* 1965, *10*, 946; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Cadmium chloride; $CdCl_2$; [10108-64-2]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L. M.; Efimushkhina, L.I.

**Zh. Neorg. Khim.* 1972, *17*, 3075-8; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1972, *17*, 1617-9.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions
t/°C = 25

$CdCl_2$		$ZrOCl_2$		Density	Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	g cm^{-3}	
0	0	37.60	3.383	1.492	A
4.03	0.355	34.11	3.096	1.527	A
8.53	0.794	32.88	3.150	1.600	A
14.73	1.50	31.65	3.314	1.700	A
19.35	2.10	30.48	3.411	1.747	A
23.72	2.72	28.67	3.381	1.771	A
29.66	3.72	26.90	3.476	1.820	A+B
29.04	3.54	26.20	3.286	1.825	B
29.07	3.45	24.96	3.048	1.827	B
33.52	3.93	20.00	2.416	1.843	B
38.08	4.56	16.39	2.021	1.871	B
39.51	4.72	14.84	1.825	1.873	B
40.10	4.86	14.89	1.857	1.892	B+C
40.28	4.90	14.87	1.861	1.889	C
44.34	5.24	9.53	1.16	1.817	C
46.87	6.36	4.91	0.685	1.745	C
49.74	6.77	2.21	0.310	1.731	C
53.05	6.16	0	0	1.757	C

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $1.75CdCl_2 \cdot ZrOCl_2 \cdot 10H_2O$;
C: $CdCl_2 \cdot 2.5H_2O$ [7790-78-5].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for unspecifed period of time. Zr and Cd were determined titrimetrically with EDTA, total Cl^- content determined by Volhard's method. The source paper also lists electrical conductivities and viscosities of each of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) Not specified. Presumably $ZrOCl_2 \cdot 8H_2O$ was reagent grade and recrystallized from 6 mol dm^{-3} HCl as in the authors' previous work (ref 1).

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, from ref 1).
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Belyaev, I.N.; Lobas, L.M. *Zh. Neorg. Khim.* 1965, *10*, 946; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Copper(II) chloride; $CuCl_2$; [7447-39-4]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.; Efimushkina, L.I.; Dvoskina, V.N.

**Zh. Neorg. Khim.* <u>1971</u>, *16*, 3392-3; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1971</u>, *16*, 1795-7.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:[a]

Composition of Saturated Solutions at 25°C

$CuCl_2$		$ZrOCl_2$		Nature of the Solid Phase[c]
mass%	m_2/mol kg^{-1}[b]	mass%	m_1/mol kg^{-1}[b]	
0	0	37.60	3.38	A
3.27	0.393	34.77	3.15	A
6.39	0.774	32.19	2.94	A
10.80	1.34	28.10	2.62	A
16.46	2.10	25.36	2.45	A
21.17	2.79	22.35	2.22	A
22.40	2.99	21.85	2.20	A+B
25.22	3.34	18.68	1.87	B
30.64	4.08	13.45	1.35	B
35.52	4.67	7.90	0.784	B
40.50	5.43	3.02	0.306	B
43.50	5.73	0	0	B

a. In the original document only graphical representation of the solubility isotherm was given. The numerical data for this compilation were made available by the authors.

b. Calculated by compiler

c. $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $CuCl_2 \cdot 2H_2O$ [10125-13-0].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for unspecified period of time. Zr was determined titrimetrically with EDTA against Xylenol Orange, Cu was titrated with EDTA against Murexide in the filtrate after precipitation of Zr hydroxide. Cl^- determined by Volhard's method. Solid phases were identified by chemical analysis and by Schreinemaker's method.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Magnesium chloride; $MgCl_2$; [7786-30-3]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

Zh. Neorg. Khim. 1968, *13*, 2295-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 1185-7.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hàla and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

$MgCl_2$		$ZrOCl_2$		Density	Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	ρ/g cm^{-3}	
0	0	37.60	3.383	1.492	A
4.00	0.457	28.97	2.426	1.420	A
11.08	1.202	18.36	1.461	1.344	A
15.50	1.614	11.01	0.841	1.297	A
18.64	1.912	6.74	0.507	1.266	A
20.02	2.045	5.07	0.380	1.248	A
25.14	2.596	0.76	0.0576	1.241	A
29.70	3.254	0.45	0.0362	1.278	A
32.65	3.714	0.08	0.0068	1.309	A
34.87[c]	4.110	0.20	0.0173	1.332	A+B
35.08	4.135	0	0	1.333	B

a. Calculated by compilers

b. A: $ZrOCl_2\cdot 8H_2O$ [13520-92-8]; B: $MgCl_2\cdot 6H_2O$ [7791-18-6]

c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experimental details stated to be similar to those reported in earlier work (refs 1,2). Isothermal method was used. Solutions with excess solid were stirred for 8-10 h at 25°C. Total Cl content determined by Volhard's method, Zr determined by chelatometric titration in 5 mol dm^{-3} HCl. Method for analysis of Mg not given. Solid phases were analysed using the Schreinemakers' method of wet residues.

In the source paper, the authors also report the viscosities (η) and electrical conductivities (κ) for each of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2\cdot 8H_2O$ was recrystallized from 6 mol dm^{-3} HCl (refs 1,2).

(2) Reagent grade $MgCl_2\cdot 6H_2O$ was recrystallized from water.

(3) Sources and purities of water and HCl were not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, refs 1, 2).
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Belyaev, I.N.; Lobas, L.M. *Zh. Neorg. Khim.* 1965, *10*, 946. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512.
2. Belyaev, I.N.; Lobas, L.M. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1967, *3*, 285.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Calcium chloride; $CaCl_2$; [10043-52-4]

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

ORIGINAL MEASUREMENTS

Kamaeva, I.C.; Serebrennikov, V.V.

Tr. Tomsk. Gos. Univ. 1963, *157*, 131-4.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 25°C

$CaCl_2$		$ZrOCl_2$		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0	0	36.96	3.28	A
0.21	0.0299	36.50	3.24	A
3.19	0.443	31.95	2.77	A
7.78	1.064	26.34	2.24	A
8.70	1.166	24.05	2.01	A
12.61	1.67	19.31	1.59	A
15.80	2.03	14.10	1.13	A
20.75	2.65	8.60	0.683	A
23.94	3.11	6.68	0.541	A
26.91	3.46	3.04	0.244	A
31.16	4.15	1.11	0.0920	A
36.47	5.20	0.33	0.0293	A
44.20	7.14	0.07	0.00705	A+B
45.23	7.44	0	0	B

Composition of Saturated Solutions at 50°C

$CaCl_2$		$ZrOCl_2$		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0	0	39.98	3.73	A
6.56	0.945	31.50	2.86	A
11.04	1.57	25.58	2.27	A
23.03	3.12	10.55	0.892	A
27.24	3.70	6.47	0.548	A
30.56	4.23	4.35	0.375	A
33.80	4.77	2.40	0.211	A
47.00	8.10	0.71	0.0762	A
54.85	11.10	0.64	0.0807	A+B
56.95	11.92	0	0	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $CaCl_2 \cdot 6H_2O$ [7774-34-7]

Continued on the next page. . .

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Calcium chloride; $CaCl_2$; [10043-52-4]

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

ORIGINAL MEASUREMENTS:

Kamaeva, I.C.; Serebrennikov, V.V.

Tr. Tomsk. Gos. Univ. 1963, *157*, 131-4.

VARIABLES:

T/K = 298, 323
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 2 h. Zr determined either by titration with EDTA or gravimetrically as ZrO_2, Ca determined by titration with EDTA, Cl^- by Volhard's method. Solid phases were identified by chemical analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, containing 0.5-1% Hf, 3-times recrystallized from water.

(2) $CaCl_2 \cdot 6H_2O$, reagent grade.

(3) Source and purity of water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]
(2) Calcium chloride; $CaCl_2$; [10043-52-4]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS

Kamaeva, I.G.; Serebrennikov, V.V.

**Zh. Neorg. Khim.* <u>1963</u>, *8*, 2151-4;
Russ. J. Inorg. Chem. (Engl. Transl.) <u>1963</u>, *8*, 1124-5.

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

$CaCl_2$		HCl		$ZrOCl_2$		Nature of the Solid Phase[g]
mass%	m_2/mol kg^{-1}[a]	mass%	m_3/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0	0	0		36.96	3.29	A
0.24	.0342	0		36.50	3.24	A
3.19	.443	0		31.95	2.77	A
7.78	1.06	0		26.34	2.24	A
8.70	1.17	0		24.05	2.01	A
12.61	1.67	0		19.31	1.59	A
15.80	2.03	0		14.10	1.13	A
20.75	2.65	0		8.60	.683	A
26.91	3.42	0		2.10	.166	A
31.16	4.15	0		1.11	.0920	A
36.47	5.20	0		.33	.0293	A
44.20	7.15	0		.07	.00705	A+C
45.23	7.44	0		0	0	C
0[b]	0	5.00	1.97	25.51	2.06	A
3.73	.476	4.92	1.91	20.75	1.65	A
6.83	.855	4.75	1.81	16.44	1.28	A
10.47	1.30	4.75	1.80	12.49	.970	A
14.18	1.74	4.80	1.79	7.42	.566	A
18.06	2.22	4.86	1.82	3.76	.288	A
22.33	2.81	5.11	1.88	.92	.0721	A
26.55	3.15	5.06	2.04	.29	.0239	A
27.88	3.77	5.13	2.11	.35	.0295	A
29.74	4.13	5.11	2.16	.26	.0225	A
31.92	4.59	5.20	2.28	.26	.0233	B
34.09	5.05	4.86	2.19	.17	.0157	B
41.18	6.90	4.70	2.40	.37	.0386	B+D
43.10	7.49	5.03	2.66	0	0	D
0[c]	0	10.00	3.64	14.70	1.10	A
4.18	.494	9.82	3.53	9.76	.719	A
7.05	.836	9.78	3.53	7.21	.533	A
9.13	1.08	10.20	3.67	4.41	.325	A
10.87	1.29	10.12	3.66	3.17	.235	A
12.77	1.54	9.91	3.63	2.42	.181	A
13.13	1.59	10.28	3.79	2.11	.159	A
18.12	2.30	10.08	3.89	.78	.0617	A
22.35	3.00	9.84	4.01	.59	.0493	A
22.93	3.10	9.83	4.04	.52	.0438	B
27.16	3.87	10.10	4.38	.46	.0408	B
31.58	4.92	9.84	4.67	.75	.0728	B
32.75[f]	5.26	10.14	4.96	1.04	.104	B
33.90	5.60	9.92	4.98	1.60	.165	B
34.73	5.82	9.93	5.07	1.57	.164	B+E
34.93	5.82	9.97	5.06	1.04	.108	E
35.46	5.94	9.88	5.04	.91	.0950	E
36.02	6.07	9.70	4.97	.80	.0840	E
37.54	6.55	10.14	5.38	.66	.0717	E+D
37.30	6.38	10.00	5.20	0	0	D

[g] A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $ZrOCl_2 \cdot 6H_2O$; C: $CaCl_2 \cdot 6H_2O$ [7774-34-7] D: α-$CaCl_2 \cdot 4H_2O$; E: $(ZrOCl_2)_2 \cdot CaCl_2 \cdot HCl \cdot 12H_2O$; F: $ZrOCl_2 \cdot CaCl_2 \cdot 0.5HCl \cdot 10H_2O$; G: β-$CaCl_2 \cdot 4H_2O$

Both α- and β-$CaCl_2 \cdot 4H_2O$ [25094-02-4]
$ZrOCl_2 \cdot 6H_2O$ [25339-81-9]

Continued on the next page. . .

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6] (2) Calcium chloride; $CaCl_2$; [10043-52-4] (3) Hydrogen chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Kamaeva, I.G.; Serebrennikov, V.V. **Zh. Neorg. Khim.* 1963, *8*, 2151-4; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1963, *8*, 1124-5.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 25°C

$CaCl_2$		HCl		$ZrOCl_2$		Nature of the Solid Phase[g]
mass%	m_2/mol kg^{-1}[a]	mass%	m_3/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0[d]	0	15.00	5.25	6.60	.473	A
3.42	.396	15.16	5.34	3.54	.255	A
6.67	.787	15.00	5.39	1.97	.145	A
10.28	1.26	14.90	5.55	1.13	.0861	A
11.88	1.49	15.15	5.77	.94	.0733	A
14.45	1.86	14.70	5.76	.83	.0665	A
15.28	2.00	15.20	6.06	.71	.0580	B
20.35	2.85	14.70	6.28	.72	.0629	B
23.66	3.60	15.30	7.08	1.75	.166	B
25.64	4.04	14.94	7.16	2.17	.213	B
26.21	4.19	14.70	7.15	2.72	.271	B+F
26.59	4.24	15.25	7.40	1.66	.165	F
29.20	4.88	15.25	7.75	1.60	.166	F
31.30	5.43	15.01	7.93	1.75	.189	F
32.00	5.89	14.70	7.82	1.72	.187	F+D+G
31.80	5.39	15.00	7.73	0	0	D+G
0[e]	0	20.00	7.03	2.00	.144	A
2.60	.309	20.10	7.28	1.60	.119	A
4.47	.541	19.88	7.32	1.18	.0890	A
6.77	.843	19.93	7.56	1.01	.0784	A
7.46	.943	20.30	7.81	.98	.0772	A+B
8.28	1.05	19.75	7.63	.98	.0775	B
9.62	1.24	19.75	7.77	.88	.0708	B
10.99	1.44	19.70	7.88	.75	.0614	B
14.10	1.94	19.70	8.27	.87	.0748	B
17.38	2.59	19.88	9.00	2.20	.204	B
17.52	2.66	20.00	9.25	3.20	.303	B
17.90	2.71	19.77	9.13	2.92	.276	B
18.18	2.88	20.10	9.70	4.90	.484	B
18.42	2.93	19.86	9.61	5.04	.499	B
18.85	2.94	20.00	9.48	3.30	.320	E
20.08	3.19	20.16	9.75	3.06	.303	E
20.16	3.20	20.10	9.72	3.05	.302	E
21.36	3.49	20.19	10.03	3.25	.331	E
21.70	3.55	20.20	10.05	2.96	.301	F
22.97	3.81	19.70	9.94	2.98	.308	F
23.72	4.00	19.73	10.12	3.08	.323	F
25.28	4.54	19.80	10.84	4.84	.543	F+D+G
28.80	5.07	20.00	10.71	0	0	D+G

a. Calculated by compiler

b. Initial HCl concentration 5 mass% for this and the following 13 data points

c. Initial HCl concentration 10 mass% for this and the following 19 data points

d. Initial HCl concentration 15 mass% for this and the following 15 data points

e. Initial HCl concentration 20 mass% for this and the following 22 data points

f. The original paper lists also mass% H_2O obtained by difference. For this experimental point the sum of mass% ($HCl+CaCl_2+ZrOCl_2$) was printed mistakenly instead of mass% H_2O. Continued on the next page.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]
(2) Calcium chloride; $CaCl_2$; [10043-52-4]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Kamaeva, I.G.; Serebrennikov, V.V.

**Zh. Neorg. Khim.* 1963, *8*, 2151-4; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1963, *8*, 1124-5.

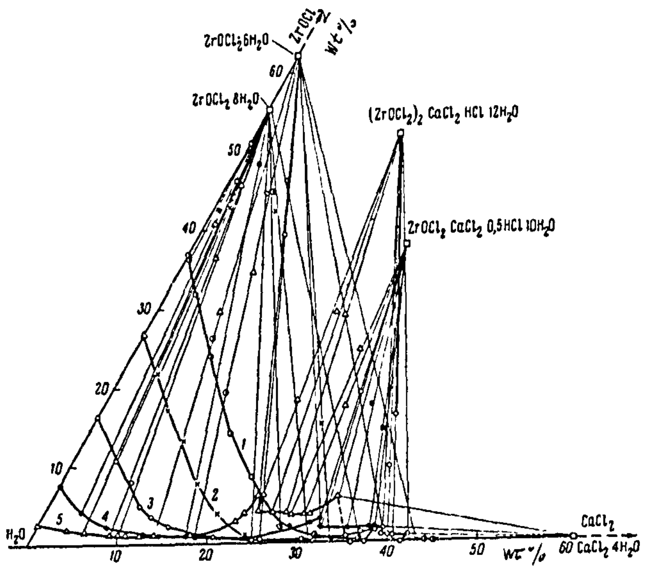
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



g. A: $ZrOCl_2 \cdot 8H_2O$; [13520-92-8] B: $ZrOCl_2 \cdot 6H_2O$; [25339-81-9]
C: $CaCl_2 \cdot 6H_2O$; [7774-34-7] D: α-$CaCl_2 \cdot 4H_2O$; [25094-02-4]
E: $(ZrOCl_2)_2 \cdot CaCl_2 \cdot HCl \cdot 12H_2O$ F: $ZrOCl_2 \cdot CaCl_2 \cdot 0.5HCl \cdot 10H_2O$
G: β-$CaCl_2 \cdot 4H_2O$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. After equilibration the systems were filtered in a thermostated apparatus. Zr and Ca were determined titrimetrically with EDTA using Eriochrome T as indicator. Free HCl was titrated in a heated aliquot against Methyl Orange. Solid phases were identified by Schreinemakers' method, by the method of indifferent additions using $FeCl_3$, and by microscopic analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, containing 0.5-1% Hf, 3-times recrystallized;

(2) $CaCl_2 \cdot 6H_2O$, reagent grade, twice recrystallized.

(3) HCl prepared from reagent grade NaCl and H_2SO_4.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Strontium chloride; $SrCl_2$; [10476-85-4]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

Zh. Neorg. Khim. 1968, *13*, 2295-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 1185-7.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

$SrCl_2$		$ZrOCl_2$		Density	Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	g cm^{-3}	
0	0	37.60	3.38	1.492	A
1.59	0.156	34.34	3.01	1.484	A
5.39	.523	29.58	2.55	1.483	A
12.50	1.22	22.90	1.99	1.479	A
19.29	1.88	16.19	1.41	1.470	A
24.35	2.40	11.65	1.02	1.474	A
25.22[c]	2.51	11.33	1.00	1.475	A+B
26.94	2.65	8.99	.788	1.454	B
28.35	2.78	7.40	.647	1.431	B
34.54	3.33	0	0	1.382	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $SrCl_2 \cdot 6H_2O$ [10025-70-4]

c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experimental details stated to be similar to those reported in earlier work (refs 1,2). Isothermal method was used. Solutions with excess solid were stirred for 8-10 h at 25°C. Total Cl content determined by Volhard's method, Zr determined by chelatometric titration in 5 mol dm^{-3} HCl. Method for analysis of Sr not given. Solid phases were analyzed using the Schreinemakers' method of wet residues.

In the source paper, the authors also report the viscosities (η) and electrical conductivities (κ) for each of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3} HCl.

(2) $SrCl_2 \cdot 6H_2O$, reagent grade, recrystallized from water.

(3) Source and purity of water and HCl not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, refs 1, 2).
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Belyaev, I.N.; Lobas, L.M. *Zh. Neorg. Khim.* 1965, *10*, 946, *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512.
2. Belyaev, I.N.; Lobas, L.M. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1967, *3*, 285.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6] (2) Strontium chloride; $SrCl_2$; [10476-85-4] (3) Hydrogen chloride; HCl; [7647-01-0] (4) Water; H_2O; [7732-18-5]	Belyaev, I.N.; Lobas, L.M.; Efimushkina, L.I. Kantserova, L.V. **Zh. Neorg. Khim.* 1973, *18*, 544-6; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) 1973, *18*, 285-6.

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

$SrCl_2$		HCl		$ZrOCl_2$		Density	Nature of the Solid Phase[f]
mass%	m_2/mol kg^{-1a}	mass%	m_3/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	g cm^{-3}	
0[b]	0	2.42	1.011	31.96	2.734	1.439	A
1.27	0.117	1.68	0.672	28.48	2.332	1.438	A
2.90	0.264	2.31	0.913	25.40	2.055	1.432	A
4.75	0.427	5.22	2.042	19.92	1.595	1.425	A
14.26[e]	1.236	7.24	2.729	5.73	0.442	1.410	A
18.34	1.618	7.31	2.804	2.85	0.224	-	A
25.70[c]	2.401	2.00	0.813	4.79	0.398	1.411	A+B
27.16	2.518	2.04	0.822	2.76	0.228	1.404	B
29.66	2.804	2.25	0.925	1.37	0.115	1.367	B
32.49	3.098	1.35	0.560	0	0	1.374	B
0[d,e]	0	7.52	2.912	21.66	1.717	1.258	A
5.46	0.462	5.89	2.172	14.29	1.079	1.289	A
11.93	0.050	8.64	3.307	7.78	0.610	1.286	A
16.39	1.449	10.28	3.951	1.97	0.155	1.295	A
20.68[c]	1.882	7.33	2.901	2.69	0.217	1.320	A+B
21.39[e]	1.937	7.08	2.787	1.86	0.150	1.315	B
21.48[e]	1.982	8.51	3.413	1.63	0.134	1.318	B
23.87	2.217	7.62	3.077	0.58	0.048	1.308	B
24.40	2.227	6.50	2.580	0	0	1.297	B

a. Calculated by compilers

b. Initial [HCl] = 1.0 mol dm^{-3} for first 10 data points.

c. Eutonic points: each eutonic point was measured twice with identical results.

d. Initial [HCl] = 3.0 mol dm^{-3} for the last 9 data points.

e. The original paper reports mass% of HCl, $SrCl_2$, $ZrOCl_2$ and H_2O, with H_2O obtained by difference; the sum of mass% for these points does not equal 100, and the compilers assume that a typographical error (an average of + 2%) is associated with the concentration of HCl, $SrCl_2$, or $ZrOCl_2$, in addition to the estimated experimental precision of ± 2-5%.

f. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $SrCl_2 \cdot 6H_2O$ [10025-70-4]

Continued on the next page. . .

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]
(2) Strontium chloride; $SrCl_2$; [10476-85-4]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.; Efimushkina, L.I. Kantserova, L.V.

**Zh. Neorg. Khim.* 1973, *18*, 544-6; *Russ. J. Inorg. Chem.* (*Engl. Transl.*) 1973, *18*, 285-6.

VARIABLES:

T/K = 298
Composition
m_3/mol kg^{-1} = 0.560-3.951

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Solutions containing excess solid were equilibrated for 20-25 h. Zr determined by EDTA titration with Xylenol Orange indicator, and Sr by EDTA titration in the presence of tartaric acid; Cl content by Volhard's method. Solid phases were determined by Schreinemakers' method of wet residues.
In the source paper, the authors also report the viscosities (η) and electrical conductivities (κ) for each of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) Not specified, but presumably same as in earlier work, (ref 1), i.e., $ZrOCl_2 \cdot 8H_2O$ (reagent grade) recrystallized from 6 mol dm^{-3} HCl.

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, from ref 1).
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Belyaev, I.M.; Lobas, L.M. *Zh. Neorg. Khim.* 1965, *10*, 946; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512.

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Barium chloride; $BaCl_2$; [10361-37-2]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

**Zh. Neorg. Khim.* 1968, *13*, 2295-9.
Russ. J. Inorg. Chem. (Engl. Transl.) 1968, *13*, 1185-7.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

$BaCl_2$		$ZrOCl_2$		Density	Nature of the Solid phase[b]
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	g cm^{-3}	
0	0	37.60	3.38	1.492	A
0.10[c]	0.00769	36.48	3.28	1.480	A+B
0.18	.0135	35.87	3.15	1.472	A+B
1.12	.0806	32.12	2.70	1.453	A+B
5.52	.367	22.19	1.72	1.426	A+B
10.97	.706	14.45	1.09	1.344	A+B
15.98	1.019	8.70	0.648	1.310	A+B
21.72	1.401	3.83	0.289	1.281	B
25.47	1.64	0	0	1.277	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $BaCl_2 \cdot 2H_2O$ [10326-27-9]

c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Experimental details stated to be similar to those reported in earlier work (refs 1,2). Isothermal method was used. Solutions with excess solid were stirred for 8-10 h at 25°C. Total Cl content determined by chelatometric titration in 5 mol dm^{-3} HCl. Method for analysis of Ba not given. Solid phases were analyzed using the Schreinemakers' method of wet residues.

In the source paper, the authors also report the viscosities (η) and electrical conductivities (κ) for each of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3} HCl.

(2) $BaCl_2 \cdot 2H_2O$, reagent grade, recrystallized from water.

(3) Source and purity of water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K (compiler, refs 1, 2).
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Belyaev, I.N.; Lobas, L.M. *Zh. Neorg. Khim.* 1965, *10*, 946, *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512.
2. Belaev, I.N.; Lobas, L.M. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1967, *3*, 285.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6] (2) Lithium chloride; LiCl; [7447-41-8] (3) Water; H_2O; [7732-18-5]	Belyaev, I.N.; Lobas, L.M. *Izv. Vyssh. Uchebn. Zaved., Khim. Khim. Tekhnol.* 1967, *10*, 255-8.
VARIABLES:	**PREPARED BY:**
T/K = 298 Composition	J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C				Nature of the Solid Phase[b]
LiCl		$ZrOCl_2$		
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	
0	0	37.60	3.38	A
2.07	0.748	32.62	2.80	A
2.87	1.02	30.95	2.63	A
5.54	1.90	25.76	2.11	A
10.03	3.32	18.65	1.47	A
13.67	4.40	12.97	0.993	A
19.88	6.31	5.77	0.436	A
27.80	9.23	1.12	0.0885	A
30.22	10.29	0.50	0.0405	A
33.41	11.98	0.80	0.0683	A
37.70	14.47	0.84	0.0767	A
39.00	15.33	1.00	0.0936	A
43.80	18.77	1.16	0.118	A
44.25	19.14	1.20	0.123	A,B
44.70	19.27	0.57	0.0585	B
45.87	19.99	0	0	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8] B: $LiCl \cdot H_2O$ [16712-20-2]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Isothermal method used. Solutions containing excess solid were mixed for 10-12 h. Total Cl^- content determined by Volhard's method; Zr determined gravimetrically as ZrO_2; LiCl concentration found by difference. Solid phases were identified by chemical analysis and by Schreinemakers' method.	(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3} HCl. (2) LiCl, reagent grade, recrystallized from water. (3) Source and purity of water and HCl not specified.
	ESTIMATED ERROR:
	Temp: precision ± 0.1 K. Soly: precision ± 1-2 % (compiler).
	REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Sodium chloride; NaCl; [7647-14-5]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

**Zh. Neorg. Khim.* 1965, *10*, 946-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 512-4.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

NaCl		$ZrOCl_2$		Density	Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	g cm^{-3}	
0	0	37.60	3.38	1.492	A
2.81	0.761	34.00	3.02	1.455	A
5.52	1.49	31.00	2.74	1.449	A
7.00	1.868	28.90	2.531	1.434	A
7.08c	1.886	28.70	2.509	1.432	A+B
7.51	2.01	28.53	2.505	1.421	B
8.08	2.15	27.66	2.416	1.388	B
12.50	3.17	20.02	1.67	1.345	B
13.06	3.30	19.26	1.60	1.330	B
16.51	4.07	14.14	1.14	1.296	B
20.63	4.93	7.82	0.614	1.247	B
26.71	6.24	-	-	1.195	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: NaCl [7647-14-5]

c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 8-10 h. Total Cl^- content determined by Volhard's method, Zr determined gravimetrically as ZrO_2. NaCl concentration found by difference. Solid phases were identified by Schreinemakers' method. The original paper also gives electrical conductivities and viscosities of saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3} HCl.

(2) NaCl, reagent grade, recrystallized from water.

(3) Source and purity of water and HCl not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Potassium chloride; KCl; [7447-40-7]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

**Zh. Neorg. Khim.* <u>1965</u>, *10*, 946-9; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1965</u>, *10*, 512-4.

VARIABLES:

$T/K = 298$
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

KCl		$ZrOCl_2$		Density	Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	g cm^{-3}	
0	0	37.60	3.38	1.4916	A
3.07	0.664	34.90	3.158	1.4916	A
3.92	0.857	34.71	3.175	1.4870	A
4.16c	0.908	34.40	3.143	1.4860	A+B
4.20	0.904	33.47	3.014	1.4891	B
4.45	0.937	31.85	2.81	1.454	B
7.12	1.456	27.27	2.33	1.399	B
8.85	1.778	24.37	2.05	1.354	B
11.89	2.31	19.19	1.56	1.313	B
12.16	2.36	18.64	1.51	1.303	B
16.11	3.04	12.83	1.01	1.258	B
19.50	3.59	7.60	0.585	1.200	B
26.80	4.91	-	-	1.1775	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8] B: KCl [7447-40-7]

c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 8-10 h. Total Cl^- content determined by Volhard's method, Zr determined gravimetrically as ZrO_2. KCl concentration found by difference. Solid phases were identified by Schreinemakers' method. The original paper also gives electrical conductivities and viscosities of saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3} HCl.

(2) KCl, reagent grade, recrystallized from water.

(3) Source and purity of water and HCl not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Rubidium chloride; RbCl; [7791-11-9]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

**Zh. Neorg. Khim.* 1968, *13*, 1149-54; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 601-4.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

RbCl		$ZrOCl_2$		Density	Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	g cm^{-3}	
0	0	37.60	3.383	1.492	A
3.92	0.538	35.80	3.334	1.530	A
12.31	1.82	31.84	3.200	1.582	A
15.89	2.47	31.01	3.279	1.600	A
19.22	3.10	29.51	3.231	1.634	A
20.61[c]	3.32	28.13	3.081	1.639	A,B
20.80	3.35	27.80	3.036	1.631	B
22.14	3.52	25.78	2.779	1.625	B
28.28	4.37	18.18	1.906	1.564	B
36.46	5.73	10.89	1.161	1.531	B
48.50	7.79	0	0	1.487	B

a. Calculated by compiler

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: RbCl [7791-11-9]

c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 8-10 h. Total Cl^- content determined by Volhard's method. Zr determined gravimetrically as ZrO_2. RbCl content found by difference. Solid phases were identified by Schreinemakers' method. The source paper also lists viscosities and electrical conductivities of saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$ reagent grade, recrystallized from 6 mol dm^{-3} HCl.

(2) RbCl, reagent grade, recrystallized from water.

(3) Source and purity of water and HCl not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Cesium chloride; CsCl; [7647-17-8]

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

ORIGINAL MEASUREMENTS:

Belyaev, I.N.; Lobas, L.M.

**Zh. Neorg. Khim.* 1968, *13*, 1149-54; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 601-4.

VARIABLES:

$T/K = 298$
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

CsCl mass%	CsCl m_2/mol kg^{-1} [a]	$ZrOCl_2$ mass%	$ZrOCl_2$ m_1/mol kg^{-1} [a]	Density g cm^{-3}	Nature of the Solid Phase[b]
0	.0190	37.60	3.383	1.492	A
0.20	.139	37.17	3.332	1.511	A
1.47	.431	35.91	3.219	1.541	A
4.42	.670	34.61	3.187	1.537	A
6.65	.767	34.42	3.279	1.631	A
7.50c	.952	34.45	3.332	1.642	A,B
9.21	1.337	33.31	3.253	1.664	B
12.63	1.76	31.26	3.129	1.687	B
16.38	2.23	28.36	2.881	1.725	B
19.80	2.94	27.37	2.909	1.725	B
24.93	3.38	24.73	2.758	1.778	B
27.73	4.04	23.55	2.713	1.820	B
31.95	4.75	21.04	2.513	1.861	B
35.66	5.53	19.77	2.490	1.866	B
39.60	6.37	17.88	2.361	1.897	B
43.30	6.98	16.30	2.265	1.961	B
45.53c	7.32	15.74	2.282	1.971	B,C
48.34	8.12	12.45	1.782	1.940	C
52.25	9.22	9.51	1.396	1.939	C
57.47	10.06	5.52	.837	1.932	C
61.73	11.03	1.81	.279	1.918	C
65.00		0	0	1.912	C

a. Calculated by compiler
b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $CsCl \cdot 2\ ZrOCl_2 \cdot 18H_2O$; C: CsCl [7647-17-8]
c. Eutonic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were mixed for 8-10 h. Total Cl^- content determined by Volhard's method, Zr determined gravimetrically as ZrO_2. CsCl concentration found by difference. Solid phases were identified by Schreinemakers' method. The source paper also lists viscosities and electrical conductivities of saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOCl_2 \cdot 8H_2O$, reagent grade, recrystallized from 6 mol dm^{-3}.

(2) CsCl, reagent grade, recrystallized from water.

(3) Source and purity of water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]

(2) Zirconium dinitrate oxide; $ZrO(NO_3)_2$; [13826-66-9]

(3) Hydrogen chloride; HCl; [7647-01-0]

(4) Nitric acid; HNO_3; [7697-37-2]

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

ORIGINAL MEASUREMENTS:

Farhan, F. M.; Nedjat, H.

J. Chem. Eng. Data 1976, *21*, 446-8.

EXPERIMENTAL VALUES:

Composition of the saturated solutions at 0°C

Initial Total Acidity[a]	Nitrate, NO_3^-		Chloride, Cl^-		Zirconium		Density
$(c_3 + c_4)$/ mol dm^{-3}	mass %[b]	mass %[c]	mass %[b]	mass %[c]	mass %[b]	mass %[c]	ρ/ g cm^{-3}[d]
7.94	16.8	17.6	9.16	8.4	16.25	13.95	1.500
	17.6	18.2	8.7	7.9	16.24	14.29	1.503
	18.3	18.9	8.2	7.6	16.24	14.46	1.505
	19.1	19.7	7.7	7.0	16.20	14.60	1.508
8.4	19.45	20.6	9.2	8.1	14.7	14.48	1.481
	20.26	21.6	8.7	7.6	14.7	11.51	
	21	22.3	8.2	7.1	14.65	11.88	
	21.8	22.6	7.7	7.0	14.63	12.86	
	22.6	23.5	7.25	6.5	14.60	12.88	
	24.2	24.2	6.27	6.1	14.55	13.2	
	25.0	25.1	5.8	5.6	14.52	13.4	
	25.8	26.1	5.3	4.7	14.49	11.52	
	26.5	26.6	4.8	4.4	14.47	12.2	1.507

[a] Total acidity defined as the total concentration of HCl and HNO_3 used to dissolve ZrO_2 and make up the solution. It includes both combined and free acids. Equilibrium total acidity found to be constant within 8.0 ± 0.2 mol dm^{-3}.

[b] Initial concentration.

[c] Equilibrium concentration.

[d] At 25°C.

NOTE: For all saturated solution the equilibrium solid phases were found to be solid solutions formed by inclusion of $ZrO(NO_3)_2 \cdot 5H_2O$ into the lattice of $ZrOCl_2 \cdot 8H_2O$.

Continued on the next page . . .

COMPONENTS:

(1) Zirconium dichloride oxide; $ZrOCl_2$; [7699-43-6]
(2) Zirconium dinitrate oxide; $ZrO(NO_3)_2$; [13826-66-9]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Nitric acid; HNO_3; [7697-37-2]
(5) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Farhan, F. M.; Nedjat, H.

J. Chem. Eng. Data 1976, *21*, 446-8.

VARIABLES:

T/K = 273
$c(NO_3^-)/c(Cl^-)$ ratio

PREPARED BY:

J. Hála

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Aliquots of the stock solution of Zr(IV) in a mixture of HCl and HNO_3 were mixed with 10 mol dm^{-3} solutions of acids to obtain solutions with the desired total acidity at 25°. These solutions were equilibrated at 0° in conical stoppered flasks for 100-350 days since long waiting times were needed for crystallization to take place. Crystallization times were inversely proportional to the Cl^-/NO_3^- ratios, and seeding with $ZrOCl_2 \cdot 8H_2O$ or $Zr(NO_3)_2 \cdot 5H_2O$ crystals was not effective in accelerating crystallization. When the amount of crystals seemed to remain unchanged they were filtered and washed with diethylether cooled to 0°C. Solid phases and saturated solutions were analyzed for Cl^-, NO_3^-, and Zr. Cl^- was titrated by Volhard method, NO_3^- determined alkalimetrically after reduction to NH_3 by Dewarda alloy, and Zr determined gravimetrically as ZrO_2. For each solution mass% were also calculated from molarity and density data. Calculated values were reported to be in good agreement with analytical results. Total acidity was obtained from Cl^- and NO_3^- concentrations. Solid phases were also characterized by x-ray diffraction.

AUXILIARY INFORMATION

SOURCE AND PURITY OF MATERIALS:

All chemicals used were reagent grade (their source was not specified). Solutions containing high Zr concentrations were prepared from partially dehydrated hydrous Zr oxide. The latter was prepared by precipitating Zr hydroxide with NH_4OH, washing it with water, and dehydrating the paste (containing 80% H_2O) by heterogeneous distillation with toluene. The product contained 19% H_2O and was dissolved by gentle heating in a mixture of concentrated HNO_3 and HCl to obtain a stock solution containing (in mol dm^{-3}) 3.01 ZrO^{2+}, 5.70 NO_3^-, and 2.30 Cl^-.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

Temperature error is not specified.
Soly: precision in Zr analysis ± 0.1 %, Cl^- and NO_3^- ± 0.2 %.

REFERENCES:

COMPONENTS:

(1) Ammonium hexachlorozirconate(IV); $(NH_4)_2ZrCl_6$; [19381-66-9]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Toptygina, G.M.; Barskaya, I.B.

**Zh. Neorg. Khim.* 1965, *10*, 2254-61; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226-30.

VARIABLES:

$T/K = 298$

$m_2/\text{mol kg}^{-1} = 14.30\text{-}18.91$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $(NH_4)_2ZrCl_6$ in aqueous HCl at 25°C

HCl		ZrO_2	NH_4Cl	$(NH_4)_2ZrCl_6$		Nature of the Solid Phase[b]
mass%	$m_2/\text{mol kg}^{-1}$[a]	mass%	mass%	mass%[a]	$m_1/\text{mol kg}^{-1}$[a]	
32.02	14.30	2.380	2.26	6.57	.315	A
32.58	14.47	2.050	1.52	5.66	.270	A+B
33.56	15.28	2.250	2.48	6.21	.303	A+B
34.78	15.96	1.980	1.76	5.46	.269	B
35.81	16.21	1.300	1.15	3.59	.174	B
36.92	17.20	1.525	1.34	4.21	.210	B
37.48	17.41	1.260	1.115	3.48	.173	B
39.24	18.63	1.085	.94	2.99	.152	B
39.49	18.91	1.170	1.03	3.23	.166	B

a. Calculated by compiler. The values mass% $(NH_4)_2ZrCl_6$ were calculated from mass% ZrO_2. Similar calculations from mass% NH_4Cl showed that both sets of results agreed for 3 highest mass% HCl values.

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: $(NH_4)_2ZrCl_6$ [19381-66-9]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $(NH_4)_2ZrCl_6$ were shaken for several days. Zr was determined gravimetrically as ZrO_2, NH_4^+ by Kjeldahl method, and Cl^- by Volhard's method. Solid phases were identified by chemical and microscopic analysis, and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2ZrCl_6$ was prepared by saturation with HCl gas of a hot solution of NH_4Cl and $ZrOCl_2 \cdot 8H_2O$. Source and purity of starting materials not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Potassium hexachlorozirconate(IV); K_2ZrCl_6; [18346-99-1]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Toptygina, G.M.; Barskaya, I.B.

**Zh. Neorg. Khim.* 1965, *10*, 2254-61; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226-30.

VARIABLES:

T/K = 298
m_2/mol kg^{-1} = 16.72-19.77

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		ZrO_2	KCl	K_2ZrCl_6		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1a}	mass%	mass%	mass%[a]	m_1/mol kg^{-1a}	
32.71	16.72	4.40	2.16	13.65	.662	A+B
34.01	17.06	3.65	1.92	11.32	.542	A+B
34.24	17.68	4.08	2.92	12.65	.623	A+B
35.83	18.17	3.25	3.40	10.08	.488	B+C
37.00	19.34	3.40	2.10	10.54	.526	B+C
36.60	19.35	3.71	3.79	11.51	.580	B+C
38.00	19.29	2.57	3.11	7.97	.386	D
38.70	19.77	2.455	2.97	7.61	.371	D

a. Calculated by compiler. The values of mass% K_2ZrCl_6 were calculated from mass% ZrO_2. Similar calculations from mass% KCl showed that both sets of results agreed only for 2 highest mass% HCl values where K_2ZrCl_6 is the equilibrium solid phase. At lower HCl concentrations the mass% KCl data yielded lower mass% K_2ZrCl_6 values.

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: KCl [7447-40-7]

C: $ZrOCl_2 \cdot 3H_2O$ [66905-82-6]; D: K_2ZrCl_6 [18346-99-1]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess K_2ZrCl_6 were shaken for several days. Zr and K were determined gravimetrically as ZrO_2 and K_2SO_4, respectively; Cl^- determined by Volhard's method. Solid phases were identified by chemical and microscopic analysis, and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) K_2ZrCl_6 was prepared by saturation with HCl gas of a solution of $ZrOCl_2 \cdot 8H_2O$ and KCl in aqueous HCl. The solid was dried under dry HCl gas. Source and purity of starting materials not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Rubidium hexachlorozirconate(IV); Rb_2ZrCl_6; [19381-65-8]

(2) Hydrogen chloride; HCl [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Toptygina, G.M.; Barskaya, I.B.

**Zh. Neorg. Khim.* 1965, *10*, 2254-61; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226-30.

VARIABLES:

T/K = 298
m_2/mol kg^{-1} = 10.84-18.44

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		ZrO_2	RbCl	Rb_2ZrCl_6		Nature of the Solid Phase^b
mass%	m_2/mol kg^{-1a}	mass%	mass%	mass%^{a}	m_1/mol kg^{-1a}	
27.48	10.84	.783	2.98	3.02	.0915	A+B
28.25	11.28	.790	2.10	3.04	.0932	A+B
28.26	11.25	.732	2.42	2.82	.0862	A+B
28.87	11.64	.802	1.77	3.09	.0956	A
30.01	12.19	.645	1.06	2.49	.0777	A
31.03	12.61	.389	0.73	1.50	.0468	A
32.07	13.15	.272	.52	1.05	.0331	A
33.64	14.08	.210	.42	.809	.0260	A
35.17	15.02	.162	.30	.624	.0205	A
36.10	15.65	.168	.34	.647	.0215	A
36.30	15.78	.152	.30	.586	.0196	A
38.47	17.29	.135	.27	.520	.0179	A
40.02	18.44	.120	.24	.462	.0163	A

a. Calculated by compiler. The values of mass% Rb_2ZrCl_6 were calculated from mass% ZrO_2. Similar calculations from mass% RbCl showed that both sets of results agreed only for 3 highest mass% HCl values.

b. A: Rb_2ZrCl_6 [19381-65-8]; B: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Rb_2ZrCl_6 were shaken for several days. Zr and Rb were determined gravimetrically as ZrO_2 and Rb_2SO_4, respectively. Cl^- determined by Volhard's method. Solid phases were identified by chemical and microscopic analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2ZrCl_6 was prepared by storing a diluted solution of $ZrOCl_2$ and RbCl over H_2SO_4 for a long period of time. Source and purity of starting materials not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Cesium hexachlorozirconate(IV); Cs_2ZrCl_6; [16918-86-8]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Toptygina, G.M.; Barskaya, I.B.

**Zh. Neorg. Khim.* 1965, *10*, 2254-61; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226-30.

VARIABLES:

T/K = 298
m_2/ mol kg^{-1} = 7.80-16.60

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		ZrO_2	CsCl	Cs_2ZrCl_6		Nature of the Solid Phase^b
mass%	m_2/mol kg^{-1a}	mass%	mass%	mass%^{a}	m_1/mol kg^{-1a}	
21.00	7.80	1.12	7.93	5.18	.123	A
22.20	8.31	.987	.40	4.56	.109	A
22.25	8.29	.903	.36	4.17	.0995	A+B
25.00	9.39	.430	.07	1.99	.0478	B
25.40	9.58	.405	.08	1.87	.0451	B
25.60	9.65	.360	.96	1.66	.0400	B
30.80	12.24	.043	.12	.199	.00506	B
31.08	12.40	.040	.11	.185	.00472	B
31.40	12.58	.035	.095	.162	.00415	B
31.75	12.79	.032	.087	.148	.00381	B
34.55	14.50	.023	.059	.106	.00285	B
37.65	16.60	.003	.008	.0139	.000392	B

a. Calculated by compiler. The values of mass% Cs_2ZrCl_6 were calculated from mass% ZrO_2. Similar calculations from mass% CsCl showed that both sets of results agreed only for HCl concentrations greater than 25.60 mass%.

b. A: $ZrOCl_2 \cdot 8H_2O$ [13520-92-8]; B: Cs_2ZrCl_6 [16918-86-8].

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Cs_2ZrCl_6 were shaken for several days. Zr and Cs were determined gravimetrically as ZrO_2 and Cs_2SO_4, respectively. Cl^- determined by Volhard's method. Solid phases were identified by chemical and microscopic analysis, and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2ZrCl_6 was prepared from a solution of $ZrOCl_2 \cdot 8H_2O$ and CsCl in aqueous HCl either by saturating it with HCl gas or by boiling. Source and purity of starting materials not specified.

