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NEA-TDB

CHEMICAL THERMODYNAMICS OF TECHNETIUM

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CHEMICAL THERMODYNAMICS OF TECHNETIUM

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ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Preface

This volume on technetium is the third volume in a series of critical reviews of the chemical thermodynamic properties of elements of special importance to modelling efforts for the safety assessment of radioactive waste disposal systems, and is the only one concerned with a fission product element. The first two volumes were reviews of the chemical thermodynamics of uranium and americium. Thermochemical data for neptunium and plutonium are being reviewed for a later volume.

The OECD Nuclear Energy Agency (NEA) began the Thermochemical Data Base (TDB) project in 1984 as a collaboration between the Data Bank of the NEA and the Division of Radiation Protection and Radioactive Waste Management. Review committees were recruited by Anthony Muller in 1984 and 1985 for the various elements of interest. Anthony Muller left the NEA in 1986 and was replaced by Hans Wanner.

The first meetings of the review teams took place in the autumn of 1987, at which time preliminary plans were made for the scope of each volume and sections were assigned to be written by each team member. It has taken more than ten years since the first meeting of the technetium committee to get this volume written. A main reason for taking this long was the loss of four committee members due to job changes or health reasons, which made this the smallest of the NEA review committees. However, another factor was the lack of consistent funding for the committee members, which brought the work on this book to a standstill on several occasions.

Editing of the various drafts of the volume on technetium has been performed by Hans Wanner (1986 to 1992), Ignasi Puigdomenech (1992 to 1995), M. C. Amaia Sandino (1995 to 1997), and most recently by Erik Östhols (1998 and 1999). During this time they have been assisted by members of the NEA Data Bank including Isabelle Poirot (now Muller), Isabelle Forest, Cecile Lotteau, Sasha Koo-Oshima, Frederique Joyeux and Isabelle Claudel.

The first meeting of the technetium committee took place at the NEA Data Bank in Gif-sur-Yvette, France, on October 14-15, 1987. Present were the committee chairman Jean Paquette and the committee members Malcolm H. Rand, Joseph A. Rard, and John R. Thornback, along with (from the NEA) Hans Wanner, Isabelle Poirot (Muller), and Jean-Claude Parneix. The second meeting of the committee took place at the NEA Data Bank in Gif-sur-Yvette, France, on May 14-15, 1990. Present were the chairman Joseph A. Rard and committee members Malcolm H. Rand and John Thornback, along with (from the NEA) Hans Wanner, Isabelle Forest, and K. Miyahara. The third and final meeting of the technetium committe took place at the Swiss Federal Nuclear Safety Inspectorate in Villigen, Switzerland on October 28-30, 1996. Present were the chairman Joseph A. Rard and committee members Giorgio Anderegg, Malcolm H. Rand, and Hans Wanner, along with (from the NEA) M. C. Amaia Sandino.

Jean Paquette resigned from the technetium committee early in 1988 after changing jobs to a nonnuclear field of work, and I became the new chairman. Jean Paquette's replacement, and his replacement's replacement, both left the technetium committee

within about a year after joining because of health reasons and job changes, respectively. Giorgio Anderegg was added to the technetium committee in 1993 and Hans Wanner in 1996. John Thornback left the technetium committee in 1996.

The original plans for the book on technetium included having sections on the organic compounds and complexes of technetium, and rough drafts for several of those sections were written by John Thornback. However, in order to finish this book without delaying any longer, it became necessary to reduce the scope of this book by eliminating these draft sections. A few types of the organic compounds and complexes of technetium are discussed in this book together with their corresponding inorganic compounds and complexes. The main types of these compounds and complexes are the oganometallic hydrides, nitrosyl and thionitrosyl compounds and complexes, and complexes containing organic selenide, arsenic, or antimony ligands. The NEA is preparing a separate volume on compounds and complexes of technetium and other radioactive elements of interest with selected simple organic ligands.

This volume was written as a truly collaborative effort. The sections on the aqueous redox chemistry of technetium (except for examining the claims for the existence of aqueous Tc^{2+}) and the solubility of $TcO_2{\cdot}1.6H_2O$(s) were written originally by Giorgio Anderegg and were revised and expanded by Hans Wanner. Malcolm Rand wrote the sections on technetium metal and the intermetallic compounds. The sections on anhydrous binary oxides and binary sulphides were a collaboration between Malcolm Rand and myself. All of the remaining sections were written by me. However, Malcolm Rand also made significant contributions to several of those sections by performing statistical thermodynamic calculations for technetium halides and oxohalides, and by helping to update some existing sections by reviewing recent publications. The large number of sections written by me was not due to any particular desire or talent on my part. Rather, it is due to the fact that I had financial support for a longer period of time than did any of the other team members.