ESTIMATED ERROR:

The temperature error is not specified.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zirconium bromide; $ZrBr_4$; [13777-25-8] (2) Trichloromethane (chloroform); $CHCl_3$; [67-66-3]	Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G. *Vestn. Mosk. Univ., Ser. 2: Khim.* 1963, *18* (1), 38-9.
VARIABLES:	**PREPARED BY:**
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $ZrBr_4$ at 25°C to be approximately 2.1 mass% (0.0522 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to ZrO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrBr_4$ was prepared by bromination of a mixture of ZrO_2 (source and purity not specified) and charcoal. The product was purified by vacuum distillation at 250°. Analysis (mass%, found/calculated): Zr 22.41-22.52/22.20, Br 77.85-77.95/77.80.

(2) Trichloromethane (chloroform) (source and purity not specified) was purified and dried by standard methods.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Zirconium bromide; $ZrBr_4$; [13777-25-8] (2) 1,2-Dichloroethane; $C_2H_4Cl_2$; [107-06-2]	Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G. *Vestn. Mosk. Univ., Ser. 2: Khim.* 1963, *18* (1), 38-9.
VARIABLES:	PREPARED BY:
T/K = 298	J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $ZrBr_4$ at 25°C to be approximately 4.1 mass% (0.104 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Isothermal method used. Excess $ZrBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium. After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to ZrO_2. All procedures were carried out in a dry box.	(1) $ZrBr_4$ was prepared by bromination of a mixture of ZrO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 250°C. Analysis (mass%, found/calculated): Zr 22.41-22.52/22.20, Br 77.85-77.95/77.80. (2) 1,2 Dichloroethane (source not specified) was purified and dried by standard methods.
	ESTIMATED ERROR:
	Nothing specified.
	REFERENCES:

COMPONENTS:

(1) Zirconium dibromide oxide; $ZrOBr_2$; [33712-61-7]

(2) Hydrogen bromide; HBr; [10035-10-6]

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

ORIGINAL MEASUREMENTS:

von Hevesy, G.; Wagner, O.H.

Z. Anorg. Allg. Chem. 1930, *191*, 194-200.

VARIABLES:

$T/K = 298$
$c_2/mol\ dm^{-3} = 1.046-13.17$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $ZrOBr_2$ in aqueous HBr at 25°C

HBr $c_2/mol\ dm^{-3}$	ZrO_2 $g\ dm^{-3}$	$ZrOBr_2$ $c_1/mol\ dm^{-3}$	Density $g\ cm^{-3}$
1.046	355.7	2.886	1.7488
1.301	344.5	2.795	1.7343
1.485	329.6	2.674	1.7139
3.488	190.5	1.546	1.5606
3.663	180.2	1.319	1.5525
4.500	125.3	1.017	1.4900
6.44	26.80	0.2176	1.4060
8.72	3.654	0.0297	1.4836
9.09	3.656	0.0298	1.4861
13.17	2.11	0.0172	-

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $ZrOBr_2 \cdot 8H_2O$ were mixed for several days. Methods of analysis and equilibrium solid phases not specified.

SOURCE AND PURITY OF MATERIALS:

(1) $ZrOBr_2 \cdot 8H_2O$ was prepared by dissolving Zr hydroxide in HBr, and by subsequent careful evaporation. Source and purity of starting materials not specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

3. The solubility of hafnium-containing substances.

Systems	Pages
HfF_4 + HF + H_2O	150-153
____ + KF + H_2O	154
____ + __ + CH_3COOH	155
____ + RbF + H_2O	156
____ + CsF + H_2O	157
____ + ___ + CH_3COOH	158
$KHfF_5$ + H_2O	159
$RbHfF_5$ + H_2O	160
$CsHfF_5$ + H_2O	161
$(NH_4)_2HfF_6$ + H_2O	162
K_2HfF_6 + H_2O	163-166
______ + HF + H_2O	167
Rb_2HfF_6 + H_2O	168-170
Cs_2HfF_6 + H_2O	171-173
$(NH_4)_3HfF_7$ + H_2O	174
__________ + NH_4F + H_2O	175
$HfCl_4$ + CH_3CN + $(C_5H_{11})_2O$	176, 177
$HfOCl_2$ + H_2O	178, 179
______ + HCl + H_2O	180-189
______ + NH_4Cl + H_2O	190
______ + $MgCl_2$ + H_2O	191
______ + $CaCl_2$ + H_2O	192
______ + _____ + HCl + H_2O	193-195
______ + $SrCl_2$ + H_2O	196
______ + $BaCl_2$ + H_2O	197
______ + LiCl + H_2O	198
______ + NaCl + H_2O	199
______ + KCl + H_2O	200
______ + RbCl + H_2O	201
______ + CsCl + H_2O	202, 203
$HfOCl_2 \cdot 8H_2O$ + CH_3OH	204
___________ + C_2H_5OH	205
___________ + $1\text{-}C_6H_{13}OH$	206
___________ + $1\text{-}C_7H_{15}OH$	207
___________ + $1\text{-}C_8H_{17}OH$	208
$(NH_4)_2HfCl_6$ + HCl + H_2O	209
K_2HfCl_6 + HCl + H_2O	210
Rb_2HfCl_6 + HCl + H_2O	211
Cs_2HfCl_6 + HCl + H_2O	212
$HfBr_4$ + $CHCl_3$	213
_____ + CCl_4	214
_____ + CH_2ClCH_2Cl	215
$HfOBr_2$ + HBr + H_2O	216

COMPONENTS:	EVALUATOR:
(1) Hafnium fluoride; HfF_4; [13709-52-9] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61137 Brno, Czechoslovakia June 1985

CRITICAL EVALUATION:

The solubility of hafnium fluoride in aqueous hydrogen fluoride.

The solubility of HfF_4 was determined at 298 K as a function of HF concentration by Hevesy and Wagner (ref 1) and Buslaev and Nikolaev (ref 2). An inspection of the molal (m_1/mol kg^{-1}) solubility data in the compilations shows that at low HF concentrations the two data sets differ greatly. The reason for the discrepancy is not clear. The two values of Hevesy and Wagner (ref 1) agree well with the isotherms of Buslaev and Nikolaev (ref 2) at the highest HF concentrations.

Due to the lack of agreement in the published values in the low HF concentration range the evaluator cannot recommend any data. For tentative values the evaluator suggests the data of Buslaev and Nikolaev (ref 2) for 298 K to be used (see the compilation for the numerical data).

REFERENCES:

1. von Hevesy, G.; Wagner, O. H. *Z. Anorg. Allgem. Chem.* 1930, *191*, 194.
2. Buslaev, Yu. A.; Nikolaev, N. S. *Dokl. Akad. Nauk SSSR* 1960, *135*, 1385.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Hafnium(IV) fluoride; HfF_4; [13709-52-9] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	von Hevesy, G.; Wagner, O.H. *Z. Anorg. Allg. Chem.* 1930, *191*, 194-200.

VARIABLES:	PREPARED BY:
$T/K = 298$ $c_2/\text{mol dm}^{-3} = 0\text{-}20.09$	J. Hála

EXPERIMENTAL VALUES:

Solubility of HfF_4 in aqueous HF at 25°C

HF		HfO_2	HfF_4		Density
$c_2/\text{mol dm}^{-3}$	$m_2/\text{mol kg}^{-1a}$	g dm^{-3}	$c_1/\text{mol dm}^{-3}$	$m_1/\text{mol kg}^{-1a}$	g cm^{-3}
0	0	413.6	1.964	1.82	1.577
0	0	457.6	2.258	2.35	1.537
1.06	1.12	568.3	2.700	2.86	1.654
1.06	1.12	571.2	2.711	2.87	1.655
6.03	7.20	892.1	4.235	5.06	2.036
6.03	7.22	897.1	4.260	5.10	2.040
10.05	13.27	903.9	4.290	5.67	2.050
15.05	21.14	733.6	3.481	4.72	1.899
15.03	21.33	741.8	3.523	5.00	1.902
20.09	29.14	250.6	1.190	1.73	1.394
20.09	29.14	258.9	1.229	1.78	1.404

a. Calculated by compiler by using the authors' density values

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess solid was shaken for unspecified period of time with aqueous HF. Method of analysis not specified. The composition of solid phases was not reported.

SOURCE AND PURITY OF MATERIALS:

(1) The solid used for measurements was prepared by dissolving HfO_2 in aqueous HF. The composition of the solid obtained by crystallization from 5-20 mol HF/dm^3 was $HfOF_2 \cdot H_2F_2 \cdot 2H_2O$.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS
(1) Hafnium(IV) fluoride; HfF_4; [13709-52-9] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	Buslaev, Yu.A.; Nikolaev, N.S. *Dokl. Akad. Nauk SSSR* 1960, *135*, 1385-7. *Dokl. Chem. (Engl. Trans.)* 1960, *135*, 1435-7.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 25°C

HF	HfO_2	HfF_4[a]		Nature of the Solid Phase[b]
mass%	mass%	mass%	m_1/mol kg^{-1}	
0.06	0.27	0.326	.0129	A
2.24	7.42	8.97	.393	A
3.51	9.33	11.28	.520	A
6.09	16.00	19.34	1.02	A
6.68	18.32	22.15	1.22	A
8.93	24.32	29.40	1.87	A
9.97	24.29	29.37	1.90	B
11.16	25.83	31.23	2.13	B
13.91	29.33	35.46	2.75	B
14.78	30.24	36.56	2.95	B
15.88	32.31	39.06	3.41	B
20.50	37.67	45.54	4.59	B
21.83	39.78	48.09	6.28	B
21.96	40.67	49.17	6.69	B
23.27	44.30	53.56	9.08	B+C
24.68	45.10	54.53	10.30	C
25.36	44.00	53.20	9.75	C
26.40	43.15	52.17	9.57	C
27.62	38.98	47.13	7.33	C
28.90	33.17	40.10	5.08	D
32.42	24.20	29.25	3.00	D
33.68	21.06	25.46	2.45	D
35.03	18.26	22.07	2.02	D
38.33	13.20	15.96	1.46	D
41.95	7.98	9.65	.783	D
42.91	6.32	7.64	.592	D
43.64	5.90	7.13	.569	D
48.11	2.14	2.59	.206	D
52.75	.52	.63	.0531	D
59.22	.17	.206	.0200	D

a. Calculated by compiler

b. A: $Hf(OH)F_3\cdot 0.75H_2O$; [107983-43-7]

B: $HfF_4\cdot 3H_2O$; [14929-53-4]

C: $H(HfF_5)\cdot 2H_2O$; [13864-14-7]

D: $H_2HfF_6\cdot 2H_2O$; [107944-17-2]

Continued on the next page...

COMPONENTS:

(1) Hafnium(IV) fluoride; HfF_4; [13709-52-9]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Buslaev, Yu.A.; Nikolaev, N.S.

**Dokl. Akad. Nauk SSSR* 1960, *135*, 1385-7.

Dokl. Chem. (Engl. Transl.) 1960, *135*, 1435-7.

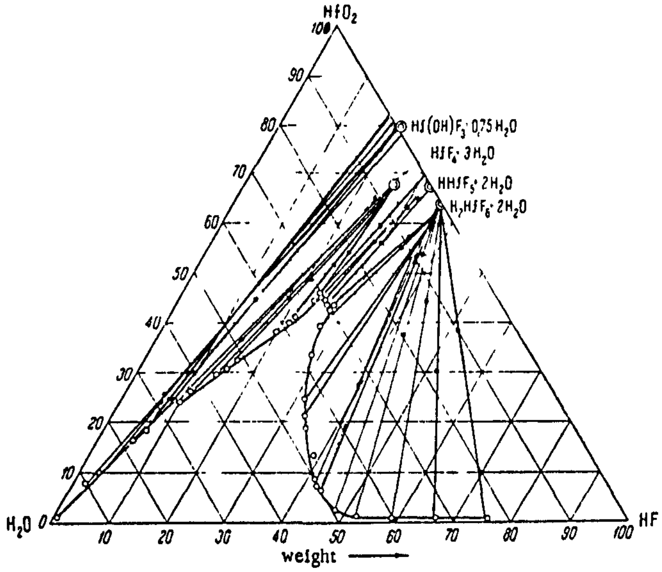
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



The system HF – HfF_4 – H_2O (25°C isotherm).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess HfF_4 was shaken with aqueous HF for 3 h. in bottles made of fluoroplast-4. Samples of solutions were taken by means of a Pt pipette. F^- in solutions containing Hf was determined alkalimetrically against phenolphthalein whereby free HF and 3/4 of F bound to Hf were titrated. HF was determined potentiometrically (ref 1); for mole ratio $HF/HfO_2 < 4$ a known amount of HCl + KF was added before titration. K_2HfF_6 was formed and excess acid was back-titrated with alkali. Hf was determined gravimetrically after removal of HF by evaporation with H_2SO_4. Solid phases were identified by chemical analysis.

ACKNOWLEDGEMENT:

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SOURCE AND PURITY OF MATERIALS:

(1) HfF_4 was prepared by dissolving HfO_2 (98.7%) in HF. The solution was evaporated and the residue used for solubility measurements. Source and purity of HF and water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 %.
Conc: precision ± 2 % HF.

REFERENCES:

1. Nikolaev, N.S.; Buslaev, Yu.A. *Zh. Neorg. Khim.* 1959, *4*, 543; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, *4*, 246-9.

COMPONENTS:

(1) Hafnium(IV) fluoride; HfF_4; [13709-52-9]

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

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 587-9.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

KF		HfF_4		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
0.11	0.0191	0.74	0.0293	A
0.45	.0796	2.28	.0921	A
0.62	.110	2.45	.0993	B
1.00	.176	2.05	.0831	B
2.23	.397	1.74	.0712	B
2.46	.438	0.98	.0399	C
3.17	.566	0.38	.0155	C
7.41	1.38	0.051	.00217	C
15.41	3.13	0.011	.00051	C

a. Calculated by compiler
b. A: $KHfF_5 \cdot H_2O$; [20910-24-1] B: K_2HfF_6; [16871-86-6] C: K_3HfF_7; [17169-17-4]

<u>Composition at the Eutonic Point</u>:

KF		HfF_4	
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]
0.66	0.117	2.49	0.101

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Mixing was carried out in teflon bottles overnight. Hf determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. K determined gravimetrically as sulfate in the filtrate after precipitation of Hf hydroxide. Solid phases were identified by chemical analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) HfF_4 prepared by dissolution of HfO_2 in bidistilled HF. Source and purity of HfO_2 not given.

(2) KF reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 %.

REFERENCES:

COMPONENTS:

(1) Hafnium fluoride; HfF_4; [13709-52-9]

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

(3) Acetic acid; $C_2H_4O_2$; [64-19-7]

ORIGINAL MEASUREMENTS:

Opalovskii, A.A.; Gudimovich, T.F. Akhmadeev, N.Kh.; Ishkova, L.D.

Zh. Neorg. Khim. 1982, *27*, 1183-5.

Russ. J. Inorg. Chem. (Engl. Transl.) 1982, *27*, 664-5.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions, $t/^{0}C$ = 25.

$KF^{a,b}$		$KHfF_5$	HfF_4		CH_3COOH	Nature of the Solid Phase
mass%	m_1/ mol kg^{-1}	mass%	mass%	m_1/ mol kg^{-1}	mass%	
1.39	0.245	0.99	0.80^b	0.0321	97.81	$KHfF_5 \cdot CH_3COOH$
4.57	0.834	1.36	1.10^b	0.0458	94.33	
7.90	1.507	2.29	1.86^b	0.0810	90.24	
10.44	2.054	2.54	2.06^b	0.0925	87.50	
13.56	2.793	2.75	2.23^b	0.104	84.12	
14.86	3.050	-	1.27	0.0595	83.87	K_2HfF_6; [16871-86-6]
18.86	4.053	-	1.05	0.0515	80.09	
21.38	4.731	-	0.84	0.0424	77.78	
21.8 [c]	4.798	-	-	-	78.2 [b]	Not reported

[a] No data given for KF. The saturated solutions were analyzed for HfF_4 and acetic acid only.

[b] Calculated by compiler.

[c] Value given in the text of the original document.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Equilibration time and details of the method not specified. Saturated solutions were analyzed for HfF_4 gravimetrically by an unspecified method and for CH_3COOH by alkalimetric titration. The composition of the solid phases was found by Schreinemakers method and by chemical and x-ray diffraction analysis.

ESTIMATED ERROR:

Nothing specified.

SOURCE AND PURITY OF MATERIALS:

(1) HfF_4 was prepared by thermal decomposition of $(NH_4)_2HfF_6$ (ref 1). Source and purity of the ammonium salt used not specified.

(2) Anhydrous KF prepared by prolonged drying of $KF.2H_2O$ over P_2O_5 in vacuum. Source and purity not specified.

(3) Acetic acid (source and purity not specified) was dried by distillation over P_2O_5.

REFERENCES:

1. Blumenthal, W. B. *The Chemical Behaviour of Zirconium*, Russian Translation, Moscow 1963, p. 73.

COMPONENTS:

(1) Hafnium(IV) fluoride; HfF_4; [13709-52-9]

(2) Rubidium fluoride; RbF; [13446-74-7]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 587-9.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

RbF		HfF_4		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]	
1.38	0.138	2.67	0.109	A
1.58	.158	2.81	.115	A
2.66	.272	3.75	.157	A+B
2.74	.280	3.60	.151	B
2.94	.301	3.47	.146	B
4.10	.424	3.28	.139	B
9.94	1.025	1.42	.0630	B
15.20	1.73	0.66	.0308	B
17.28	2.03	1.18	.0569	C
25.41	3.28	0.50	.0265	C
29.13	3.96	0.47	.0262	C

a. Calculated by compiler

b. A: $RbHfF_5 \cdot H_2O$; [20910-25-2] B: Rb_2HfF_6; [16962-20-2] C: Rb_3HfF_7; [20450-14-0]

Composition at the Eutonic Point

RbF		HfF_4	
mass%	m_2/mol kg^{-1}[a]	mass%	m_1/mol kg^{-1}[a]
2.61	0.267	3.68	0.154

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Mixing was carried out in teflon bottles overnight. Hf determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. Rb determined gravimetrically as sulfate in the filtrate after precipitation of Hf hydroxide. The composition of solid phases was deduced from chemical analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) HfF_4 prepared by dissolution of HfO_2 in bidistilled HF.

(2) RbF prepared from Rb_2CO_3 and HF. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Hafnium(IV) fluoride; HfF_4; [13709-52-9]

(2) Cesium fluoride; CsF; [13400-13-0]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 587-9.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions				Nature of the Solid Phase[b]
CsF		HfF_4		
mass%	m_2/mol kg^{-1} [a]	mass%	m_1/mol kg^{-1} [a]	
1.51	0.104	2.74	0.112	A
2.5	.174	2.94	.122	A
4.11	.293	3.52	.150	A+B
6.41	.459	1.72	.0736	B
10.5	.783	1.26	.0561	B
17.8	1.44	0.82	.0396	B
19.24	1.58	0.57	.0279	B
32.34	3.17	0.40	.0237	B
40.25	4.45	0.21	.0139	B
48.56	6.24	0.18	.0138	B
62.52	11.02	0.14	.0147	B

a. Calculated by compiler
b. A: $CsHfF_5 \cdot H_2O$; [19400-30-7] B: Cs_2HfF_6; [16919-32-7]

<u>Composition at the Eutonic Point</u>:

CsF		HfF_4	
mass%	m_2/mol kg^{-1} [a]	mass%	m_1/mol kg^{-1} [a]
3.56	0.253	3.92	0.166

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Mixing was carried out in teflon bottles overnight. Hf determined gravimetrically as sulfate in the filtrate after precipitation of Hf hydroxide. The composition of solid phases was deduced from chemical analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) HfF_4 prepared by dissolution of HfO_2 in bidistilled HF.

(2) CsF prepared from Cs_2CO_3 and HF. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 %.

REFERENCES:

COMPONENTS:

(1) Hafnium fluoride; HfF_4; [13709-52-9]

(2) Cesium fluoride; CsF; [13400-13-0]

(3) Acetic acid; $C_2H_4O_2$; [64-19-7]

ORIGINAL MEASUREMENTS:

Opalovskii, A. A.; Gudimovich, T. F. Akhmadeev, N. Kh.; Ishkova, L. D.

Zh. Neorg. Khim. 1983, *28*, 1876-8.

Russ. J. Inorg. Chem. (Engl. Transl.) 1983, *28*, 1065-6.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions

$CsF^{a,b}$		HfF_4		CH_3COOH	Nature of the Solid Phase
mass%	m_2/mol kg^{-1}	mass%	m_1/mol kg^{-1} ^{b}	mass%	
0	0	0.73^c	0.0289	99.27^b	Not reported
2.28	0.154	0.51	0.0206	97.21	$CsHfF_5$; [15803-64-2]
5.56	0.391	0.87	0.0365	93.57	
9.84	0.727	1.11	0.0490	89.05	
10.51	0.785	1.36	0.0606	88.13	
14.82	1.159	1.01	0.0472	84.17	Cs_2HfF_6; [16919-32-7]
21.23	1.795	0.93	0.0469	77.84	
29.26	2.754	0.81	0.0455	69.93	
35.16	3.605	0.63	0.0386	64.21	
41.44	4.698	0.49	0.0332	58.07	
47.22	5.936	0.41	0.0308	52.37	
50.44	6.759	0.41	0.0328	49.13	
51.6^c	7.018	-	-	48.6^b	Not reported

[a] No data given for CsF. Apparently the saturated solutions were analyzed for HfF_4 and acetic acid only.

[b] Calculated by compiler.

[c] Value given in the original document in the text.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Methods of analysis of the liquid phases not reported but apparently Hf was determined gravimetrically and CH_3COOH by alkalimetric titration, as in the authors previous work (ref 1). Equilibration time and conditions not specified. Compositions of the solid phases were found by Schreinemakers method.

SOURCE AND PURITY OF MATERIALS:

(1) HfF_4, source and purity not specified, dried over P_2O_5.

(2) CsF, source and purity not specified, dried over P_2O_5.

(3) Anhydrous acid used, source and purity not specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Opalovskii, A.A.; Gudimovich, T.F.; Akhmadeev, N.Kh.; Ishkova, L.D. *Zh. Neorg. Khim.* 1982, *27*, 1183.

COMPONENTS:

(1) Potassium pentafluorohafnate(IV); $KHfF_5$; [13815-25-3]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 587-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $KHfF_5 \cdot H_2O$ [20910-24-1] is reported as 0.1087 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $KHfF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Hf was determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. K determined gravimetrically as K_2SO_4 after the precipitation of Hf hydroxide. $KHfF_5 \cdot H_2O$ dissolved congruently and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) $KHfF_5 \cdot H_2O$ was prepared by equilibrating HfF_4 with solutions containing 0.11-0.45% KF. Under these conditions $KHfF_5 \cdot H_2O$ is obtained as the equilibrium solid phase, as follows from the measurement of the HfF_4-KF-H_2O system studied in the same document. HfF_4 was prepared by dissolution of HfO_2 in HF. KF reagent grade, source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Rubidium pentafluorohafnate(IV); $RbHfF_5$; [13844-79-6]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 587-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $RbHfF_5 \cdot H_2O$ [20910-25-2] is reported as 0.1115 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $RbHfF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Hf was determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. Rb determined gravimetrically as Rb_2SO_4 after the precipitation of Hf hydroxide. $RbHfF_5 \cdot H_2O$ dissolved congruently, and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) $RbHfF_5 \cdot H_2O$ was prepared by equilibrating HfF_4 with solutions containing 1.38-1.58 mass% RbF. Under these conditions $RbHfF_5 \cdot H_2O$ is obtained as the equilibrium solid phase, as follows from the measurement of the HfF_4-RbF-H_2O system studied in the same document. HfF_4 was prepared by dissolution of HfO_2 in HF. KF reagent grade, source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Cesium pentafluorohafnate; $CsHfF_5$ [15803-64-2]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* <u>1966</u>, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1966</u>, *11*, 587-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of $CsHfF_5 \cdot H_2O$ [19400-30-7] is reported as 0.112 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $CsHfF_5 \cdot H_2O$ were shaken overnight in teflon bottles. Hf was determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. Cs determined gravimetrically as Cs_2SO_4 after the precipitation of Hf hydroxide. $CsHfF_5 \cdot H_2O$ dissolved congruently, and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) $CsHfF_5 \cdot H_2O$ was prepared by equilibrating HfF_4 with solutions containing 1.51 mass% CsF. Under these conditions $CsHfF_5 \cdot H_2O$ is obtained as the equilibrium solid phase, as follows from the measurement of the HfF_4-CsF-H_2O system studied in the same document. HfF_4 was prepared by dissolution of HfO_2 in HF. CsF prepared from Cs_2CO_3 and HF. Source and purity not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 %.

REFERENCES:

COMPONENTS:

(1) Ammonium hexafluorohafnate(IV); $(NH_4)_2HfF_6$; [16925-24-9]

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

ORIGINAL MEASUREMENTS:

1.von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74.

2.von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.

VARIABLES:

$T/K = 273-293$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

$t/°C$	Ammonium Hexafluorohafnate(IV) $c_1/mol\ dm^{-3}$
0	0.890
20	1.425

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Hf was determined gravimetrically as HfO_2 after evaporation with H_2SO_4 and ignition of the residue of an aliquot from the saturated solution. The authors do not report on the composition of the solid phase.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2HfF_6$ was prepared by dissolution of HfO_2 in concentrated HF, and by adding a stoichiometric amount of NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) (OC-6-11)-Dipotassium hexafluorohafnate(2-); K_2HfF_6; [16871-86-6]

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

EVALUATOR:

J. Hála
Department of Inorganic Chemistry
J. E. Purkyne University
61 137 Brno, Czechoslovakia

June 1985

CRITICAL EVALUATION:

The solubility of potassium hexafluorohafnate in water.

Egerev and Pogorelyi (ref 1) report the solubility of K_2HfF_6 in water at ten degree intervals between 273.16 and 373.16 K. They fitted their data by the method of least squares to the equation $\log S = -(1637.5)/(T/\mathrm{K}) + 3.6512$, where S is mol/100 g H_2O. The regression line fits the experimental values at 273 and 373 poorly, but appears to be satisfactory at the other temperatures.

Single solubility values are reported at 298.15 K by Tananaev and Guzeeva (ref 2), 0.1244 mol dm^{-3}, and Schmitt *et al.* (ref 3), 0.128 mol dm^{-3}. The average of (0.126 ± 0.002) mol dm^{-3} is recommended. The recommended value and several values from the equation of Egerev and Pogorelyi are given below.

Table 1. The solubility of K_2HfF_6 in water.

T/K	m_1/mol kg^{-1} (ref 1)	c_1/mol dm^{-3} (ref 2,3)
283.15	0.0738	
298.15	0.144	0.126 ± 0.002
323.15	0.384	
363.15	1.387	

REFERENCES:

1. Egerev, O. I.; Pogorelyi, A. D.
   Zh. Prikl. Khim. 1966, *39*, 926-8.
   J. Appl. Chem. USSR (Engl. Transl.) 1966, *39*, 866-7.

2. Tananaev, I. V.; Guzeeva, L. S.
   Zh. Neorg. Khim. 1966, *11*, 1091.
   Russ. J. Inorg. Chem. (Engl. Transl.) 1966, *11*, 587.

3. Schmitt, R. H.; Grove, E. L.; Brown, R. D.
   J. Am. Chem. Soc. 1960, *82*, 5292.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Potassium hexafluorohafnate; K_2HfF_6; [16871-86-6] (2) Water; H_2O; [7732-18-5]	Schmitt, R. H.; Grove, E. L.; Brown, R. D. *J. Am. Chem. Soc.* 1960, *82*, 5292-5.
VARIABLES:	**PREPARED BY:**
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The solubility of K_2HfF_6 at 25°C is reported to be $c_1/\text{mol dm}^{-3} = 0.128$. The value is the average of four measurements, but neither the individual values or standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Two saturated solutions of K_2HfF_6 were prepared at 40°C and another two were prepared at 20°C. All solutions were brought to equilibrium at 25°C with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70°C, weighed, kept over P_2O_5 for several days and reweighed. All work was carried out in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) K_2HfF_6 was prepared by adding a concentrated solution of reagent grade KCl to a solution of H_2HfF_6.

The salt was filtered, washed, and recrystallized several times. Either Pt or polyethylene containers and deionized water were used in all steps.

The H_2HfF_6 solution was prepared by dissolving HfO_2 (source not specified) in excess HF. The HfO_2 was not purified since its chief impurity, Zr, was removed by the recrystallization of the H_2HfF_6.

Spectrographic analysis of the H_2HfF_6 showed only minor traces of impurities. The content was not reported.

(2) Deionized water was used.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K, (NBS calibration).
The solubility error is not specified.

COMPONENTS:

(1) Potassium hexafluorohafnate; K_2HfF_6; [16871-86-6]

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

ORIGINAL MEASUREMENTS:

Egerev, O.I.; Pogorelyi, A.D.

**Zh. Prikl. Khim.* 1966, *39*, 926-8; *J. Appl. Chem. USSR (Engl. Transl.)* 1966, *39*, 866-7.

VARIABLES:

T/K = 273-373

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Potassium Hexafluorohafnate(IV)	
T/K	g/100 g H_2O	m_1/mol kg^{-1}
273.16	2.254	0.06079
283.16	2.896	0.07811
293.16	4.308	0.11619
303.16	6.336	0.17087
313.16	9.584	0.25845
323.16	14.361	0.38729
333.15	20.757	0.55980
343.16	27.743	0.74818
353.16	37.231	1.00407
363.16	51.32	1.38410
373.16	74.1	1.99950

Least squares treatment of the data yielded for the temperature dependency of K_2HfF_6 solubility (in mol/100 g H_2O) the following equation:

$$\log S = -(1637.5/T) + 3.6512$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Each measurement was repeated 2-6 times. Samples of saturated solutions were taken by means of a pipette heated to the corresponding temperature. The samples were weighed and evaporated, the residue dried at 105°C and weighed. The authors do not report on the equilibrium solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) K_2HfF_6 was prepared from Hf metal obtained by thermal decomposition of HfI_4. Hf contained less than 1% Zr and 10^{-2}% Si, Fe, Al, and Ti. Source and purity of other chemicals not specified.

ESTIMATED ERROR: Temp: precision ± 0.1 K. The error of the arithmetic mean solubility varied from 0.04 to 1.1% depending on the number of measurements.

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorohafnate(IV); K_2HfF_6; [16871-86-6]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966, *11*, 587-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of K_2HfF_6 is reported as 0.1244 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess K_2HfF_6 were shaken overnight in teflon bottles. Hf was determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. K determined gravimetrically as K_2SO_4 after the precipitation of Hf hydroxide. K_2HfF_6 dissolved congruently, and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) K_2HfF_6 was prepared by equilibrating HfF_4 with solutions containing 0.62-2.23 mass% KF. Under these conditions K_2HfF_6 is obtained as the equilibrium solid phase, as follows from the measurement of the HfF_4-KF-H_2O system studied in the same document. HfF_4 was prepared by dissolution of HfO_2 in HF. KF reagent grade, source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Potassium hexafluorohafnate(IV); K_2HfF_6; [16871-86-6]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

1. von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74.
2. von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.

VARIABLES:

$T/K = 293$
$c_2/\text{mol dm}^{-3} = 0.125\text{-}5.89$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 20°C

Hydrogen Fluoride $c_2/\text{mol dm}^{-3}$	Potassium Hexafluorohafnate(IV) $c_1/\text{mol dm}^{-3}$
0.125	0.1008
5.89	0.1942

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Hf was determined gravimetrically as HfO_2 but no details were given. The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

Nothing specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) (OC-6-11)-Dirubidium hexafluorohafnate (2-); Rb_2HfF_6; [16962-20-2] (2) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61137 Brno, Czechoslovakia October 1985

CRITICAL EVALUATION:

The solubility of dirubidium hexafluorohafnate(2-) in water.

Two laboratories report the solubility of Rb_2HfF_6 in water at 298 K. Schmitt *et al.* (ref 1) report a value of 0.186 mol dm^{-3} as a mean of four measurements. The system was brought to equilibrium from both lower and higher temperatures with a high precision of temperature control (±0.005 K) followed by direct gravimetry of the evaporated residue. Tananaev and Guzeeva (ref 2) report a value of 0.1519 mol dm^{-3} with a temperature error of ± 0.1 K. The evaluator prefers the value of Schmitt *et al.*, and suggests its use as the tentative value.

REFERENCES:

1. Schmitt, R. H.; Grove, E. L.; Brown, R. D.
J. Am. Chem. Soc. 1960, *82*, 5292.

2. Tananaev, I. V.; Guzeeva, L. S.
Zh. Neorg. Khim 1966, *11*, 1091;
Russ. J. Inorg. Chem. (Engl. Transl.) 1966, *11*, 587.

COMPONENTS:

(1) Rubidium hexafluorohafnate; Rb_2HfF_6; [16962-20-2]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Rb_2HfF_6 at 25°C is reported to be $c_1/\text{mol dm}^{-3} = 0.186$. The value is the average of four measurements, but neither the individual values or standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Two saturated solutions of Rb_2HfF_6 were prepared at 40°C and another two were prepared at 20°C. All solutions were brought to equilibrium at 25°C with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70°C, weighed, kept over P_2O_5 for several days and reweighed. All work was carried out in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2HfF_6 was prepared by adding a concentrated solution of reagent grade RbF to a solution of H_2HfF_6.

The salt was filtered, washed, and recrystallized several times. Either Pt or polyethylene containers and deionized water were used in all steps.

SOURCE AND PURITY OF MATERIALS:

The H_2HfF_6 solution was prepared by dissolving HfO_2 (source not specified) in excess HF. The HfO_2 was not purified since its chief impurity, Zr, was removed by the recrystallization of the H_2HfF_6.

Spectrographic analysis of the Rb_2HfF_6 showed only minor traces of impurities. The Zr content was not reported.

(2) Deionized water was used.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K, (NBS calibration).

The solubility error is not specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Rubidium hexafluorohafnate(IV); Rb_2HfF_6; [16962-20-2] (2) Water; H_2O; [7732-18-5]	Tananaev, I.V.; Guzeeva, L.S. **Zh. Neorg. Khim.* <u>1966</u>, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1966</u>, *11*, 587-9.
VARIABLES:	PREPARED BY:
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Rb_2HfF_6 is reported as 0.1519 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Rb_2HfF_6 were shaken overnight in teflon bottles. Hf was determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. Rb determined gravimetrically as Rb_2SO_4 after the precipitation of Hf hydroxide. Rb_2HfF_6 dissolved congruently, and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2HfF_6 was prepared by equilibrating HfF_4 with solutions containing 2.74-15.2 mass% RbF. Under these conditions Rb_2HfF_6 is obtained as the equilibrium solid phase, as follows from the measurement of the HfF_4-RbF-H_2O system studied in the same document. HfF_4 was prepared by dissolution of HfO_2 in HF. RbF reagent, source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) (OC-6-11)-Dicesium hexfluorohafnate(2-); Cs_2HfF_6; [16919-32-7] (2) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia October 1985

CRITICAL EVALUATION:

Two values of the solubility of Cs_2HfF_6 at 298 K have been reported. Schmitt *et al.* (ref 1) report a value of 0.174 mol dm^{-3} obtained by direct gravimetry of the evaporated residue as a mean of four measurements in which the system was brought to equilibrium from both lower and higher temperatures in an experiment of high precision temperature control. Tananaev and Guzeeva (ref 2) report a value of 0.1641 mol dm^{-3} obtained with a temperature uncertainty of ± 0.1 degree. The evaluator prefers the value of Schmitt *et al.*, and classes it as the tentative value.

REFERENCES:

1. Schmitt, R. H.; Grove, E. L.; Brown, R. D.
J. Am. Chem. Soc. 1960, *82*, 5292.

2. Tananaev I. V.; Guzeeva, L. S.
Zh. Neorg. Khim. 1966, *11*, 1091;
Russ. J. Inorg. Chem. (Engl. Transl.) 1966, *11*, 587.

COMPONENTS:

(1) Cesium hexafluorohafnate; Cs_2HfF_6; [16919-32-7]

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

ORIGINAL MEASUREMENTS:

Schmitt, R. H.; Grove, E. L.; Brown, R. D.

J. Am. Chem. Soc. 1960, *82*, 5292-5.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Cs_2HfF_6 at 25°C is reported to be $c_1/\text{mol dm}^{-3} = 0.174$. The value is the average of four measurements, but neither the individual values or standard deviation are reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Two saturated solutions of Cs_2HfF_6 were prepared at 40°C and another two were prepared at 20°C. All solutions were brought to equilibrium at 25°C with constant stirring. After attaining equilibrium, known volumes of the saturated solutions were evaporated to dryness at 70°C, weighed, kept over P_2O_5 for several days and reweighed. All work was carried out in polyethylene ware.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2HfF_6 was prepared by adding a concentrated solution of an unspecified Cs halide to a solution of H_2HfF_6.

The salt was filtered, washed, and recrystallized several times. Either Pt or polyethylene containers and deionized water were used in all steps.

SOURCE AND PURITY OF MATERIALS:

The Cs_2HfF_6 solution was prepared by dissolving HfO_2 (source not specified) in excess HF. The HfO_2 was not purified since its chief impurity, Zr, was removed by the recrystallization of the Cs_2HfF_6.

Spectrographic analysis of the Cs_2HfF_6 showed only minor traces of impurities. The Zr content was not reported.

(2) Deionized water was used.

ESTIMATED ERROR:

Temp: accuracy ± 0.005 K, (NBS calibration).

The solubility error is not specified.

COMPONENTS:

(1) Cesium hexafluorohafnate(IV); Cs_2HfF_6; [16919-32-7]

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

ORIGINAL MEASUREMENTS:

Tananaev, I.V.; Guzeeva, L.S.

**Zh. Neorg. Khim.* 1966, *11*, 1091-5; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1966; *11*, 587-9.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility at 25°C of Cs_2HfF_6 is reported as 0.1641 mol dm^{-3}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess Cs_2HfF_6 were shaken overnight in teflon bottles. Hf was determined gravimetrically as HfO_2 after removal of F^- by evaporation with H_2SO_4. Cs determined gravimetrically as Cs_2SO_4 after the precipitation of Hf hydroxide. Cs_2HfF_6 dissolved congruently, and could be recrystallized from water.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2HfF_6 was prepared by equilibrating HfF_4 with solutions containing less than 6.4 mass% CsF. Under these conditions Cs_2HfF_6 is obtained as the equilibrium solid phase, as follows from the measurement of the HfF_4-CsF-H_2O system studied in the same document. HfF_4 was prepared by dissolution of HfO_2 in HF, CsF prepared from Cs_2CO_3 and HF. Source and purity not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Ammonium heptafluorohafnate(IV); $(NH_4)_3HfF_7$; [17169-53-8]

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

ORIGINAL MEASUREMENTS:

1. von Hevesy, G.; Christiansen, J.A.; Berglund, V. *Z. Anorg. Allg. Chem.* 1925, *144*, 69-74.
2. von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.

VARIABLES:

T/K = 273-293

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	Ammonium Heptafluorohafnate(IV)
t/°C	c_1/mol dm^{-3}
0	0.425
20	0.588

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Hf was determined gravimetrically as HfO_2 after evaporation with H_2SO_4 and ignition of the residue of an aliquot from the saturated solution. The authors do not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_3HfF_7$ was prepared by dissolution of HfO_2 in concentrated HF, and by adding an excess of NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS: (1) Ammonium heptafluorohafnate(IV); $(NH_4)_3HfF_7$; [17169-53-8] (2) Ammonium fluoride; NH_4F; [12125-01-8] (3) Water; H_2O; [7732-18-5]	**ORIGINAL MEASUREMENTS:** von Hevesy, G. *Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk.* 1925, *6*, 1-149.
VARIABLES: T/K = 293 c_2/mol dm^{-3} = 0-5.01	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

Solubility of $(NH_4)_3HfF_7$ in aqueous NH_4F at 20°C

Ammonium Fluoride c_2/mol dm^{-3}	Ammonium Heptafluorohafnate(IV) c_1/mol dm^{-3}
0	0.588
0.992	0.261
1.971	0.108
5.01	0.0258

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken in ebonite bottles for several hours. Hf was determined gravimetrically as HfO_2 after evaporation with H_2SO_4 and ignition of the residue of an aliquot from the saturated solution. NH_4^+ concentration determined by Kjeldahl's method. The author does not report on the composition of the solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_3HfF_7$ was prepared by dissolution of HfO_2 in concentrated HF, and by adding an excess of NH_4F. Source and purity of chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Hafnium(IV) chloride; $HfCl_4$; [13499-05-3]
(2) Acetonitrile; C_2H_3N; [75-05-8]
(3) Bis(3-methylbutyl) ether, or *isoamyl ether*; $C_{10}H_{22}O$; [544-01-4]

ORIGINAL MEASUREMENTS:

Larsen, E.M.; Trevorrow, L.E.

J. Inorg. Nucl. Chem., 1956, *2*, 254-9.

VARIABLES:

T/K = 298
Solvent composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Experimental data were given in graphical form as the phase diagram for the $ZrCl_4/CH_3CN$/isoamyl ether system at 25°C, with the corresponding points for $HfCl_4$ indicated by primed letters.* The solubility line A′B′ represents the solubility of the solid phase in liquid mixtures of varying composition. The solid phase existing in equilibrium with the solutions along the entire A′B′C′ line was $HfCl_4 \cdot 2CH_3CN$. Numerical data were given for the following points:

	Solvent Composition		Solubility
Point	CH_3CN mass%	Isoamyl ether mass%	$HfCl_4$ mass%
A′	12	86	2.0
B′	66	18	16
C′	79.6±0.4	-	20.4±0.4
D′	-	89.5	10.5

* See diagram on the next page. . .

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility of $HfCl_4$ in CH_3CN/isoamyl ether mixtures was obtained from the ternary $HfCl_4/CH_3CN$/isoamyl ether phase diagram at 25°C. To prepare the 3-component mixtures, $HfCl_4$ was sublimed *in vacuo* into a cell fitted with serum-bottle caps at sidearms; the cell was brought to atm. pressure by admission of dry air, transferred to a paraffin oil-sealed stirrer assembly, thermostated, and the solvents added through the bottle caps with hypodermic syringes. The location of points A′ and B′ on the phase diagram was determined by the interaction of the solubility line with the liquid-liquid curves. The CH_3CN-rich side of the binodal curve was constructed from clear and cloud points obtained by alternately titrating with each solvent. The points on the ether-rich side were obtained by titrating with a solution of $HfCl_4$ in CH_3CN of

Continued on the next page. . .

SOURCE AND PURITY OF MATERIALS:

(1) $HfCl_4$ was prepared by passing Cl_2 gas over a mixt. of HfO_2 (containing 1 or 2% ZrO_2) and charcoal at 600°C, and purified by first subliming in an atmosphere of H_2 and then resubliming several times *in vacuo*. It was kept in sealed ampoules. The atomic mass of Hf was corrected for the Zr content.
(2) CH_3CN was dried over P_2O_5 and

Continued on the next page. . .

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Hafnium(IV) chloride; $HfCl_4$; [13499-05-3]
(2) Acetonitrile; C_2H_3N; [75-05-8]
(3) Bis(3-methylbutyl) ether, or *isoamyl ether*; $C_{10}H_{22}O$; [544-01-4]

ORIGINAL MEASUREMENTS:

Larsen, E.M.; Trevorrow, L.E.

J. Inorg. Nucl. Chem., 1956, *2*, 254-9.

VARIABLES:

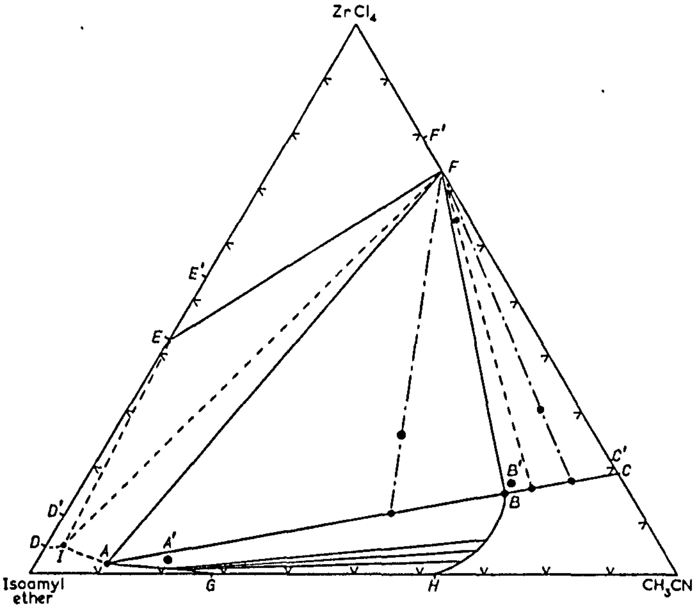
T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The ternary systems with $ZrCl_4$ and with $HfCl_4$ are similar. Only the complete $ZrCl_4$ system is shown. The corresponding $HfCl_4$ points are indicated by the primed letters.