This volume contains a detailed description of the phase relations, reaction chemistry, and physicochemical properties of technetium and its various compounds, complexes, and aqueous species. The discussion is much more detailed than was given in the earlier volumes on uranium and americium, and was necessary because of the extreme complexity of the chemistry of technetium. This complexity arises because of the ability of technetium to form compounds with technetium valences ranging from -1 to +7, and because of its strong tendency to form binuclear and polynuclear compounds and complexes. Its chemistry is so complex that much of it is poorly understood, and many of the phase relations (including the technetium-oxygen system) are incompletely characterised. The authors of this volume hope that by presenting a detailed discussion of what is known and what is not known about the chemistry and thermodynamics of technetium, some of the readers will be inspired to determine some of the missing information or to reconcile discrepancies between seemingly contradictory information or conclusions published in the literature.

Livermore, California, October 1997 Joseph A. Rard, Chairman

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The entire manuscript of this book has undergone a peer review by an independent international group of reviewers, according to the procedures in the TDB-6 guideline, available from the NEA. The peer reviewers have viewed and approved the modifications made by the authors in response to their comments. The peer review comment

records may be obtained on request from the OECD Nuclear Energy Agency. The peer reviewers are:

Dr. John Baldas, Australian Radiation Laboratory, Yallambie, Victoria, Australia,

Prof. Leo Brewer, Chemistry Department, University of California, Berkeley, California, USA,

Dr. Konstantin E. Guerman, Technetium Radiochemistry and Ecology Group, Institute of Physical Chemistry RAS, Moscow, Russia, and

Dr. David J. Jobe, College of Pharmacy and Nutrition, University of Saskatchewan, Saskatoon, Canada.

Their contributions are gratefully acknowledged.

Foreword

This is the third volume of a series of expert reviews of the chemical thermodynamics of key chemical elements in nuclear technology and waste management. A volume on neptunium and plutonium is currently in progress. The recommended thermodynamic data are the result of a critical assessment of published information.

The data base system developed at the Data Bank of the OECD Nuclear Energy Agency (NEA), *cf.* Section II.6, ensures consistency not only within the recommended data set on technetium but also among all the data sets to be published in the series.

The NEA Data Bank provides a number of services that may be useful to the reader of this book.

- The recommended data can be obtained via Internet directly from the NEA Data Bank.
- The NEA Data Bank maintains a library of computer programs in various areas. This includes geochemical codes such as PHREEQE, EQ3/6, MINEQL, MINTEQ, PHRQPITZ, *etc.*, in which chemical thermodynamic data like those presented in this book are required as the basic input data. These computer codes can be obtained on request from the NEA Data Bank.

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Chapter I

Introduction

I.1 Background

If hazardous waste is stored in an underground tank or in a geological formation, the principal mode of transport of the hazardous components away from the repository will be, in most cases, through the aqueous phase, either as dissolved species or as suspended material. It is obviously essential to understand, to model, and to predict the reactions that will occur between the hazardous waste components and the groundwater, between the hazardous waste components and the container in which they were initially enclosed, and between the waste components and the surrounding geological material. This will allow estimates to be made of the amounts of the hazardous components being transported away from the repository. To do the necessary calculations requires that the groundwater composition and temperature be known, along with the chemical composition of the rocks in the surrounding geological media. In addition, the thermodynamic stabilities and solubilities of the compounds and complexes that can form under these conditions must also be known. In other words, a reliable, critically assessed, thermodynamic data base is required for all of the hazardous components.

In the area of radioactive waste management, the hazardous radioactive constituents consist, to a large extent, of fission products, residual fuel, and actinides produced by the operation of nuclear reactors, in addition to lesser amounts from other sources such as waste from medical procedures done with radioactive isotopes. The fission product ^{99}Tc is produced in appreciable amounts during the burning of nuclear fuel, with a fission yield of about 6.1% from the thermal neutron fission of ^{235}U and 5.9% from fission of ^{239}Pu [70LAV/POZ, 87LIE/BAU, 93LIE]. Much of this technetium ends up in the high activity waste of reprocessing plants. Part of the technetium is also present in the intermetallic (Mo, Tc, Ru, Rh, Pd) “white phases” in spent nuclear fuel, which are difficult to dissolve.

In recognition of the need for an internationally acceptable, high quality, and (so far as possible) comprehensive data base for the safety assessment of nuclear waste disposal, in 1984 the Radioactive Waste Management Committee (RWMC) of the OECD Nuclear Energy Agency decided to initiate the Nuclear Energy Agency Thermochemical Data Base Project (NEA-TDB) [85MUL, 88WAN, 90WAN].

The highest priority was assigned by the RWMC to performing critical reviews for the chemical thermodynamic properties of the compounds and aqueous species of uranium, americium, technetium, neptunium, and plutonium. The first two volumes of this series on uranium [92GRE/FUG] and americium [95SIL/BID] have since been

published. The present effort constitutes the third volume of this series.

I.2 Focus of the review

As mentioned in the previous section, the primary focus of this volume is to provide a critical review of the chemical-thermodynamic properties of technetium relevant to the safety assessment of radioactive waste repositories in the geosphere. Major considerations of this review thus include examining data relevant to the release of hazardous waste components from a repository into the geosphere, including the chemical interaction of the hazardous waste components with its primary container, with the "backfill" material, with groundwater, and with the geological "near field" materials. Groundwaters and porewaters provide the primary media for the transport of these hazardous components away from a repository and for their transport through the surrounding geological media and the biosphere. Thus a knowledge of the chemical and thermodynamic properties of the various hazardous waste components and their interaction with groundwaters of various chemical compositions is of fundamental importance to this review.

A secondary focus of this review is to examine data relevant to understanding the chemical state of technetium in spent fuel, under conditions in which it might be emitted from a nuclear reactor, and under conditions used in reprocessing of spent nuclear fuel. Thus, some discussion is devoted to the intermetallic compounds of technetium and to the phase diagrams of technetium with other metals and with carbon, and to the high-temperature thermodynamics of technetium and some of its compounds, *e.g.*, Tc(g), TcO(g), TcC(g), TcS(g), TcF_6(g), TcO_3F(g), *etc*.

A major effort was made for assessing the thermodynamic properties of aqueous species of technetium at ambient temperature conditions. There is a remarkable lack of thermodynamic data for technetium and its compounds and complexes above room temperature. The available data are mainly restricted to vapour pressure measurements and partial phase diagrams for a few systems. The method selected in this review for the thermodynamic analysis of ionic interactions between ionic components in water is the specific ion interaction equation (SIT), see Appendix C. This method allows the selected evaluated thermodynamic data of this review to be used in a general and consistent manner for thermodynamic modelling calculations, regardless of the type and chemical composition of the groundwater, subject to the restriction that the maximum ionic strengths not exceed those imposed by the available experimental data evaluated in this review.

The most important solid phases for predicting the maximum concentrations of technetium in aqueous solutions and of the release of technetium from a repository are (at different values of E_h) probably Tc(cr), TcO_2(cr), $TcO_2 \cdot 1.6H_2O$(s), and various less-soluble pertechnetate salts such as $KTcO_4$(cr). Reasonably complete thermodynamic data are available for these compounds, data which, in most cases, are of fairly high quality. There are also fairly high quality thermodynamic data for most of the aqueous species in the technetium-water system: TcO_4^- and the various hydrolysed forms of Tc(IV). However, the available data for Tc(III) is ambiguous because of un-

certainties about its actual degree of hydrolysis, and there is a lack of thermodynamic data for most of the complexes of technetium(III) and Tc(IV) with inorganic ions. A few stability constants have been measured for these aqueous ions, but in most cases, insufficient data is available to permit calculation of their Gibbs energies of formation.

This review also contains a detailed discussion of the chemistry and reactions of technetium. In some cases this chemical information can provide valuable information about whether certain technetium complexes will form under repository conditions, even when a lack of thermodynamic data precludes a rigorous thermodynamic modelling calculation. For example, the aqueous ions $TcCl_6^{2-}$ and $TcBr_6^{2-}$ are very well known, but the available thermodynamic data for them is not complete enough to calculate their Gibbs energies of formation. However, the available chemical information indicates that they form only in solutions possessing both high acidity and high concentrations of the corresponding halide ions, and that these TcX_6^{2-} will undergo essentially complete hydrolysis in a typical groundwater. Thus, the lack of Gibbs energies of formation for them, in the assessed thermodynamic data base, will have no adverse impact on modelling calculations related to an underground repository.

Although the main focus of this review is to obtain a critically-evaluated chemical-thermodynamic data base for technetium, doing these calculations requires thermodynamic data for various other chemical elements and compounds. These auxiliary data were taken from the most recent CODATA Key Values [89COX/WAG] whenever possible. Thermodynamic values for certain other compounds and aqueous species were selected in the volume on uranium [92GRE/FUG]. The internal consistency of all selected thermodynamic data is ensured by software developed at the NEA Data Bank. To retain this consistency in applications of the thermodynamic data base for technetium, it is imperative that the selected auxiliary thermodynamic data be used for all calculation.