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Continued from preceding page. . .

a homogeneous ether-rich solvent mixture until the 2-liquid phase region was reached. The points on the line representing equilibrium between the solid phase and the mixed solvent were determined by adding various solvent mixtures to $HfCl_4$ until the solid phase disappeared. The composition of the equilibrium solid phase was obtained by the method of wet residues. Hf in liquid or solid samples was determined by adding the samples to an excess of water, distilling off the solvent with steam, and precipitating hydrated Hf oxide with NH_3 solution. To determine N in the solid phases, samples were dissolved in glacial acetic acid and N determined by the Kjeldahl method. The ether was obtained by difference.

SOURCE AND PURITY OF MATERIALS:

Continued from preceding page. . .

distilled (n_D^{25} = 1.3418).

3) Isoamyl ether was purified from peroxides, dried with $CaCl_2$ and Na ribbon, and distilled (N_D^{25} = 1.4059). Atmospheric moisture was excluded during distillation of the solvents.

ESTIMATED ERROR:

See previous page.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

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

ORIGINAL MEASUREMENTS:

Blinova, Z. N.; Komissarova, L. N.

Zh. Neorg. Khim. 1972, *17*, 2520-5.

Russ. J. Inorg. Chem. (Engl.Transl.) 1972, *17*, 1318-21.

EXPERIMENTAL VALUES:

Composition of the staurated solutions.

Temperature		HfO_2	Cl^-	$HfOCl_2$		
$t/^\circ C$	T/K	mass %	mass %	mass %[a]	mass %[b]	m_1/mol kg^{-1}[c]
0	273	35.05	11.85	44.21	44.35	2.994
15	288	35.70	12.23	45.03	45.76	3.132
25	298	36.25	12.46	45.73	46.64	3.234
40	313	37.64	12.84	47.48	48.06	3.446
50	323	38.85	13.13	49.01	49.14	3.631
60	333	39.50	13.20	49.83	49.41	3.711
70	343	40.36	13.89	50.91	51.99	3.993
80	353	42.57	14.23	53.70	53.26	4.332
90[d]	363	44.17	14.75	55.72	55.21	4.693
100[d]	373	44.55	-	56.20	-	4.835
110[d]	383	47.77	-	60.26	-	5.714
120[d]	393	51.55	-	65.03	-	7.007

Calculated by compiler:

[a] from mass% HfO_2

[b] from mass% Cl

[c] from the average of the calculated mass% $HfOCl_2$

[d] The solubility value reported as being average of several measurements but the individual data were not given.

NOTE: In the temperature range of 0-80°C the Hf:Cl ratio in saturated solutions and solid phases varied within 1:1.98 - 1:2.04 and 1:1.89 - 1:1.97, respectively. The smooth inflection at 90-100°C on the solubility versus temperature plot was ascribed by the authors to increasing hydrolysis and polymerization with the formation of a new compound whose solubility also increases with increasing temperature. Increasing hydrolysis of $HfOCl_2$ at high temperatures was indicated by appreciable loss of HCl through the seal of the vessels. Although not stated explicitly the data suggest that the solid phase at <80°C was apparently the hydrate $HfOCl_2 \cdot 8H_2O$.

Continued on the next page . . .

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

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

ORIGINAL MEASUREMENTS:

Blinova, Z. N.; Komissarova, L. N.

Zh. Neorg. Khim. 1972, *17*, 2520-5.

Russ. J. Inorg. Chem. (Engl.Transl.) 1972, *17*, 1318-21.

VARIABLES:

$T/K = 273 - 393$

PREPARED BY:

J. Hála

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated with water at the desired temperature for 1-2 h in glass vessels with liquid paraffine hydraulic seal. The vessels were thermostated in water (15-60°), in glycerine above 60°, or in ice at 0°. Samples of the saturated solutions and solid phases were analyzed for Hf and Cl gravimetrically as HfO_2 and AgCl, respectively. At higher temperatures samples of saturated solutions were withdrawn with a heated pipette. Samples of solid phases were taken only from measurements at <80° since at higher temperatures the mother liquor crystallized rapidly. The solid phases were also characterized by a polarizing microscope.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2 (99.33 mass% Hf, 0.55 mass% Zr). HfO_2 was heated with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4 to 300-450°, the melt was dissolved in distilled water, and Hf was precipitated with concentrated NH_4OH. Hf hydroxide was washed free from sulfate by decantation, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization. HCl used was reagent grade.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

COMPONENTS:	EVALUATOR:
(1) Hafnium oxide chloride; $HfOCl_2$; [13759-17-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia February 1985

CRITICAL EVALUATION:

An evaluation of the solubility of $HfOCl_2$ in aqueous hydrogen chloride solutions.

There are four literature sources on the $HfOCl_2$ + HCl + H_2O system available (ref 1 - 4). The work of Hevesy (ref 1) gives the solubility in mol dm^{-3} at 293 K whereas in the other documents the solubility was presented in mass % of either $HfOCl_2$ (ref 3), or HfO_2 (ref 2, 4) from which the solubilities were calculated in mol kg^{-1}.

There are great differences in the solubilities at low acidities between the data of Goroshchenko and Spasibenko (ref 2) and the data in the other papers (ref 3, 4). In (ref 3, 4) the $HfOCl_2$ solubility decreases as the HCl solubility increases while the solubilities reported by Goroshchenko and Spasibenko increase with HCl concentration. The reason is that they started with hydrated HfO_2 as the solid. Thus, the low acidity region of paper (ref 2) has been disregarded.

There are two general features of the solubility of $HfOCl_2$ in HCl solutions. They are (*i*) an increase in the solubility with increasing temperature, and (*ii*) the appearance of a shallow minimum (at 25-30 mass % HCl in solution) on the solubility *vs.* m_{HCl} plot (ref 1-4). The increase in the solubility of $HfOCl_2$ at acidities > 30 mass% HCl is caused by the formation of anionic chlorocomplexes of Hf(IV) in solution.

The data sets of Kamaneva *et al.* (ref 3) and Blinova and Komissarova (ref 4) are compared for 298 K and the data sets of Goroshchenko and Spasibenko (ref 2) and Blinova and Komissarova (ref 4) are compared for 273 K (see Figures 1 and 2). For both temperatures a reasonable agreement of data is observed at acidities > 18 mass % HCl, although there is some discrepabcy for the solubility increase above 30 mass % at 273 K.

Both sets of data were smoothed by a linear regression of the data to a fifth order polynomial in HCl mass %. At 298 K (Figure 1) the equation for the HCl mass % range of 18 to 39 is [Eqn (1)]

$$(m_1/\text{mol kg}^{-1}) = 11.9049 - 1.5070(100w_2) + 6.5960 \times 10^{-2}(100w_2)^2$$

$$- 9.0494 \times 10^{-4}(100w_2)^3 - 9.4593 \times 10^{-6}(100w_2)^4 + 2.5099\times10^{-7}(\downarrow)^5$$

$100w_2$

At 273 K there is a disagreement in the data above 32 mass % HCl (Figure 2). The data of Blinova and Komissarova (ref 4) show the generally accepted increase in solubility of $HfOCl_2$ with increasing HCl mass %. The data of Goroshchenko and Spasibenko (ref 2) do not show the expected increase. The evaluator believes the data of Blinova and Komissarova should be given preferance in the high HCl region. The smoothing equation below was prepared by a linear regression which did not include the three experimental points of Goroshchenko and Spasibenko above 31.5 mass % HCl.

$$(m_1/\text{mol kg}^{-1}) = 5.7634 - 0.63134(100w_2) + 2.0545 \times 10^{-2}(100w_2)^2 +$$

$$7.5962\times10^{-5}(100w_2)^3 - 1.5377\times10^{-5}(100w_2)^4 + 2.1147\times10^{-7}(100w_2)^5$$

The solid line of Figure 2 was calculated from the above equation [Eqn(2)]. The equation below [Eqn (3)] was obtained from a linear regression which included the Goroshchenko and Spasibenko data above 31.5 mass % HCl. The equation is:

$$(m_1/\text{mol kg}^{-}) = 6.2671 - 0.68204(100w_2) + 2.1591 \times 10^{-2}(100w_2)^2 +$$

$$1.0237\times10^{-4}(100w_2)^3 - 1.6081\times10^{-5}(100w_2)^4 + 2.0871\times10^{-7}(100w_2)^5$$

See the dashed line in Figure 2, which show a deviation from [Eqn (2)] at high HCl concentrations.

COMPONENTS:	EVALUATOR:
(1) Hafnium oxide chloride; $HfOCl_2$; [13759-17-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia February 1985

CRITICAL EVALUATION:

An evaluation of the solubility of $HfOCl_2$ in aqueous hydrogen chloride solutions (continued).

Additional discrepancies can be noted for the higher temperature data. The values of Kamaeva *et al.* (ref 3) at 298 K are higher than the Goroshchenko and Spasibenko values at 303 K in the high acidity region, although it is known that the solubility increases with temperature. The data of Blinova and Komissarova (ref 4) for 12 to 14.15 mass % HCl appear to be unreasonably high, and correspond to values for low acidities in other documents (ref 2, 3). The reason for this is not clear, although supersaturated solutions are a possibility. The evaluator suggests these data be classed as doubtful.

The molalities of HCl calculated from the mass % HCl data of (ref 4) pass through a minimum in spite of the increasing HCl concentration (the water concentration increases in the system along with that of HCl). A similar, but less pronounced effect, is observed for the HCl molalities calculated from the data of (ref 2). Therefore the mass % HCl rather than the mol kg^{-1} scale has been chosen for the graphical comparisons of data in Figures 1 and 2.

Tentative values: The evaluator suggests the following be used as tentative values.
At 273 K use values calculated from [Eqn (2)].
At 298 K use values calculated from [Eqn (1)].
At 303 and 323 K use the data of Goroshchenko and Spasibenko (ref 2).

REFERENCES:

1. von Hevesy, G.
Kgl. Danske Videnskab. Selskab. 1925, *6*, No. 7.

2. Goroshchenko, Ya. G.; Spasibenko, T. P.
Zh. Neorg. Khim. 1965, *10*, 2156.

3. Kamaeva, I. G.; Melnik, L. A.; Serebrennikov, V. V.
Zh. Neorg. Khim. 1968, *13*, 1974.

4. Blinova, Z. N.; Komissarova, L. N.
Zh. Neorg. Khim. 1972, *17*, 2520.

COMPONENTS:	EVALUATOR:
(1) Hafnium oxide chloride; $HfOCl_2$; [13759-17-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia February 1985

CRITICAL EVALUATION:

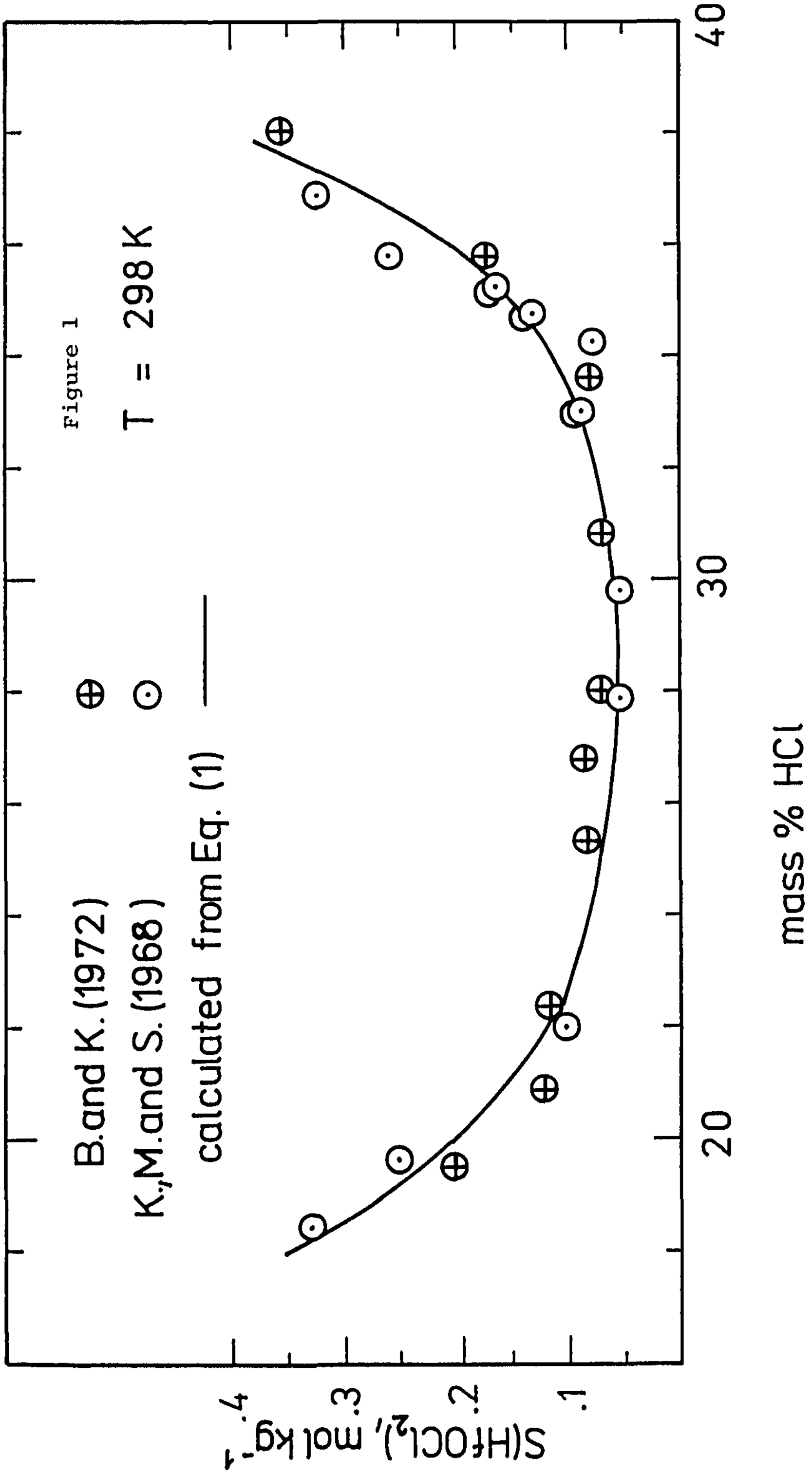


Figure 1

COMPONENTS:	EVALUATOR:
(1) Hafnium oxide chloride; $HfOCl_2$; [13759-17-6] (2) Hydrogen chloride; HCl; [7647-01-0] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne UNiversity 61 137 Brno, Czechoslovakia February 1985

CRITICAL EVALUATION:

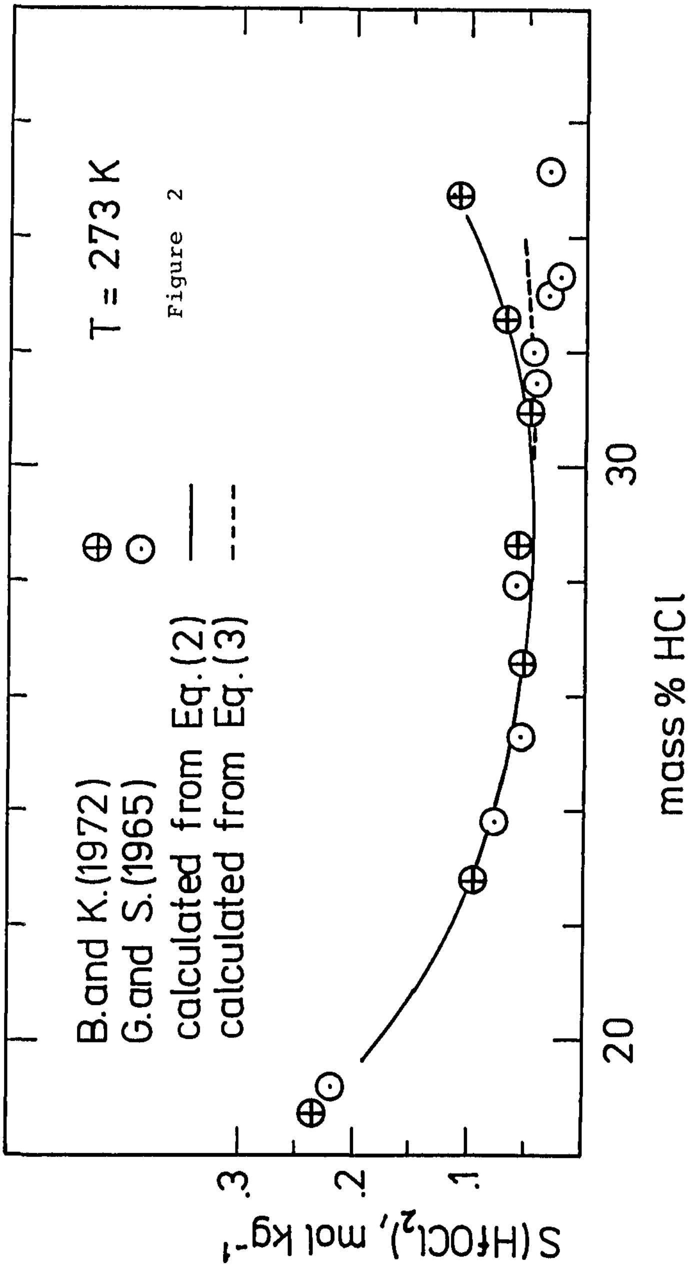


Figure 2

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

von Hevesy, G.

Mat.-Fys. Medd.-K. Dan. Vidensk. Selsk. 1925, *6*, 1-149.

VARIABLES:

$T/K = 293$
$c_2/\text{mol dm}^{-3} = 5.64\text{-}11.28$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $HfOCl_2$ in aqueous HCl at 20°C

HCl $c_2/\text{mol dm}^{-3}$	$HfOCl_2$ $c_1/\text{mol dm}^{-3}$
5.64	0.167
6.48	0.1030
9.02	0.0530
10.33	0.0668
10.56	0.0801
11.28	0.1509

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Hf was determined gravimetrically as HfO_2 after evaporation of the samples with H_2SO_4. Total Cl^- content determined by Volhard's method, HCl concentration found by difference. The author does not report on the composition of solid phases.

SOURCE AND PURITY OF MATERIALS:

(1) HfO_2 containing 5% ZrO_2 was converted to $HfOCl_2 \cdot 8H_2O$ which was heated in a stream of HCl to yield $HfOCl_2 \cdot 3H_2O$.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Goroshchenko, Ya.G.; Spasibenko, T.P.

**Zh. Neorg. Khim.* 1965, *10*, 2156-62; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1173-6.

VARIABLES:

T/K = 273, 303, 323
HCl/mass% = 0.85-36.60

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 0°C

HCl	HfO_2	$HfOCl_2$[a]		Nature of the Solid Phase[b]
mass%	mass%	mass%	m_1/mol kg^{-1}	
1.96	2.68	3.38	.135	A
2.02	3.75	4.73	.191	A
2.84	5.30	6.69	.279	A
2.97	6.05	7.63	.322	A
4.43	10.63	13.41	.615	A
4.64	11.00	13.88	.642	A
7.83	14.80	18.67	.957	A
10.64	22.51	28.39	1.75	A
13.63	24.77	31.25	2.14	A+B
14.23	14.81	18.68	1.05	B
16.36	7.81	9.85	.503	B
19.22	3.55	4.48	.221	B
23.88	1.22	1.54	.0778	B
25.29	.86	1.08	.0552	B
27.96	.83	1.05	.0557	B
31.50	.60	.757	.0421	B+C
33.00	.38	.479	.0271	C
33.29	.31	.391	.0222	C
35.16	.44	.555	.0325	C

Continued on the next page. . .

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess of either Hf hydroxide or $HfOCl_2 \cdot 8H_2O$ were mixed for unspecified long period of time. Where Hf hydroxide was used, it was prepared by passing $HfOCl_2$ solution through a column of EDE-10P anion exchanger in OH form. The product contained 88.41% HfO_2, 0.46% HCl and 11.13% H_2O. Analytical methods not specified. The composition of solid phases was determined by chemical analysis and X-ray diffraction. Hf hydroxide which was in equilibrium with solutions of low acidity (<13 wt % HCl) was analyzed after drying. The composition of $HfOCl_2 \cdot 3H_2O$ was also confirmed by Schreinemakers' method and by the method of indifferent addition.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2 containing 0.55% ZrO_2, 0.1% TiO_2, 0.003% Fe_2O_3 and 0.02% Al_2O_3. The product was twice recrystallized from aqueous HCl.

(2,3) Source and purity of HCl and water not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS

Goroshchenko, Ya.G.; Spasibenko, T.P.

***Zh. Neorg. Khim.* 1965, *10*, 2156-62; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1173-6.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 30°C

HCl	HfO_2	$HfOCl_2$[a]		Nature of the Solid Phase[b]
mass%	mass%	mass%	m_1/mol kg^{-1}	
1.81	3.61	4.55	.183	A
2.44	8.20	10.34	.447	A
3.23	12.58	15.87	.739	A
3.68	14.69	18.53	.898	A
5.60	21.20	26.74	1.49	A
6.53	22.07	27.84	1.60	A
9.74	25.72	32.44	2.12	A
10.38	26.82	33.83	2.28	A
11.52	28.97	36.54	2.65	A
13.08	30.98	39.08	3.08	A+B
13.84	25.02	31.56	2.18	B
14.89	18.73	23.62	1.45	B
16.11	11.54	14.56	.791	B
17.58	7.55	9.52	.492	B
20.00	3.35	4.22	.210	B
25.13	1.60	2.02	.104	B
29.68	1.17	1.48	.0810	B
32.75	1.28	1.61	.0924	B+C
33.29	1.67	2.10	.122	C
36.19	2.30	2.90	.179	C
36.60	2.39	3.01	.188	C

Composition of Saturated Solutions at 50°C

HCl	HfO_2	$HfOCl_2$[a]		Nature of the Solid Phase[b]
mass%	mass%	mass%	m_1/mol kg^{-1}	
.85	2.63	3.31	.130	A
1.46	4.57	5.76	.234	A
1.65	6.57	8.29	.346	A
2.27	10.59	13.36	.597	A
2.59	13.83	17.45	.822	A
2.61	13.94	17.58	.830	A
2.72	14.99	18.91	.909	A
3.66	16.80	21.19	1.08	A
4.01	20.38	25.72	1.38	A
4.88	24.00	30.27	1.76	A
7.50	31.03	39.14	2.76	A
7.55	31.13	39.27	2.78	A
9.48	36.63	46.20	3.76	A
12.50	38.80	48.94	4.78	A+B
13.57	31.53	39.77	3.10	B
15.24	23.08	29.11	1.97	B
16.03	16.21	20.45	1.21	B
17.90	10.15	12.80	.696	B
19.81	5.97	7.53	.390	B
23.78	2.87	3.62	.188	B
25.52	2.50	3.15	.166	B
26.78	1.97	2.48	.132	B
29.40	1.85	2.33	.129	B
32.48	5.30	6.69	.414	B+C
33.06	5.72	7.22	.456	C

a. Calculated by compilers

b. A: $HfO_2 \cdot xHCl \cdot yH_2O$ (x = 0.05-0.25, y = 1.41-2.79);

B: $HfOCl_2 \cdot 8H_2O$; [14456-34-9]

C: $HfOCl_2 \cdot 3H_2O$; [107924-80-1]

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Kamaeva, I.G.; Melnik, L.A.; Serebrennikov, V.V.

**Zh. Neorg. Khim.* 1968, *13*, 1974-80; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 1026-9.

VARIABLES:

$T/K = 298$
$m_2/\text{mol kg}^{-1} = 0\text{-}17.40$

PREPARED BY:

J. Hála and M. Salomon

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl mass%	HCl $m_2/\text{mol kg}^{-1a}$	$HfOCl_2$ mass%	$HfOCl_2$ $m_1/\text{mol kg}^{-1a}$	Nature of the Solid Phase^b
0	0	45.60	3.158	A
2.11	1.008	40.47	2.656	A
3.64	1.653	35.98	2.245	A
6.03	2.63	31.00	1.855	A
18.40	6.73	6.62	.333	A
19.59	7.12	4.99	.249	A
22.03	7.96	2.07	.103	A
27.78	10.70	1.04	.0550	A
29.73	11.77	0.99	.0538	A
33.01	13.83	1.51	.0869	B
33.02	13.84	1.54	.0887	B
34.22	14.56	1.30	.0760	B
34.77	15.12	2.16	.129	B
34.90	15.21	2.17	.130	B
35.19	15.53	2.68	.163	B
35.21	15.55	2.70	.164	B
35.73	16.29	4.12	.258	B
36.92	17.40	4.91	.318	B

a. Calculated by compilers

b. A: $HfOCl_2 \cdot 8H_2O$; [14456-34-9] B: $HfOCl_2 \cdot HCl \cdot 6.5H_2O$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used as described previously (ref 1). Solutions containing excess solid were mechanically mixed, and equilibrium was assumed to be reached in 8 days by analogy to previous results (ref 1). Hf was determined titrimetrically with EDTA against Xylenol Orange, HCl was titrated with alkali. Solid phases were identified by Schreinemakers' method and by microscopy.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ prepared by hydrolysis of $HfCl_4$. The product was twice recrystallized from aqueous HCl. Source and purity of $HfCl_4$ not specified.

(2) HCl prepared from CP grade NaCl and H_2SO_4.

(3) Distilled water was used.

ESTIMATED ERROR:

Temp: precision ± 0.05 K.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Kamaeva, I.G.; Serebrennikov, V.V. *Zh. Neorg. Khim.* 1963, *8*, 2151; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1963, *8*, 1124.

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Blinova, Z. N.; Komissarova, L. N.

Zh. Neorg. Khim. 1972, *17*, 2520-5.

Russ. J. Inorg. Chem. (Engl.Transl.) 1972, *17*, 1318-21.

EXPERIMENTAL VALUES:

Solubility of $HfOCl_2$ in aqueous HCl at 0 and 25°C

Temperature		HCl		HfO_2	$HfOCl_2$		Nature of the Solid Phase[b]
$t/^{\circ}C$	T/K	mass %	m_2/mol kg^{-1} [a]	mass %	mass %[a]	m_1/mol kg^{-1} [a]	
0	273	11.98	7.52	35.15	44.34	3.825	A
		12.33	7.39	33.25	41.94	3.456	A
		12.52	7.01	30.52	38.50	2.962	A
		12.99	6.58	26.06	32.87	2.288	A
		15.84	5.87	8.05	10.15	1.947	A
		18.69	6.70	3.81	4.81	0.237	A
		22.77	8.30	1.57	1.97	0.0986	A
		26.31	9.33	0.83	1.047	0.0543	A
		28.66	11.19	0.86	1.085	0.0582	B
		30.97	12.47	0.71	0.896	0.0496	B
		32.55	13.49	0.99	1.249	0.0711	C
		34.76	15.06	1.55	1.955	0.116	D
		41.63	23.38	7.56	9.54	0.736	D
25	298	12.85	8.28	36.05	45.47	4.111	A
		13.00	8.15	34.27	43.23	3.721	A
		13.21	7.64	31.21	39.37	3.128	A
		13.29	7.58	30.61	38.61	3.025	A
		14.15	6.90	23.45	29.58	1.981	A
		15.25	6.29	14.48	18.27	1.036	A
		16.48	6.26	8.98	11.33	0.591	A
		19.52	7.01	3.24	4.09	0.202	A
		20.87	7.47	1.98	2.50	0.123	A
		22.34	8.14	1.87	2.36	0.118	A
		25.34	9.52	1.30	1.640	0.0846	A
		26.81	10.27	1.28	1.616	0.0851	B
		28.01	10.49	1.05	1.324	0.0680	B
		30.80	12.44	1.01	1.274	0.0707	B
		33.58	14.16	1.09	1.375	0.0797	E
		35.75	15.96	2.23	2.81	0.172	E
		38.01	18.41	4.24	5.35	0.356	E
		39.41	21.79	8.71	10.99	0.835	not reported

[a] Calculated by compiler.

[b] Solid phases

A: $HfOCl_2 \cdot 8H_2O$; [14456-34-9]

B: $HfOCl_2 \cdot 7H_2O$

C: $HfOCl_2 \cdot 6H_2O$; [41468-24-0]

D: $HfOCl_2 \cdot 3.5H_2O$

E: $HfOCl_2 \cdot (3\text{-}3.5)H_2O$

Note: The increase in the solubility of $HfOCl_2$ in solutions containing >31 mass % HCl was ascribed by the authors to the formation of the chlorocomplexes of the type $HfCl_n^{(4-n)+}$.

Continued on the next page . . .

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Blinova, Z. N.; Komissarova, L. N.

Zh. Neorg. Khim. 1972, *17*, 2520-5.

Russ. J. Inorg. Chem. (Engl. Transl.) 1972, *17*, 1318-21.

VARIABLES:

T/K = 273, 298

$m_2/\text{mol kg}^{-1}$ = 5.87-23.38 at 273 K
6.26-21.79 at 298 K

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

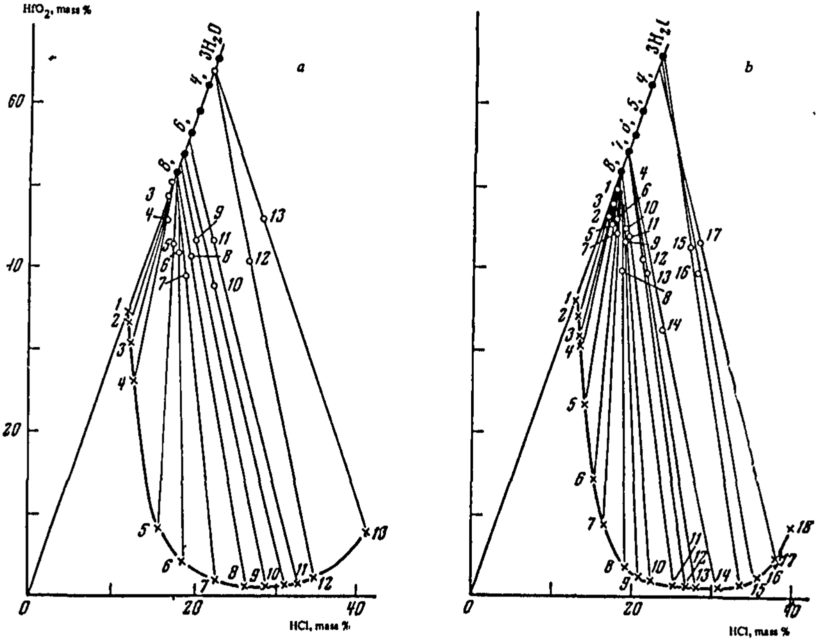


Figure Solubility isotherm for hafnium oxide chloride in HCl solutions at 0°C (*a*) and 25°C (*b*).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated in a thermostated bath with HCl solutions of the desired concentration in glass vessels with liquid paraffine hydraulic seal. Solutions of HCl with d. > 1.19 g cm^{-3} were prepared by saturating concentrated HCl solution with HCl gas. Equilibrium was established within 5-6 days at 0^0, and in 2 days at 25^0. Samples of the saturated solutions and solid phases were analyzed gravimetrically for Hf and Cl as HfO_2 and AgCl, respectively. Solid phases were also characterized by optical microscopy and the method of wet residues.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2 (99.33 mass % Hf, 0.55 mass % Zr). HfO_2 was heated with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4 to 300-450 , the melt was dissolved in distilled water, and Hf was precipitated with concentrated NH_4OH. Hf hydroxide was washed free from sulfate by decantation, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization.

(2) Reagent grade HCl was used.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Ammonium chloride; NH_4Cl; [12125-02-9]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

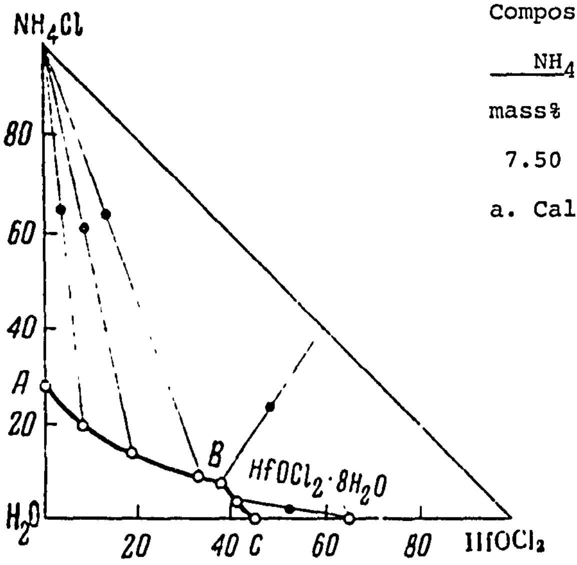
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

NH_4Cl		$HfOCl_2$	
mass%	m_2/mol kg^{-1} a	mass%	m_1/mol kg^{-1} a
7.50	2.50	37.50	2.52

a. Calculated by compiler

$HfOCl_2\cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2\cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. NH_4Cl concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2\cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) NH_4Cl, reagent grade. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]
(2) Magnesium chloride; $MgCl_2$; [7786-30-3]
(3) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

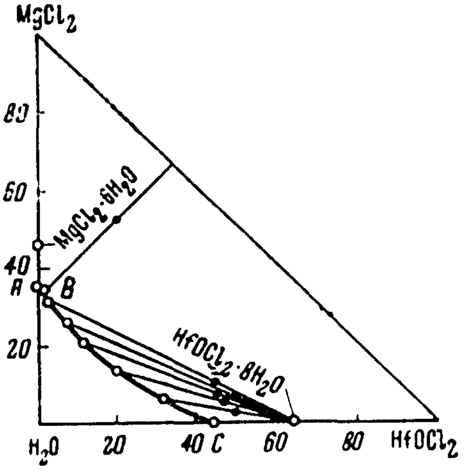
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

$MgCl_2$		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
34.20	5.55	1.13	0.0658

a. Calculated by compiler

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2 \cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. $MgCl_2$ concentration found by difference. Solid phases identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) $MgCl_2 \cdot 6H_2O$, reagent grade. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Calcium chloride; $CaCl_2$; [10043-52-4]

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

ORIGINAL MEASUREMENTS:

Kamaeva, I.G.; Serebrennikov, V.V.

Zh. Neorg. Khim. 1967, *12*, 3224-6;
Russ. J. Inorg. Chem. (Engl. Transl.) 1967, *12*, 1706-7.
Tr. Tomsk. Gos. Univ. 1971, *204*, 66-9

VARIABLES:

T/K = 298, 323
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

	$CaCl_2$		$HfOCl_2$		Nature of the Solid Phase[b]
t/°C	mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	
25	0	0	45.60	3.16	A
	4.11	0.643	38.33	2.51	A
	8.02	1.166	30.01	1.82	A
	12.22	1.698	22.92	1.33	A
	16.42	2.20	16.30	0.913	A
	20.85	2.74	10.53	.578	A
	28.59	3.69	1.69	.0913	A
	35.45	4.99	0.57	.0336	A
	37.21	5.36	0.20	.0120	A
	43.52	6.95	0.09	.00601	A+B(A+C)[c]
	45.23	7.44	0	0	B(C)[c]
50	0	0	47.96	3.47	A
	3.81	0.615	40.44	2.73	A
	8.42	1.258	31.28	1.95	A
	12.62	1.82	24.91	1.50	A
	18.29	2.56	17.22	1.00	A
	26.56	3.59	6.87	0.389	A
	32.15	4.45	2.72	.157	A
	39.49	6.06	1.76	.113	A
	54.61	11.02	0.75	.0633	A+C
	56.95	11.92	0	0	C

a. Calculated by compiler
b. A: $HfOCl_2 \cdot 8H_2O$; B: $CaCl_2 \cdot 6H_2O$[7774-34-7]; C: $CaCl_2 \cdot 2H_2O$[10035-04-8]
c. Data from the 1971 document

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess solid were shaken for 8 h. Samples for analysis were taken by means of a pipette heated previously to 25 or 50°C, and filtered through thermostated Schott crucibles. Hf and Ca were determined titrimetrically with EDTA against Xylenol Orange and Murexide respectively as indicators. Solid phases were identified by chemical and microscopic analysis and by Schreinemakers' method.

Note: Footnote b. above
A: $HfOCl_2 \cdot 8H_2O$; [14456-34-9]

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2 of unspecified purity. The oxide was melted with borax and Na_2CO_3, the melt dissolved in HCl, and the product recrystallized three times.

(2) $CaCl_2 \cdot 2H_2O$ (pure) was recrystallized from water.

ESTIMATED ERROR:

Temp: precision ± 0.05 K.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]
(2) Calcium chloride; $CaCl_2$; [10043-52-4]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS

Tsurik, L.A.; Kamaeva, I.G., Serebrennikov, V.V.

**Zh. Neorg. Khim.* 1977, *22*, 1366-71; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1977, *22*, 744-7.

EXPERIMENTAL VALUES

Composition of Saturated Solutions at 25°C

$CaCl_2$		HCl		$HfOCl_2$		Nature of the Solid Phase[g]
mass%	m_2/mol kg^{-1a}	mass%	m_3/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	
0^b	0	5.00	2.22	33.09	2.01	A
3.55	.458	5.25	2.06	21.41	1.56	A
6.18	.778	5.11	1.96	17.14	.902	A
9.58	1.17	4.71	1.75	11.71	.596	A
13.65	1.61	4.93	1.77	5.07	.250	A
19.80	2.43	4.83	1.80	1.93	.0990	A
21.36	2.67	5.64	2.14	.87	.0454	A
26.12	3.44	5.27	2.11	.25	.0138	A
31.21^f	4.41	4.69	2.02	.27	.0159	A
35.49	5.40	5.22	2.42	.11	.00700	A
40.17^f	6.66	4.90	2.47	.6	.0416	A+B
42.09	7.24	5.10	2.67	.40	.0288	B
0^{cf}	0	10.00	4.24	25.27	1.47	A
3.06	.392	10.18	3.97	16.35	.875	A
6.61	.792	9.97	3.64	8.26	.414	A
10.23	1.22	9.93	3.62	4.57	.229	A
13.43^f	1.63	9.86	3.64	2.44	.124	A
21.32	2.84	10.20	4.13	.80	.0445	A
24.18	3.35	10.16	4.29	.70	.0406	A
32.57	5.14	10.02	4.81	.30	.0198	C
36.96	6.35	10.06	5.26	.54	.0388	C
37.62	6.51	9.69	5.10	.59	.0427	C
38.87	6.96	10.41	5.67	.37	.0272	C+B
40.18	7.24	9.83	5.39	0	0	B
0^d	0	15.00	5.65	12.20	.631	A
2.87	.343	15.71	5.71	6.01	.300	A
2.90^f	.342	14.58	5.23	6.13	.302	A
8.15	.994	14.91	5.53	3.03	.154	A
15.47	2.03	14.55	5.82	1.40	.0769	A
19.90	2.79	15.03	6.42	.85	.0499	A
20.93	3.03	15.43	6.79	1.3	.0786	A
24.05^f	3.59	14.81	6.73	.82	.0512	A
25.53	3.94	15.05	7.06	.99	.0638	A+C
26.68^f	4.22	15.25	7.34	1.06	.0701	C
27.50^f	4.41	15.22	7.44	1.15	.0772	C
28.77	4.84	15.89	8.13	1.74	.122	C
29.91^f	5.15	15.05	7.88	2.68	.193	D
32.26^f	5.90	15.25	8.49	3.24	.248	D
34.34^f	6.60	15.13	8.86	3.67	.295	D
35.28^f	6.88	14.81	8.79	3.72	.303	D
36.12	7.27	15.27	9.35	3.82	.321	D+B+E
36.31	6.93	14.87	8.64	1.64	.131	B+E
37.83^f	7.35	15.39	9.10	.40	.0325	B+E

Continued on the next page. . .

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]
(2) Calcium chloride; $CaCl_2$; [10043-52-4]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Tsurik, L.A.; Kamaeva, I.G., Serebrennikov, V.V.

**Zh. Neorg. Khim.* 1977, *22*, 1366-71; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1977, *22*, 744-7.

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

$CaCl_2$		HCl		$HfOCl_2$		Nature of the Solid Phase[g]
mass%	m_2/mol kg^{-1a}	mass%	m_3/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}	
0[e]	0	20.00	7.09	2.60	.127	A
4.26	.521	20.04	7.46	2.01	.103	A
4.63	.568	20.54	7.67	1.38	.0708	A
6.36	.795	20.23	7.70	1.35	.0706	A
8.79	1.14	20.48	8.09	1.30	.0706	A
10.32	1.36	19.85	7.94	1.23	.0676	A
12.48	1.69	19.90	8.19	.98	.0554	A
12.92	1.76	19.93	8.26	1.01	.0575	A
13.93	1.95	20.61	8.79	1.17	.0686	A
15.06[f]	2.11	19.50	8.30	1.02	.0597	A
18.92	2.85	20.36	9.33	.90	.0567	C
20.03[f]	3.06	19.69	9.17	1.36	.0870	C
20.97	3.28	20.00	9.51	1.34	.0875	C
21.64	3.42	20.07	9.66	1.28	.0846	C
21.80	3.54	19.80	9.78	2.90	.197	C
22.63[f]	3.97	20.37	10.88	5.63	.413	C+B+E
23.55[f]	4.07	20.31	10.70	4.07	.295	B+E
24.51[f]	4.25	19.90	10.50	3.61	.262	B+E
25.09	4.31	19.90	10.40	2.54	.182	B+E
25.65	4.39	19.70	10.27	2.04	.146	B+E
27.17	4.70	19.00	10.00	1.75	.127	B+E
29.02	5.20	20.01	10.91	.68	.0509	B+E

a. Calculated by compiler

b. Initial HCl concentration 5 mass% for this and the following 11 data points

c. Initial HCl concentration 10 mass% for this and the following 11 data points

d. Initial HCl concentration 15 mass% for this and the following 18 data points

e. Initial HCl concentration 20 mass% for this and the following 21 data points

f. Inconsistent numerical data. The original paper also lists mass% H_2O obtained by difference. For this point the sum does not equal 100% which suggests a typographical error (ranging from approx. 0.5 to 9.4%) associated with either the HCl, $CaCl_2$, or $ZrOCl_2$ concentrations, in addition to the estimated experimental precision of ±2-5%.

g. A: $HfOCl_2 \cdot 8H_2O$; B: α-$CaCl_2 \cdot 4H_2O$; C: $HfOCl_2 \cdot 6H_2O$;
D: $HfOCl_2 \cdot CaCl_2 \cdot 0.5HCl \cdot 12H_2O$, which could also be written as $Ca_2[HfOCl_4]_2 \cdot HCl \cdot 24H_2O$ or $Ca[HfOCl_3 \cdot H_2O]_2 \cdot CaCl_2 \cdot HCl \cdot 22H_2O$;
E: β-$CaCl_2 \cdot 4H_2O$

Note registry numbers: $HfOCl_2 \cdot 8H_2O$; [14456-34-9]
$HfOCl_2 \cdot 6H_2O$; [41463-24-0]
α- and β-$CaCl_2 . 4H_2O$; [25094-02-4]

Continued on the next page. . .

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]
(2) Calcium chloride; $CaCl_2$; [10043-52-4]
(3) Hydrogen chloride; HCl; [7647-01-0]
(4) Water; H_2O; [7732-18-5]

ORIGINAL MEASUREMENTS:

Tsurik, L.A.; Kamaeva, I.G., Serebrennikov, V.V.

Zh. Neorg. Khim. 1977, *22*, 1366-71; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1977, *22*, 744-7.

VARIABLES:

$T/K = 298$
Composition
$m_3/\text{mol kg}^{-1} = 2.22\text{-}10.91$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

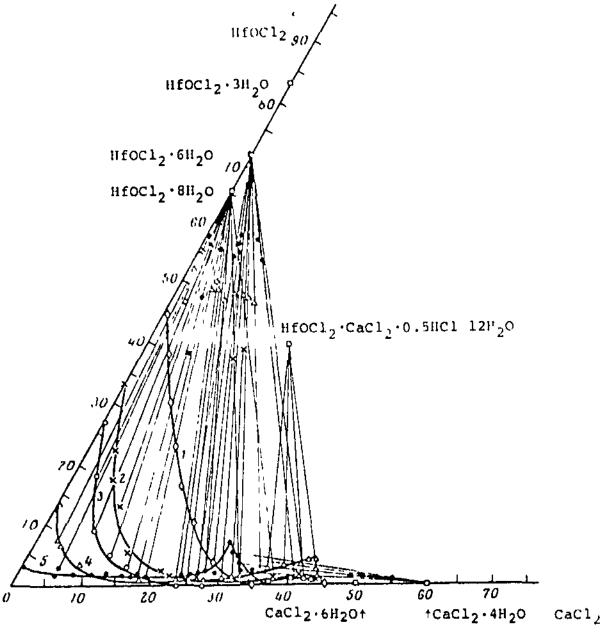


Figure Acid-free projection of the 25°C isotherm of the system. 1) Solubility of hafnium oxide chloride in aqueous solutions of calcium chloride, 2) in 5% hydrochloric acid, 3) in 10% hydrochloric acid, 4) in 15% hydrochloric acid, 5) in 20% hydrochloric acid.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. After equilibration the systems were filtered in a thermostated apparatus. Hf and Ca were determined titrimetrically with EDTA using Eriochrome T as indicator. Free HCl was titrated in a heated aliquot against Methyl Orange. Solid phases were identified by Schreinemakers' method, by the method of indifferent additions using $FeCl_3$, and by microscopic analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ prepared by hydrolysis of $HfCl_4$, reagent grade, and twice recrystallized from concentrated HCl.