Literature coverage for this review is intended to be complete through 1994 and most of 1995. However, a few references from 1996-1998 are also cited.

I.3 Known isotopes of technetium

All 21 isotopes of technetium with mass numbers from ^{90}Tc to ^{110}Tc have been reported, as have 7 nuclear isomers: ^{93m}Tc, ^{94m}Tc, ^{95m}Tc, ^{96m}Tc, ^{97m}Tc, ^{99m}Tc, and ^{102m}Tc. However, in several cases the identifications of the isotopes are tentative. All isotopes of technetium are radioactive. The majority of these isotopes have half lives ranging from 0.82 seconds (^{110}Tc) to 61.2 days (^{97m}Tc) and are therefore not a significant concern for the disposal of nuclear waste. Kirby [82KIR] has given a complete list of these isotopes, their half-lives, the method first used to prepare each isotope, and references to the original publications.

Only three of these isotopes have long enough half lives to be a concern for the disposal of nuclear waste, ^{97}Tc with $t_{1/2} = 2.6 \times 10^6$ years, ^{98}Tc with $t_{1/2} = 4.2 \times 10^6$ years, and ^{99}Tc with $t_{1/2} = 2.14 \times 10^5$ years. Two of these isotopes are prepared by irradiation of molybdenum with deuterons or protons. The third of these long-lived isotopes, ^{99}Tc, is the most important one for nuclear waste disposal since several tonnes

are produced each year as fission products in nuclear reactors. Significant amounts of ^{99m}Tc are also prepared in "technetium generators" by irradiation of ^{99}Mo (usually as molybdenum trioxide) with neutrons. This isotope decays very cleanly with a half-life of $t_{1/2} = 6.02$ hours to form ^{99}Tc, by emission of a nearly monoenergetic 140 keV gamma ray [82KIR, 93JUR/BER]; ^{99m}Tc has been extensively used in nuclear medicine [82SEI].

Virtually all of the technetium used in the thermodynamic measurements is ^{99}Tc, and thus all evaluated thermodynamic values given in this review pertain to this isotope.

I.4 The discovery and natural occurrence of technetium and its utilisation

In 1869 Dmitri Ivanovich Mendeleev reported his periodic table in a reasonably complete form, which provided a systematic ordering of the elements based on their molar masses. Mendeleev predicted that two of the gaps in this table would be filled by heavier analogs of manganese, which he named eka-manganese and dvi- or dwi-manganese (from the Sanskrit words for one and two), and that their "atomic weights" would be approximately 100 and 190, respectively. "Dwi-manganese" is now known as rhenium.

The search for new elements in various rocks and minerals became more systematic after the publication of Mendeleev's periodic table, since chemically similar elements might be expected to be found in the same types of ores. There were numerous claims for the discovery of new elements, some of which proved to be correct. However, the majority of the claims for the purported new elements were erroneous, and usually resulted from mixtures of several elements being misidentified as being a single element. Several of these claimed new elements seemed to have "atomic weights" or chemical properties that appeared to correspond to eka-manganese. There are a number of published descriptions of the convoluted history of the search for Mendeleev's eka-manganese [59BOY2, 62KEN, 68KOT/PAV, 82KIR, 93KUR]. Two of these descriptions are fairly detailed [62KEN, 82KIR], and were used as the source of information for the following discussion.

The first of the candidate elements for eka-manganese was reported by Osann in 1828 as an extract from platinum ores, and was named polinium by him. He later acknowledged that this "element" was actually an impure fraction or iridium. In 1846 Hermann reported the isolation of the "element" ilmenium from various ores, which was reportedly found occurring with niobium and tantalum. However, other workers claimed that ilmenium was actually a mixture of titanium, niobium, and tantalum or that it was an impure sample of niobium. In 1877 Kern reported the discovery of the new "element" davyum (which was named after Sir Humphrey Davy) which he believed belonged to the platinum group metals. He originally predicted that davyum (Da) would have an "atomic weight" of about 100. Kern later determined that it had an "atomic weight" of 154, which made it too heavy to be the elusive eka-manganese. Barrière claimed in 1896 to have isolated an "element" from monazite sand that had an "atomic weight" of 104 and named it lucium. However, Crookes showed that lucium was mainly yttrium, along with lesser amounts of several other rare earth elements.