(2) $CaCl_2 \cdot 6H_2O$, reagent grade.

(3) HCl prepared from reagent grade NaCl and H_2SO_4.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 2-5 % (compiler).

REFERENCES:

1. Kamaeva, I.C.; Serebrennikov, V.V. *Zh. Neorg. Khim.* 1967, *12*, 3224; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1967, *12*, 1706.

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Strontium chloride; $SrCl_2$; [10476-85-4]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

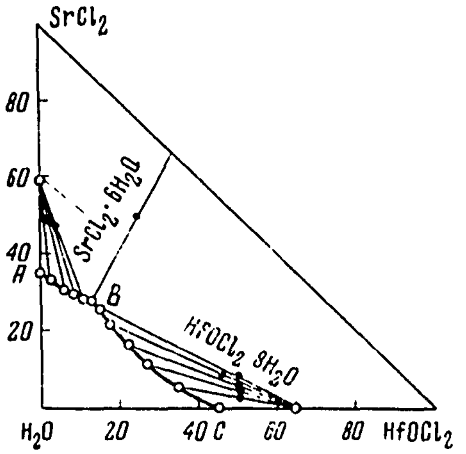
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

$SrCl_2$		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
27.55	2.90	12.50	.786

a. Calculated by compiler

Equilibrium Solids:

$SrCl_2\cdot 6H_2O$; [10025-70-4]
$HfOCl_2\cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical data given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2\cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. $SrCl_2$ concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2\cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) $SrCl_2\cdot 2H_2O$, reagent grade. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Barium chloride; $BaCl_2$; [10361-37-2]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

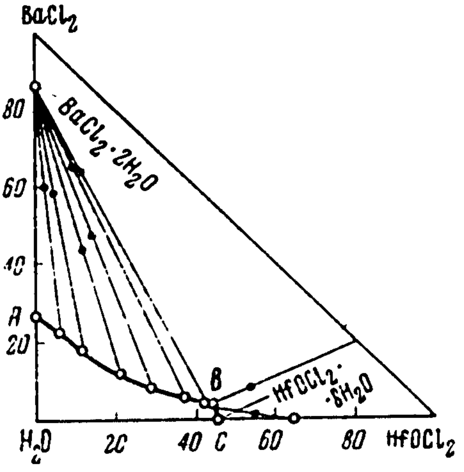
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

$BaCl_2$		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
3.97	0.367	44.10	3.20

a. Calculated by compiler

Equilibrium Solids:

$BaCl_2 \cdot 2H_2O$; [10326-27-9]

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2 \cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. $BaCl_2$ concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) $BaCl_2 \cdot 2H_2O$ reagent grade. Source and purity of other chemicals not specified.

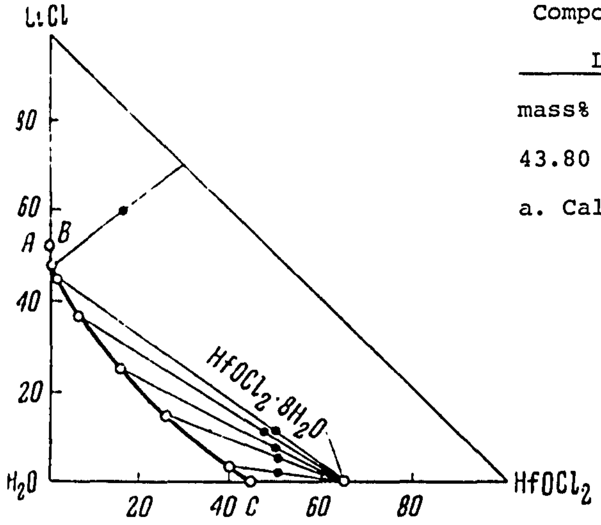
ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS: (1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6] (2) Lithium chloride; LiCl; [7447-41-8] (3) Water; H_2O; [7732-18-5]	**ORIGINAL MEASUREMENTS:** Barskaya, I.B.; Morozov, I.S. **Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.
VARIABLES: *T*/K = 298 Composition	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

LiCl		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
43.80	18.62	0.705	0.0479

a. Calculated by compiler

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2 \cdot 8H_2O$ were shaken for 3-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. LiCl concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) LiCl, reagent grade. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Sodium chloride; NaCl; [7647-14-5]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

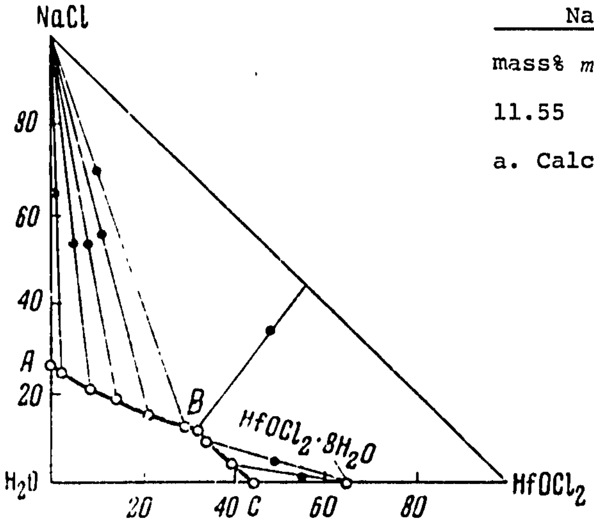
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

NaCl		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
11.55	3.50	32.00	2.14

a. Calculated by compiler

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl \cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's mehtod. NaCl concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) NaCl, reagent grade. Source and purity of other chemicals not specified.

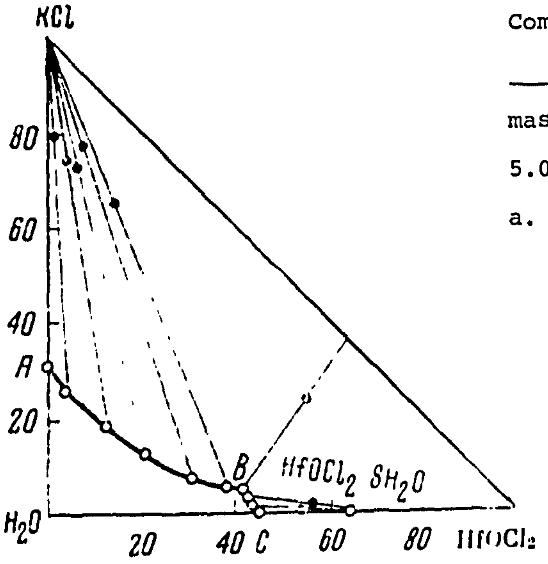
ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6] (2) Potassium chloride; KCl; [7447-40-7] (3) Water; H_2O; [7732-18-5]	Barskaya, I.B.; Morozov, I.S. **Zh. Neorg. Khim.* 1968, *13*, 1408-11, *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.
VARIABLES:	**PREPARED BY:**
T/K = 298 Composition	J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

KCl		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
5.05	1.27	41.50	2.93

a. Calculated by compiler

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Isothermal method used. Solutions containing excess $HfOCl_2 \cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. KCl concentration found by difference. Solid phases identified by Schreinemakers' method.	(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl. (2) KCl, reagent grade. Source and purity of other chemicals not specified.
	ESTIMATED ERROR:
	Temp: precision ± 0.1 K. The solubility error is not specified.
	REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Rubidium chloride; RbCl; [7791-11-9]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

VARIABLES:

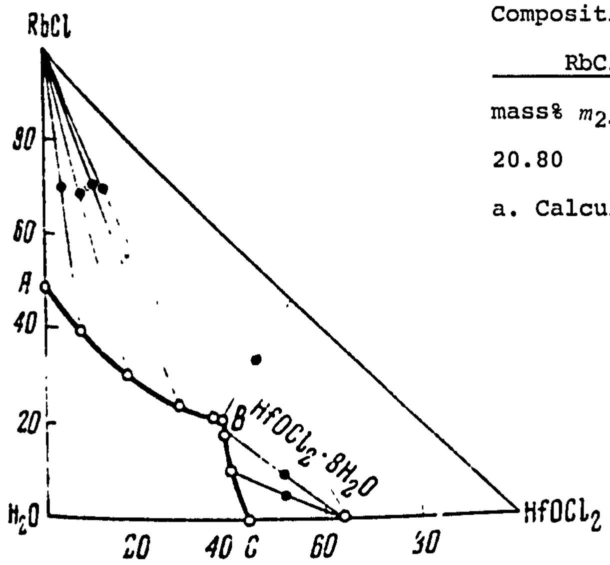
T/K = 298

Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

RbCl		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
20.80	4.18	38.00	3.48

a. Calculated by compiler

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2 \cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. RbCl concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) RbCl, reagent grade. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision 0.1 K.

The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Cesium chloride; CsCl; [7647-17-8]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Morozov, I.S.

**Zh. Neorg. Khim.* 1968, *13*, 1408-11; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1968, *13*, 738-40.

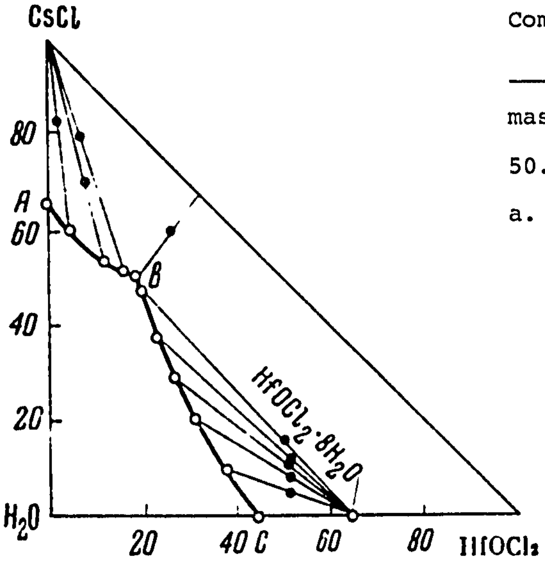
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Point

CsCl		$HfOCl_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
50.20	9.68	19.00	2.32

a. Calculated by compiler

$HfOCl_2 \cdot 8H_2O$; [14456-34-9]

The original document presented only a graphical form of the solubility isotherm (concentrations given in mass%). Numerical values given for the eutonic point. A later reinvestigation of the system showed also the formation of the compound $2HfOCl_2 \cdot CsCl \cdot 10H_2O$ (ref 1) (see next page).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOCl_2 \cdot 8H_2O$ were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. CsCl concentration found by difference. Solid phases were identified by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) CsCl, reagent grade. Source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

REFERENCES:

1. Barskaya, I.B.; Toptygina, G.M. *Zh. Neorg. Khim.* 1970, *15*, 2572, *Russ. J. Inorg. Chem. (Engl. Transl.)* 1970, *15*, 1333.

COMPONENTS:

(1) Hafnium dichloride oxide; $HfOCl_2$; [13759-17-6]

(2) Cesium chloride; CsCl; [7647-17-8]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Toptygina, G.M.

**Zh. Neorg. Khim.* <u>1970</u>, *15*, 2572-3; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1970</u>, *15*, 1333.

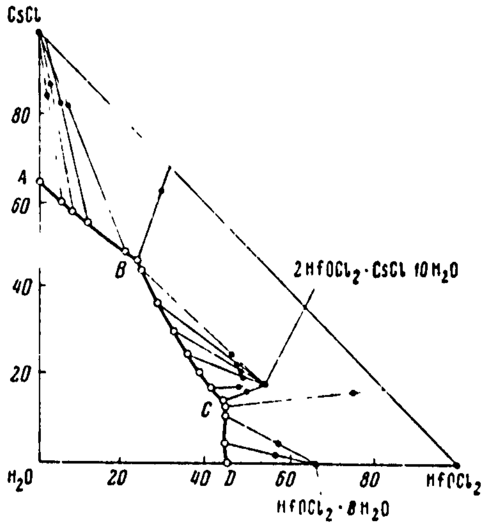
VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



Composition at the Eutonic Points

CsCl		HfOCl$_2$	
mass%	m_2/mol kg^{-1a}	mass%	m_1/mol kg^{-1a}
13.52	1.805	42.00	3.558
46.20	8.968	23.20	2.857

a. Calculated by compiler

Equilibrium Solids:

CsCl; [7647-17-8]

$2HfOCl_2.CsCl\cdot 10H_2O$;

$HfOCl_2\cdot 8H_2O$; [14456-34-9]

The authors report numerical values for only two saturated solutions, at the eutonic points. The remaining solubility data were presented graphically.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method (ref 1) used. Solutions containing excess solid were shaken for 8-12 h. Hf was determined gravimetrically as HfO_2, total Cl^- content by Volhard's method. CsCl concentration found by difference. Equilibrium solid phases were studied by X-ray diffraction, thermal analysis, microscopy, and IR spectroscopy.

SOURCE AND PURITY OF MATERIALS:

(1) As in the authors' previous work (ref 1), $HfOCl_2\cdot 8H_2O$ was prepared by crystallization from solutions of $HfCl_4$ in HCl.

(2) CsCl, reagent grade, source and purity of other chemicals not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1-2 % (compiler).

REFERENCES:

1. Barskaya, I.B.; Morozov, I.S. *Zh. Neorg. Khim.* <u>1968</u>, *13*, 1408; *Russ. J. Inorg. Chem. (Engl. Transl.)* <u>1968</u>, *13*, 738.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Hafnium dichloride oxide octahydrate; $HfOCl_2 \cdot 8H_2O$; [14456-34-9] (2) Methanol; CH_4O; [67-56-1]	Blinova, Z. N.; Komissarova, L. N. *Zh. Neorg. Khim.* 1972, *17*, 2520-5. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1972, *17*, 1318-21.
VARIABLES:	PREPARED BY:
T/K = 298	J. Hála

EXPERIMENTAL VALUES:

The solubility of $HfOCl_2 \cdot 8H_2O$ is reported to be 30.12 mass % HfO_2 or 58.54 mass % $HfOCl_2$. The equilibrium solid phase was $HfOCl_2 \cdot 8H_2O$.

NOTE: The latter value apparently represents the solubility of the hydrated salt. From the mass % HfO_2 the compiler calculated the solubility of the equilibrium solid from the mass % HfO_2 to be 58.60 mass % or 3.456 mol kg^{-1} $HfOCl_2 \cdot 8H_2O$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated in a thermostated bath with the solvent. Equilibrium was established in 12-15 days. Samples of the saturated solutions were analyzed for Hf content gravimetrically as HfO_2. Solid phase was characterized by chemical and microscopical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2(99.33 mass% Hf, 0.55 mass% Zr). HfO_2 was heated to 300-450° with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4, the melt was dissolved in water, and Hf was precipitated with NH_4OH. Hf hydroxide was washed free from sulfate ions, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization. HCl used was reagent grade.

(2) Grade "pure" methanol was used. Nothing was mentioned about drying the solvent.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Hafnium dichloride oxide octahydrate; $HfOCl_2 \cdot 8H_2O$; [14456-34-9] (2) Ethanol; C_2H_6O; [64-17-5]	Blinova, Z. N.; Komissarova, L. N. *Zh. Neorg. Khim.* 1972, *17*, 2520-5. *Russ. J. Inorg. Chem. (Engl.Transl.)* 1972, *17*, 1318-21.
VARIABLES:	PREPARED BY:
T/K = 298	J. Hála

EXPERIMENTAL VALUES:

The solubility of $HfOCl_2 \cdot 8H_2O$ at 25°C is reported to be 19.23 mass % HfO_2 or 37.40 mass % $HfOCl_2$. The equilibrium solid phase was $HfOCl_2 \cdot 8H_2O$.

NOTE: The latter value apparently represents the solubility of the hydrated salt. From the mass % HfO_2 the compiler calculated the solubility of $HfOCl_2 \cdot 8H_2O$ to be 37.41 mass % or 1.460 mol kg^{-1}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated in a thermostated bath with the solvent. Equilibrium was established in 12-15 days. Samples of the saturated solutions were analyzed for Hf content gravimetrically as HfO_2. Solid phase was characterized by chemical and microscopical analysis.	(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2(99.33 mass% Hf, 0.55 mass% Zr). HfO_2 was heated to 300-450° with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4, the melt was dissolved in water, and Hf was precipitated with NH_4OH. Hf hydroxide was washed free from sulfate ions, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization. HCl used was reagent grade. (2) Grade "pure" ethanol was used. Nothing was mentioned about drying the solvent.
	ESTIMATED ERROR:
	Temp: precision ± 0.1 K. Solubility error is not specified.

COMPONENTS:

(1) Hafnium dichloride oxide octahydrate; $HfOCl_2 \cdot 8H_2O$; [14456-34-9]

(2) 1-Hexanol; $C_6H_{14}O$; [111-27-3]

ORIGINAL MEASUREMENTS:

Blinova, Z. N.; Komissarova, L. N.

Zh. Neorg. Khim. 1972, *17*, 2520-5.

Russ. J. Inorg. Chem. (Engl. Transl.) 1972, *17*, 1318-21.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of $HfOCl_2 \cdot 8H_2O$ at 25°C is reported to be 2.46 mass % HfO_2 or 4.78 mass % $HfOCl_2$. The equilibrium solid phase was $HfOCl_2 \cdot 8H_2O$.

NOTE: The latter value apparently represents the solubility of the hydrated salt. From the mass % HfO_2 the compiler calculated the solubility of $HfOCl_2 \cdot 8H_2O$ to be 4.79 mass % or 0.123 mol kg^{-1}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated in a thermostated bath with the solvent. Equilibrium was established in 12-15 days. Samples of the saturated solutions were analyzed for Hf content gravimetrically as HfO_2. Solid phase was characterized by chemical and microscopical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2(99.33 mass% Hf, 0.55 mass% Zr). HfO_2 was heated to 300-450° with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4, the melt was dissolved in water, and Hf was precipitated with NH_4OH. Hf hydroxide was washed free from sulfate ions, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization. HCl used was reagent grade.

(2) Grade "pure" 1-hexanol was used. Nothing was mentioned about drying the solvent.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Hafnium dichloride oxide octahydrate; $HfOCl_2 \cdot 8H_2O$; [14456-34-9] (2) 1-Heptanol; $C_7H_{16}O$; [111-70-6]	Blinova, Z. N.; Komissarova, L. N. *Zh. Neorg. Khim.* 1972, *17*, 2520-5. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1972, *17*, 1318-21.
VARIABLES:	PREPARED BY:
T/K = 298	J. Hála

EXPERIMENTAL VALUES:

The solubility of $HfOCl_2 \cdot 8H_2O$ at 25°C is reported to be 1.56 mass % HfO_2 or 3.02 mass % $HfOCl_2$. The equilibrium solid phase was $HfOCl_2 \cdot 8H_2O$.

NOTE: The latter value apparently represents the solubility of the hydrated salt. From the mass % HfO_2 the compiler calculated the solubility of $HfOCl_2 \cdot 8H_2O$ to be 3.04 mass % or 0.0766 mol kg^{-1}.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated in a thermostated bath with the solvent. Equilibrium was established in 12-15 days. Samples of the saturated solutions were analyzed for Hf content gravimetrically as HfO_2. Solid phase was characterized by chemical and microscopical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2(99.33 mass% Hf, 0.55 mass% Zr). HfO_2 was heated to 300-450° with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4, the melt was dissolved in water, and Hf was precipitated with NH_4OH. Hf hydroxide was washed free from sulfate ions, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization. HCl used was reagent grade.

(2) Grade "pure" 1-heptanol was used. Nothing was mentioned about drying the solvent.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

COMPONENTS:

(1) Hafnium dichloride oxide octahydrate; $HfOCl_2 \cdot 8H_2O$; [14456-34-9]

(2) 1-Octanol; $C_8H_{18}O$; [111-87-5]

sec-Octanol; $C_8H_{10}O$;

ORIGINAL MEASUREMENTS:

Blinova, Z. N.; Komissarova, L. N.

Zh. Neorg. Khim. 1972, *17*, 2520-5.

Russ. J. Inorg. Chem. (Engl. Transl.) 1972, *17*, 1318-21.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of $HfOCl_2 \cdot 8H_2O$ at 25°C is reported to be 1.03 mass % HfO_2 or 2.00 mass % $HfOCl_2$. The equilibrium solid phase was $HfOCl_2 \cdot 8H_2O$.

Note 1: The latter value apparently represents the solubility of the hydrated salt. From the mass % HfO_2 the compiler calculated the solubility of $HfOCl_2 \cdot 8H_2O$ to be 2.00 mass % or 0.0498 mol kg^{-1}.

Note 2: *sec*-octanol (2-octanol, 3-octanol, or 4-octanol (not clear)) solubility < 0.002 mass % HfO_2 after 2.5 months (below limit of detection of method).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfOCl_2 \cdot 8H_2O$ was equilibrated in a thermostated bath with the solvent. Equilibrium was established in 12-15 days. Samples of the saturated solutions were analyzed for Hf content gravimetrically as HfO_2. Solid phase was characterized by chemical and microscopical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOCl_2 \cdot 8H_2O$ was prepared from HfO_2(99.33 mass% Hf, 0.55 mass% Zr). HfO_2 was heated to 300-450° with a mixture of $(NH_4)_2SO_4$ and concentrated H_2SO_4, the melt was dissolved in water, and Hf was precipitated with NH_4OH. Hf hydroxide was washed free from sulfate ions, dissolved in concentrated HCl, and $HfOCl_2 \cdot 8H_2O$ obtained by crystallization. HCl used was reagent grade.

(2) Grade "pure" 1-octanol was used. Nothing was mentioned about drying the solvent.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

COMPONENTS:

(1) Ammonium hexachlorohafnate(IV); $(NH_4)_2HfCl_6$; [19381-62-5]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1967, *12*, 29-33; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1967, *12*, 14-16.

VARIABLES:

T/K = 298

m_2/mol kg^{-1} = 13.79-20.72

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		HfO_2	NH_4Cl	$(NH_4)_2HfCl_6$		Nature of the Solid Phase^b
mass%	m_2/mol kg^{-1a}	mass%	mass%	mass%^{a}	m_1/mol kg^{-1a}	
31.03	13.70	3.35	5.50	6.80	.322	A+B
35.10	16.14	2.58	1.28	5.24	.258	A
35.75	16.56	2.48	1.235	5.03	.250	A
36.74	17.00	1.96	1.00	3.98	.197	A
39.64	19.04	1.60	.815	3.25	.167	A
39.75	19.12	1.59	.80	3.23	.167	A
42.05	20.72	1.13	.565	2.29	.121	A

a. Calculated by compiler. The values of mass% $(NH_4)_2HfCl_6$ were calculated from mass% HfO_2. Similar calculations from mass% NH_4Cl yielded lower values except for the value for 31.03% HCl which was higher.

b. A: $(NH_4)_2HfCl_6$ [19381-62-5]; B: $HfOCl_2 \cdot 8H_2O$ [14456-34-9]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess of either $(NH_4)_2HfCl_6$ or of a mixture of NH_4Cl and $HfCl_4$ were shaken for several hours to several days. Hf was determined gravimetrically as HfO_2, NH_4^+ by the Kjeldahl method, and Cl^- by Volhard's method. Solid phases were identified by chemical and microscopic analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) $(NH_4)_2HfCl_6$ was prepared by saturation with HCl gas of a hot solution of $HfCl_4$ and NH_4Cl. $HfCl_4$ was prepared by chlorination in the presence of carbon of HfO_2, whose source and purity was not specified. Source and purity of NH_4Cl and HCl were not given.

ESTIMATED ERROR:

Soly: precision ± 2-5 % (compiler). The temperature error is not specified.

REFERENCES:

1. Toptygina, G.M.; Barskaya, I.B. *Zh. Neorg. Khim.* 1965, *10*, 2254; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226.

COMPONENTS:

(1) Potassium hexachlorohafnate(IV); K_2HfCl_6; [19381-63-6]

(2) Hydrogen Chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Toptygina, G.M.

***Zh. Neorg. Khim.* 1967, *12*, 29-33; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1967, *12*, 14-16.

VARIABLES:

T/K = 298

m_2/mol kg^{-1} = 17.93-19.58

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		HfO_2	KCl	K_2HfCl_6		Nature of the Solid Phase[b]
mass%	m_2/mol kg^{-1} [a]	mass%	mass%	mass%[a]	m_1/mol kg^{-1} [a]	
36.23	17.93	3.74	1.70	8.34	.321	A+B
39.52	19.58	2.30	1.63	5.13	.197	C

a. Calculated by compiler. The values of mass% K_2HfCl_6 were calculated from mass% HfO_2. Similar calculations from mass% KCl yielded an identical result for 39.52 mass% HCl where K_2HfCl_6 is the equilibrium solid phase. The result for 36.23 mass% HCl was lower than that calculated from mass% HfO_2.

b. A: KCl [7447-40-7]; B: $HfOCl_2 \cdot 8H_2O$ [14456-34-9];

C: K_2HfCl_6 [19381-63-6]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess of either K_2HfCl_6 or of a mixture of $HfCl_4$ and KCl were shaken for several hours to several days. Hf and K were determined gravimetrically as HfO_2 and K_2SO_4, respectively, Cl^- determined by Volhard's method. Solid phases were identified by chemical and microscopic analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) K_2HfCl_6 was prepared by saturation with HCl gas of a solution of $HfCl_4$ and KCl in aqueous HCl. $HfCl_4$ was prepared by chlorination in the presence of carbon of HfO_2, whose source and purity was not specified. The solid was dried under dry HCl gas (ref 1). Source and purity of HCl and KCl were not given.

ESTIMATED ERROR:

Soly: precision ± 2-5 % (compiler). The temperature error is not specified.

REFERENCES:

1. Toptygina, G.M.; Barskaya, I.B. *Zh. Neorg. Khim.* 1965, *10*, 2254; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226.

COMPONENTS:

(1) Rubidium hexachlorohafnate(IV); Rb_2HfCl_6; [19276-22-3]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1967, *12*, 29-33; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1967, *12*, 14-16.

VARIABLES:

$T/K = 298$
$m_2/\text{mol kg}^{-1} = 10.22\text{-}11.39$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		HfO_2	RbCl	Rb_2HfCl_6		Nature of the Solid Phase[b]
mass%	$m_2/\text{mol kg}^{-1\,a}$	mass%	mass%	mass%[a]	$m_1/\text{mol kg}^{-1\,a}$	
25.86	10.22	1.77	2.36	4.73	.121	A+B
29.30	12.02	1.44	1.69	3.85	.102	A
30.10	12.25	.94	1.09	2.51	.0663	A
35.42	15.24	.309	.331	.825	.0230	A
39.92	18.39	.209	.23	.558	.0167	A

a. Calculated by compiler. The values of mass% Rb_2HfCl_6 were calculated from mass% HfO_2. Similar calculations from mass% RbCl yielded higher values.

b. A: Rb_2HfCl_6 [19276-22-3]; B: $HfOCl_2 \cdot 8H_2O$ [14456-34-9]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess of either Rb_2HfCl_6 or of a mixture of $HfCl_4$ and RbCl were shaken for several hours to several days. Hf and Rb were determined gravimetrically as HfO_2 and Rb_2SO_4, respectively. Cl^- determined by Volhard's method. Solid phases were identified by chemical and microscopic analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) Rb_2HfCl_6 was prepared by storing a diluted solution of $HfCl_4$ and RbCl over H_2SO_4 for a long period of time (ref 1). $HfCl_4$ was prepared by chlorination in the presence of carbon of HfO_2, whose source and purity were not specified. Source and purity of RbCl and HCl not given.

ESTIMATED ERROR:

Soly: precision ± 2-5 % (compiler). The temperature error is not specified.

REFERENCES:

1. Toptygina, G.M.; Barskaya, I.B. *Zh. Neorg. Khim.* 1965, *10*, 2254; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226.

COMPONENTS:

(1) Cesium hexachlorohafnate(IV); Cs_2HfCl_6; [16918-89-7]

(2) Hydrogen chloride; HCl; [7647-01-0]

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

ORIGINAL MEASUREMENTS:

Barskaya, I.B.; Toptygina, G.M.

**Zh. Neorg. Khim.* 1967, *12*, 29-33; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1967, *12*, 14-16.

VARIABLES:

$T/K = 298$
$m_2/\text{mol kg}^{-1} = 7.60\text{-}18.31$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions at 25°C

HCl		HfO_2	CsCl	Cs_2HfCl_6		Nature of the Solid Phase^b
mass%	$m_2/\text{mol kg}^{-1a}$	mass%	mass%	mass%^{a}	$m_1/\text{mol kg}^{-1a}$	
20.26	7.60	2.11	7.68	6.59	.137	A+B
22.19	8.45	1.85	4.10	5.77	.122	A+B
25.61	9.90	1.095	1.70	3.42	.0733	A
25.62	9.90	1.083	1.69	3.38	.0725	A
29.09	11.55	.324	.505	1.01	.0220	A
34.70	14.63	.086	.135	.268	.00627	A
39.97	18.31	.053	.083	.165	.00420	A

a. Calculated by compilers. The values of mass% Cs_2HfCl_6 were calculated from mass% HfO_2. Similar calculations from mass% CsCl yielded reasonable agreement only for 3 highest HCl concentrations.

b. A: Cs_2HfCl_6 [16918-89-7]; B: $HfOCl_2 \cdot 8H_2O$ [14456-34-9]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess of either Cs_2HfCl_6 or of a mixture of $HfCl_4$ and CsCl were shaken for several hours to several days. Hf and Cs determined gravimetrically as HfO_2 and Cs_2SO_4, respectively. Cl^- determined by Volhard's method. Solid phases were identified by chemical and microscopic analysis and by Schreinemakers' method.

SOURCE AND PURITY OF MATERIALS:

(1) Cs_2HfCl_6 was prepared from a solution of $HfCl_4$ and CsCl either by saturating it with HCl gas or by boiling (ref 1). $HfCl_4$ was prepared by chlorination in the presence of carbon of HfO_2, whose source and purity were not specified. Source and purity of CsCl and HCl not specified.

ESTIMATED ERROR:

Soly: precision ± 2-5 % (compiler).

The temperature error is not specified.

REFERENCES:

1. Toptygina, G.M.; Barskaya, I.B. *Zh. Neorg. Khim.* 1965, *10*, 2254; *Russ. J. Inorg. Chem. (Engl. Transl.)* 1965, *10*, 1226.

COMPONENTS:

(1) Hafnium bromide; $HfBr_4$; [13777-22-5]

(2) Trichloromethane (chloroform); $CHCl_3$; [67-66-3]

ORIGINAL MEASUREMENTS:

Berdonosov, S. S.; Lapitskii, A. V.
Vlasov, L. G.

Vestn. Mosk. Univ., Ser. 2: Khim. 1963, *18* (1), 38-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $HfBr_4$ at 25°C to be approximately 1.5 mass% (0.0306 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to HfO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $HfBr_4$ was prepared by bromination of a mixture of HfO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 250°C. Analysis (mass%, found/calculated):
Hf 35.68-35.87/35.83,
Br 64.25-64.31/64.17.

(2) Trichloromethane (chloroform) (source and purity not specified) was purified and dried by standard methods.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Hafnium bromide; $HfBr_4$; [13777-22-5] (2) Tetrachloromethane; CCl_4; [56-23-5]	Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G. *Vestn. Mosk. Univ., Ser. 2: Khim.* 1963, *18* (1), 38-9.
VARIABLES:	**PREPARED BY:**
T/K = 298	J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $HfBr_4$ at 25°C to be approximately 0.2 mass% (0.0040 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60°C and then ignited to HfO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $HfBr_4$ was prepared by bromination of a mixture of HfO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 250°C. Analysis (mass%, found/calculated): Hf 35.68-35.87/35.83, Br 64.25-64.31/64.17.

(2) Tetrachloromethane (source and purity not specified) was purified and dried by standard methods.

REFERENCES:

COMPONENTS:

(1) Hafnium bromide; $HfBr_4$; [13777-22-5]

(2) 1,2-Dichloroethane; $C_2H_4Cl_2$; [107-06-2]

ORIGINAL MEASUREMENTS:

Berdonosov, S. S.; Lapitskii, A. V. Vlasov, L. G.

Vestn. Mosk. Univ., Ser. 2: Khim. 1963, *18* (1), 38-9.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The original document presented only one experimental value in a graph. From it the compiler estimated the solubility of $HfBr_4$ at 25 ^{0}C to be approximately 4.1 mass% (0.0858 mol kg^{-1}).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess $HfBr_4$ was agitated with 5 cm^3 of the solvent in a stoppered test-tube in a thermostated bath for three hours, which was found sufficient to reach equilibrium.

After centrifugation, a 1.0-1.5 g sample of the saturated solution was hydrolyzed in water in a crucible at 50-60 ^{0}C and then ignited to HfO_2.

All procedures were carried out in a dry box.

SOURCE AND PURITY OF MATERIALS:

(1) $HfBr_4$ was prepared by bromination of a mixture of HfO_2 (source and purity not specified) with charcoal. The product was purified by vacuum distillation at 250 ^{0}C. Analysis (mass%, found /calculated): Hf 35.68-35.87/35.83, Br 64.25-64.31/ 64.17.

(2) 1,2-Dichloroethane (source and purity not specified) was purified and dried by standard methods.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Hafnium dibromide oxide; $HfOBr_2$; [14118-72-0]

(2) Hydrogen bromide; HBr; [10035-10-6]

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

ORIGINAL MEASUREMENTS:

von Hevesy, G.; Wagner, O.H.

Z. Anorg. Allg. Chem. 1930, *191*, 194-200.

VARIABLES:

$T/K = 298$
$c_2/\text{mol dm}^{-3} = 0.351\text{-}13.36$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of $HfOBr_2$ in aqueous HBr at 25°C

HBr $c_2/\text{mol dm}^{-3}$	HfO_2 g dm^{-3}	$HfOBr_2$ $c_1/\text{mol dm}^{-3}$	Density g cm^{-3}
0.351	694.5	3.299	2.0838
3.620	314.5	1.493	1.6989
6.568	48.90	0.2321	1.4348
8.77	10.60	0.0503	1.4984
13.36	0.80	0.0038	1.7157

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions containing excess $HfOBr_2 \cdot 8H_2O$ were mixed for several days. Methods of analysis and equilibrium solid phases not specified.

SOURCE AND PURITY OF MATERIALS:

(1) $HfOBr_2 \cdot 8H_2O$ was prepared by dissolving Hf hydroxide in HBr, and by subsequent careful evaporation. Source and purity of starting materials not specified.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

4. The solubility of vanadium-containing halide and oxyhalide substances.

Systems	Pages
$VF_5 + UF_6$	218
$VOF_2 + HF + H_2O$	219, 220
$VOF_3 + HF + H_2O$	221
____ $+ UF_6$	222
$VCl_2 + LiCl + (CH_3)_2SO$	223
$VCl_3 + LiCl + (CH_3)_2SO$	224

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Vanadium fluoride; VF_5; [7783-72-4] (2) Uranium fluoride; UF_6; [7783-81-5]	Mears, W. H.; Townend, R. V.; Broadley, R. D.; Tarissini, A. D.; Stahl, R. F. *Ind. Eng. Chem.* 1958, *50*, 1771-3.
VARIABLES:	PREPARED BY:
T/K = 343	J. Hála

EXPERIMENTAL VALUES:

The solubility of VF_5 at 70 °C is reported to be > 10 mass %. This corresponds to a solubility of m_1/mol kg^{-1} > 0.76 as calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Weighed amounts of UF_6 and VF_5 were distilled into Fluorothene tubes under vacuum. A single liquid phase free of any solid was taken as evidence of complete solubility.

SOURCE AND PURITY OF MATERIALS:

(1) VF_5 was prepared by the reaction between V metal and F_2 gas at 500 °C according to (ref 1). The product contained 35.0 % V (calculated 34.9 %).

(2) UF_6. Specification grade material from US AEC, Oak Ridge, TN.

ESTIMATED ERROR:

REFERENCES:

1. Emeleus, H. J.; Gutman, V. J. *J. Chem. Soc.* 1949, 2979.

COMPONENTS:

(1) Vanadium oxide fluoride; VOF_2; [13814-83-0]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Buslaev, Yu. A.; Gustyakova, M. P.

**Izv. Akad. Nauk SSSR, Ser. Khim.* 1963, 1533-7.

Bull. Div. Chem. Sci. (Engl.Transl.) 1963, 1399-1402.

VARIABLES:

T/K = 298
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions

HF mass %	VO_2 mass %	Nature of the Solid Phases[a]	HF mass %	VO_2 mass %	Nature of the Solid Phases[a]
2.53	5.42	A	27.04	9.81	B
2.80	6.62	A	37.62	4.22	B + C
3.28	7.35	A	42.48	2.17	C
4.62	9.60	A	49.33	1.51	C
5.57	11.56	A	51.93	1.54	C
5.51	13.40	A	54.12	1.58	C
7.93	16.04	A	57.17	1.35	C
8.76	18.20	A	59.59	1.71	C
9.93	20.20	A + B	63.30	1.77	C
11.51	15.53	B	66.78	2.99	C
12.12	15.67	B	71.07	10.16	C
15.30	10.58	B	62.37	6.76	D
25.26	5.99	B	68.45	3.34	D
35.28	4.65	B	71.01	1.53	D
45.85	10.35	B	73.07	1.35	D
48.40	12.85	B	80.98	0.61	D

See bottom of following page for identification of the solid phases.

Continued on the following page . . .

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions of HF containing excess $VOF_2\cdot4H_2O$ were equilibrated for various time periods depending on the composition of the solid phases in equilibrium with the solution. The equilibrium time was 5-6 h for systems containing solid VO_2 and $VOF_2\cdot4H_2O$, whereas 2-3 days were necessary for those containing $VOF_2\cdot2H_2O$ and VOF_2 due to slow dehydration processes. Slow attainment of equilibrium prevented studies in solutions with > 81 mass% HF. V(IV) in the saturated solutions was determined by titration with $KMnO_4$, F^- was determined by an unspecified potentiometric method. Solid phases were identified by chemical analysis.

SOURCE AND PURITY OF MATERIALS:

(1) $VOF_2\cdot4H_2O$, pale-blue crystalline solid, was prepared by dissolving VO_2 (containing < 1% V(V)) in HF. Source and purity of materials used not specified.

ESTIMATED ERROR:

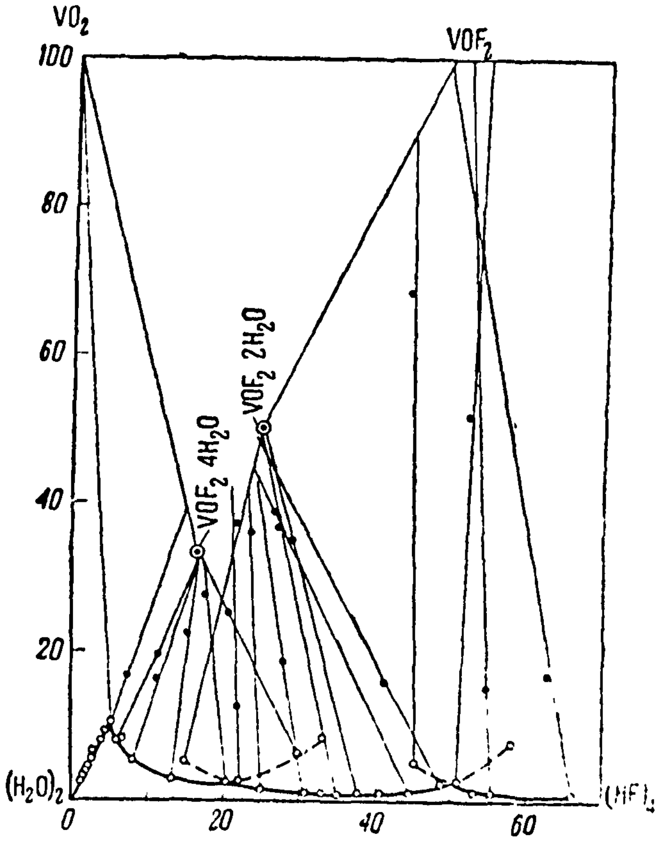
Nothing specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Vanadium oxide fluoride; VOF_2; [13814-83-0] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	Buslaev, Yu. A.; Gustyakova, M. P. **Izv. Akad. Nauk SSSR, Ser. Khim.* <u>1963</u>, 1533-7. *Bull. Div. Chem. Sci. (Engl. Transl)* <u>1963</u>, 1399-1402.

PHASE DIAGRAM OF THE VOF_2-HF-H_2O SYSTEM

Phase diagram of the VOF_2-HF-H_2O system



[a] Solid phases

A: VO_2,[12036-21-4]

B: $VOF_2 \cdot 4H_2O$

C: $VOF_2 \cdot 2H_2O$

D: VOF_2; [13814-83-0]

COMPONENTS:

(1) Vanadium oxide trifluoride; VOF_3; [13709-31-4]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N. S.; Buslaev, Yu. A.

Khim. Redk. Elem., Akad. Nauk SSSR, Inst. Obsh. i Neorg. Khim. 1955, *2*, 57-63.

Chem. Abstr. 1956, *50*, 3056*e*.

VARIABLES:

T/K = 289, 298
Composition

PREPARED BY:

J. Hála
M. Salomon

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature $t/°C$	T/K	HF mass%	V_2O_5 mass%	VOF_3 mass%[a]	Nature of the Solid Phase[b]
16	289	44.2	45.1	61.47	A
		46.6	45.4	61.88	A
		50.0	44.6	60.79	A
		53.0	45.0	61.34	A
		54.5	43.5	59.29	B
		56.8	40.4	55.07	B
		61.2	35.6	48.52	B
		63.0	33.4	45.52	B
		65.1	31.4	42.80	B
		68.0	29.8	40.62	C
		71.0	26.8	36.53	C
		75.5	23.4	31.89	C
		77.8	22.8	31.08	C
		78.5	22.7	30.94	C
25	298	6.7	10.5	14.31	D
		10.8	15.9	21.67	D
		15.2	22.3	30.39	D
		21.5	30.4	41.43	D
		29.0	32.7	44.57	E
		35.0	35.1	47.84	E
		38.2	40.0	54.52	E
		41.3	46.4	63.24	E

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solutions of HF were equilibrated with excess V_2O_5 at 25°C (C_{HF} < 41.3 mass%) or 16°C (C_{HF} > 44.2 mass%) for 2-3 days. Paraffine coated and ebonite or Pt vessels were used for measurements at lower and higher HF concentration ranges, respectively. Samples of the solutions were taken into a weighed paraffine coated vessel containing water or ice. V was determined in the presence of F^- titrimetrically with $KMnO_4$ after reduction to V(III) with Zn amalgam in the presence of H_3BO_3. F^- in the presence of V was determined by potentiometric titration with NaOH. Solid phases were identified by chem. analysis, the phase B also by microscopy.

SOURCE AND PURITY OF MATERIALS:

V_2O_5 used reagent grade, source not specified.

ESTIMATED ERROR:

Temp: precision ± 0.5 K at 298 K; precision ± 1 at 289 K.
The solubility error is not specified.

Footnotes: [a] Calculated by compiler.

[b] Solid phases.

A: $4VOF_3.3HF.3H_2O$;
B: $2VOF_3.3HF.H_2O$;
C: VOF_3, [13709-31-4]
D: V_2O_5, [1314-62-1]
E: $3VO_2F.HF.H_2O$ [16999-41-0]

COMPONENTS:

(1) Vanadium oxide trifluoride; VOF_3; [13709-31-4]

(2) Uranium fluoride; UF_6; [7783-81-5]

ORIGINAL MEASUREMENTS:

Mears, W. H.; Townend, R. V.; Broadley, R. D.; Tarissini, A. D.; Stahl, R. F.

Ind. Eng. Chem. 1958, *50*, 1771-3.

VARIABLES:

T/K = 343, 348

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

Temperature		VOF_3	
t/°C	T/K	mass%	m_1/mol kg^{-1} [d]
70	343	0.6[a]	0.049
		0.8[b]	0.065
75	348	0.7[c]	0.057

[a] Isothermal method.

[b] Freezing point lowering (probably a high value)

[c] Vapor pressure measurement.

[d] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Method A is an isothermal method. Weighed amounts of UF_6 and excess VOF_3 were distilled into Flourothene tubes under vacuum. Several such tubes were equilibrated with excess VOF_3 at 70°C for 1 week with hourly shaking each day. The tubes were allowed to stand undisturbed for two days while any excess VOF_3 floated to the top. Finally the tubes were quenched in liquid N, and their bottom sections, containing the saturated solution, were sealed off, dropped into water and analyzed for U and V. Methods of analysis not given. Method C: an excess of VOF_3 was added to pure UF_6 in a vapor-liquid apparatus and brought to equilibrium at 75°C. Samples of the liquid phase were analyzed for V. Method of analysis not given.

SOURCE AND PURITY OF MATERIALS:

(1) VOF_3 was prepared by the reaction of V_2O_5 with F gas at 450° according to ref (1), and degassed at liquid N temperature. It contained 40.9 - 41.3% V (calculated: 41.1%).

(2) UF_6, specification grade material from U.S.A.E.C., Oak Ridge.

ESTIMATED ERROR:

REFERENCES:

1. Haendler, H. M.; Bartram, S. F.; Becker, R. S.; Bernard, W. J.; Bukata, S. W. *J. Am. Chem. Soc.* 1954, *76*, 2177.

COMPONENTS:

(1) Vanadium chloride; VCl_2; [10580-52-6]

(2) Lithium chloride; LiCl; [7447-41-8]

(3) Sulfinylbismethane or dimethylsulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Melendres, C. A.

U. S. Energy Comm. Report UCRL-16330, 1965, 67 pp. (*Masters Thesis*).

Chem. Abstr. 1966, *64*, 10462d.

VARIABLES:

T/K = 298.15

PREPARED BY:

M. Salomon

EXPERIMENTAL VALUES: Composition of saturated solutions, $t/^{\circ}C$ = 25.00.

Lithium Chloride			Vanadium Chloride			Density
g/100 g(3)	mol $kg^{-1\,a}$	mol $dm^{-3\,a}$	g/100 g(3)	mol $kg^{-1\,a}$	mol $dm^{-3\,a}$	ρ/g cm^{-3}
9.037[b]	2.132	2.281[c]	0.0	-	-	1.1666
16.793	3.961	3.976	0.0897	0.00736	0.00863	1.1732
0.0	-	-	0.1796[d]	0.01474	0.01615	1.0976
0.0	-	-	0.0	-	-	1.0955

[a] Calculated by the compiler.
[b] Composition of solid is $LiCl\cdot(CH_3)_2SO$. The solid is crystalline and white.
[c] Author calculates 2.487 mol dm^{-3} which is probably an error.
[d] Composition of the solid phase could not be determined after repeated analysis.

ADDITIONAL PROPERTIES OF SATURATED SOLUTIONS:

Composition (g/100 g(3))		Viscosity	Electrolytic Conductivity
LiCl	VCl_2	η/cP	$10^3\kappa$/ S cm^{-1}
9.037	0.0	23.158	2.917
16.793	0.0897	31.319	2.365
0.0	0.1796	2.271	0.4875
0.0	0.0	1.98	1.5×10^{-4}

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Solute and solvent combined in a 250 ml flask protected from the atmosphere by argon atmosphere in a dry box and by a buret vacuum system. No thermal effect was observed during solution. The flask was sealed and mechanically agitated for at least one week in a water thermostat. Temperature was measured with a calibrated thermometer. Equilibrated solutions were allowed to settle 2-3 days, and the solution then filtered through a fritted glass disc under Ar pressure into a 250 ml flask. Weighed aliquots analyzed for Cl by either $AgNO_3$ titration with dichlorofluorescein indicator or potentiometrically.

An analysis of the wet residue (dried under 60-70 mmHg) for total C, H, S, and Cl gave an empirical formula from which the solvate formula was derived. The VCl_2 + DMSO system did not give a rational empirical formula. It appears that a solute of unknown composition is present in that equilibrated solid phase.

SOURCE AND PURITY OF MATERIALS:

1. VCl_2, anhydrous, 99.9 % purity (K & K Laboratories). Used as received.
2. Dimethylsulfoxide (DMSO) (Crown Zellerbach Corp.) was treated with solid NaOH in a polyethylene bottle for 0.5 hour. Type 4A molecular sieves were added and allowed to stand for 24 hours with periodic shaking. The DMSO was fractionated at 5 mmHg and 70-80 °C. The middle 3/5 to 1/2 fraction was retained for use. K. Fisher analysis gave a maximum water content of 0.01 mass %.

ESTIMATED ERROR:

Temp: precision ± 0.02 K.
Soly: precision ± 2 % (author);
precision ± 3-5 % (compiler, because duplicate analyses not done).

COMPONENTS:

(1) Vanadium chloride; VCl_3; [7718-98-1]

(2) Lithium chloride; LiCl; [7447-41-8]

(3) Sulfinylbismethane or dimethylsulfoxide; C_2H_6OS; [67-68-5]

ORIGINAL MEASUREMENTS:

Melendres, C. A.

U. S. Energy Comm. Report UCRL-16330, 1965, 67 pp. (*Masters Thesis*).

Chem. Abstr. 1966, *64*, 10462d.

VARIABLES:

T/K = 298.15
Composition

PREPARED BY:

M. Salomon

EXPERIMENTAL VALUES: Composition of saturated solutions, t/°C = 25.00.

Lithium Chloride			Vanadium Chloride		
g/100 g(3)	mol kg^{-1}[a]	mol dm^{-3}[a]	g/100 g(3)	mol kg^{-1}[a]	mol dm^{-3}[a]
9.037[b]	2.132	2.281[c]	0.0	---	---
9.929	2.342	2.500	0.0708	0.00450	0.00481
0.0	---	---	0.2088[d]	0.01327	0.01456

[a] Calculated by compiler.

[b] Solid phase is $LiCl\cdot(CH_3)_2SO$, a white crystalline solid.

[c] Author calculated 2.487 mol dm^{-3} which is probably an error.

[d] Solid phase is $VCl_3\cdot4(CH_3)_2SO$, a light grey-green solid.

ADDITIONAL PROPERTIES OF SATURATED SOLUTIONS, t/°C = 25.00.

Composition (g/100 g(3))		Viscosity	Electrolytic Conductivity	Density
LiCl	VCl_2	η/cP	$10^3\kappa$/ S cm^{-1}	ρ/g cm^{-3}
9.037	0.0	23.158	2.917	1.1666
9.929	0.0708	31.681	2.235	1.1743
0.0	0.2088	2.169	0.7732	1.0995
0.0	0.0	1.98-2.10	2.5×10^{-4}	1.0955

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Solute and solvent combined in a 250 ml flask protected from the atmosphere by argon atmosphere in a dry box and by a buret vacuum system. No thermal effect was observed during solution. The flask was sealed and mechanically agitated for at least one week in a water thermostat. Temperature was measured with a calibrated thermometer. Equilibrated solutions were allowed to settle 2-3 days, and the solution then filtered through a fritted glass disc under Ar pressure into a 250 ml flask. Weighed aliquots analyzed for Cl by either $AgNO_3$ titration with dichlorofluorescein indicator or potentiometrically.

An analysis of the wet residue (dried under 60-70 mmHg) for total C, H, S, and Cl gave an empirical formula from which the solvate formula was derived.

SOURCE AND PURITY OF MATERIALS:

(1) VCl_3, anhydrous, 99.9% purity (K & K Laboratories). Used as received.

(2) Dimethylsulfoxide (DMSO) (Crown Zellerbach Corp.) was treated with solid NaOH in a polyethylene bottle for 0.5 hour. Type 4A molecular sieves were added and allowed to stand for 24 hours with periodic shaking. The DMSO was fractionated at 5 mmHg and 70-80°C. The middle 3/5 to 1/2 fraction was retained for use. K. Fisher analysis gave a maximum water content of 0.01 mass %.

ESTIMATED ERROR:

Temp: precision ± 0.02 K.
Soly: precision ± 2 % (author);
precision ± 3-5 % (compiler, because duplicate analyses not done).

5. The solubility of niobium-containing halide and oxyhalide substances.

Systems	Pages
NbF_5 + HF + H_2O	226, 227
____ + BrF_3	228
____ + UF_6	229
NbO_2F + HF + H_2O	230-235
_____ + __ + HNO_3 + H_2O	236
$AgNbF_6$ + HF	237
$KNbF_6$ + HF + H_2O	238
K_2NbF_7 + HF + H_2O	239-241
______ + KF + H_2O	242
______ + __ + HF + H_2O	243
K_2NbOF_5 + H_2O	244
$NaNbCl_6$ + CCl_2=CClCCl=CCl_2	245
$KNbCl_6$ + CCl_2=CClCCl=CCl_2	246
$NbCl_4$ + CCl_2=CClCCl=CCl_2	247
$NbCl_5$ + C_6H_6	248
_____ + $(C_2H_5)_2O$	249
_____ + $C_4H_6O_3$	250
_____ + CCl_2=CClCCl=CCl_2	251
_____ + $CH_2ClCOOH$	252
_____ + $TiCl_4$	253-259
$NbOCl_3$ + $NbCl_5$	260-262
______ + $TiCl_4$	263
$NbBr_5$ + $(C_2H_5)_2O$	264

COMPONENTS:

(1) Niobium fluoride; NbF_5; [7783-68-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N. S.; Buslaev, Yu. A.

***Zh. Neorg. Khim.* 1959, *4*, 205-12.

Russ. J. Inorg. Chem. (Engl.Transl.) 1959, *4*, 84-9.

EXPERIMENTAL VALUES:

Composition of saturated solutions at $t/^{\circ}C = 20$.

HF	Nb_2O_5	Nb [a,b]		Nature of Solid Phase [c]
mass%	mass%	mass%	m/mol kg^{-1}	
2.89	3.82	2.67	0.304	A
13.65	18.05	12.62	1.84	A
14.60	21.65	15.14	2.32	A
20.56	28.24	19.74	3.56	A
26.45	35.26	24.65		A
28.81	35.83	25.05		A
32.02	43.52	30.43		A
33.56	46.30	32.37		A
35.62	47.61	33.28		A
37.05	49.01	34.26		A
38.81	50.50	35.31		A
40.01	50.59	35.37		A
41.00	51.79	36.21		A
41.80	53.65	37.51		A
43.60	52.58	36.76		B
44.74	51.82	36.23		B
45.62	50.82	35.53		B
49.60	47.99	33.55		B
52.02	47.13	32.95		B
53.62	47.43	33.16		B + C
54.77	46.24	32.33		C
57.32	42.70	29.85		C
66.40	32.57	22.77		C
71.72	28.21	19.72		C
76.41	25.23	17.64		C
79.95	24.77	17.32		C
80.37	25.87	18.09		C
81.41	25.77	18.02		C
60.88	57.55	40.23		D
61.04	56.48	39.49		D
66.15	49.51	34.61		D
75.48	35.35	24.71		D
80.07	29.51	20.63		D
83.58	24.45	17.09		D
85.50	21.31	14.90		D
86.34	19.70	13.77		D
88.28	17.22	12.04		D

[a] Calculated by the compiler.

[b] The molal values calculated for comparison with the data of Ferris (ref 2) in the low HF concentration range.

[c] Solid phases:

A: $Nb_2O_5 \cdot 2H_2O$

B: $HNb_2F_{11} \cdot 4H_2O$

C: $HNbF_6 \cdot H_2O$

D: NbF_5; [7783-68-8]

Continued on the next page . . .

COMPONENTS:

(1) Niobium fluoride; NbF_5; [7783-68-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Nikolaev, N. S.; Buslaev, Yu. A.

**Zh. Neorg. Khim.* 1959, *4*, 205-12.

Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 84-9.

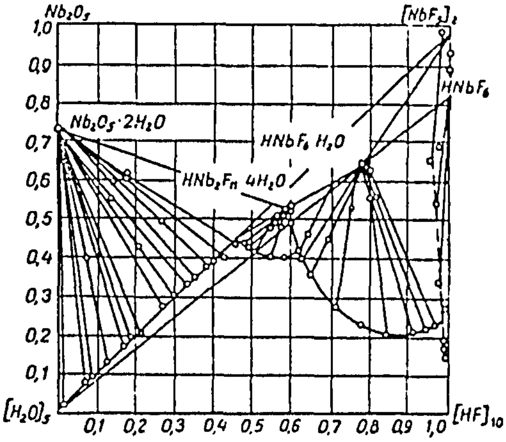
VARIABLES:

T/K = 293
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:



NbF_5 + HF + H_2O
Mole Fraction, 293 K

Phase diagram of the NbF_5 + HF + H_2O system.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Teflon bottles equipped with stirrers and heavy fluoro-carbon hydraulic sealing were used. Solutions containing excess of hydrous Nb_2O_5 were equilibrated for at least 3-4 hr., in some experiments for 2 or more days. At high HF concentrations NbF_5 was used as the solute. In such cases the solutions were prepared by adding water to NbF_5 solution in anhydrous HF. Samples of saturated solutions were taken by and weighed in a Pt pipette after filtration in a Pt apparatus. Nb was determined gravimetrically as Nb_2O_5 after precipitation with tanine, F^- in the presence of Nb was titrated with NaOH against methyl red. Solutions containing > 80% HF, and the solid phases were analyzed for H_2O content by Fischer method modified for HF solutions (1). The composition of the solid phases was determined by chemical and microscopical analysis and also graphically from the phase diagram.

SOURCE AND PURITY OF MATERIALS:

Nb_2O_5 was prepared from Nb metal by dissolving it in a mixture of HF + H_2O_2 and fluorination of the product with ClF_3 in liquid HF. The product was hydrolyzed to yield hydrous Nb_2O_5. NbF_5 was prepared by fluorination with ClF_3 of Nb metal. Source and purity of starting materials not specified except for the Ta content (0.2 mol%) in Nb metal.

ESTIMATED ERROR:

Temp: precision ± 0.1 K

Soly: precision ± 2.5 %.

REFERENCES:

1. Nikolaev, N. S.: Alenchikova, I.F. *Zavodskaya Lab*. 1958, *24*, 418.
2. Ferris, L. M. *J. Chem. Eng. Data* 1966, *11*, 343.

COMPONENTS:

(1) Niobium fluoride; NbF_5; [7783-68-8]

(2) Bromine trifluoride; BrF_3; [7787-71-5]

ORIGINAL MEASUREMENTS:

Sheft, I.; Hyman, H. H.; Katz, J. J.

J. Am. Chem. Soc. 1953, *75*, 5221-3.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The authors report the solubility of NbF_5 in BrF_3 at 25 °C as (15.7 ± 0.01) g Nb/100 g solution or as the mole fraction of the species $BrF_2^+NbF_6^-$, $x = 0.341$.

The compiler calculated the solubility of the species NbF_5 as 31.75 g/100 g solution or m_1/mol kg^{-1} = 2.476, and the species $BrF_2^+NbF_6^-$ solubility as m/mol kg^{-1} = 3.75.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Measurements were carried out in a solubility apparatus made of Cu and brass, and consisting of a Cu mixing tube with a fritted Fluorothene filter disc at the bottom end to which a sampling compartment was connected. Excess NbF_5 was first mixed with BrF_3 in a quartz tube, and Br_2 and HF were removed by short evacuation. The slurry was then poured into the Cu mixing tube. The apparatus was assembled in a constant temperature air box which was lying on the rocker platform. The rocker was shaken for about 20 h. The displacement was such that at no time could the liquid come into contact with the filter disc. After equilibrium had been attained the box was turned upright, He pressure applied, and the saturated solution was forced through the filter into the weighed collecting tube. The sampling compartment was opened, the collecting tube sealed with a Fluorothene cap and weighed. The saturated solution was then hydrolyzed, Nb precipitated with cupferron, and ignited to Nb_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) NbF_5 was prepared by fluorination by BrF_3 of Nb_2O_5 (source and purity not specified). The volatile impurities, Br_2 and HF, were removed under vacuum, and the resulting slurry was used as such.

(2) BrF_3 (Harshaw Chem. Comp.) was purified from Br_2, HBr, BrF_5, HF, and nonvolatile fluorides by vacuum distillation in an all-nickel still. The fraction used (b.p. 95-95.5° at 250 mmHg) was pale yellow and was stored in Ni container. It was used in less than 3 days after distillation.

ESTIMATED ERROR:

Temp: precision ± 0.75 K.

Soly: precision ± 0.6 %.

COMPONENTS: (1) Niobium fluoride; NbF_5; [7783-68-8] (2) (OC-6-11)-Uranium fluoride; UF_6; [7783-81-5]	**ORIGINAL MEASUREMENTS:** Nikolaev, N. S.; Sadikova, A. T. *At. Ener.* 1975, *39*, 338-43. *Sov. At. Energy (Engl. Transl.)* 1975, *39*, 338-43.
VARIABLES: $T/K = 373$	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

At 100 °C the solubility of NbF_5 in UF_6 is reported to be 0.37 mol kg^{-1} (6.86 mass %).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility was determined in a Cu autoclave placed in a crucible furnace. Excess solid was equilibrated under constant mixing with 6 ml UF_6 for 30-40 h, and then allowed to stand for another 40 h at the desired temperature, which exceeded 3-4 times the time necessary to reach the equilibrium. After that the autoclave was rapidly cooled in liquid N. A sample of the frozen saturated solution was transfered to ice to hydrolyze the components, and analyzed. Methods of analysis were not given. All procedures were carried out in a dry box at -20°C.

SOURCE AND PURITY OF MATERIALS:

The fluorides were prepared by the authors. No details were specified except for the fact that the products were strictly anhydrous.

ESTIMATED ERROR:

Temp: precision ± 5 K.

Solubility error is not specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Niobium fluoride oxide; NbO_2F; [13597-25-6] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia October 1985

CRITICAL EVALUATION:

An evaluation of the solubility of NbO_2F in aqueous HF solutions.

Nikolaev and Buslaev (ref 1) measured the solubility of either $Nb_2O_5 \cdot xH_2O$ or NbF_5 in aqueous HF solutions to nearly 100 % HF at 293 K. Ferris (ref 2) measured the solubility of NbO_2F in aqueous HF solutions up to about 24 mass percent HF at 298 K. Although the data were measured at temperatures that differed by five degrees, the results (Figure 1) agree well enough to believe that the same system is being studied by the two laboratories over the common part of the HF range.

Nikolaev and Buslaev equilibrated their mixtures from 3-4 hours up to two days. They reported the equilibrium solid to be $Nb_2O_5 \cdot 2H_2O$. Ferris equilibrated the system for up to four months. His data shows less scatter than the data of Nikolaev and Buslaev. Ferris carefully characterized the solid as NbO_2F by both chemical analysis and by X-ray diffraction. The evaluator accepts what appears to be the more careful work of Ferris that NbO_2F is the thermodynamically stable solid. Ferris' data is preferred over the 0 to 24 mass percent HF range. Ferris points out that if Nikolaev and Buslaev used a very large excess of $Nb_2O_5 \cdot xH_2O$ over HF that all of the HF could have been consumed without markedly depleting the oxide present. This could explain the difference in the identification of the solid phase.

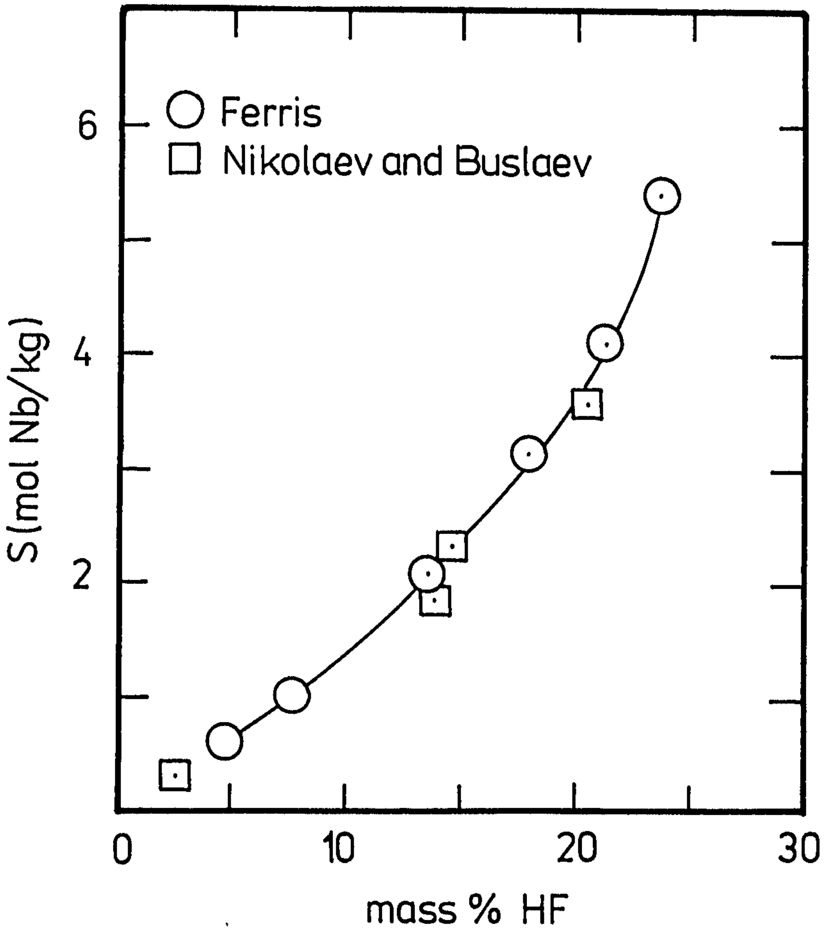
REFERENCES:

1. Nikolaev, N. S.; Buslaev, Yu. A.
   Zh. Neorg. Khim. 1959, *4*, 205.

2. Ferris, L. M.
   J. Chem. Eng. Data 1966, *11*, 343.

COMPONENTS:	EVALUATOR:
(1) Niobium fluoride oxide; NbO_2F; [13597-25-6] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia October 1985

CRITICAL EVALUATION:



$NbO_2F + HF + H_2O$

m/mol Nb kg^{-1} *vs.* HF/mass%

T/K = 293 Nikolaev and Buslaev

= 298 Ferris

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Niobium fluoride oxide; NbO_2F; [13597-25-6] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	Nikolaev, N. S.; Buslaev, Yu. A. *Zh. Neorg. Khim.* 1959, *4*, 205-12. *Russ. J. Inorg. Chem. (Engl. Transl.)* 1959, *4*, 84-9.
VARIABLES:	PREPARED BY:
T/K = 293 Composition	J. Hála

EXPERIMENTAL VALUES:

Nikolaev and Buslaev did not indentify NbO_2F as the solid phase in this system. Subsequent work of Ferris (ref 1) strongly indicates the equilibrium solid to be the NbO_2F and not the $Nb_2O_5 \cdot 2H_2O$ identified by Nikolaev and Buslaev. For Nikolaev and Buslaev's complete data see the data sheets on the NbF_5 + HF + H_2O system (pp. 226-7).

HF	Nb_2O_5	$Nb^{a, b}$	
mass %	mass %	mass %	m/mol kg^{-1}
2.89	3.82	2.67	0.304
13.65	18.05	12.62	1.84
14.60	21.65	15.14	2.32
20.56	28.24	19.74	3.56

[a] Calculated by the compiler.

[b] The molal values, which could represent NbO_2F, are compared with the values of Ferris on p. 231.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Teflon bottles equiped with stirrers and heavy fluoro-carbon hydraulic seals were used. Solutions containing as excess of Nb_2O_5 were equilibrated for at least 3-4 hr., in some experiments for 2 or more days. Samples were taken by and weighed in a Pt pipette after filtration in a Pt apparatus. Nb was determined gravimetrically as Nb_2O_5.

SOURCE AND PURITY OF MATERIALS:

Nb_2O_5 was prepared from Nb metal by dissolving it in a mixture of HF + H_2O_2 and fluorination of the product with ClF_3 in liquid HF. The product was hydrolyzed to yield hydrous Nb_2O_5. Source and purity of the starting materials was not specified except for the Ta content (0.2 mol %) in Nb metal.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 2.5 %

REFERENCES:

1. Ferris, L. M. *J. Chem. Eng. Data* 1966, *11*, 343.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Niobium fluoride oxide; NbO_2F [13597-25-6] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	Ferris, L. M. *J. Chem. Eng. Data* 1966, *11*, 343-6.

EXPERIMENTAL VALUES:

Composition of Solutions at 25°C. (Starting solid was hydrous NbO_2F. The solutions were equilibrated for about two years.)[a]

Fluorine[b] c/mol dm^{-3}	Niobium c/mol dm^{-3}	Density ρ/g cm^{-3}
0.41	0.082	1.0144
0.67	0.145	1.0366
1.47	0.293	1.0448
3.89	0.932	-
4.42	0.921	-
4.58	1.06	-
5.01	1.06	-
19.0	4.60	-
21.2	4.50	-

[a] The equilibrium solid in all solutions was was identified as $NbO_2F \cdot (1/2)H_2O$

[b] Total concentration.

NOTE: The F/Nb atomic ratio in the saturated solutions varied from 4.12 to 5.00, and the concentration of free F^- ions was negligible. The solubilization of NbO_2F proceeded via the equilibrium

$$NbO_2F(s) + 4\ HF(aq) \rightleftarrows H_2NbOF_5(aq) + H_2O$$

Composition of Solutions at 25°C. (Starting solid was Nb_2O_5. The solutions were equilibrated for about four months.)[a]

Fluorine[b]	HF	Nb_2O_5	Niobium		Density
c/mol dm^{-3}	mass%	mass%	c/mol dm^{-3}	m/mol kg^{-1} [c]	ρ/g cm^{-3}
0.237	-	-	0.053	-	1.0079
1.06	-	-	0.237	-	1.0334
2.63[d]	4.87	7.26	0.589	0.607	1.0773
4.44[d]	7.83	11.2	0.956	1.00	1.1326
6.26	-	-	1.23	-	-
8.69[d]	13.8	19.9	1.88	2.07	1.2594
10.6	-	-	2.34	-	1.3143
12.4[d]	18.0	26.4	2.74	3.13	1.3805
14.3	-	-	3.23	-	1.4394
15.6[d]	21.2	31.0	3.40	4.08	1.4644
17.4	-	-	3.69	-	1.5003
18.9[d]	23.8	36.4	4.34	5.40	1.5857
25.2	-	-	5.29	-	-

[a] The equilibrium solid phases were mixtures of $Nb_2O_5 \cdot xH_2O$ and $NbO_2F \cdot (1/2)H_2O$ in all cases.

[b] Total concentration.

[c] Calculated by the compiler.

[d] Free F^- ion concentration determined to be <0.003 mol dm^{-3}.

NOTE: The F/Nb atom ratio in the saturated solutions varied from 4.35 to 5.09, and the concentration of free F^- ions was negligible.

Continued on the next page . . .

COMPONENTS:	ORIGINAL MEASUREMNTS:
(1) Niobium fluoride oxide; NbO_2F; [13597-25-6] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	Ferris, L. M. *J. Chem. Eng. Data* <u>1966</u>, *11*, 343-6.

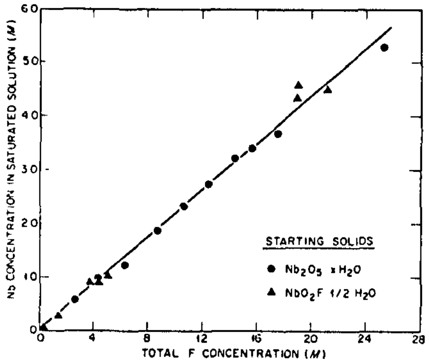
EXPERIMENTAL VALUES:

NOTE: (continued) The solubilization of Nb_2O_5 proceeded via the equilibrium

$$Nb_2O_5(s) + 6\ HF(aq) \rightleftarrows NbO_2F(s) + H_2NbOF_5(aq) + 2\ H_2O$$

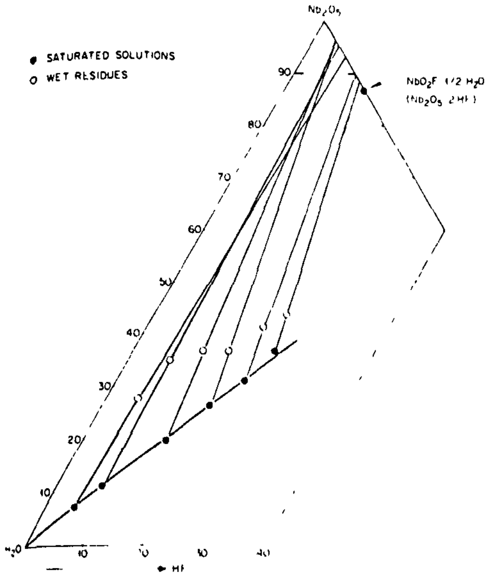
Both sets of data (starting with either $Nb_2O_5 \cdot xH_2O$ or $NbO_2F \cdot (1/2)H_2O$ as the solid) fit a single straight line when the niobium concentration in the saturated solution is plotted against the total fluorine concentration. This indicates that the NbO_2F is the thermodynamically stable solid phase.

See the figures below.



Solubility of niobium in hydrofluoric acid solutions at 25° C

Slope of line, 0 220, corresponding to F/Nb ratio of 4 54 in saturated solutions



Portion of Nb_2O_5-HF-H_2O system at 25° C.

Composition in weight %

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Continued on the next page . . .

COMPONENTS:

(1) Niobium fluoride oxide; NbO_2F; [13597-25-6]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGNINAL MEASUREMENTS:

Ferris, L. M.

J. Chem. Eng. Data 1966, *11*, 343-6.

VARIABLES:

$T/K = 298$
HF Concentration
Starting solid

PREPARED BY:

J. Hála

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal. Excess of either hydrous $Nb_2O_5 \cdot \frac{1}{2}H_2O$ or $NbO_2F \cdot \frac{1}{2}H_2O$ was equilibrated with HF solutions. Solutions containing initially hydrous Nb_2O_5 attained equilibrium in a few days, equilibration of systems containing initially $NbO_2F.1/2H_2O$ required nearly 2 years. After equilibration samples of the saturated solutions were clarified by centrifugation at 25°, and analyzed. Solid phases were recovered by filtration, washed with water and air-dried. Their composition was determined by chemical analysis and x-ray diffraction. Solid phases from solutions equilibrated with hydrous Nb_2O_5 were also identified by the method of wet residues. Nb in solutions and solid phases was determined by both x-ray absorption (ref 1) and by ignition of samples to Nb_2O_5. Total F in solutions and in wet residues was determined by differential potentiometric titration with NaOH (ref 2). In solid compounds F was also determined by pyrohydrolysis (refs 3,4) after drying the sample in the presence of a mixture of WO_3 and Na_2WO_4. The concentration of free F^- in solutions was determined by spectrophotometric titration with Th(IV) solution as a titrant, and SPDNS as the indicator (ref 5). Raman spectra of selected saturated solutions were recorded to confirm the presence of the $NbOF_5^{2-}$ ion.

SOURCE AND PURITY OF MATERIALS:

(1) Hydrated NbO_2F was obtained by dissolving high purity Nb metal in boiling 16 mol dm^{-3} HNO_3 + 1 mol dm^{-3} HF (F:Nb atom ratio < 5) in a teflon vessel. The product was filtered, washed with acetone, and dried first in air and then over Drierite. Analysis (mass %): found Nb 61.6, F 12.4, H_2O 5.12; calculated for $NbO_2F.1/2H_2O$ Nb 60.8, F 12.4, H_2O 5.89. The existence of the hydrate was confirmed by ir analysis. Hydrous Nb_2O_5 was obtained by dissolving sintered Nb_2O_5 (Kawecki Chem. Co.; total metal impurities < 300 ppm) in HF, and precipitating the hydrous oxide with NH_4OH. The precipitate was alternately washed with water and 0.1 mol dm^{-3} HNO_3 and air-dried at room temperature. It contained about 50% Nb, 25% H_2O, 0.1% F, and < 0.5% N.

(2) HF, reagent grade.

(3) Distilled water was used.

ESTIMATED ERROR:

Temp: precision ± 1 K.
Soly: precision ± 3 % as Nb.

REFERENCES:

(1) Dunn, H. W. *Anal. Chem.* 1962, *34*, 116.

(2) Nikolaev, N. S.; Buslaev, Yu.A. *Russ. J. Inorg. Chem.* 1959, *4*, 84.

(3) Horton, A. D. USAEC Report TID-7015, 1958.

(4) Mennis, O. USAEC Report TID-7015, 1961, Suppl. 3.

(5) Laing, W. R. USAEC Report ORNL-3750, 1965.

COMPONENTS:

(1) Niobium fluoride oxide; NbO_2F; [13597-25-6]

(2) Hydrogen fluoride; HF; [7664-39-3]

(3) Nitric acid; HNO_3; [7697-37-2]

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

ORIGINAL MEASUREMENTS:

Ferris, L. M.

J. Chem. Eng. Data 1966, *11*, 343-6.

VARIABLES: $T/K = 298$

$c_2/\text{mol dm}^{-3} = 0.20 - 5.37$

$c_3/\text{mol dm}^{-3} = 4.42 - 21.3$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of NbO_2F in aqueous HF + HNO_3 at 25°C

HNO_3 mol dm^{-3}	Fluorine[a] mol dm^{-3}	Niobium mol dm^{-3}
5.35	0.353	0.087
4.93	0.758	0.138
4.94	1.58	0.449
4.68	5.37	0.572
4.42	5.06	1.02
9.66	0.421	0.080
9.62	0.742	0.132
8.89	1.82	0.361
9.30	2.68	0.493
8.98	4.74	0.932
12.4	0.200	0.031
12.5	1.03	0.204
21.3	0.198	0.030
20.6	0.916	0.173
19.7	1.56	0.243

[a] Total concentration.

Note: The equilibrium solid phase was $NbO_2F.1/2H_2O$ in all solutions. The F/Nb atom ratio in the saturated solutions varied within the range of 3.51 - 6.69.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess of hydrous Nb_2O_5 was equilibrated with HF/HNO_3 wolutions for about 1 year. After equilibration samples of the saturated solutions were clarified by centrifugation at 25°, and analyzed. Nb was determined by both x-ray absorption (ref 1) and by ignition of samples to Nb_2O_5. Total F content was determined by differential potentiometric titration with NaOH (ref 2). Solid phases were identified by x-ray diffraction.

SOURCE AND PURITY OF MATERIALS:

(1) Hydrous Nb_2O_5 was obtained by dissolving sintered oxide (Kawecki Chem. Co., total metal impurities < 300 ppm) in HF, and precipitating the hydrous oxide with NH_4OH. The precipitate was washed alternately with water and 0.1 mol dm^{-3} HNO_3 and air-dried at room temperature. It contained about 50% Nb, 25% H_2O, 0.1% F, and < 0.5% N.

(2) HF, reagent grade.

(3) HNO_3, reagent grade.

(4) Distilled water was used.

ESTIMATED ERROR:

Temp: precision ± 1 K.

Soly: precision ± 3 % as Nb.

REFERENCES:

(1) Dunn, H. W. *Anal. Chem.* 1962, *34*, 116.

(2) Nikolaev, N. S.; Buslaev, Yu.A. *Russ. J. Inorg. Chem.* 1959, *4*, 84.

COMPONENTS:

(1) Silver hexafluoroniobate(1-); $AgNbF_6$; [12062-11-2]

(2) Hydrogen fluoride; HF; [7664-39-3]

ORIGINAL MEASUREMENTS:

Gut, R.; Rueede, J.

J. Coord. Chem. 1978, *8*, 47-53.

VARIABLES:

T/K = 273

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Both the solubility and solubility product of $AgNbF_6$ in liquid HF at 0 °C are reported. The values are 0.752 g in 100 g HF from which the compiler calculated m_1/mol kg^{-1} = 0.0239, and $-\log K_{s0} = 3.01$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility was determined by isothermal method followed by chemical analysis of saturated solutions. Details were not reported. The solubility product was obtained from titrations of solutions of $KNbF_6$ in HF with a AgF solution in HF during which solid $AgNbF_6$ was formed. Details of calculations not reported. In the titrations the $[Ag^+]/[NbF_6]$ ratio varied 10-50-fold and the ionic strength varied within 0.15 ± 0.03 mol dm^{-3} due to changes in supporting electrolyte concentration. The titrations were carried out in a Kel-F apparatus with a burette made of a precision drilled Kel-F rod, using a Ag indicator electrode and $Ag/AgBF_4(sat)/KBF_4(sat)/HF$ or $Ag/AgNbF_6(sat)$/liquid HF systems as reference electrodes. The titration apparatus was handled at 0^0 in a refrigerator. The Ag electrode responded reversibly to the concentration of free Ag^+ ions over the range of pAg = 1.5-20. Equilibrium potentials were reached in seconds and were constant over long periods of time.

SOURCE AND PURITY OF MATERIALS:

(1) $AgNbF_6$ was prepared from AgF and NbF_5 in anhydrous HF and recrystallized. NbF_5 used was prepared by condensing excess HF onto freshly sublimed $NbCl_5$, and subliming the crude NbF_5 in vacuum. AgF used was prepared by evaporation of HF from $AgHF_2$ which in turn was prepared in the following way. Excess HF gas was condensed on a wet filter cake of freshly precipitated Ag_2O and the solution obtained was evaporated to dryness by heating at 150^0 in a stream of N gas. The residue was dissolved in anhydrous HF, cooled to -78^0 to obtain crystals of AgF.5HF which decomposed to $AgHF_2$ on heating to 25^0.

(2) Anhydrous HF distilled from commercial (source not specified) 99.9% product in steel tanks was redistilled 2-3-times over AgF to remove traces of H_2S. The conductivity of the product corresponded to water content $< 10^{-4}$ mol dm^{-3}.

ESTIMATED ERROR:

Error of solubility product

± 0.04 log units (reproducibility).

Temperature and solubility errors are not reported. The authors stated that the solubility calculated from K_{s0} was somewhat higher than the isothermal value, due to the salt effect.

COMPONENTS:

(1) Potassium hexafluoroniobate; $KNbF_6$; [16919-14-5]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1946, *19*, 1093-1105.

VARIABLES:

$T/K = 298$
HF/mass % = 40.9-59.0

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Solubility of $KNbF_6$ in aqueous HF at 25°C

HF	NbF_5	KF	$KNbF_6$	
mass%	mass%	mass%	mass%[a]	m_1/mol kg^{-1} [b]
40.90	12.07	4.03	15.79	1.482
45.00	11.88	3.90	15.55	1.602
47.50	11.84	4.00	15.50	1.703
54.00	11.60	-	15.14	1.994
57.30	11.30	3.80	14.78	2.152
59.00	11.25	3.68	14.72	2.277

[a] Calculated by authors from the NbF_5 data.

[b] Calculated by compiler.

Note:
As follows from the study of the K_2NbF_7-HF-H_2O system also carried out in this document the $KNbF_6$ salt is unstable in solutions containing < 40 mass% HF. The equilibrium solid phase was reported to be $KNbF_6$ [16919-14-5] in all solutions since the KF/NbF_5 mole ratio in saturated solutions varied within the range of 1.06-1.09.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility measurements were carried out in a Ag vessel. Mixtures were equilibrated by stirring for 7-10 hours. Four samples were taken from each saturated solution. In 2 of them the sum of free HF and Nb was titrated with alkali against methylorange in the presence of $CaCl_2$. In the other 2 samples Nb was determined gravimetrically as Nb_2O_5 after evaporation of the sample with H_2SO_4+H_3BO_3 mixture and hydrolytic precipitation of niobic acid. In the filtrate K was determined gravimetrically as K_2SO_4 after evaporation of the filtrate with HF+H_2SO_4 to remove H_3BO_3. Free HF content was obtained by difference. Independent experiments showed that 5 moles of alkali were consumed per 1 mole Nb.

SOURCE AND PURITY OF MATERIALS:

(1) $KNbF_6$ was prepared from Nb metal of unspecified source and purity. The metal was dissolved in HF+HNO_3 mixture, the solution was evaporated to a small volume and by addition of a 70-80% HF solution the HF concentration was adjusted to 50-60%. $KNbF_6$ was precipitated by addition of a solution of KHF_2 in 50-60% HF. The product was recrystallized from 50-55% HF, analysis not reported.

(2) Concentrated HF was obtained by distillation of a mixture of equal volumes of 40% HF and concentrated H_2SO_4.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

COMPONENTS:

(1) Dipotassium heptafluoroniobate (2-); K_2NbF_7; [16924-03-1]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Ruff, O.; Schiller, E.

Z. Anorg. Chem. 1911, *72*, 329-57.

VARIABLES:

T/K = 289, 358
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions.

Temperature		HF	KF[a]	NbF_5	Nb[d]	Salt[e]		Nature of the Solid Phase[f]
$t/°C$	T/K	mass%	mass%	mass%	mass%	mass%	m_1/mol kg^{-1}	
16	289	0.35[b]	2.98	5.19	2.57	7.79*	0.301	A
16	289	4.34[b]	5.33	7.07	3.50	-	-	A+B
16	289	10.43[c]	2.32	4.33	2.14	7.01**	0.279	B
85	358	0.35[b]	14.68	30.39	15.03	45.63*	2.994	A+C

[a] KF not present as a component and not considered in calculating molalities of the salts; the values given represent the content of potassium in the saturated solutions.

[b] K_2NbF_7 equilibrated with water; HF produced by hydrolysis of the salt.

[c] K_2NbF_7 equilibrated with 10.95 mass% HF solution.

[d] Calculated by compiler.

[e] Calculated by compiler for the salt corresponding to the respective equilibrium solid phase (*K_2NbOF_5; **K_2NbF_7).

[f] A: $K_2NbOF_5 \cdot H_2O$, [19200-74-9]; B: K_2NbF_7; [16924-03-1];
C: unidentified solid phase.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess of K_2NbF_7 was shaken in Pt bottles with either water or a HF solution for 3 hours and filtered through a Pt funnel. In one aliquot of the filtrate, Nb and free HF were determined alkametrically according to ref (1); in another, Nb was determined gravimetrically as Nb_2O_5 after precipitation with NH_3 solution. Precipitation was repeated twice (after dissolution of hydrous Nb_2O_5 in HF) to remove adsorbed potassium, and in the collected filtrates potassium was determined (method not specified). Solid phases were identified by optical microscopy.

SOURCE AND PURITY OF MATERIALS:

(1) K_2NbF_7 (source or method of preparation not specified) was separated from K_2TaF_7 according to (ref 2), then repeatedly recrystallized from concentrated HF solution and finally dried at 120° to remove HF.

(2) HF solutions were prepared from nonaqueous HF to avoid the presence of H_2SiF_6.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Winteler, H. *Z. Angew. Chem.* 1902, *15*, 33.

2. Marignac, M. C. *Ann. Chim. Phys.* 1866, *9*[*4*], 249.

COMPONENTS:

(1) Dipotassium heptafluoroniobate(2-); K_2NbF_7; [16924-03-1]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1946, *19*, 1093-1105 (measurements at 298 K)

Zh. Prikl. Khim. 1947, *20*, 385-90. (measurements at 348 K)

EXPERIMENTAL VALUES:

HF		NbF_5	KF	K_2NbF_7		Nature of the Solid Phase[d]
mass%	m_2/mol kg^{-1} [c]	mass%	mass%	mass%[b]	m_1/mol kg^{-1} [c]	
Composition of saturated solutions, $t/^{0}C = 25$.						
1.51[a]	0.8572	6.45	-	10.44	0.3899	A
3.61[a]	2.129	7.20	4.15	11.63	0.4512	A
4.12[a]	2.448	7.27	4.82	11.76	0.4597	A
5.20[a]	3.152	7.62	4.94	12.33	0.4916	A
5.30[a]	3.234	7.90	4.98	12.78	0.5130	A
6.30[a]	3.909	8.12	5.20	13.14	0.5364	A
6.60[a]	4.139	8.47	5.30	13.70	0.5653	A
6.94	4.374	8.50	-	13.75	0.5701	B
7.16	4.528	8.53	-	13.80	0.5741	B
7.20	4.571	8.75	-	14.16	0.5914	B
8.00	5.117	8.56	-	13.85	0.5828	B
9.35	5.911	7.16	4.61	11.58	0.4816	B
12.20	7.708	5.37	3.43	8.69	0.3612	B
16.34	10.49	3.59	2.30	5.80	0.2450	B
19.18	12.85	3.83	2.37	6.19	0.2727	B
20.50	13.97	3.81	2.48	6.16	0.2762	B
24.60	17.64	3.53	2.32	5.71	0.2694	B
27.40	20.54	3.53	2.20	5.71	0.2816	B
31.58	26.17	5.02	2.63	8.11	0.4422	B
37.87	38.25	7.82	5.22	12.64	0.8399	B
40.32		8.88	6.60	-		B
46.67		7.68	7.38	-		C
61.73		6.41	8.20	-		C
Composition of saturated solutions, $t/^{0}C = 75$.						
2.70	1.583	7.45	-	12.06	0.4653	A
5.00	4.421	23.77	14.38	38.47	2.238	A+B
6.00	5.211	22.52	15.28	36.45	2.083	B
9.60	7.958	18.60	-	30.10	1.641	B
11.40	9.206	16.50	9.58	26.70	1.418	B
15.00	11.96	13.80	-	22.33	1.172	B
20.20	16.29	11.00	6.80	17.80	0.9441	B
20.70	16.94	11.25	7.19	18.21	0.9802	B
29.00	27.84	11.70	7.12	18.94	1.196	B
32.10	34.54	13.24	7.87	21.43	1.516	B
33.60	43.19	17.00	-	27.51	2.326	B

[a] HF formed by hydrolysis of K_2NbF_7; the initial mixture contained K_2NbF_7 and water only.

[b] Calculated by authors from the NbF_5 data.

[c] Calculated by compiler.

[d] A: $K_2NbOF_5.H_2O$; B: K_2NbF_7, [16924-03-1]; C: $KNbF_6$, [16919-14-5]. [19200-74-9]

Continued on the next page . . .

COMPONENTS:

(1) Dipotassium heptafluoroniobate(2-); K_2NbF_7; [16924-03-1]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. <u>1946</u>, *19*, 1093-1105 (measurements at 298 K)

Zh. Prikl. Khim. <u>1947</u>, *20*, 385-90. (measurements at 348 K)

EXPERIMENTAL VALUES:

Note:

In experiments with equilibrium HF concentration $\leq$ 6.60 mass%, HF was not added to the initial mixtures. The increasing HF concentration in these measurements was the result of increasing amount of K_2NbF_7 introduced into the initial mixture. Increasing solubility of Nb in this region is explained by gradual stabilization of the NbF_7^{2-}ion in the solution on increasing equilibrium HF concentration:

$$K_2NbOF_5 + 2\ HF \rightarrow K_2NbF_7 + H_2O$$

Another increase in solubility observed at equilibrium HF concentration > 27 mass% was explained by the formation of the NbF_6^- ion in solution, and finally also in the solid phase:

$$K_2NbF_7 + HF \rightarrow KNbF_6 + KHF_2$$

The solubility in this region represents the solubility of $KNbF_6$ in HF solutions containing KHF_2.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility measurements were carried out in a Ag vessel. Mixtures were equilibrated with stirring for 7-10 hours at 25°C or for 4 hours at 75°C. In measurements with equilibrium HF concentration $\leq$ 6.60 mass%, K_2NbF_7 was equilibrated with water only. Samples of saturated solutions were analyzed for Nb, K, and free HF. Nb was determined gravimetrically as Nb_2O_5 after evaporation of the sample with $H_2SO_4 + H_3BO_3$ and hydrolytic precipitation of niobic acid. In the filtrate K was determined gravimetrically as K_2SO_4 after evaporation of the filtrate with HF + H_2SO_4 to remove H_3BO_3. In another aliquot of the saturated solution, the sum of free HF and Nb were titrated with alkali against methyl orange in the presence of $CaCl_2$. Free HF content was obtained by difference. Independent experiments showed that 5 moles of alkali are consumed per 1 mole of Nb. K_2NbF_7 as the solid phase was deduced from the fact that the NbF_5/KF mole ratio was close to 2 in the corresponding HF concentration ranges. Nothing was mentioned about the identification of $KNbF_6$ and $K_2NbOF_5.H_2O$.

SOURCE AND PURITY OF MATERIALS:

(1) K_2NbF_7 was prepared by addition of KF to a HF solution of NbF_5. The product was filtered, washed with water-alcohol mixture containing HF, then with pure alcohol, and recrystallized from 10% HF, and dried at 110°C. On drying K_2NbF_7 lost HF continuously turning partly into $K_2NbOF_5.H_2O$. According to authors this was not important for the solubility measurements. NbF_5 was prepared by dissolving Nb metal (unspecified origin and purity) in a mixture of HF + HNO_3 and subsequent evaporation of HNO_3.

(2) HF used for mixtures containing up to 35 mass% HF was prepared from 40% acid obtained from the acid doubly distilled in a Pt apparatus. Mixtures with higher HF content were prepared from 60-90 mass% HF obtained by distillation of a mixture of equal volumes of 40% HF and concentrated H_2SO_4.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

The solubility error is not specified.

COMPONENTS:

(1) Dipotassium heptafluoroniobate (2-); K_2NbF_7; [16924-03-1]

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

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

ORIGINAL MEASUREMENTS:

Ruff, O.; Schiller, E.

Z. Anorg. Chem. 1911, *72*, 329-57.

VARIABLES:

T/K = 289, 353
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions.

Temperature		KF		NbF_5	Nb[c]	K_2NbOF_5[c]		Nature of the Solid Phase[f]
$t/^\circ C$	T/K	mass%[a]	mass%[b]	mass%	mass%	mass%	m_1/mol kg^{-1}[d]	
16	289	7.41	5.54	1.16	0.573	1.74	0.066	A
16	289	7.39	6.04	2.67	1.320	e	e	A+B
80	353	4.81	10.08	11.66	5.765	17.51	0.786	A+C

[a] Initial concentration.

[b] Equilibrium concentration found by analysis. At 16°C it was lower than the concentration of KF used initially. The authors explained this by the formation of a new solid phase richer in K than both K_2NbF_7 and $K_2NbOF_5.H_2O$ which, however, could not be detected by optical microscopy. The value at 80° corresponds to the sum of concentrations of KF used and of K dissociated from the salt dissolved.

[c] Calculated by compiler for the salt corresponding to the equilibrium solid phase (K_2NbOF_5).

[d] Equilibrium mass% KF corrected for K dissociated from K_2NbOF_5 dissolved.

[e] Not calculated because of the coexistence of two soluble solid phases.

[f] A: $K_2NbOF_5.H_2O$; B: K_2NbF_7 [16924-03-1]; C: unidentified solid phase.

Note: There is some uncertainty about the two measurements at 16°. With initially the same KF concentration, different solid phases were reported. For the measurement with 7.39 mass% KF the saturated solution was reported to contain also 5.39 mass% HF although it was stated that K_2NbF_7 was shaken with solutions containing KF only.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess K_2NbF_7 was shaken with KF solutions for 3 hours in Pt bottles and filtered through a Pt funnel. In the filtrate Nb was determined gravimetrically as Nb_2O_5 after precipitation with NH_3 solution. Precipitation was repeated twice (after dissolution of hydrous Nb_2O_5 in HF) to remove adsorbed K, and in the collected filtrates K was determined (method not specified). Solid phases were identified by optical microscopy.

Note: Footnote f above.
A: $K_2NbOF_5 \cdot H_2O$; [19200-74-9]

SOURCE AND PURITY OF MATERIALS:

(1) K_2NbF_7 (source and purity not specified) was first separated from K_2TaF_7 according to ref (1), and then repeatedly recrystallized from concentrated HF solution and finally dried at 120° to remove HF.

ESTIMATED ERROR:

REFERENCES:

1. Marignac, M. C. *Ann. Chim. Phys.* 1866, *9*[*4*], 249.

COMPONENTS:

(1) Dipotassium heptafluoroniobate(2-); K_2NbF_7; [16924-03-1]

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

(3) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1947, *20*, 385-90.

VARIABLES:

$T/K = 298$
c_2/mass % = 0 - 10
c_3/mass % = 1 - 10

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Solubility of K_2NbF_7 in aqueous KF + HF at 25°C

HF mass %[a]	KF mass %[a]	K_2NbF_7 mass %	HF mass %[a]	KF mass %[a]	K_2NbF_7 mass %
1	0	5.20	5	0	6.35
	1	3.35		1	4.90
	2	3.04		2	4.80
	5	2.00		5	3.24
	10	0.25		10	0.81
2	0	5.95	10	0	6.86
	1	4.42		1	5.40
	2	3.62		2	4.60
	5	2.40		5	3.81
	10	0.70		10	1.45

[a] Initial concentration.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

As in the authors' previous work (ref 1) isothermal method was used. Excess K_2NbF_7 was equilibrated with KF-HF solutions in a Ag vessel by stirring for 8 hours. Saturated solutions were analyzed for Nb gravimetrically as Nb_2O_5 after evaporation of the sample with a mixture of H_2SO_4 + H_3BO_3 and hydrolytic precipitation of niobic acid. Solid phases were not investigated.

SOURCE AND PURITY OF MATERIALS:

(1) K_2NbF_7 was prepared by addition of KF to a HF solution of NbF_5 (the latter was prepared by dissolving Nb metal of unspecified source and purity in a mixture of HF + HNO_3 and subsequent evaporation of HNO_3). The product was filtered, washed with water-alcohol mixture containing HF, then with pure alcohol, recrystallized from 10% HF, and dried at 110°C. The authors

SOURCE AND PURITY OF MATERIALS: (continued)

stated that on drying K_2NbF_7 lost HF continuously turning partly to $K_2NbOF_5.H_2O$.

(2) HF used was prepared from 40% HF obtained from the acid doubly distilled from a Pt apparatus.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error not specified.

REFERENCES:

1. Savchenko, G. S.; Tananaev, I. V. *Zh. Prikl. Khim.* 1946, *19*, 1093.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Dipotassium (OC-6-21)-pentafluorooxoniobate(2-); K_2NbOF_5; [17523-77-2] (2) Water; H_2O; [7732-18-5]	Marignac, M. C. *Ann. Chim. Phys.* 1866, *8*[*4*], 5-75.
VARIABLES:	PREPARED BY:
$T/K = 292 \pm 2$	J. Hála

EXPERIMENTAL VALUES:

One part of $K_2NbOF_5 \cdot H_2O$ was reported to be soluble in 12.5 - 13 parts of water at 17 - 21°C (0.256 - 0.267 mol kg^{-1}; calculated by compiler for K_2NbOF_5).

The solubility of $K_2NbOF_5 \cdot H_2O$ was reported to increase with temperature but no data were given.

$K_2NbOF_5 \cdot H_2O$; [19200-74-9]

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:	SOURCE AND PURITY OF MATERIALS:
No details given.	(1) $K_2NbOF_5 \cdot H_2O$ was prepared from mixed Nb+Ta oxides obtained from the mineral columbite of different localities. From it, a mixture of $K_2NbOF_5 \cdot H_2O$ and K_2TaF_7 was prepared by dissolving the oxides in a solution of HF and adding KF. The two salts were separated by repeated crystallization making use of the difference in their solubilities. Pure $K_2NbOF_5 \cdot H_2O$ was obtained as thin rhomboedral plates. Analysis (mass%): found H_2O 5.87, Nb 31.12, K 25.92, F 31.72; calculated H_2O 5.98, Nb 31.23, K 25.91, F 31.56.
	ESTIMATED ERROR:
	Temp: precision ± 2 K.

COMPONENTS:

(1) Sodium hexachloroniobate; $NaNbCl_6$; [16920-10-8]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.
**Zh. Fiz. Khim.* 1964, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl. Transl.) 1964, *38*, 710-1.

VARIABLES:

T/K = 298. 323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$NaNbCl_6$
$t/^0C$	T/K	10^3c_1/mol dm^{-3}
25	298	10.59
50	323	12.62

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $NaNbCl_6$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Nb in samples taken periodically over 15 days. Nb in the sample was determined gravimetrically as Nb_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Nb into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $NaNbCl_6$ was prepared by heating stoichiometric amounts of NaCl and $NbCl_5$ in a sealed ampoule in vacuum at 220-300°. $NbCl_5$ used was prepared by chlorination of Nb metal with Cl gas at 250-500°;

SOURCE AND PURITY OF MATERIALS: (continued)

m.p. 204°. NaCl was recrystallized and ignited before use.

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

COMPONENTS:

(1) Potassium hexachloroniobate; $KNbCl_6$; [16919-88-3]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.
Zh. Fiz. Khim. 1964, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl. Transl.) 1964, *38*, 710-1.

VARIABLES:

T/K = 298, 323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$KNbCl_6$
$t/^\circ C$	T/K	$10^3 c_1/\text{mol dm}^{-3}$
25	298	1.94
50	323	3.53

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $KNbCl_6$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Nb in samples taken periodically over 15 days. Nb in the sample was determined gravimetrically as Nb_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Nb into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $KNbCl_6$ was prepared by heating stoichiometric amounts of KCl and $NbCl_5$ in a sealed ampoule in vacuum at 220-300°. $NbCl_5$ used was prepared by chlorination of Nb metal with Cl gas at

SOURCE AND PURITY OF MATERIALS: (continued)

250-500°; m.p. 204°. KCl was recrystallized and ignited before use.

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

COMPONENTS:

(1) Niobium chloride; $NbCl_4$; [13569-70-5]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Shevtsova, L. M.; Shadrova, L. G. Kogan, L. M.
**Zh. Fiz. Khim.* 1964, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl.Transl.) 1964, *38*, 710-1.

VARIABLES:

T/K = 298, 323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$NbCl_4$
$t/^0C$	T/K	$10^3c_1/\text{mol dm}^{-3}$
25	298	4.09
50	323	18.41

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $NbCl_4$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equiped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Nb in samples taken periodically over 15 days. Nb in the sample was determined gravimetrically as Nb_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Nb into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_4$ was prepared by reduction of $NbCl_5$ with Nb powder (ref 1). $NbCl_5$ was prepared by chlorination of 99.0-99.5 % purity Nb metal (impurities not specified) with Cl_2 gas at 250-500 °C. The $NbCl_5$ m.p. was 204 °C.

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

1. Schäfer, H.; Göser, C.; Bayer, L. *Z. Anorg. Allgem. Chem.* 1951, *265*, 258.

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) Benzene; C_6H_6; [71-43-2]

ORIGINAL MEASUREMENTS:

Fairbrother, F.; Nixon, J. F.; Prophet, H.

J. Less-Common Met. 1965, *9*, 434-6.

VARIABLES:

$T/K = 292.7 - 323.2$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Niobium chloride; $NbCl_5$	
$t/^{\circ}C$	T/K^a	g/100 g solvent	$m_1/mol\ kg^{-1\,a}$
19.5	292.7	0.810	0.0300
23.5	296.7	0.879	0.0325
29.0	302.2	1.139	0.0422
36.2	309.4	1.598	0.0591
41.5	314.7	1.710	0.0633
50.0	323.2	2.640	0.0977

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $NbCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $NbCl_5$. The method of Niobium analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ was prepared by direct chlorination of Nb metal and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as specified in earlier work (2)

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.
2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) 1,1'-Oxybisethane (diethyl ether); $C_4H_{10}O$; [60-29-7]

ORIGINAL MEASUREMENTS:

Cowley, A.; Fairbrother, F.; Scott, N.

J. Chem. Soc. 1958, 3133-7.

VARIABLES:

T/K = 275.8 - 298.1

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Niobium chloride; $NbCl_5$	
$t/^\circ C$	T/K	g/100 g solvent	m_1/mol kg^{-1} [a]
2.6	275.8	10.93	0.405
10.1	283.3	12.99	0.481
15.7	288.9	14.99	0.555
20.0	293.2	18.32	0.678
22.6	295.8	23.37	0.865
24.9	298.1	24.92	0.922

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. The Pyrex glass apparatus (ref 1) consisted of the solvent pretreatment line, the saturation, and the sampling vessels. In the pretreatment section, the solute was repeatedly pretreated by successive sublimations of the halide and condensation at -195°C of the solvent onto it. Both components were transferred into the saturation vessel which was connected to the sampling compartment through a sintered glass disc. The vessel was rocked for 24 h, the saturated solution filtered into the sampling ampoule which was then sealed off, weighed, and broken under water to hydrolyze the halide. After standing for 4-5 h, the solution was heated to 90°C, cooled and filtered, and the oxide was ignited and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ was prepared from pure metal sheet and dry Cl gas at 300-350°C (ref 2). The product was purified by 5 or 6 fractional sublimations *in vacuo*, and finally sublimed into fragile hook-ended ampoule.

(2) Diethylether (anesthetic) was distilled from 1/5 of its volume of H_2SO_4, kept over P_2O_5 for at least a week, decanted, fractionated under dry N gas, and stored over Na wire.

ESTIMATED ERROR:

Temp: precision ± >0.1 K.

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc., London* 1956, 1164.

2. Alexander, K. M.; Fairbrother, F. *J. Chem. Soc., London* 1949, S 223.

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) 4-Methyl-1,3-dioxalan-2-one (propylene carbonate); $C_4H_6O_3$; [108-32-7]

ORIGINAL MEASUREMENTS:

Harris, W. S.

U. S. At. Energy Comm. Report UCRL-8381, 1958, 77 pp.

Chem. Abstr. 1959, *53*, 4966b.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of $NbCl_5$ in propylene carbonate at 25 ^{0}C was estimated to be approximately 85 g $NbCl_5$/100 g of solvent. The compiler calcuated a molal solubility of m_1/mol kg^{-1} = 3.15.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An isothermal method was used. Saturated solutions were prepared by agitating excess solid with the solvent for at least three days in a glass cell shaped in the form of an inverted T with a ball-joint cap. The cell was thermostated in a water bath. Atmospheric moisture was excluded by use of a dry box. The method of Nb determination in the saturated solutions was not specified.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ (Stauffer Chemical Co., purity not specified) was used without purification.

(2) Propylene carbonate (Jefferson Chemical Co.) was purified by fractionating the solvent twice. The first fractionation was conducted at

SOURCE AND PURITY OF MATERIALS: (continued)

50 mmHg and a reflux ratio of 5:1. Small portions containing high and low boiling impurities were rejected. The remainder was re-fractionated at 20 mmHg and a reflux ratio from 15:1 to 25:1. The middle 4/5 of this was used.

ESTIMATED ERROR:

Temp: precision ± 0.01 K.
The solubility value reported is considered only an approximate estimate.

REFERENCES:

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.
**Zh. Fiz. Khim.* 1964, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl. Transl.) 1964, *38*, 710-1.

VARIABLES:

T/K = 298 323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$NbCl_5$
$t/{}^\circ C$	T/K	10^3c_1/mol dm^{-3}
25	298	45.33
50	323	86.11

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $NbCl_5$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Nb in samples taken periodically over 15 days. Nb in the sample was determined gravimetrically as Nb_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Nb into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ was prepared by chlorination of Nb metal with Cl gas at 250-500°. M.p. 204°. The product was stored in a dry box. The purity of Nb metal used was 99.0-99.5% as determined by

SOURCE AND PURITY OF MATERIALS: (continued)

emission spectrography; impurities not specified.

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) Chloroacetic acid; $C_2H_3ClO_2$; [79-11-8]

ORIGINAL MEASUREMENTS:

Malhotra, K. C.; Sud, R. G.

J. Inorg. Nucl. Chem. 1974, *36*, 3767-72.

VARIABLES:

$T/K = 366.5$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of $NbCl_5$ is reported to be 64.32 g in 100 g of solvent at 93.5 °C. From the value the compiler calculated $m_1/\text{mol kg}^{-1} = 6.67$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Chloroacetic acid was added to a dry ampoule containing a sufficient amount of $NbCl_5$. The ampoule was sealed and shaken for 24 hours. The ampoule was then broken, the contents quickly filtered through a sintered glass in a dry atmosphere, and a sample of known weight taken. The method of Nb determination was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$. Source and purity not specified.

(2) Chloroacetic acid, B. D. H., purified by distillation under reduced pressure and recrystallized from benzene.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Solubility error is not specified.

REFERENCES:

COMPONENTS:	EVALUATOR:
(1) Niobium chloride; $NbCl_5$; [10026-12-7] (2) Titanium chloride; $TiCl_4$; [7550-45-0]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia

CRITICAL EVALUATION:

An evaluation of the solubility of $NbCl_5$ in $TiCl_4$ at temperatures between 273 and 373 K.

Five sets of data are available for the temperature dependence of the solubility of $NbCl_5$ in $TiCl_4$ (ref 1-5). In all of the papers the solubility values were determined by an isothermal method and by analysis of the saturated solutions. In two cases (ref 2, 3) a polythermal method was also used in the region of higher solubilities. The solubility values obtained by the isothermal method are compared in Figure 1. Of these, the data of Tarasenkov and Komandin (ref 1) are much lower than the data of the other authors. The authors (ref 1) themselves state the low precision of their data, and these data can be rejected. [The poor quality of their data can be seen in the $NbCl_5/TaCl_5$ solubility ratio in $TiCl_4$ they report. Their values show $TaCl_5$ being 25 to 60 times more soluble than $NbCl_5$ (in mass %). The solubility ratio from other workers (ref 2-5) show the two solutes have solubilities of the same order of magnitude, which one would expect from the properties of Nb and Ta.]

It is not possible to give preference to any of the remaining four sets of data. Figure 1 show some regions of fair agreement. The data of Niselson and Perekhrest (ref 3) show fair agreement with the data of Morozov and Toptygin (ref 2) over the temperature range of 15 to 40 °C, and good agreement with the value of Long (ref 5) at 60 °C. It is worth noting that direct, although different, methods of analysis of the solutions were used in (ref 2, 3, 5), but that an indirect analysis (based on the sum of Ti and Nb and the total chloride content) was employed in (ref 4).

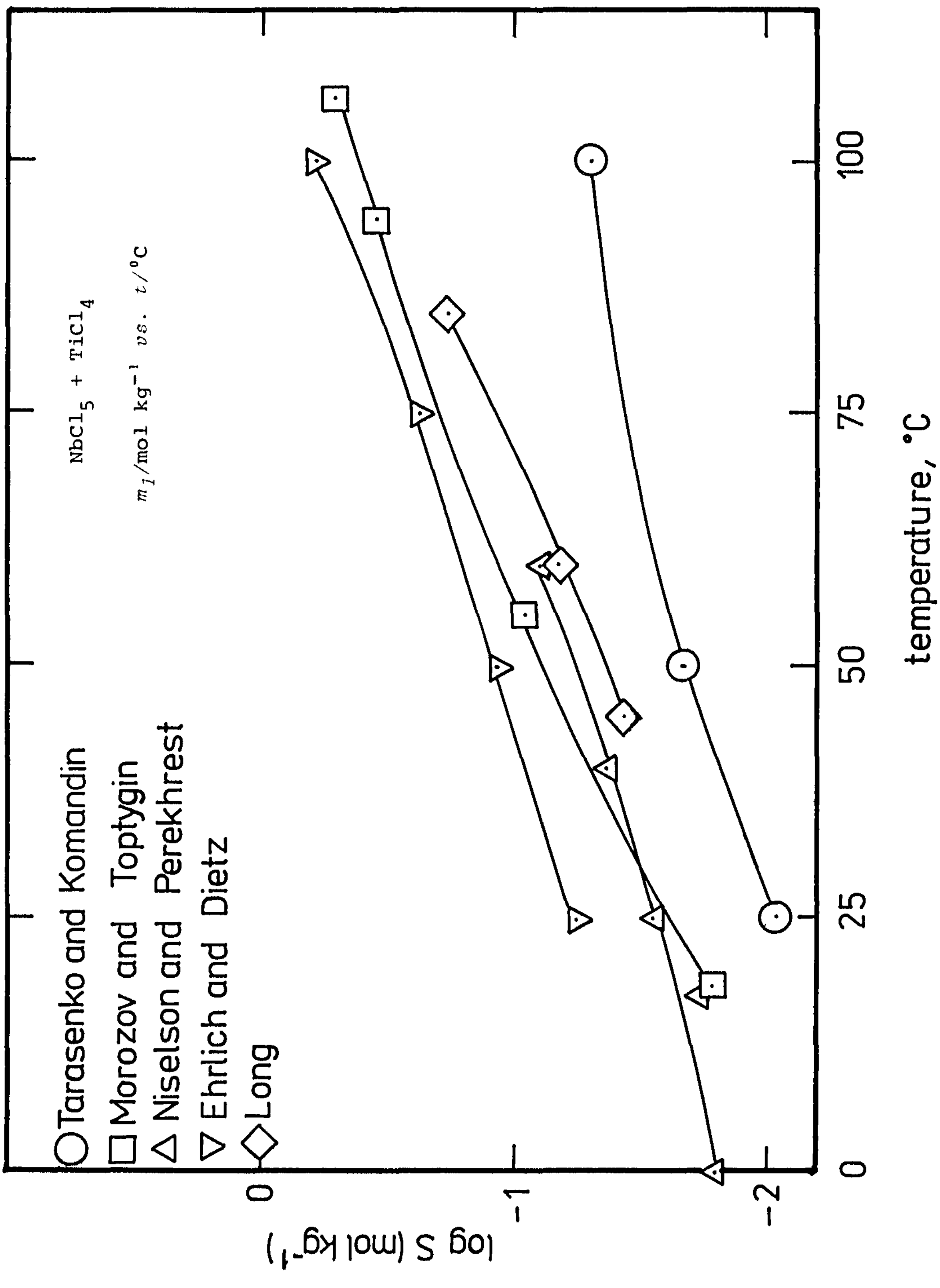
The two data sets obtained by the polythermal method (ref 2, 3) differ considerably. The values of Niselson and Perekhrest (ref 3) are 5 to 10 mass% $NbCl_5$ lower at a given temperature than the values of Morozov and Toptygin (ref 2). There are two possible explanations for the difference. There is a strong tendency to form supersaturated solutions in the $NbCl_5 + TiCl_4$ systems (ref 3) which prevents the liquidus temperature to be determined from cooling curves with reasonable accuracy. It has also been pointed out (ref 2) that the presence of $NbCl_3O$ in the $NbCl_5$ could lead to erroneous interpretation of the cooling curves since precipitation of $NbCl_3O$ could be mistakenly taken for the first appearance of crytals of $NbCl_5$. Morozov and Toptygin (ref 2) took great care to remove $NbCl_3O$ from the $NbCl_5$ used in their measuremnts.

REFERENCES:

1. Tarasenkov, P. N.; Komandin, A. V.
   Zh. Obsch. Khim. 1940, *10*, 1319.
2. Morozov, I. S.; Toptygin, D. Ya.
   Zh. Neorg. Khim. 1957, *2*, 1915.
3. Niselson, L. A.; Perekhrest, G. L.
   Zh. Neorg. Khim. 1958, *3*, 2150.
4. Ehrlich, P.; Dietz, G.
   Z. Anorg. Allg. Chem. 1960, *305*, 158.
5. Long, A. M.
   Aust. J. Chem. 1969, *22*, 853.

COMPONENTS:	EVALUATOR:
(1) Niobium chloride; $NbCl_5$; [10026-12-7] (2) Titanium chloride; $TiCl_4$; [7550-45-0]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia

CRITICAL EVALUATION:



COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Tarasenkov, P. N.; Komandin, A. V.

Zh. Obshch. Khim. 1940, *10*, 1319-27.

VARIABLES:

$T/K = 298 - 373$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$NbCl_5$	
$t/^\circ C$	T/K	mass %	$m_1/mol\ kg^{-1}$ [a]
25	298	0.24	0.0089
50	323	0.58	0.0216
100	373	1.32	0.0495

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. $TiCl_4$ was distilled onto excess solid $NbCl_5$ and the mixture was equilibrated in a tube closed with Hg seal and equipped with a stirrer. Nb content in the saturated solution was determined gravimetrically with tanine method.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ was prepared from K_2NbOF_5 via Nb_2O_5 according to ref (1).

(2) $TiCl_4$, tech. grade, was purified by fractional distillation after preliminary treatment with Hg metal. The product boiled at 136°/743 mmHg.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

The authors state low precision of the data and suggest the data be considered as qualitative.

REFERENCES:

1. Honigschmidt, O.; Winterberger, K. *Z. Anorg. Allg. Chem.* 1934, *219*, 161.

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Morozov, I. S.; Toptygin, D. Ya.

Zh. Neorg Khim. 1957, *2*, 1915-21.

J. Inorg. Chem. (USSR)(Engl.Transl.) 1957, *2*(8), 322-33.

VARIABLES:

$T/K = 291 - 464$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		$NbCl_5$	
$t/^0C$	T/K	mass%[b]	$m_1/\text{mol kg}^{-1}$[a]
18	291	0.45	0.0167
55	328	2.4	0.0910
94	367	8.7	0.353
106	379	12.2	0.514
114	387	14.9	
123	396	21.4	
145	418	35.4	
151	424	39.8	
163	436	49.2	
165	438	54.3	
167	440	60.2	
172	445	65.3	
175	448	69.2	
182	455	79.4	
191	464	88.1	

[a] Calculated by compiler.

[b] Only approximate values were reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubilities over the temperature range of 18-106° were obtained by isothermal method. Mixtures of $TiCl_4$ and $NbCl_5$ were distilled into a test-tube with a side arm. The test-tube was sealed off, kept at the desired temperature for 20-40 h, and a part of the saturated solution was poured into the side arm. The latter was then sealed off, cooled, and weighed. Prior to analysis, most of the $TiCl_4$ was removed by distillation in the presence of NaCl. The final separation of Nb from the remaining Ti was achieved by means of phenylarsonic acid. The solubilities above 110° were obtained from thermal analysis. The mixtures of $TiCl_4$ and $NbCl_5$ were prepared by weighing, melted, and cooling curves were recorded.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ was prepared by chlorination with Cl gas of Nb metal (source and purity not specified). The product was repeatedly passed in a stream of Cl gas over heated carbon to convert eventual $NbCl_3O$ into $NbCl_5$, and contained finally approximately 0.01% $NbCl_3O$.

(2) Commercially available $TiCl_4$ (source not specified) was distilled twice. The fraction boiling at 136°C at 760 mmHg was used.

ESTIMATED ERROR:

Nothing specified.

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Niselson, L. A.; Perekhrest, G. L.

Zh. Neorg. Khim. 1958, *3*, 2150-5.

J. Inorg. Chem. (USSR) (Engl.Transl.) 1958, *3*(9), 215-22.

VARIABLES:

T/K = 249.0 - 477.9

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Liquidus Temperature		Niobium Chloride; $NbCl_5$		
$t/^\circ C$	T/K^d	mass %	mol %	m_1/mol kg$^{-1\,d}$
-24.0[a]	249.2	0	0	0
-24.2[b]	249.0	0.222	0.160	-
0.0	273.2	0.425	0.300	0.0158
17.5	290.7	0.474	0.333	0.0176
25.0	298.2	0.758	0.533	0.0283
40.0	313.2	1.13	0.80	0.0423
60.0	333.2	2.02	1.43	0.0763
84.5	357.7	4.87	3.47	-
114.3	387.5	11.7	8.56	-
141.5	414.7	25.5	19.4	-
157.0	430.2	40.7	32.4	-
175.0	448.2	59.7	51.2	-
179.5	452.7	63.1	56.8	-
187.8	461.0	75.5	68.4	-
204.7[c]	477.9	100.0	100.0	-

[a] Taken from ref. (1).

[b] Eutectic temp., calculated by authors according to ref. (2).

[c] Taken from ref. (3)

[d] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

At higher (>4.87 mass%) $NbCl_5$ concentrations, the liquidus curve was obtained by visual polythermal method. $NbCl_5$ and $TiCl_4$ were weighed into a glass tube previously dried *in vacuo* at 350-400°C. The tube was sealed, heated in a furnace to melt the mixture, and then allowed to cool slowly in a thermostated glycerine bath under constant rotation at 60 rpm. The liquidus temp. was taken as the average of temperatures of appearance and disappearance of crystals in the melt recorded at successive cooling and heating of the system. At lower $NbCl_5$ concentrations, isothermal method was used. Ampoules containing $TiCl_4$ and $NbCl_5$ were equilibrated for 30 h at 40 and 60°C, and for 60 h at 0 and 17.5°C. A sample of the saturated solution was hydrolyzed, the precipitate ignited to oxides, and the Nb concentration was determined spectrographically. The eutectic temp. was calculated according to (3).

SOURCE AND PURITY OF MATERIALS:

Source of $TiCl_4$ and $NbCl_5$ not specified. The halides were purified by rectification and were stored in sealed ampoules.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Clabaugh, W. S.; Leslie, R. T.; Gilchrist, R. J. *Res. Nat. Bur. Stand* 1955, *55*, 261.
2. Kordes, E. *Z. Anorg. Chem.* 1927, *167*, 97.
3. Schafer, H.; Pietruck, C. *Z. Anorg. Allgem. Chem.* 1951, *267*, 174.

COMPONENTS:

(1) Niobium chloride; $NbCl_5$; [10026-12-7]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Ehrlich, P.; Dietz, G.

Z. Anorg. Allg. Chem. 1960, *305*, 158-68.

VARIABLES:

T/K = 298 - 373

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions

Temperature		$NbCl_5$	
t/ C	T/K	mass %	m_1/mol kg^{-1} [a]
25	298	1.5	0.0564
50	323	3	0.114
75	348	6	0.236
100	373	14	0.603

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Distillation of the solvent, dissolution, sampling, and hydrolyzing the saturated solutions were carried out in an all-glass apparatus in which transfer of liquids was carried out by means of dry N gas. Samples for analysis were taken from the dissolution vessel through a tube thermostated to a temperature higher by 2°C than that of the vessel, and were hydrolyzed in diluted acid. After hydrolysis, an indirect analysis was used where the sum of Ti + Nb and total Cl^- were determined.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$ was prepared according to ref (1). Its purity was not specified.

(2) $TiCl_4$, tech. grade, was purified by refluxing with 1.5 g $CuSO_4 \cdot 5H_2O$ and 10 g charcoal per 300 ml $TiCl_4$ for 2 h. A colorless product distilled at 136 °C and showed elec. conductivity of $<10^{-9}$ S cm^{-1}.

ESTIMATED ERROR:

Temp: precision ± 0.2 K.

The solubility error is not specified.

REFERENCES:

1. Brauer, G. Handbuch der anorganische preparative Chemie 1954, F. Enke-Verlag, Stuttgart.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Niobium chloride; $NbCl_5$; [10026-12-7] (2) Titanium chloride; $TiCl_4$; [7550-45-0]	Long, A. M. *Austral. J. Chem.* 1969, *22*, 853-4.

VARIABLES:	PREPARED BY:
T/K = 318 - 358	J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

Temperature		$NbCl_5$	
$t/^{\circ}C$	T/K	mass %	m_1/mol kg^{-1} [a]
45	318	1.0	0.0374
60	333	1.8	0.0678
85	348	4.8	0.187

[a] Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Saturated solutions were prepared in a sealed, N filled apparatus (1), for 21-90 hr. After equilibration, a sample of the filtered saturated solution was collected in a detachable ampoule. Dissolving and sampling operations were carried out in a thermostated waterbath. Each ampoule with the sample was broken under 3N HNO_3 in a sealed bottle, and hydrous oxides of Nb+Ti were precipitated by NH_3. After filtration and ignition at 800°C, the mixed oxides were analyzed x-ray spectrographically.

SOURCE AND PURITY OF MATERIALS:

(1) $NbCl_5$, laboratory grade (Alfa Inorganics) was used as obtained.

(2) $TiCl_4$ (source not specified) was purified by treatment with Cu powder and distillation, and collected in sealed ampoules.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: precision ± 2 %.

REFERENCES:

1. Long, A. M. *Chem. Ind.* 1968, *50*, 1764.

COMPONENTS:

(1) Niobium Chloride oxide; $NbCl_3O$; [13597-20-1]

(2) Niobium chloride; $NbCl_5$; [10026-12-7]

EVALUATOR:

J. Hála
Department of Inorganic Chemistry
J. E. Purkyne University
61137 Brno, Czechoslovakia

October 1985

CRITICAL EVALUATION:

The solubility of niobium chloride oxide in niobium chloride.

Two papers (ref 1 and 2) report measurements of the solubiltiy of $NbCl_3O$ in $NbCl_5$ by a polythermal method. The two data sets differ considerably. The liquidus curve of Niselson and Gavrilov (ref 2) is at a much higher temperature than that of Meyer and coworkers (ref 1). The reason for the discrepancy is not clear and it is not possible to give one data set preference over the other. The two papers do agree well on the eutectic temperature which is given as 203.3-203.4 (ref 1) and 203 (ref 2) ^0C.

REFERENCES:

1. Meyer, G.; Oosterom, J. F.; VanOeveren, W. J. *Rec. Trav. Chim.* 1961, *80*, 502.

2. Niselson, L. A.; Gavrilov, O. R. *Zh. Neorg. Khim.* 1967, *12*, 3166.

COMPONENTS:

(1) Niobium chloride oxide; $NbOCl_3$; [13597-20-1]

(2) Niobium chloride; $NbCl_5$; [10026-12-7]

ORIGINAL MEASUREMENTS:

Meyer, G.; Oosterom, J. F.; Van Oeveren, W. J.

Recl. Trav. Chim. Pays-Bas. 1961, *80*, 502-12.

VARIABLES:

T/K = 476.8 - 505

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

$NbCl_5$ mol %	$NbOCl_3$ mol %	Liquidus Temperature $t/^{\circ}C$	T/K^a
96.5	3.5	204.5	477.7
95.6	4.4	204.1	477.3
95.2	4.8	203.9	477.1
94.9	5.1	203.7	476.9
94.8	5.2	203.6	476.8
94.4	5.6	208	481
94.1	5.9	219	492
93.4	6.6	232	505

[a] Calculated by compiler.

Note: Extrapolation of the two branches of the phase diagram yielded the eutectic compn. of 94.4 mol % $NbCl_5$ + 5.6 (± 0.2) mol % $NbOCl_3$ with the eutectic temp. at 203.3 - 203.4 °C. The melting point of pure $NbCl_5$ was estimated to be (206.8 ± 0.3) °C.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Polythermal method. Mixtures of $NbOCl_3$ and $NbCl_5$ were condensed into evacuated tubes under exclusion of atm. moisture. The tubes were sealed and slowly warmed up under shaking in a salt bath until the solid phase disappeared. Temperature was measured by using calibrated Anschutz thermometers.

SOURCE AND PURITY OF MATERIALS:

Source of $NbCl_5$ and $NbOCl_3$ was not specified. Only negligible traces of impurities were detected in the chemicals by spectrographic analysis. Contrary to other authors (1,2) it was not possible to obtain pure $NbCl_5$ by distn. and subsequent sublimation. The product contained 97.4 mass % $NbCl_5$ at the most, the rest being $NbOCl_3$.

ESTIMATED ERROR:

Comp. of the mixture: ± 0.2 mol % due to the inaccuracy of the analysis of the starting materials.
Liquidus temp: ± 0.15 °C, ± 1 °C, and ± 2 °C for measurements with $NbOCl_3$ content of 3.5 - 5.2, 5.6, and 5.9 mol %, resp.

REFERENCES:

(1) Alexander, K. M.; Fairbrother, F. *J. Chem. Soc., Suppl.* 1949, 223.

(2) Süe, M. P. *Bull. Soc. Chim. France* 1939, *6*, 830.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Niobium Chloride oxide; $NbOCl_3$; [13597-20-1] (2) Niobium chloride; $NbCl_5$; [10026-12-7]	Niselson, L. A.; Gavrilov, O. R. *Zh. Neorg. Khim.* 1967, *12*, 3166-71. *Russ. J. Inorg. Chem. (Engl. Transl.* 1967, *12*, 1674-8.
VARIABLES:	**PREPARED BY:**
T/K = 475.6 - 701.4	J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Liquidus Temperature		$NbOCl_3$		Liquidus Temperature		$NbOCl_3$	
$t/^0C$	T/K	mass %	x_1[a]	$t/^0C$	T/K	mass %	x_1[a]
204.2	477.4	0.0	0.0	295.0	568.2	6.80	0.084
202.4	475.6[b]	0.50	0.00627	300.0	573.2	7.57	0.093
203.0	476.2	0.84	0.010	346.4	619.6	15.20	0.183
204.0	477.2	0.88	0.011	366.0	639.2	22,00	0.261
209.1	482.3	0.93	0.012	369.9	643.1	25.00	0.295
221.0	494.2	1.58	0.020	385.5	658.7	31.00	0.361
225.0	498.2	1.78	0.022	390.7	663.9	36.80	0.422
230.0	503.2	1.90	0.024	397.2	670.4	42.50	0.481
231.0	504.2	2.27	0.028	398.0	671.2	44.40	0.501
256.2	529.4	3.13	0.039	404.0	677.2	49.10	0.548
264.4	537.6	3.90	0.048	413.5	686.7	60.35	0.656
267.2	540.4	4.00	0.050	420.7	693.9	70.00	0,745
270.0	543.2	4.31	0.054	424.2	697.4	75.78	0.797
280.9	554.1	5.00	0.062	426.7	699.9	84.70	0.874
283.6	556.8	5.17	0.064	427.0	700.2	91.67	0.932
290.0	563.2	6.40	0.079	428.2	701.4	100.00	1

[a] Calculated by compiler

[b] Eutectic point

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Liquidus temperatures were obtained by visual-polythermal method. Ampoules with the mixture of both components were shaken in a molten salt bath whose temp. was measured with a calibrated thermocouple (ref 1).

SOURCE AND PURITY OF MATERIALS:

(1) $NbOCl_3$ was prepared by oxidation of gaseous $NbCl_5$ with oxygen at 400° and purified by sublimation.

(2) $NbCl_5$, source not specified, was purified by distillation and contained < 10^{-3}% of unspecified impurities.

ESTIMATED ERROR:

Temp: precision ± 0.5 K.
Soly: Nothing specified.

REFERENCES:

1. Niselson, L. A.; Perekhrest, G. L. *Zh. Neorg. Khim.* 1958, *3*, 2150.

COMPONENTS:

(1) Niobium chloride oxide; $NbCl_3O$; [13597-20-1]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Morozov, I. S.; Toptygin, D. Ya.

Zh. Neorg Khim. 1957, *2*, 1915-21.

J. Inorg. Chem. (USSR)(Engl.Transl.) 1957, *2*(8), 322-33.

VARIABLES:

T/K = 553, 573

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		$NbCl_3O$	
$t/^0C$	T/K	mass%[b]	m_1/mol kg^{-1}[a]
280	553	0.1-0.2	0.0047-0.0093
300	573	1.5-2.0	0.071 -0.095

[a] Calculated by compiler.

[b] Only approximate values were reported.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

An isothermal method was used, but no details are given. The procedure was presumably similar to that used in this document for the $NbCl_5$ + $TiCl_4$ system.

SOURCE AND PURITY OF MATERIALS:

(2) Commercially available $TiCl_4$ (source not specified) was distilled twice. The fraction boiling at 136 ^0C at 760 mmHg was used.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Niobium bromide; $NbBr_5$; [13478-45-0]

(2) 1,1'-Oxybisethane (diethyl ether); $C_4H_{10}O$; [60-29-7]

ORIGINAL MEASUREMENTS:

Cowley, A.; Fairbrother, F.; Scott, N.

J. Chem. Soc. 1958, 3133-7.

VARIABLES:

T/K = 275.4 - 294.1

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Niobium bromide; $NbBr_5$	
$t/^{\circ}C$	T/K	g/100 g solvent	m_1/mol kg^{-1} [a]
2.2	275.4	2.99	0.0607
5.6	278.8	3.20	0.0650
10.0	283.2	3.53	0.0717
14.6	287.8	3.65	0.0741
17.1	290.3	3.73	0.0757
20.9	294.1	4.34	0.0881

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. The Pyrex glass apparatus (ref 1) consisted of the solvent pretreatment line, the saturation, and the sampling vessels. In the pretreatment section, the solute was repeatedly pretreated by successive sublimations of the halide and condensation at -195°C of the solvent onto it. Both components were transferred into the saturation vessel which was connected to the sampling compartment through a sintered glass disc. The vessel was rocked for 24 h, the saturated solution filtered into the sampling ampoule which was then sealed off, weighed, and broken under water to hydrolyze the halide. After standing for 4-5 h, the solution was heated to 90°C, cooled and filtered, and the oxide was ignited and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) $NbBr_5$ free from hydrolytic products was prepared by reacting dry Br with Nb metal sheet in a closed system at 400-450°C. The product was purified by 5 or 6 fractional sublimations *in vacuo*, and finally sublimed into fragile hook-ended ampoule.

(2) Diethylether (anesthetic) was distilled from 1/5 of its volume of H_2SO_4, kept over P_2O_5 for at least a week, decanted, fractionated under dry N gas, and stored over Na wire.

ESTIMATED ERROR:

Temp: precision ± >0.1 K.

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc., London* 1956, 1164.

6. The solubility of tantalum-containing halide and oxyhalide substances.

Systems	Pages
TaF_5 + HF + H_2O	266, 267
____ + UF_6	268
____ + $C_4H_6O_3$	269
$AgTaF_6$ + HF	270
$KTaF_6$ + HF + H_2O	271
K_2TaF_7 + HF + H_2O	272-280
______ + __ + KF + H_2O	281, 282
______ + __ + K_2NbOF_5 + H_2O	283
Rb_2TaF_7 + H_2O	284
Na_3TaF_8 + H_2O	285
$TaCl_4$ + CCl_2=CClCCl=CCl_2	286
$TaCl_5$ + *c*-C_6H_{12}	287
_____ + C_6H_6	288
_____ + C_7H_8	289
_____ + C_8H_{10}	290
_____ + C_9H_{12}	291
_____ + $(C_2H_5)_2O$	292
_____ + $C_4H_6O_3$	293
_____ + CCl_4	294, 295
_____ + CCl_2=CClCCl=CCl_2	296
_____ + CS_2	297
_____ + $TiCl_4$	298-305
$NaTaCl_6$ + CCl_2=CClCCl+CCl_2	306
$KTaCl_6$ + CCl_2=CClCCl=CCl_2	307
$TaBr_5$ + $(C_2H_5)_2O$	308
_____ + CCl_4	309
_____ + C_2H_5Br	310
TaI_5 + $(C_2H_5)_2O$	311

COMPONENTS:

(1) Tantalum fluoride; TaF_5; [7783-71-3]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Buslaev, Yu. A.; Nikolaev, N. S.

Zh. Neorg. Khim. 1959, *4*, 465-71.

Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 210-4.

VARIABLES:

T/K = 293
Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of saturated solutions at 20°C.

HF mass %	Ta_2O_5 mass %	Nature of the Solid Phases[a]	HF mass %	Ta_2O_5 mass %	Nature of the Solid Phases[a]
10.97	23.11	A	41.62	57.35	C
14.95	35.44		42.82	56.02	
18.31	42.55		43.78	54.25	
20.49	46.95		44.17	53.84	
25.38	54.11		48.78	48.32	
26.80	56.52		52.25	46.43	
25.45	60.23		57.25	42.44	
28.86	59.90		61.49	40.95	
29.32	63.62		66.38	38.46	
29.10	65.76		66.41	38.92	
30.28	64.68	B	68.94	38.30	
32.58	62.50		42.05	70.12	D
35.76	60.50		60.72	59.21	D
36.74	59.50		51.39	59.55	E
37.26	59.21		62.80	45.58	E
38.26	58.72		70.70	36.20	E
39.81	58.78				

The solid phases are identified at the bottom of the following page.

Continued on the next page . . .

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. The procedure was essentially that used for the analogous $NbF_5/HF/H_2O$ system (ref 1). Teflon bottles equipped with stirrers and heavy fluorocarbon hydraulic sealing were used. Solutions containing excess hydrous Ta_2O_5 were equilibrated for at least 3-4 h, in some experiments for 2 or more days. At high HF concentrations TaF_5 was used as the solute. In such cases the solutions were prepared by adding water to TaF_5 solutions in anhydrous HF. Samples of saturated solutions were taken by and weighed in a Pt pipette after filtration in a Pt apparatus. Ta was determined gravimetrically as Ta_2O_5, F^- in the presence of Ta was titrated with NaOH against phenolphthaleine. Solutions containing high HF concentrations and the solid phases were analyzed for H_2O by Fischer method modified for HF solutions (ref 2). The composition of the solid phases was determined by chemical and microscopical analysis and also by the method of wet residues.

Continued on the next page . . .

SOURCE AND PURITY OF MATERIALS:

(1) TaF_5 was prepared by fluorination with ClF_3 of Ta metal (source and purity not specified except for the Nb content, 0.34%). Hydrous Ta_2O_5 was obtained by hydrolyzing a solution of Ta in liquid HF.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 1 % in Ta;
precision ± 2.5 % in F^-.

REFERENCES:

1. Nikolaev, N. S.; Buslaev, Yu. A. *Zh. Neorg. Khim.* 1959, *4*, 205.
2. Nikolaev, N. S.; Alenchikova, I.F. *Zavodskaya Lab.* 1958, *24*, 418.

COMPONENTS:

(1) Tantalum fluoride; TaF_5; [7783-71-3]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

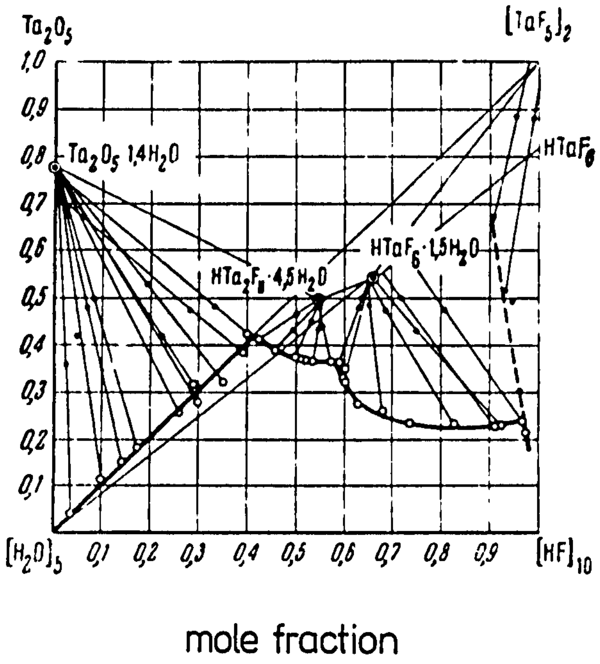
Buslaev, Yu. A.; Nikolaev, N. S.

Zh. Neorg. Khim. 1959, *4*, 465-71.

Russ. J. Inorg. Chem. (Engl. Transl.) 1959, *4*, 210-4.

EXPERIMENTAL VALUES:

Phase diagram of the TaF_5 + HF + H_2O System.



[a] Solid phases

A: $Ta_2O_5 \cdot 1.4\ H_2O$

B: $HTa_2F_{11} \cdot 4.5\ H_2O$

C: $HTaF_6 \cdot 1.5\ H_2O$

D: TaF_5, [7783-71-3]

E: not given.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum fluoride; TaF_5; [7783-71-3] (2) (OC-6-11)-Uranium fluoride; UF_6; [7783-81-5]	Nikolaev, N. S.; Sadikova, A. T. *At. Ener.* 1975, *39*, 338-43. *Sov. At. Energy (Engl. Transl.)* 1975, *39*, 338-43.
VARIABLES:	PREPARED BY:
T/K = 373	J. Hála

EXPERIMENTAL VALUES:

At 100°C the solubility of TaF_5 in UF_6 is reported to be 0.10 mol kg^{-1} (2.86 mass %).

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility was determined in a Cu autoclave placed in a crucible furnace. Excess solid was equilibrated under constant mixing with 6 ml UF_6 for 30-40 h, and then allowed to stand for another 40 h at the desired temperature, which exceeded 3-4 times the time necessary to reach the equilibrium. After that the autoclave was rapidly cooled in liquid N. A sample of the frozen saturated solution was transfered to ice to hydrolyze the components, and analyzed. Methods of analysis were not given. All procedures were carried out in a dry box at -20°C.

SOURCE AND PURITY OF MATERIALS:

The fluorides were prepared by the authors. No details were specified except for the fact that the products were strictly anhydrous.

ESTIMATED ERROR:

Temp: precision ± 5 K.
Solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Tantalum fluoride; TaF_5; [7783-71-3]

(2) Propylene carbonate (4-methyl-1, 3-dioxalan-2-one); $C_4H_6O_3$; [108-32-7]

ORIGINAL MEASUREMENTS:

Fischer, H. W.; Schwabe, K.

Korrosion (Dresden) 1980, *11*, 105-15.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The approximate solubility of TaF_5 at $t/°C = 25$ is reported to be 12 g TaF_5/100 g solvent.

The compiler calculates $m_1/\text{mol kg}^{-1} = 0.43_5$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Although not stated explicitly, the solubility was apparently determined in the apparatus described for the electrolysis experiments. The apparatus was connected to a vacuum line, and extreme care was taken to avoid access of air moisture. No details were given about the time of equilibration or analysis of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) TaF_5 (Ferak, West Berlin), 99% purity, was used without further purification.

(2) Propylene carbonate (Ferak, West Berlin) was distilled before use.

ESTIMATED ERROR:

Neither temperature or solubility error were specified.

REFERENCES:

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Silver hexafluorotantalate(1-); $AgTaF_6$; [61104-79-8] (2) Hydrogen fluoride; HF; [7664-39-3]	Gut, R.; Rueede, J. *J. Coord. Chem.* 1978, *8*, 47-53.
VARIABLES:	PREPARED BY:
$T/K = 273$	J. Hála

EXPERIMENTAL VALUES:

Both the solubility and solubility product of $AgTaF_6$ in liquid HF at 0°C are reported. The values are 1.23 g in 100 g HF from which the compiler calculated $m_1/\text{mol kg}^{-1} = 0.0305$, and $-\log K_{s0} = 2.61$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Solubility was determined by isothermal method followed by chemical analysis of saturated solutions. Details were not reported. The solubility product was obtained from titrations of solutions of $KTaF_6$ in HF with a AgF wolution in HF during which solid $AgTaF_6$ was formed. Details of calculations not reported. In the titrations the $[Ag^+]/[TaF_6^-]$ ratio varied 10-50-fold and the ionic strength varied within 0.15 ± 0.03 mol dm^{-3} due to changes in supporting electrolyte concentration. The titrations were carried out in a Kel-F apparatus with a burrette made of a precision drilled Kel-F rod, using a Ag indicator electrode and $Ag/AgBF_4(sat)/KBF_4(sat)$ /liquid HF or $Ag/AgTaF_6(sat)$/liquid HF systems as reference electrodes. The titration apparatus was handled at 0° in a refrigerator. The Ag electrode responded reversibly to the concentration of free Ag^+ ions over the range of pAg = 1.5-20. Equilibrium potentials were reached in seconds and were constant over long periods of time.

SOURCE AND PURITY OF MATERIALS:

(1) $AgTaF_6$ was prepared from AgF and TaF_5 in anhydrous HF and recrystallized. TaF_5 used was prepared by condensing excess HF onto freshly sublimed $TaCl_5$, and subliming the crude TaF_5 in vacuum. AgF used was prepared by evaporation of HF from $AgHF_2$ which in turn was prepared in the following way. Excess HF gas was condensed on a wet filter cake of freshly precipitated Ag_2O and the solution obtained was evaporated to dryness by heating at 150° in a stream of N gas. The residue was dissolved in anhydrous HF, cooled to -78° to obtain crystals of AgF.5HF which decomposed to $AgHF_2$ on heating to 25°.

(2) Anhydrous HF distilled from commercial (source not specified) 99.9% product in steel tanks was redistilled 2-3-times over AgF to remove traces of H_2S. The conductivity of the product corresponded to water content $< 10^{-4}$ mol dm^{-3}.

ESTIMATED ERROR:

Precision of solubility product

± 0.04 log units.

Temperature and solubility errors are not reported. The authors stated that the solubility calculated from K_{s0} was somewhat higher than the isothermal value, due to the salt effect.

COMPONENTS:

(1) Potassium hexafluorotantalate; $KTaF_6$; [20137-53-5]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1946, *19*, 1093-1105.

VARIABLES:

$T/K = 298$

HF/mass% = 42.4 - 65.5

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Solubility of $KTaF_6$ in aqueous HF at 25°C

HF	TaF_5	KF	$KTaF_6$	
mass%	mass%	mass%	mass%[a]	m_1/mol kg^{-1}[b]
42.40	13.98	3.73	16.88	1.241
50.00	13.30	2.94	16.06	1.417
53.15	13.20	3.06	15.93	1.542
56.00	13.20	-	15.93	1.699
59.90	13.70	3.20	16.53	2.099
63.85	14.26	3.35	17.21	2.720
65.50	14.40	4.07	17.40	3.046

[a] Calculated by authors from the TaF_5 data.

[b] Calculated by compiler.

Note:
As follows from the study of the K_2TaF_7-HF-H_2O system also carried out in this document the $KTaF_6$ salt is unstable in solutions containing < 45 mass% HF. The equilibrium solid phase was reported to be $KTaF_6$ [20137-53-5] in all solutions since the KF/TaF_5 mole ratio in saturated solutions varied within the range of 1.06 - 1.11.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility measurements were carried out in a Ag vessel. Mixtures were equilibrated by stirring for 7-10 hours. Four samples were taken from each saturated solution. In 2 of them the sum of free HF and Ta was titrated with alkali against methylred in the presence of $CaCl_2$. It was found in independent experiments that 4.4-4.7 moles of alkali were consumed per 1 mole of Ta. In other 2 samples Ta was determined gravimetrically as Ta_2O_5 after precipitation with NH_4OH (without removal of HF), and K as K_2SO_4 in the filtrate after the determination of Ta. The content of free HF was obtained by subtraction considering the average value of 4.5 mole alkali per 1 mole Ta.

SOURCE AND PURITY OF MATERIALS:

(1) $KTaF_6$ was prepared from Ta metal of unspecified source and purity. The metal was dissolved in HF+HNO_3 mixture, the solution was evaporated to a small volume and by addition of 70-80% HF solution the HF concentration was adjusted to 50-60%. $KTaF_6$ was precipitated by addition of a solution of KHF_2 in 50-60% HF. The product was recrystallized from 50-55% HF. Analysis: found 54.31% Ta, 11.60% K; calculated 54.23% Ta, 11.69% K.

(2) Concentrated HF was obtained by distillation of a mixture of equal volumes of 40% HF and concentrated H_2SO_4.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

COMPONENTS:	EVALUATOR:
(1) Dipotassium heptafluorotantalate(2-);K_2TaF_7;[16924-00-8] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61137 Brno, Czechoslovakia October, 1985

CRITICAL EVALUATION:

The solubility of potassium heptafluorotantalate in aqueous hydrogen fluoride.

Six documents (ref 1-6) report the solubility of potassium heptafluorotantalate in this system. Only the documents of Babaeva and Klyachko-Gurvich (ref 1), Savchenko and Tananaev (ref 2 and 3), and Ruff and Schiller (ref 4), which cover a wide range of HF concentration and temperature, need to be considered. The data of Marignac (ref 5) are for the solubility of K_2TaF_7 in water containing a small unspecified concentration of HF. The data of Meerson *et al.* (ref 6) were reported in graphical form only. Therefore, the data from these documents (ref 5 and 6) were not considered further.

The data from documents (ref 1 - 3) agree qualitatively in both the trend of the solubility increasing with HF concentration and with temperature. Some discrepancies can be noted concerning the temperature dependence of the solubility (see Figure on following page). The data of Savchenko and Tananaev (ref 3) for 348 K (75 °C) are higher than those of Babaeva and Klyachko-Gurvich (ref 1) for 353 K (80 °C) at low HF concentration, but the Savchenko and Tananaev values are lower at high HF concentrations. Although less pronounced, a problem also exists between the data for 293 K (20 °C) (ref 1) and for 298 K (25 °C) (ref 2) in that the two data sets almost coincide. There are no reasons to prefer one data set over the other. All (ref 1 - 3) are classed as tentative. The data of Ruff and Schiller (ref 4) seems to be too high and can be rejected.

REFERENCES:

1. Babaeva, A. V.; Klyachko-Gurvich, L. L. *Zh. Obsh. Khim.* 1935, *5*, 220.

2. Savchenko, G. S.; Tananaev, I. V. *Zh. Prikl. Khim.* 1946, *19*, 1093.

3. Savchenko, G. S.; Tananaev, I. V. *Zh. Prikl. Khim.* 1947, *20*, 385

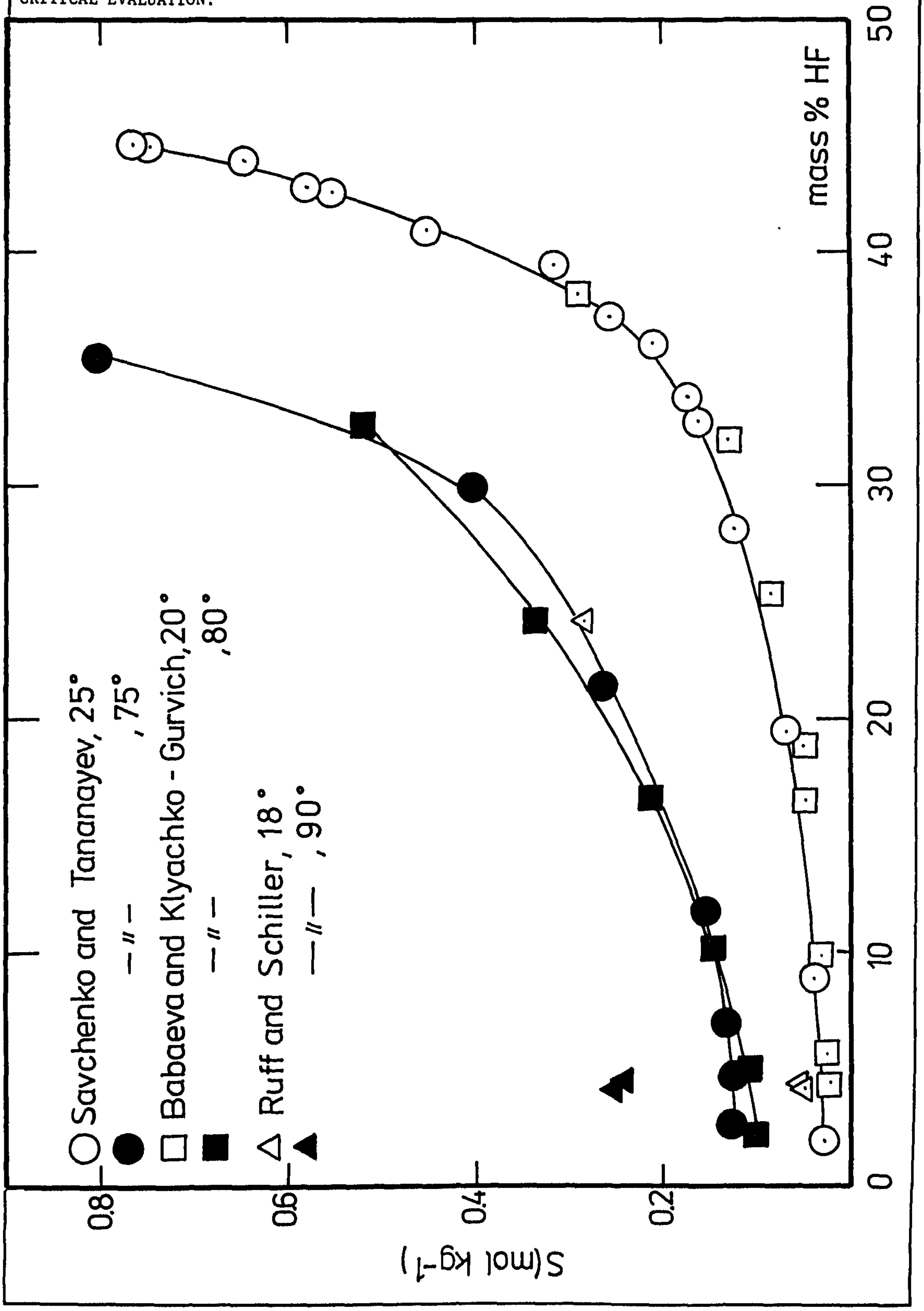
4. Ruff, O.; Schiller, E. *Z. Anorg. Chem.* 1911, *72*, 329.

5. Marignac, M. C. *Ann. Chim. Phys.* 1866, *9* [4], 247.

6. Meerson, G. A.; Zverev, G. L.; Zubkova, F. M. *Tsvetnye Metally* (Nonferrous Metals) 1939, No. 8, 97.

COMPONENTS:	EVALUATOR:
(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61137 Brno, Czechoslovakia October 1985

CRITICAL EVALUATION:



COMPONENTS: (1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8] (2) Hydrogen fluoride; HF; [7664-39-3] (3) Water; H_2O; [7732-18-5]	**ORIGINAL MEASUREMENTS:** Marignac, M. C. *Ann. Chim. Phys.* <u>1866</u>, *9* [*4*], 247-76.
VARIABLES: *T*/K = 288	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

The solubility of K_2TaF_7 at 15°C is reported as 1 part of the salt being soluble in 200 parts of water (0.0128 mol kg^{-1}; compiler). The water was reported to contain a very small though unspecified concentration of HF.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE: No details reported.	**SOURCE AND PURITY OF MATERIALS:** Nothing specified.
	ESTIMATED ERROR: Nothing specified.
	REFERENCES:

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Meerson, G. A.; Zverev, G. L.; Zubkova, F. M.

Tsvetnye Metal. (Nonferrous Metals) 1939, No. 8, 97-101.

VARIABLES:

T/K = 294, 333

HF/mass % = 1

PREPARED BY:

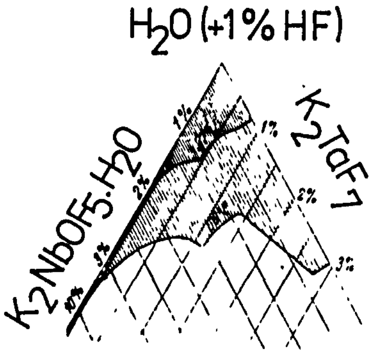
J. Hála

EXPERIMENTAL VALUES:

The solubility of K_2TaF_7 in 1 mass percent aqueous HF solution was reported at 21 and 60 °C in graphical form, see Figure to right. The values can be read on the H_2O (+1 % HF) - K_2TaF_7 side of the triangular H_2O(+1% HF) + K_2NbOF_5 + K_2TaF_7 phase diagram.

To two significant figures the values are 0.68 mass% at 21 °C and 2.9 mass % at 60 °C.

The compiler calculates solubilities of m_1/mol kg^{-1} = 0.021 and 0.093 at 294 and 333 K, respectively.



upper curve, 21°C
lower curve, 60°C

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess K_2TaF_7 was equilibrated with 1 mass % HF solution in ebonite beaker. A weighed portion of the saturated solution was evaporated in a Pt dish and the residue was weighed. The results so obtained were confirmed in measurements where solutions saturated initially at higher temperatures were allowed to cool down and equilibrate at the desired temperature.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 (source not specified) was repeatedly recrystallized from 1 mass % HF solution. The product contained 56.4% Ta_2O_5 (calculated 56.34% - compiler), 0.003% Fe, 0.04% Si, 0.01% Ti, and 0.02% Sn.

(2) HF was purified from H_2SiF_6, which suppressed the solubility of K_2TaF_7, by treating the HF solution with solid K_2TaF_7 to allow for the precipitation of the Si-Ta heteropolyacid. (The authors did not mention the amount of K_2TaF_7 used for this purification process or eventual K_2TaF_7 concentration present in the purified HF.)

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
The solubility error is not specified.

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-9]

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

ORIGINAL MEASUREMENTS:

Ruff, O.; Schiller, E.

Z. Anorg. Chem. 1911, *72*, 329-57.

VARIABLES:

T/K = 291-363

HF/mass% = 0.03-24.3

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions.

Temperature		HF	KF^b	TaF_5	Ta^c	$K_2TaF_7{}^c$		Nature of the Solid Phase[d]
$t/^\circ C$	T/K	mass%	mass%	mass%	mass%	mass%	m_1/mol kg^{-1}	
18	291.2	0.029[a]	0.12	0.25	0.164	0.36	0.00922	A+B
18.5	291.7	4.2	0.52	1.24	0.813	1.76	0.0477	A
18	291.2	4.47	0.56	1.33	0.827	1.89	0.0515	A
18	291.2	24.3	2.25	5.35	3.51	7.60	0.285	A
85	358.2	0.85[a]	1.69	2.18	1.430	3.10	0.0823	A+B
90	363.2	4.2	2.52	6.00	3.935	8.53	0.249	A
90	363.2	4.47	2.41	5.73	3.757	8.14	0.238	A
90	363.2	24.3	4.59	10.91	7.15	15.50	0.657	A

[a] K_2TaF_7 shaken with water; HF produced by hydrolysis of K_2TaF_7.

[b] KF not used as the solute; the values correspond to K dissociated from the salt dissolved and were not considered in calculating molalities of K_2TaF_7.

[c] Calculated by compiler.

[d] A: K_2TaF_7, [16924-00-8]; B: solid phase of variable composition referred to as $K_xTa_yO_zF_u$ in the original document. Its composition depended on that of the corresponding equilibrium saturated solution and approached that of the Marignac's (ref 2) insoluble salt $K_4Ta_4O_5F_{14}$ on repeated boiling with fresh water.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess K_2TaF_7 was shaken with either water or a HF solution in Pt bottles for 3 hours and filtered through a Pt funnel. In one aliquot of the filtrate, Ta and free HF were determined alkalimetrically (ref 1); in another, Ta was determined gravimetrically as Ta_2O_5 after precipitation with NH_3 solution. Precipitation was repeated twice (after dissolution of hydrous Ta_2O_5 in HF) to remove adsorbed potassium, and in the collected filtrates K was determined by an unspecified method. Solid phases were identified by optical microscopy.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 (source or method of preparation not specified) was first separated from K_2NbF_7 according to ref (2), then repeatedly recrystallized from concentrated HF solution, and finally dried at 120° to remove HF.

(2) HF solutions were prepared from non-aqueous HF to avoid the presence of H_2SiF_6.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Winteler, H. *Z. Angew. Chem.* 1902, *15*, 33.

2. Marignac, M. C. *Ann. Chim. Phys.* 1866, *9*[*4*], 247.

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Babaeva, A. V.; Klyachko-Gurvich, L. L.

Zh. Obsh. Khim. 1935, *5*, 220-3.

EXPERIMENTAL VALUES:

Solubility of K_2TaF_7 in aqueous HF

HF		K_2TaF_7	
mass %	m_2/mol kg^{-1} [a]	mass %	m_1/mol kg^{-1} [a]
Composition at 0°C			
0.105[b]	0.05260	0.114	0.002913
0.610	0.3075	0.246	0.006327
1.757	0.8966	0.287	0.007472
3.750	1.955	0.364	0.009680
6.545	3.518	0.454	0.01245
11.207	6.350	0.579	0.01674
17.273	10.54	0.815	0.02537
24.099	16.15	1.326	0.04534
38.366	33.57	4.500	0.2009
Composition at 20°C			
0.214[b]	0.1075	0.266	0.006816
0.288[b]	0.1448	0.319	0.008185
1.223[c]	0.6224	0.555	0.01441
1.520	0.7764	0.620	0.01616
1.770	0.9066	0.645	0.01686
4.234	2.228	0.783	0.02102
5.778	3.092	0.838	0.02288
9.859	5.529	1.015	0.02904
16.520	10.065	1.440	0.04476
19.047	12.00	1.609	0.05171
25.420	17.60	2.368	0.08362
32.025	24.95	3.825	0.1521
38.157	34.37	6.345	0.2915
Composition at 80°C			
2.170	1.148	3.367	0.09089
5.023	2.755	3.843	0.1075
7.550	4.281	4.305	0.1245
10.230	6.022	4.863	0.1461
16.690	10.84	6.331	0.2097
24.233	18.09	8.820	0.3360
32.610	29.14	11.444	0.5216

[a] Calculated by compiler.

[b] Initial mixture contained only K_2TaF_7 and water, HF formed by hydrolysis of the salt.

[c] 0.233 given in the original document which is an obvious misprint.

Note: K_2TaF_7, [16924-00-8] was the equilibrium solid phase in all cases except for the measurements marked b) where a basic salt $K_xTa_yF_zO_n$ of unspecified composition coexisted with K_2TaF_7.

Continued on the next page . . .

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Babaeva, A. V.; Klyachko-Gurvich, L. L.

Zh. Obsh. Khim. 1935, *5*, 220-3.

VARIABLES: T/K = 273, 293, and 353

HF/mass% = 0.1-38.4 at 273 K,
0.2-38.2 at 293 K,
2.2-32.6 at 353 K

PREPARED BY:

J. Hála

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. All measurements were carried out in either Pt or bakelite test tubes immersed in a thermostat. Mixtures of K_2TaF_7 and HF solution were stirred until equilibrium was reached. At 0°C the mixtures were stirred with a vertical stirrer and equilibrium was reached within 3-4 hours. No equilibrium times were reported for measurements at higher temperatures. The mixtures were allowed to stand for 1 hour and samples of saturated solutions were withdrawn by using either a paraffine coated glass pipette (at 0 and 20°C) or a heated rubber pipette (at 80°C). Four samples were taken from each measurements and always weighed into a Pt crucible containing water. In two samples the sum of HF and Ta was determined by titration with NaOH against phenolphthaleine. In the remaining two samples K_2TaF_7 was decomposed by heating with concentrated H_2SO_4 and then Ta was determined gravimetrically as Ta_2O_5 by precipitation with ammonia, and K gravimetrically as K_2SO_4 in the filtrate after Ta determination. Composition of the solid phases was determined by chemical analysis and microscopic observation.

AUXILIARY INFORMATION

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 was prepared from technical grade mixture of Nb+Ta oxides containing 95.4% oxides. Raw oxide mixture was purified from Fe, Mn, and Sn to obtain a product containing 47.3% Ta_2O_5, 52.0% Nb_2O_5, and 0.74% TiO_2. This was dissolved in HF, and K_2TaF_7 was separated from double fluorides of Nb and Ti by repeated recrystallization from HF solutions. For some experiments K_2TaF_7 was also prepared from a technical grade product by 5-6 times recrystallizing it from HF solutions. Analysis: found 56.38% Ta_2O_5, 19.74% K; calculated 56.41% Ta_2O_5, 19.92% K.

SOURCE AND PURITY OF MATERIALS:

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1946, *19*, 1093-1105. (measurements at 298 K)

Zh. Prikl. Khim. 1947, *20*, 385-90. (measurements at 348 K)

EXPERIMENTAL VALUES:

Solubility of K_2TaF_7 in aqueous HF at 25°C

HF		TaF_5	KF	K_2TaF_7	
mass%	m_2/mol kg^{-1} [b]	mass%	mass%	mass% [a]	m_1/mol kg^{-1} [b]
1.97	1.014	0.67	0.22	0.95	0.0250
9.51	5.327	0.89	0.34	1.26	0.0360
19.54	12.45	1.41	0.58	2.00	0.0650
28.20	20.58	2.32	0.93	3.30	0.123
32.82	25.95	2.78	1.00	3.95	0.159
33.86	27.31	2.93	1.41	4.16	0.171
36.14	30.61	3.41	1.61	4.85	0.210
37.26	32.66	4.02	1.67	5.71	0.255
39.49	36.63	4.67	2.25	6.63	0.314
40.90	40.71	6.25	3.06	8.88	0.451
42.64	45.16	7.15	3.35	10.16	0.549
42.80	45.86	7.43	4.02	10.55	0.577
44.00	49.18	7.94	3.87	11.28	0.643
44.56	51.94	8.84	4.39	12.56	0.747
44.64	52.39	8.99	4.15	12.77	0.765
45.29		10.49	4.93		
46.32		10.30	5.64		
46.66		9.86	6.00		
47.60		9.54	6.45		
49.62		8.49	6.71		
51.12		6.95	9.89		
52.36		8.74	6.00		
60.09		5.18	11.97		
68.67		8.00	8.08		

[a] Calculated by authors from the TaF_5 data.

[b] Calculated by compiler.

Note: The decrease of the solubility of K_2TaF_7 above 45 mass% HF is caused by the conversion of K_2TaF_7 to $KTaF_6$,

$$K_2TaF_7 + HF \rightarrow KTaF_6 + KHF_2$$

The ternary K_2TaF_7-HF-H_2O system thus turns into a quarternary one, $KTaF_6$-HF-KF-H_2O, and the solubility data for TaF_5 correspond to the solubility of $KTaF_6$ in the presence of KHF_2. Schreinemakers' method of wet residue did not yield an unequivocal proof for the formation of $KTaF_6$ (possibly because of incomplete conversion of K_2TaF_7) but its existence was proved by the synthesis of $KTaF_6$ by precipitation with KHF_2 of a solution of Ta metal in 50-60 mass% HF.

Over the concentration range of HF of 1.97 - 44.64 mass% the KF/TaF_5 mole ratio in the saturated solutions varied within the range of 1.74 - 2.31 which was taken as evidence for K_2TaF_7 [16924-00-8] being the equilibrium solid phase.

Continued on the following page . . .

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1946, *19*, 1093-1105. (measurements at 298 K)

Zh. Prikl. Khim. 1947, *20* , 385-90. (measurements at 348 K)

VARIABLES:

T/K = 298 and 348

m_1/mass% = 2-68.7 at 298 K; 2.7-35.5 at 348 K

PREPARED BY:

J. Hala

EXPERIMENTAL VALUES:

Solubility of K_2TaF_7 in aqueous HF at 75°C

HF		TaF_5	KF	K_2TaF_7	
mass%	m_2/mol kg^{-} [b]	mass%	mass%	mass%[a]	m_1/mol kg^{-} [b]
2.70	1.455	3.20	1.52	4.55	0.125
4.86	2.675	3.05	1.37	4.33	0.122
7.12	4.029	3.25	-	4.55	0.131
11.80	7.085	3.48	1.65	4.95	0.152
21.52	15.12	5.15	-	7.32	0.262
30.00	24.82	6.74	-	9.58	0.404
35.50	36.18	10.87	4.69	15.45	0.803

[a] Calculated by authors from the TaF_5 data.

[b] Calculated by compiler.

Note: The mole ratio of KF/TaF_5 in the saturated solutions was constant throughout the whole concentration range of HF and varied within the limits of 2.08 - 2.25. This was taken as a proof for K_2TaF_7 [16924-00-8] being the equilibrium solid phase in all solutions.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Solubility measurements were carried out in a Ag vessel. Mixtures were equilibrated by stirring for 7-10 hours at 25°C or for 4 hours at 75°C. Four samples were taken from each saturated solution. In two of them the sum of free HF and Ta was titrated with alkali against methylred in the presence of $CaCl_2$. It was found in independent experiments that 4.4-4.7 moles of alkali were consumed per 1 mole Ta. In the other 2 samples Ta was determined gravimetrically as Ta_2O_5 after precipitation with NH_4OH (without removal of HF), and K as K_2SO_4 in the filtrate after the determination of Ta. The content of free HF was obtained by subtraction considering the average value of 4.5 moles alkali per 1 mole of Ta.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 (Kahlbaum), purity not specified.

(2) HF used for mixtures containing up to 35 mass% HF was prepared from 40 mass% HF obtained from the acid doubly distilled from a Pt apparatus. Mixtures with higher HF content were prepared from 60-90 mass% HF obtained by distillation of a mixture of equal volumes of 40% HF and concentrated H_2SO_4.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

The solubility error is not specified.

REFERENCES:

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) Hydrogen fluoride; HF; [7664-39-3]

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

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

ORIGINAL MEASUREMENTS:

Ruff, O.; Schiller, E.

Z. Anorg. Chem. 1911, *72*, 329-57.

VARIABLES:

T/K = 289-353

Composition

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES: Composition of the saturated solutions.

Temperature		KF		HF	TaF_5	Ta[d]	K_2TaF_7[d,f]		Nature of the Solid Phase[e]
$t/^\circ C$	T/K	mass%[a]	mass%[b]	mass%	mass%	mass%	mass%	m_1/mol kg^{-1}	
16	289	7.35	6.73	0.015[c]	0.09	0.0590	0.128	0.00350	A+B
18	291	4.77	4.79	0.074[c]	0.10	0.0656	0.142	0.00381	A+B
18	291	21.92	21.93	10.44	0.036	0.0236	0.0512	0.00193	A
85	358	4.77	5.27	1.17[c]	0.96	0.630	1.36	0.0376	A+B
90	363	21.92	22.42	10.44	1.18	0.774	1.68	0.0652	A

[a] Initial concentration used in the measurement.

[b] Equilibrium concentration found by analysis.

[c] Formed during hydrolysis of K_2TaF_7; see also footnote (e) for the solid phase B.

[d] Calculated by compiler.

[e] A: K_2TaF_7, [16924-00-8]; B: solid phase of variable composition referred to as $K_xTa_yO_zF_u$ in the original document. Its composition depended on that of the corresponding equilibrium saturated solution and, on repeated boiling with fresh water, approached that of the Marignac's (ref 2) insoluble salt $K_4Ta_4O_5F_{14}$.

[f] In calculating molalities the experimental KF concentration values were corrected for KF dissociated from K_2TaF_7.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Excess K_2TaF_7 was shaken with solutions of desired composition in Pt bottles for 3 hours and filtered through a Pt funnel. In one aliquot of the filtrate, Ta and free HF were determined alkalimetrically (ref 1); in another, Ta was determined gravimetrically as Ta_2O_5 after precipitation with NH_3 solution. Precipitation was repeated twice (after dissolution of hydrous Ta_2O_5 in HF) to remove adsorbed potassium, and in the collected filtrates K was determined by an unspecified method. Solid phases were identified by optical microscopy.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 (source or method of preparation not specified) was first separated from K_2NbF_7 according to ref (2), then repeatedly recrystallized from concentrated HF solution, and finally dried at 120° to remove HF.

(2) HF solutions were prepared from non-aqueous HF to avoid the presence of H_2SiF_6.

ESTIMATED ERROR:

Nothing specified.

REFERENCES:

1. Winteler, H. *Z. Angew. Chem.* 1902, *15*, 33.

2. Marignac, M. C. *Ann. Chim. Phys.* 1866, *9*[*4*], 247.

COMPONENTS:

(1) Dipotassium heptafluorotantalate (2-); K_2TaF_7; [16924-00-8]

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

(3) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Savchenko, G. S.; Tananaev, I. V.

Zh. Prikl. Khim. 1947, *20*, 385-90.

VARIABLES:

$T/K = 298$

c_2/mass% = 0-10

c_3/mass% = 1-10

PREPARED BY:

J. Hala

EXPERIMENTAL VALUES:

Solubility of K_2TaF_7 in aqueous HF + KF at 25°C

HF mass %[a]	KF mass %[a]	K_2TaF_7 mass %	HF mass %[a]	KF mass %[a]	K_2TaF_7 mass %
1	0	0.80	5	0	1.10
	1	0.078		1	0.125
	2	0.05		2	0.072
	5	0.022		5	0.036
	10	0.020		10	0.025
2	0	0.95	10	0	1.30
	1	0.084		1	0.13
	2	0.053		2	0.063
	5	0.025		5	0.040
	10	0.023		10	0.032

[a] Initial concentration.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

As in the authors' previous work (ref 1) isothermal method was used. Excess K_2TaF_7 was equilibrated by stirring with HF-KF solutions in a Ag vessel for 8 hours. Saturated solutions were analyzed for Ta content gravimetrically as Ta_2O_5 after precipitation with ammonia without removal of HF. Solid phases were not investigated.

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 (Kahlbaum), purity not specified.

(3) HF used was prepared from 40% HF obtained from the doubly distilled acid from a Pt apparatus (ref 1).

(2) KF, source and purity not specified.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Solubility error is not specified.

REFERENCES:

1. Savchenko, G. S.; Tananaev, I.V. *Zh. Prikl. Khim.* 1946, *19*, 1093.

COMPONENTS:

(1) Dipotassium heptafluorotantalate(2-); K_2TaF_7; [16924-00-8]

(2) (OC-6-21)-Dipotassium pentafluorooxoniobate(2-); K_2NbOF_5; [17523-77-2]

(3) Hydrogen fluoride; HF; [7664-39-3]

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

ORIGINAL MEASUREMENTS:

Meerson, G. A.; Zverev, G. L.; Zubkova, F. M.

Tsvetnye Metally (Nonferrous Metals) 1939, No. 8, 97-101.

VARIABLES:

T/K = 294 - 348
Composition

PREPARED BY:

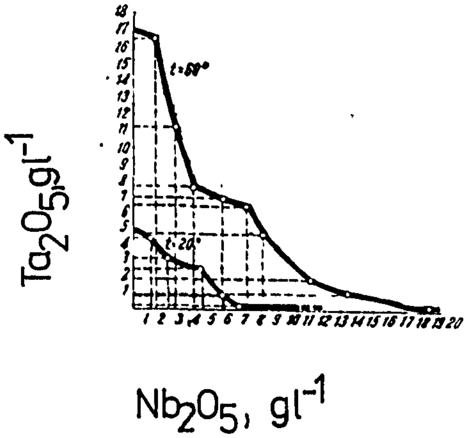
J. Hála

EXPERIMENTAL VALUES:

The salting out of K_2TaF_7 by K_2NbOF_7 in 1 mass % HF aqueous solutions was reported at 21 and 60 °C in graphical form. See the Figure to the right.

Also reported were the solubility ratios, $K_2TaF_7/K_2NbOF_5 \cdot H_2O$, as a function of temperature.

Temperature		Solubility ratio
t/°C	*T*/K	$K_2TaF_7/K_2NbOF_5 \cdot H_2O$
21	294	1:11.9
40	313	1:11.6
60	333	1:10.1
75	348	1:11



AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal salting-out of K_2TaF_7 from its saturated solutions by solid $K_2NbOF_5.H_2O$ was used. Known amounts of the latter salt was added to saturated solutions of K_2TaF_7 at the desired temperature in the presence of 1 mass% HF in paraffine-coated beakers. The mixture was stirred for 40 minutes and then allowed to stand for 20 minutes. The K_2TaF_7 precipitated out of the solution was filtered, washed with alcohol, dried in a Pt dish, and weighed.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

The solubility error is not specified.

$K_2NbOF_5 \cdot H_2O$; [19200-74-9]

SOURCE AND PURITY OF MATERIALS:

(1) K_2TaF_7 (source not specified) was repeatedly recrystallized from 1 mass% HF solution. The product contained 56.4% Ta_2O_5 (calculated 56.34% - compiler), 0.003% Fe, 0.04% Si, 0.01% Ti, and 0.02% Sn.

(2) $K_2NbOF_5.H_2O$ (source not specified) was repeatedly recrystallized from 1 mass% HF. The product contained 51.23% Nb_2O_5 (calculated 44.28% - compiler), 0.09% Fe, 0.01% Si, 0.13% TiO_2, 0.03% Sn, and 0.1-0.2% Ta_2O_5.

(3) HF was purified from H_2SiF_6, which suppressed the solubility of K_2TaF_7 and $K_2NbOF_5.H_2O$, by treating the HF solution with solid K_2TaF_7 and $K_2NbOF_5.H_2O$ to allow for the precipitation of Si-Ta and Si-Nb heteropolyacids. (The authors did not mention the amount of salts used in this purification process, or their eventual concentration in the purified HF solution.)

COMPONENTS:

(1) Rubidium heptafluorotantalate; Rb_2TaF_7; [76056-60-5]

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

ORIGINAL MEASUREMENTS:

Balke, C. W.

J. Am. Chem. Soc. 1905, *27*, 1140-57.

VARIABLES:

$T/K = 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

The solubility of Rb_2TaF_7 in water at 25°C is reported to be approximately 1 g salt in 40 g (parts) water. From the value the compiler calculated the solubility in water to be $m_1/\text{mol kg}^{-1} = 0.052$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Saturated solutions of the salt were obtained by allowing the crystals to remain in contact with the solution for several hours in a rubber beaker with occasional stirring. The clear liquid was decanted into a weighed Pt dish. The solution was evaporated with few drops of HF being added when the evaporation was nearly complete. The dish with the residue was dried and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) The starting material was Ta_2O_5 which was obtained from the columbite of South Dakota. Crude K_2TaF_7 was first obtained as crystalline precipitate upon the addition of KF to the HF solution of $(Ta, Nb)_2O_5$ and processed to obtain pure Ta_2O_5 in the following manner. K_2TaF_7 was three times recrystallized from water containing enough HF to prevent the formation of the oxysalt. Pt and rubber ware was used. In each step large amount of salt was allowed to remain in the mother liquor to ensure a complete removal of K_2NbOF_5 and other impurities. The K_2TaF_7 so obtained was next purified from Si by evaporating the salt with excess of concentrated H_2SO_4. The residue was boiled up repeatedly with water, and Ta_2O_5 produced was repeatedly washed. Chemical tests showed absence of Fe, W, and Ti. To the solution of the oxide in diluted HF RbF was added. Rb_2TaF_7 was then recrystallized from water containing a small amount of HF to prevent the formation of the insoluble oxysalt. Analysis (mass %, found/calculated): RbF 42.90-43.26/42.91, TaF_5 56.93-57.05/57.09.

COMPONENTS:

(1) Trisodium octafluorotantalate(3-); Na_3TaF_8; [17456-13-2]

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

ORIGINAL MEASUREMENTS:

Balke, C. W.

J. Am. Chem. Soc. 1905, *27*, 1140-57.

VARIABLES:

T/K = 298

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Two measurements of the solubility of Na_3TaF_8 in water at 25 °C were reported as 1 g of salt dissolves in 20.9 and 20.5 g (parts) of water. From the average value of 1 g salt per 20.7 g water the compiler calculated the solubility of Na_3TaF_8 in water to be m_1/mol kg^{-1} = 0.120.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Saturated solutions of the salt were obtained by allowing the crystals to remain in contact with the solution for several hours in a rubber beaker with occasional stirring. The clear liquid was decanted into a weighed Pt dish. The solution was evaporated with few drops of HF being added when the evaporation was nearly complete. The dish with the residue was dried and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) The starting material was Ta_2O_5 which was obtained from the columbite of South Dakota. Crude K_2TaF_7 was first obtained as crystalline precipitate upon the addition of KF to the HF solution of $(Ta, Nb)_2O_5$ and processed to obtain pure Ta_2O_5 in the following manner. K_2TaF_7 was three times recrystallized from water containing enough HF to prevent the formation of the oxysalt. Pt and rubber ware was used. In each step large amount of salt was allowed to remain in the mother liquor to ensure a complete removal of K_2NbOF_5 and other impurities. The K_2TaF_7 so obtained was next purified from Si by evaporating the salt with excess of concentrated H_2SO_4. The residue was boiled up repeatedly with water, and Ta_2O_5 produced was repeatedly washed. Chemical tests showed absence of Fe, W, and Ti. The oxide was dissolved in HF and first $Na_2TaF_7.H_2O$ was obtained by concentrating and cooling a solution containing NaF and large excess TaF_5. On recrystallization of this salt from a diluted solution of HF, Na_3TaF_8 was obtained. HF used was distilled from a Pt retort with KOH added to hold back SiO_2.

Analysis (mass %, found/calculated): NaF 31.28-31.32/31.19, TaF_5 68.45-68.9/68.81.

ESTIMATED ERROR:

The temperature error is not specified.

Soly: precision ± 1 % (compiler).

COMPONENTS:

(1) Tantalum chloride; $TaCl_4$; [13569-72-7]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.
**Zh. Fiz. Khim.* <u>1964</u>, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl. Transl.) <u>1964</u>, *38*, 710-1.

VARIABLES:

T/K = 298, 323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$TaCl_4$
$t/^{\circ}C$	T/K	10^3c_1/mol dm^{-3}
25	298	3.13
50	323	54.62

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $TaCl_4$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Ta in samples taken periodically over 15 days. Ta in the sample was determined gravimetrically as Ta_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Ta into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_4$ was prepared by reduction of $TaCl_5$ with Al powder (ref 1,2). Unreacted $TaCl_5$ and $AlCl_3$ formed were removed by distillation at 210-220°. $TaCl_5$ used was prepared from 99.99% Ta metal by chlorination with Cl gas at 250-500°; m.p. 220°.

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

1. Schäfer, H.; Bayer, L.; Lehmann, H. *Z. Anorg. Allgem. Chem.* <u>1952</u>, *268*, 268.

2. Ruff, O.; Thomas, F. *Z. Anorg. Allgem. Chem.* <u>1925</u>, *148*, 1.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Cyclohexane; C_6H_{12}; [110-82-7]	Fairbrother, F.; Nixon, J. F.; Prophet, H. *J. Less-Common Met.* 1965, *9*, 434-6.
VARIABLES:	**PREPARED BY:**
T/K = 292.8 - 332.4	J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Tantalum chloride; $TaCl_5$	
$t/^{\circ}C$	T/K^a	g/100 g solvent	m_1/mol kg^{-1a}
19.6	292.8	0.454	0.0127
29.9	303.1	0.709	0.0198
39.5	312.7	1.129	0.0315
49.5	322.7	1.666	0.0465
59.2	332.4	2.572	0.0718

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $TaCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $TaCl_5$. The method of tantalum analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by direct chlorination of Ta metal, and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as in earlier work (ref 2).

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.
2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Benzene; C_6H_6; [71-43-2]	Fairbrother, F.; Nixon, J. F.; Prophet, H. *J. Less-Common Met.* 1965, *9*, 434-6.
VARIABLES:	**PREPARED BY:**
T/K = 293.3 - 332.5	J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Tantalum chloride; $TaCl_5$	
$t/^{\circ}C$	T/K^a	g/100 g solvent	m_1/mol kg$^{-1 a}$
20.1	293.3	0.716	0.0200
29.8	303.0	1.151	0.0321
39.7	312.9	1.819	0.0508
49.5	322.7	2.733	0.0763
59.3	332.5	4.178	0.1166

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $TaCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $TaCl_5$. The method of tantalum analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by direct chlorination of Ta metal, and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as in earlier work (ref 2).

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.
2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS: (1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Toluene; C_7H_8; [108-88-3]	**ORIGINAL MEASUREMENTS:** Fairbrother, F.; Nixon, J. F.; Prophet, H. *J. Less-Common Met.* 1965, *9*, 434-6.
VARIABLES: T/K = 293.1 - 318.7	**PREPARED BY:** J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Tantalum chloride; $TaCl_5$	
$t/^{\circ}C$	T/K^a	g/100 g solvent	$m_1/\text{mol kg}^{-1\,a}$
19.9	293.1	0.805	0.0225
29.3	302.5	1.248	0.0348
39.8	313.0	1.873	0.0523
45.5	318.7	2.338	0.0653

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $TaCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $TaCl_5$. The method of tantalum analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by direct chlorination of Ta metal, and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as in earlier work (ref 2).

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.
2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) m-Xylene; C_8H_{10}; [108-38-3]	Fairbrother, F.; Nixon, J. F.; Prophet, H. *J. Less-Common Met.* 1965, *9*, 434-6.
VARIABLES:	**PREPARED BY:**
T/K = 293.8 - 332.9	J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Tantalum chloride; $TaCl_5$	
$t/^{\circ}C$	T/K^a	g/100 g solvent	m_1/mol kg^{-1} ^{a}
20.6	293.8	0.735	0.0205
29.5	302.7	1.131	0.0316
39.5	312.7	1.660	0.0463
49.7	322.9	2.564	0.0716
59.7	332.9	3.562	0.0994

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $TaCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $TaCl_5$. The method of tantalum analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by direct chlorination of Ta metal, and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as in earlier work (ref 2).

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.
2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Mesitylene; C_9H_{12}; [108-67-8]	Fairbrother, F.; Nixon, J. F.; Prophet, H. *J. Less-Common Met.* 1965, *9*, 434-6.
VARIABLES:	**PREPARED BY:**
T/K = 292.8 - 332.7	J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Tantalum chloride; $TaCl_5$	
t/°C	T/K[a]	g/100 g solvent	m_1/mol kg^{-1}[a]
19.6	292.8	0.743	0.0207
29.7	302.9	1.145	0.0320
39.4	312.6	1.601	0.0447
50.7	323.9	2.446	0.0683
59.5	332.7	3.449	0.0963

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $TaCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $TaCl_5$. The method of tantalum analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by direct chlorination of Ta metal, and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as in earlier work (ref 2).

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.
2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) 1,1'-Oxybisethane (diethyl ether); $C_4H_{10}O$; [60-29-7]

ORIGINAL MEASUREMENTS:

Cowley, A.; Fairbrother, F.; Scott, N.

J. Chem. Soc. 1958, 3133-7.

VARIABLES:

$T/K = 267.4 - 293.7$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Tantalum Chloride; $TaCl_5$	
$t/°C$	T/K	g/100 g solvent	m_1/mol kg^{-1} [a]
-5.8	267.4	13.24	0.370
1.8	275.0	14.78	0.413
7.0	280.2	15.78	0.441
16.3	289.5	18.39	0.513
18.5	291.7	21.08	0.588
20.5	293.7	26.61	0.743

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. The Pyrex glass apparatus (ref 1) consisted of the solvent pretreatment line, the saturation, and the sampling vessels. In the pretreatment section, the solute was repeatedly pretreated by successive sublimations of the halide and condensation at -195°C of the solvent onto it. Both components were transferred into the saturation vessel which was connected to the sampling compartment through a sintered glass disc. The vessel was rocked for 24 h, the saturated solution filtered into the sampling ampoule which was then sealed off, weighed, and broken under water to hydrolyze the halide. After standing for 4-5 h, the solution was heated to 90°C, cooled and filtered, and the oxide was ignited and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by passing dry HCl gas over Ta metal sheet at 350-400°C. The product was purified by 5 or 6 fractional sublimations *in vacuo*, and finally sublimed into fragile hook-ended ampoule.

(2) Diethylether (anaesthetic) was distilled from 1/5 of its volume of H_2SO_4, kept over P_2O_5 for at least a week, decanted, fractionated under dry N gas, and stored over Na wire.

ESTIMATED ERROR:

Temp: precision ± >0.1 K.

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc., London* 1956, 1164.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Propylene carbonate (4-methyl-1, 3-dioxalan-2-one); $C_4H_6O_3$; [108-32-7]	Fischer, H. W.; Schwabe, K. *Korrosion (Dresden)* 1980, *11*, 105-15.
VARIABLES:	**PREPARED BY:**
$T/K = 298$	J. Hála

EXPERIMENTAL VALUES:

The approximate solubility of $TaCl_5$ at $t/°C = 25$ is reported to be 26 g $TaCl_5$/100 g solvent. The compiler calculates $m_1/mol\ kg^{-1} = 0.73$.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Although not stated explicitly, the solubility was apparently determined in the apparatus described for electrolysis experiments. The apparatus was connected to a vacuum line, and extreme care was taken to avoid access of air moisture. No details were given about the time of equilibration or the analysis of the saturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ (Merck) contained $\leq$ 0.003% Nb and $\leq$ 0.015% of other metals, and was used without further purification.

(2) Propylene carbonate (Ferak, West Berlin) was purified by distillation.

ESTIMATED ERROR:

Neither temperature or solubility error were specified.

REFERENCES:

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Tetrachloromethane; CCl_4; [56-23-5]

ORIGINAL MEASUREMENTS:

Namoradze, Z. G.; Zvyagintsev, O. E.

Zh. Prikl. Khim. 1939, *12*, 603-8.

VARIABLES:

$T/K = 293\text{-}311$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Ta_2O_5[a]	$TaCl_5$	
$t/^0C$	T/K	g/10 ml satd sln	g/100 ml satd sln	c_1/mol dm^{-3}[b]
20	293	0.0516	0.8365	0.02335
30	303	0.0770	1.2494	0.03489
38	311	0.0960	1.5563	0.04345

[a] Average from 2 or 3 measurements calculated by authors. Individual measurements not reported.

[b] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method was used. Freshly distilled $TaCl_5$ was used for all measurements. The vessel with collected $TaCl_5$ was briefly disconnected from the chlorination app., stoppered, and placed in a thermostat. A portion of the dry solvent was added and the mixture was stirred for 10-14 hours at the desired temperature. The stirrer was equipped with a Hg seal. After equilibration the mixture was allowed to stand for several hours, and a 10 ml sample was withdrawn with a pipette with a cotton filter. On evaporating the solvent $TaCl_5$ hydrolyzed, and Ta content in the sample was determined gravimetrically as Ta_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by chlorination with Cl gas in the presence of charcoal at 600-700° of Ta_2O_5. The product was twice distilled and collected in the vessel for solubility measurement; m.p. 211.3°. Analysis: found 48.67% Cl, 51.25% Ta; calculated 49.5% Cl, 50.5% Ta. The Ta_2O_5 used was separated from Nb_2O_5 in the mixture of Nb and Ta oxides (obtained from ilmenorutile) according to Marignac (ref 1) and Memberg and Winzer (ref 2).

(2) CCl_4 was purified and dried by standard methods.

REFERENCES:

1. Marignac, M. C. *Ann. Chim. Phys.* 1865, *8*, 49.
2. Memberg, E.; Winzer, K. *Z. Angew. Chem.* 1913, *26*, 157.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Tetrachloromethane; CCl_4; [56-23-5]	Fairbrother, F.; Nixon, J. F.; Prophet, H. *J. Less-Common Met.* 1965, *9*, 434-6.
VARIABLES:	PREPARED BY:
T/K = 291.3 - 322.2	J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		Tantalum chloride; $TaCl_5$	
$t/^{\circ}C$	T/K^a	g/100 g solvent	m_1/mol kg^{-1a}
18.1	294.3	0.555	0.0155
28.6	301.8	0.702	0.0196
37.9	311.1	1.061	0.0296
49.0	322.2	1.360	0.0380

^{a} Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The solubility measurements were carried out in a closed system by an isothermal method described earlier by the authors (ref 1). Previously dried pure solvent was pretreated 3-4 times with $TaCl_5$ and distilled *in vacuo* into the solubility apparatus. The procedure removed residual moisture and other impurities which would otherwise react with $TaCl_5$. The method of tantalum analysis was not given.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by direct chlorination of Ta metal, and purified by fractional sublimation *in vacuo*.

ESTIMATED ERROR:

Temp: precision ± 0.1 K as in earlier work (ref 2).
Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc.* 1956, 1164.

2. Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.

**Zh. Fiz. Khim.* <u>1964</u>, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl. Transl.) <u>1964</u>, *38*, 710-1.

VARIABLES:

T/K = 298,323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$TaCl_5$
$t/^0C$	T/K	10^3c_1/mol dm^{-3}
25	298	48.7
50	323	117.09

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $TaCl_5$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Ta in samples taken periodically over 15 days. Ta in the sample was determined gravimetrically as Ta_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Ta into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared from 99.99% purity Ta metal by chlorination with Cl gas at 250-500^0. The product m. at 220^0 and was stored in a dry box.

SOURCE AND PURITY OF MATERIALS:(continued)

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Carbon disulphide; CS_2; [75-15-0]

ORIGINAL MEASUREMENTS:

Namoradze, Z. G.; Zvyagintsev, O. E.

Zh. Prikl. Khim. 1939, *12*, 603-8.

VARIABLES:

$T/K = 273 - 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Ta_2O_5 [a]	$TaCl_5$	
$t/^{\circ}C$	T/K	g/10 ml satd sln	g/100 ml satd sln	$c_1/mol\ dm^{-3}$ [b]
0	273	0.0793	1.2850	0.03587
14	287	0.1628	2.6393	0.07368
20	293	0.1992	3.1175	0.08703
25	298	0.2308	3.7436	0.1045

[a] Average from 2 or 3 measurements calculated by authors. Individual measurements not reported.

[b] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method was used. Freshly distilled $TaCl_5$ was used for all measurements. The vessel with collected $TaCl_5$ was briefly disconnected from the chlorination app., stoppered, and placed in a thermostat. A portion of the dry solvent was added and the mixture was stirred for 12 hours at the desired temperature. The stirrer was equipped with a Hg seal. After equilibration the mixture was allowed to stand for several hours, and a 10 ml sample was withdrawn with a pipette with a cotton filter. On evaporating the solvent $TaCl_5$ hydrolyzed, and Ta content in the sample was determined gravimetrically as Ta_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by chlorination with Cl gas in the presence of charcoal at 600-700° of Ta_2O_5. The product was twice distilled and collected in the vessel for solubility measurement; m.p. 211.3°. Analysis: found 48.67% Cl, 51.25% Ta; calculated 49.5% Cl, 50.5% Ta. The Ta_2O_5 used was separated from Nb_2O_5 in the mixture of Nb and Ta oxides (obtained from ilmenorutile) according to Marignac (ref 1) and Memberg and Winzer (ref 2).

(2) CS_2 was purified and dried by standard methods.

REFERENCES:

1. Marignac, M. C. *Ann. Chim. Phys.* 1865, *8*, 49.
2. Memberg, E.; Winzer, K. *Z. Angew. Chem.* 1913, *26*, 157.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

EVALUATOR:

J. Hála
Department of Inorganic Chemistry
J. E. Purkyne University
61 137 Brno, Czechoslovakia

October 1985

CRITICAL EVALUATION:

An evaluation of the solubility of $TaCl_5$ in $TiCl_4$ between 273 and 403 K.

Six sets of data are available for the temperature dependence of the solubility of $TaCl_5$ in $TiCl_4$ (ref 1-6). In all of the papers the solubilities were determined by an isothermal method and by analysis of the saturated solutions. In two papers (ref 2, 3) a polythermal method was also used in the region of higher solubilities. The solubility values obtained by the isothermal method are compared in Figure 1. Of these, the data of Tarasenkov and Komandin are much higher than the data of the other authors. The authors (ref 1) themselves state the low precision of their data, and these data can be rejected. [The poor quality of their data can be seen in their $NbCl_5/TaCl_5$ solubility ratio in $TiCl_4$ which indicates a much larger difference in solubility than expected from the properties of Nb and Ta.]

The remaining five data sets show good agreement, especially those of (ref 4-6). The measurements in these three documents do not extend below 25 °C, and they cannot be compared with the data of (ref 2 and 3) which appear to be slightly lower at the higher temperatures. Because of the different temperature ranges studied in these papers it is not possible to give a preference to any of these data. All of the data from (ref 2-6) were treated by a linear regression to obtain the equation

$$\log (m_1/\text{mol kg}^{-1}) = -1.919 + 0.014285\ (t/^{\circ}\text{C})$$

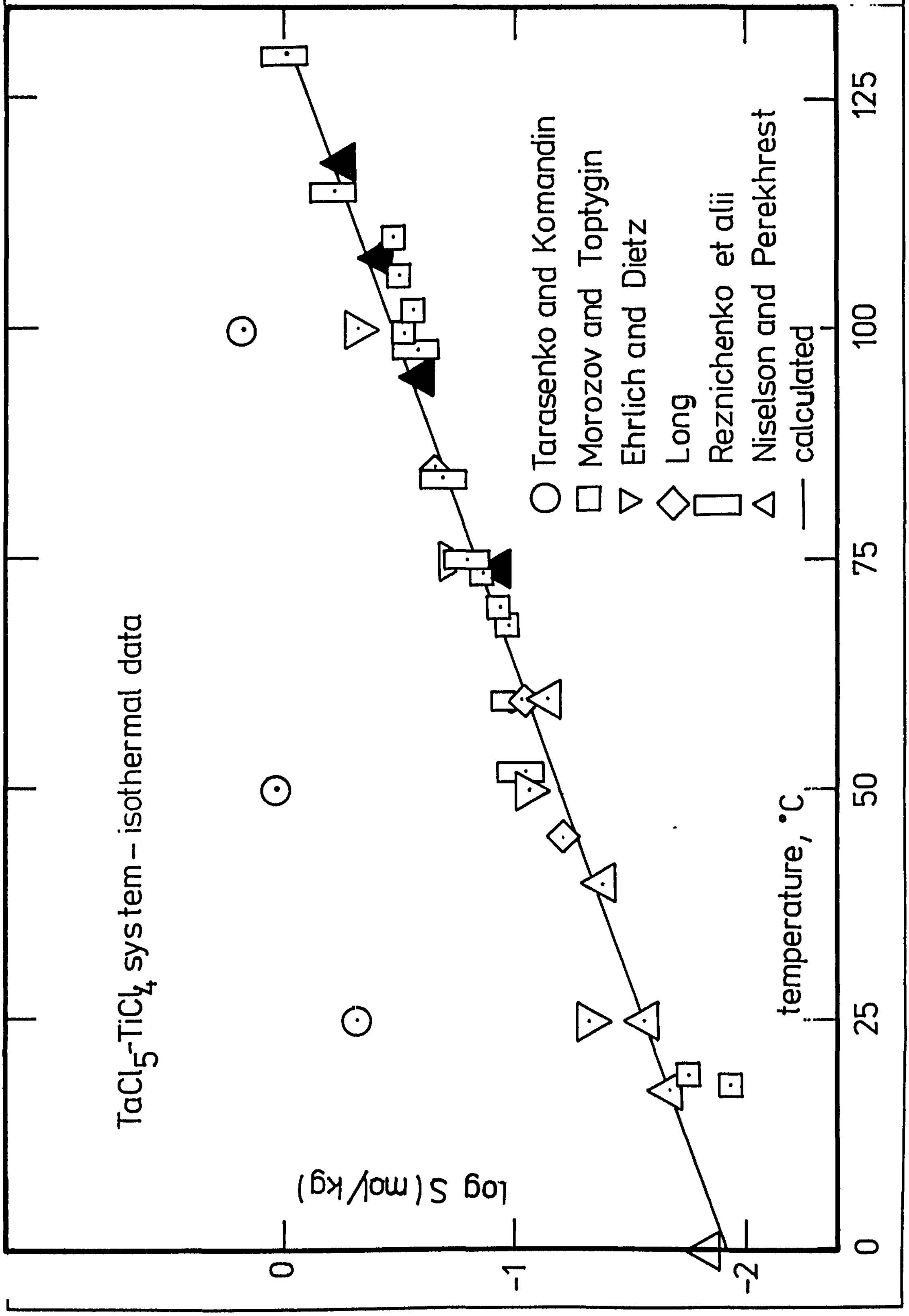
for the 0 to 130 °C temperature interval.

The two data sets obtained by the polythermal method (ref 2 and 3) differ considerably. The values of Niselson and Perekhrest (ref 3) are lower than those of Morozov and Toptygin (ref 2) at a given temperature by 5-10 mass% $TaCl_5$. The reason may be the strong tendency to form super saturated solutions in the system (ref 3) which makes it difficult to determine the liquidus temperature from cooling curves. The Niselson and Perekherst polythermal values agree well with the isothermal values of other authors (black triangles in Fig 1), and their data should be given preference.

REFERENCES:

1. Tarasenkov, P. N.; Komandin, A. V. *Zh. Obsch. Khim.* 1940, *10*, 1319.
2. Morozov, I. S.; Toptygin, D. Ya. *Zh. Neorg. Khim.* 1957, *2*, 1915.
3. Niselson, L. A.; Perekhrest, G. L. *Zh. Neorg. Khim.* 1958, *3*, 2150.
4. Ehrlich, P.; Dietz, G. *Z. Anorg. Allg. Chem.* 1960, *305*, 158.
5. Long, A. M. *Australian J. Chem.* 1969, *22*, 853.
6. Reznichenko, V. A.; Moinov, S. G.; Egorov, S. I.; Laktyushin,V.S. *Izv. Akad. Nauk. SSSR, Metally* 1969, No. 3, 56.

COMPONENTS:	EVALUATOR:
(1) Tantalum chloride; $TaCl_5$; [7721-01-9] (2) Titanium chloride; $TiCl_4$; [7550-45-0]	J. Hála Department of Inorganic Chemistry J. E. Purkyne University 61 137 Brno, Czechoslovakia October 1985



COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Tarasenkov, P. N.; Komandin, A. V.

Zh. Obshch. Khim. 1940, *10*, 1319-27.

VARIABLES:

T/K = 298 - 415

PREPARED BY:

J. Hala

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$TaCl_5$	
$t/^{0}C$	T/K	mass %	m_1/mol kg^{-1} [a]
25	298	14.3	0.466
50	323	27.1	1.04
100	373	33.9	1.43
141.8 [b]	415	39.3	1.81

[a] Calculated by compiler

[b] B.p. of $TiCl_4$ saturated with $TaCl_5$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Both isothermal and polythermal methods were used. In the isothermal method $TiCl_4$ was distilled onto excess $TaCl_5$ and the mixture was equilibrated in a tube closed with Hg seal and equipped with a stirrer. $TaCl_5$ content in the saturated solution was determined from the total Cl^- content as determined by Volhard's method after hydrolysis of the sample and removal of the hydrolytic products. In the polythermal method known amounts of both chlorides were slowly heated in a closed vessel and the temperature of the disappearance of the last crystals was read. The system was then cooled slowly and the temperature of crystallization was read. The procedure was repeated several times and the average temperature was taken. It is not clear from the document which of the methods was used to obtain the data reported.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by chlorination of Ta metal. The product was stored in sealed ampoules.

(2) $TiCl_4$, tech. grade, was purified by fractional distillation after preliminary treatment with Hg metal. The product boiled at 136^{0}/743 mmHg.

ESTIMATED ERROR:

Temp: precision ± 0.1 K for the isothermal method.

The authors state low precision of the data and suggest the data be taken as qualitative.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Morozov, I. S.; Toptygin, D. Ya.

Zh. Neorg Khim. 1957, *2*, 1915-21.

J. Inorg. Chem. (USSR)(Engl.Transl.) 1957, *2*(8), 322-33.

VARIABLES:

T/K = 291 - 470

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Temperature		$TaCl_5$	
$t/^{\circ}C$	T/K	mass%	m_1/mol kg^{-1} [a]
Isothermal method			
18		0.40	0.0112
19		0.6	0.0169
68		3.6	0.104
70		3.9	0.113
74		4.8	0.141
100		9.6	0.296
102		8.8	0.269
106		10.0	0.310
110		10.7	0.334
Polythermal method			
65		7.5	
88		15.0	
108		21.5	
129		34.8	
142		44.1	
145		48.8	
156		60.2	
164		64.2	
180		73.2	
192		80.2	
197		88.5	

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

In the isothermal method mixtures of $TiCl_4$ and $TaCl_5$ were distilled into a test-tube with a side arm. The test-tube was sealed off, kept at the desired temperature for 20-40 h, and a part of the saturated solution was poured into the side arm. The latter was then sealed off, cooled, and weighed. Prior to analysis, most of the $TiCl_4$ was removed by distillation in the presence of NaCl. The final separation of Ta from the remaining Ti was achieved by means of phenylarsonic acid. In the polythermal method, mixtures of $TiCl_4$ and $TaCl_5$ were prepared by weighing, melted, and cooling curves were recorded.

NOTE: The two data sets do not coincide because the systems tend to form supersaturated solutions.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ was prepared by chlorination of Ta metal with Cl_2 gas.

(2) Commercially available $TiCl_4$ (source not specified) was distilled twice. The fraction boiling at 136°C at 760 mmHg was used.

ESTIMATED ERROR:

REFERENCES:

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Niselson, L. A.; Perekhrest, G. L.

Zh. Neorg. Khim. 1958, *3*, 2150-5.

J. Inorg. Chem. (USSR) (Engl. Transl.) 1958, *3*(9), 215-22.

VARIABLES:

T/K = 249.0 - 489.7

PREPARED BY:

J. Hala

EXPERIMENTAL VALUES: Composition of saturated solutions.

Liquidus Temperature		Tantalum chloride; $TaCl_5$		
t/ C	T/K[d]	mass %	mol %	m_1/mol kg^{-1}[d]
-24.0[a]	249.2	0	0	0
-24.2[b]	249.0	0.266	0.141	-
0	293.2	0.50	0.266	0.0140
17.5	290.7	0.75	0.398	0.0211
25	298.2	0.93	0.495	0.0262
40	313.2	1.41	0.75	0.0399
60	333.2	2.50	1.34	0.0716
74.0	347.2	4.13	2.23	0.120
94.8	368.0	8.02	4.47	0.243
108.0	381.2	11.6	6.52	0.366
118.0	391.2	16.3	9.30	0.544
148.5	421.7	33.4	22.0	
182.2	455.4	64.4	48.8	
204.5	477.7	87.3	78.6	
216.5[c]	489.7	100.0	100.0	

[a] Taken from ref (1)

[b] Eutectic temperature calculated by authors according to ref (2)

[c] Taken from ref (3)

[d] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

At higher $TaCl_5$ concentrations (≥4.13 mass%) the liquidus curve was obtained by visual polythermal method. $TaCl_5$ and $TiCl_4$ were weighed into a glass tube previously dried *in vacuo* at 350-400°. The tube was sealed, heated in a furnace to melt the mixture, and then allowed to cool slowly in a thermostated glycerine bath under constant rotation at 60 rpm. The liquidus temperature was taken as the average of temperatures of appearance and disappearance of crystals in the melt recorded at successive cooling and heating of the system. At lower $TaCl_5$ concentrations, isothermal method was used. Ampoules containing $TaCl_5$ and $TiCl_4$ were equilibrated for 30 h at 40 and 60°, and for 60 h at 0 and 17.5°. A sample of the sautrated solution was hydrolyzed, the precipitate ignited to oxides, and the Ta concentration was determined spectrographically.

SOURCE AND PURITY OF MATERIALS:

Source of $TaCl_5$ and $TiCl_4$ not specified. Both halides were purified by rectification and stored in sealed ampoules.

ESTIMATED ERROR:

REFERENCES:

1. Clabaugh, W. S.; Leslie, R. T.; Gilchrist, R. J. *Res. Nat. Bur. Stand* 1955, *55*, 261.
2. Kordes, E. *Z. Anorg. Chem.* 1927, *167*, 97.
3. Schafer, H.; Pietruck, C. *Z. Anorg. Allgem. Chem.* 1951, *267*, 174.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Ehrlich, P.; Dietz, G.

Z. Anorg. Allg. Chem. 1960, *305*, 158-68.

VARIABLES:

T/K = 298 - 373

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solutions

Temperature		$TaCl_5$	
t/ C	T/K	mass %	m_2/mol kg^{-1} [a]
25	298	1.6	0.0454
50	323	2.9	0.0834
75	348	5.8	0.172
100	373	14.0	0.454

[a] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. An all-glass apparatus was used in which the unit for distilling the solvent, equipment for solubility determination, and sampling and hydrolyzing the saturated solutions were coupled together. Transfer of liquids in the system was carried out by means of nitrogen gas pressure. Samples for analysis were taken from the dissolution vessel through an immersed tube thermostated to a temperature higher by 2° than that of the dissolution vessel. The samples were hydrolyzed in diluted acid and Ta was separated from Ti by repeated precipitation with N-benzoyl-N-phenylhydroxylamine (ref 1.).

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ prepared according to ref (2). Its purity was not specified.

(2) $TiCl_4$, tech. grade, was purified by refluxing it with 1.5 g $CuSO_4 \cdot 5H_2O$ and 10 g charcoal per 300 ml $TiCl_4$ for 2 h. A colorless product was obtained, b. 136°, electric conductivity < 10^{-9} cm^{-1}.

ESTIMATED ERROR:

Temp: precision ± 0.2 K

Solubility error not specified.

REFERENCES:

1. Moshier, R. W.; Schwarberg, J. E. *Anal. Chem.* 1957, *29*, 947.

2. Brauer, G. *Handbuch der Preparative Anorganische Chemie* 1954, F. Enke-Verlag, Stuttgart.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Long, A. M.

Austral. J. Chem. 1969, *22*, 853-4.

VARIABLES:

$T/K = 318 - 358$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of Saturated Solution

Temperature		$TaCl_5$	
$t/^{\circ}C$	T/K	mass %	$m_1/\text{mol kg}^{-1}$[a]
45	318	2.1	0.0599
60	333	3.1	0.0893
85	348	7.5	0.226

[a] Calculated by compiler

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

The saturated solutions were prepared in a sealed, nitrogen-filled apparatus (ref 1), for 21-90 hours. After equilibration a sample of the filtered solution was collected in a detachable ampoule. Dissolving and sampling were carried out in a thermostated waterbath. Each ampoule with the sample was broken under 3 mol dm^{-3} HNO_3 in a sealed bottle, and hydrous oxides of Ta and Ti were precipitated by ammonia. After filtration and ignition at 800° the mixed oxides were analyzed by x-ray spectrography.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ (Alfa Inorganics), lab. grade, was used as obtained.

(2) $TiCl_4$ was purified by treatment with Cu powder and distillation. It was stored in sealed ampoules.

ESTIMATED ERROR:

Temp: precision ± 0.5 K
Soly: precision ± 2 %

REFERENCES:

1. Long, A. M.
Chemistry and Industry 1968, *50*, 1764.

COMPONENTS:

(1) Tantalum chloride; $TaCl_5$; [7721-01-9]

(2) Titanium chloride; $TiCl_4$; [7550-45-0]

ORIGINAL MEASUREMENTS:

Reznichenko, V. A.; Moinov, S. G.; Egorov, S. I.; Laktyushin, V. S.

Izv. Akad. Nauk SSSR, Metal. 1969, No. 3, 56-60.

VARIABLES:

$T/K = 325.2 - 403.2$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Temperature		$TaCl_5$								
$t/^{\circ}C$	T/K^{c}	mass %^{a}							mass %^{b}	$m_1/\text{mol kg}^{-1\,c}$
52.0	325.2	2.2	3.8	2.5	2.1	5.0	2.7		3.05	0.0878
60.0	333.2	3.4	2.8	2.7	3.6	3.2	3.7		3.23	0.0932
75.0	348.2	6.6	6.5	4.7	5.6	5.8	4.6	5.2	5.57	0.165
84.0	357.2	6.2	6.9	7.2	6.8	6.8			6.78	0.203
97.5	370.9	8.2	9.6	8.3	8.1	8.3			8.50	0.259
115.0	388.2	16.5	17.3	17.9	17.8	17.2	17.3		17.33	0.585
130.0	403.2	26.0	25.2	25.0	24.6	26.6	24.6		25.33	0.947

[a] Determined for various equilibration times (see the procedure).

[b] Average.

[c] Calculated by compiler.

Note: By least squares treatment of the data the authors obtained the following equation for the solubility of $TaCl_5$ in $TiCl_4$ (solubility S expressed in mole fractions):

$$\log S = -1689/T + 3.336$$

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. A thermostated glass vessel equipped with a stirrer, thermometer and a glass pipette for withdrawing the samples, and sealed with silicone oil, was used. The system was mixed for 1 h at a desired temperature and then allowed to stand at this temperature for a prolonged period of time during which samples were taken at 3 h intervals. Ta was determined gravimetrically as the oxide by precipitation with ammonia after separation of Ti and Ta hydrated oxides in HCl medium.

SOURCE AND PURITY OF MATERIALS:

(1) $TaCl_5$ of unspecified origin contained (in mass %) 0.01 Mn, 0.01 Si, 0.15 Ni, 0.01 Fe, 0.01 Cu, and 0.03 Nb.

(2) $TiCl_4$ (source not specified) was purified by using Cu filings. It contained (in mass %) 0.005 Mn, Si, and Mg, and 0.01 Fe.

ESTIMATED ERROR:

Temp: precision ± 0.2 K.

Solubility error not specified.

REFERENCES:

COMPONENTS:

(1) Sodium hexachlorotantalate(1-); $NaTaCl_6$; [16920-14-2]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.

***Zh. Fiz. Khim.* 1964, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl.Transl.) 1964, *38*, 710-1.

VARIABLES:

T/K = 298, 323

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		$NaTaCl_6$
$t/^{0}C$	T/K	$10^3 c_1$/mol dm^{-3}
25	298	5.56
50	323	7.41

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $NaTaCl_6$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Ta in samples taken periodically over 15 days. Ta in the sample was determined gravimetrically as Ta_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Ta into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $NaTaCl_6$ was prepared by heating stoichiometric amounts of $TaCl_5$ and NaCl in a sealed ampoule in vacuum at 220-300°. $TaCl_5$ used was prepared from 99.99% purity Ta metal by chlorination with Cl gas at 250-500°; m.p. 200°. NaCl was recrystallized and ignited before use.

SOURCE AND PURITY OF MATERIALS: (continued)

(2) Hexachloro-1,3-butadiene (source not specified) was purified to obtain a product with d_4^{20} = 1.6807 and n_D^{20} = 1.5543.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

COMPONENTS:

(1) Potassium hexachlorotantalate; $KTaCl_6$; [16918-73-3]

(2) 1,1,2,3,4,4-Hexachloro-1,3-butadiene; C_4Cl_6; [87-68-3]

ORIGINAL MEASUREMENTS:

Bolshakov, K. A.; Safronov, V. V.; Kogan, L. M.; Shevtsova, Z. N.; Shadrova, L. G.
***Zh. Fiz. Khim.* 1964, *38*, 1305-6.

Russ. J. Phys. Chem. (Engl. Transl.) 1964, *38*, 710-1.

VARIABLES:

$T/K = 298.\ 323$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of saturated solutions.

Temperature		$KTaCl_6$
$t/^0C$	T/K	$10^3c_1/mol\ dm^{-3}$
25	298	0.99
50	323	1.87

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. Excess $KTaCl_6$ was introduced to the solvent in a dry box. The mixture was equilibrated for 5-10 days in a thermostated vessel equipped with a hydraulic stopper to prevent both solvent evaporation and access of atmospheric moisture. Attainment of equilibrium was checked by analyzing the liquid phase for Ta in samples taken periodically over 15 days. Ta in the sample was determined gravimetrically as Ta_2O_5 either after direct ignition of the samples of the saturated solutions or after extraction of Ta into concentrated HCl and subsequent precipitation of the hydrated oxide.

SOURCE AND PURITY OF MATERIALS:

(1) $KTaCl_6$ was prepared by heating stoichiometric amounts of $TaCl_5$ and KCl in a sealed ampoule in vacuum at 220-300°. $TaCl_5$ used was prepared from 99.99% purity Ta metal by chlorination with Cl

SOURCE AND PURITY OF MATERIALS: (continued)

gas; m.p. 220°. KCl was recrystallized and ignited before use.

(2) Hexachloro-1,3-bitadiene (source not specified) was purified to obtain a product with $d_4^{20} = 1.6807$ and $n_D^{20} = 1.5543$.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.
Soly: precision ± 0.2-0.5 %.

REFERENCES:

COMPONENTS:

(1) Tantalum bromide; $TaBr_5$; [13451-11-1]

(2) 1,1'-Oxybisethane (diethyl ether); $C_4H_{10}O$; [60-29-7]

ORIGINAL MEASUREMENTS:

Cowley, A.; Fairbrother, F.; Scott, N.

J. Chem. Soc. 1958, 3133-7.

VARIABLES:

$T/K = 276.2 - 294.6$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Tantalum bromide; $TaBr_5$	
$t/^{\circ}C$	T/K	g/100 g solvent	$m_1/\text{mol kg}^{-1}$ [a]
3.0	276.2	6.41	0.110
8.5	281.7	7.52	0.130
18.9	292.1	8.80	0.152
21.4	294.6	10.09	0.174

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. The Pyrex glass apparatus (ref 1) consisted of the solvent pretreatment line, the saturation, and the sampling vessels. In the pretreatment section, the solute was repeatedly pretreated by successive sublimations of the halide and condensation at -195°C of the solvent onto it. Both components were transferred into the saturation vessel which was connected to the sampling compartment through a sintered glass disc. The vessel was rocked for 24 h, the saturated solution filtered into the sampling ampoule which was then sealed off, weighed, and broken under water to hydrolyze the halide. After standing for 4-5 h, the solution was heated to 90°C, cooled and filtered, and the oxide was ignited and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) $TaBr_5$ free from hydrolytic products was prepared by reacting dry Br with Ta metal sheet in a closed system at 400-450°C. The product was purified by 5 or 6 fractional sublimations *in vacuo*, and finally sublimed into fragile hook-ended ampoule.

(2) Diethylether (anesthetic) was distilled from 1/5 of its volume of H_2SO_4, kept over P_2O_5 for at least a week, decanted, fractionated under dry N gas, and stored over Na wire.

ESTIMATED ERROR:

Temp: precision ± >0.1 K.

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc. London* 1956, 1164.

COMPONENTS:

(1) Tantalum bromide; $TaBr_5$; [13451-11-1]

(2) Tetrachloromethane; CCl_4; [56-23-5]

ORIGINAL MEASUREMENTS:

Namoradze, Z. G.; Zvyagintsev, O. E.

Zh. Prikl. Khim. 1939, *12*, 603-8.

VARIABLES:

T/K = 293 and 303

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Ta_2O_5 [a]	$TaBr_5$	
$t/^\circ C$	T/K	g/10 ml satd sln	g/100 ml satd sln	c_1/mol dm^{-3} [d]
20[b]	293	0.0242	0.3921	0.006755
30[c]	303	0.0534	1.4651	0.02524

[a] Average from 2 or 3 measurements calculated by authors. Individual measurements not reported.

[b] Equilibrium time 19 hours.

[c] Equilibrium time 10 hours.

[d] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method was used. Freshly distilled $TaBr_5$ was used for all measurements. The vessel with collected $TaBr_5$ was briefly disconnected from the bromination app.; stoppered, and placed in a thermostat. A portion of the dry solvent was added and the mixture was stirred for 10-14 hours at the desired temperature. The stirrer was equipped with a Hg seal. After equilibration the mixture was allowed to stand for several hours, and a 10 ml sample was withdrawn with a pipette with a cotton filter. On evaporating the solvent $TaBr_5$ hydrolyzed, and Ta content in the sample was determined gravimetrically as Ta_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) $TaBr_5$ was prepared by bromination of a mixture of Ta_2O_5 with charcoal by Br gas at 600-700° using CO_2 as a carrier gas for bromine. The product was twice distilled and collected in the vessel used for solubility measurements. Analysis: found 67.7-67.8% Br, 32.2-32.5% Ta; calculated 68.9% Br, 31.1% Ta. The Ta_2O_5 used was separated from Nb_2O_5 in the mixture of Nb and Ta oxides (obtained from ilmenorutile) according to Marignac (ref 1) and Memberg and Winzer (ref 2).

(2) CCl_4 was purified and dried by standard methods.

REFERENCES:

1. Marignac, M. C. *Ann. Chim. Phys.* 1865, *8*, 49.

2. Memberg, E.; Winzer, K. *Z. Angew. Chem.* 1913, *26*, 157.

COMPONENTS:

(1) Tantalum bromide; $TaBr_5$; [13451-11-1]

(2) Bromoethane; C_2H_5Br; [74-96-4]

ORIGINAL MEASUREMENTS:

Namoradze, Z. G.; Zvyagintsev, O. E.

Zh. Prikl. Khim. 1939, *12*, 603-8.

VARIABLES:

$T/K = 273 - 298$

PREPARED BY:

J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Ta_2O_5 [a]	$TaBr_5$	
$t/^\circ C$	T/K	g/10 ml satd sln	g/100 ml satd sln	$c_1/mol\ dm^{-3}$ [f]
0	273	0.0158[b]	0.2560	0.004410
0	273	0.0162[c,e]	0.2624	0.004520
20	293	0.0246[d]	0.3985	0.006865
25	298	0.0264[c]	0.4277	0.007368

[a] Average from 2 or 3 measurements calculated by authors. Individual measurements not reported.

[b] Equilibrium time 12 hours.

[c] Equilibrium time 10 hours.

[d] Equilibrium time 17 hours.

[e] Saturated solutions obtained at 25°C and then cooled down to 0°C.

[f] Calculated by compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method used. Freshly distilled $TaBr_5$ was used for all measurements. The vessel with collected $TaBr_5$ was briefly disconnected from the bromination app.; stoppered, and placed in a thermostat. A portion of the dry solvent was added and the mixture was stirred for 10-14 hours at the desired temperature. The stirrer was equipped with a Hg seal. After equilibration the mixture was allowed to stand for several hours, and a 10 ml sample was withdrawn with a pipette with a cotton filter. On evaporating the solvent $TaBr_5$ hydrolyzed, and Ta content in the sample was determined gravimetrically as Ta_2O_5.

SOURCE AND PURITY OF MATERIALS:

(1) $TaBr_5$ was prepared by bromination of a mixture of Ta_2O_5 with charcoal by Br gas at 600-700° using CO_2 as a carrier gas for bromine. The product was twice distilled and collected in the vessel used for solubility measurements. Analysis: found 67.7-67.8% Br, 32.2-32.5% Ta; calculated 68.9% Br, 31.1% Ta. The Ta_2O_5 used was separated from Nb_2O_5 in the mixture of Nb and Ta oxides (obtained from ilmenorutile) according to Marignac (ref 1) and Memberg and Winzer (ref 2).

REFERENCES:

1. Marignac, M. C. *Ann. Chim. Phys.* 1865, *8*, 49.

2. Memberg, E.; Winzer, K. *Z. Angew. Chem.* 1913, *26*, 157.

COMPONENTS:	ORIGINAL MEASUREMENTS:
(1) Tantalum iodide; TaI_5; [14693-81-3] (2) 1,1'-Oxybisethane (diethyl ether); $C_4H_{10}O$; [60-29-7]	Cowley, A.; Fairbrother, F.; Scott, N. *J. Chem. Soc.* 1958, 3133-7.
VARIABLES:	**PREPARED BY:**
$T/K = 276.2 - 293.2$	J. Hála

EXPERIMENTAL VALUES:

Composition of the saturated solutions.

Temperature		Tantalum iodide; TaI_5	
$t/^\circ C$	T/K	g/100 g solvent	m_1/mol kg^{-1} [a]
3.0	276.2	2.29	0.0281
5.8	279.0	2.43	0.0298
9.0	282.2	2.56	0.0314
15.7	288.9	2.94	0.0361
20.0	293.2	3.27	0.0401

[a] Calculated by the compiler.

AUXILIARY INFORMATION

METHOD/APPARATUS/PROCEDURE:

Isothermal method. The Pyrex glass apparatus (ref 1) consisted of the solvent pretreatment line, the saturation, and the sampling vessels. In the pretreatment section, the solute was repeatedly pretreated by successive sublimations of the halide and condensation at -195°C of the solvent onto it. Both components were transferred into the saturation vessel which was connected to the sampling compartment through a sintered glass disc. The vessel was rocked for 24 h, the saturated solution filtered into the sampling ampoule which was then sealed off, weighed, and broken under water to hydrolyze the halide. After standing for 4-5 h, the solution was heated to 90°C, cooled and filtered, and the oxide was ignited and weighed.

SOURCE AND PURITY OF MATERIALS:

(1) TaI_5 was prepared from Ta metal heated in an induction furnace in the presence of iodine vapors (ref 2). The product was purified by 5 or 6 fractional sublimations *in vacuo*, and finally sublimed into fragile hook-ended ampoule.

(2) Diethylether (anesthetic) was distilled from 1/5 of its volume of H_2SO_4, kept over P_2O_5 for at least a week, decanted, fractionated under dry N gas, and stored over Na wire.

ESTIMATED ERROR:

Temp: precision ± 0.1 K.

Solubility error is not specified.

REFERENCES:

1. Fairbrother, F.; Scott, N.; Prophet, H. *J. Chem. Soc. London* 1956, 1164.
2. Alexander, K. M.; Fairbrother, F. *J. Chem. Soc., London* 1949, S 223.

Page numbers preceded by E refer to evaluation texts whereas those not preceded by E refer to compiled tables.
In this index diammonium and dipotassium halates are indexed under ammonium and potassium.

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

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