Ogawa, in 1909, reported the isolation of a new "element" from thorianite, reinite, and molybdenite which he named nipponium (Np). It had an "atomic weight" of about 100. Evans had claimed the discovery of an "element" the previous year and which had essentially identical properties. These two "elements" are usually assumed to be identical. There were no lines in the X-ray emission spectrum of this "element" that could not be attributed to known elements, and its identity remains uncertain. Moseley in 1913 described the use of the X-ray emission spectrum frequencies to determine the atomic number of elements, and thereby showed that the eka-manganese of Mendeleev should fall between elements molybdenum (atomic number 42) and ruthenium (atomic number 44). Thus it should have an atomic number of 43. Gerber attempted to isolate element 43 from various molybdenum and tungsten ores but without success. However, in 1917, he proposed that the as yet undiscovered element 43 should be named neo-molybdenum rather than eka-manganese, because of his belief that its chemistry should resemble that of molybdenum more closely than that of manganese. In contrast, Bosanquet and Keeley had the opposite viewpoint that the chemistry of element 43 should resemble that of manganese, and searched for it in manganese ores. Their results, published in 1924, were also negative. They proposed that element 43, once discovered, should be named moseleyum (Ms).

The most substantial claim for the isolation of element 43 came from Noddack, Tacke, and Berg in 1925. They isolated a concentrate of material extracted from colombite, $Fe_2Nb_2O_6$, which they estimated contained 5% of element 75 and 0.5% of element 43. Their discovery of element 75, which they named rhenium, was verified by others. Evidence for element 43 was based on three X-ray emission lines which fell close to their anticipated frequencies. Noddack, Tacke, and Berg named the element 43 masurium (Ma) after the East Prussian area of Masuria. The spectroscopic plates upon which this identification was made were later reported to have been broken, and no further evidence for masurium was obtained. However, the name masurium continued to be used in the scientific literature until the late 1940s.

These searches for element 43 in natural minerals were based on the reasonable expectation that it was present along with the other heavy elements when the earth formed ca. 4.6×10^9 years ago, and that, although it might be rare, it would still be present in the earth's crust. However, as noted above, all isotopes of technetium are radioactive and the one with the longest half-life,

^{98}Tc, has a half-life of $t_{1/2} = 4.2 \times 10^6$ years. About $(4.6 \times 10^9)/(4.2 \times 10^6) \approx 1095$ half-lives of this isotope have occurred since it was deposited on the primordial earth, and thus the fraction still remaining should be $(1/2)^{1095} = 2 \times 10^{-330}$ for this isotope and even less for the other isotopes. Obviously no detectable amounts of this primordial technetium still exist.

The first verified identification of element 43 was made by Perrier and Segrè, who published their results in 1937 and 1939 [37PER/SEG, 39PER/SEG]. Their sample was extracted from a molybdenum plate that had been irradiated with a deuteron beam and its associated secondary neutrons in the cyclotron at Berkeley, California. Short lived isotopes of element 43 could not be detected since there was a six week delay in the chemical processing of the molybdenum plate, during which time the plate was being shipped from Berkeley to Italy. Perrier and Segrè [37PER/SEG] carried out some fairly

complicated chemical separations in order to isolate element 43 from this irradiated molybdenum. A variety of chemical treatments and precipitation sequences were used to remove zirconium and molybdenum. Since none of these other precipitates were radioactive, and since the solution phase remained radioactive, they concluded that the radioactivity was due to some other element which could only be element 43. Some of the chemical properties of element 43 were determined, and, as expected, were similar to those of rhenium. In 1946 they named this element technetium after the Greek word for artificial, $\tau\varepsilon\chi\nu\iota\kappa\acute{o}\varsigma$.

The original isotope isolated by Perrier and Segrè was undoubtedly ^{97m}Tc which was produced from ^{96}Mo by a (d, n) reaction [82KIR].

The isotope ^{99}Tc is produced in major amounts in fission reactors and thus is expected to be present in uranium ores from the spontaneous fission of ^{238}U. However, as noted by Kenna and Kuroda [61KEN/KUR], the steady-state concentration of technetium expected in uranium ores is quite small given the $\approx 8 \times 10^{15}$ years half-life for spontaneous fission of ^{238}U. They estimated that a sample of pitchblende containing 50 mass-% uranium would contain about 10^{-10} g of ^{99}Tc per kg of ore, which corresponds to a mass fraction of 10^{-13}. To isolate technetium in such extremely small amounts would obviously require extremely careful and sophisticated chemical processing of the ore.

The first indisputable identification of "natural" ^{99}Tc was made from an uranium ore by Kenna and Kuroda [61KEN/KUR]. Starting with 3.3 kg of pitchblende from the former Belgian Congo, they removed most fission products and decay products by using a complicated series of chemical separations. They succeeded in separating about 1 pg of ^{99}Tc, which they detected by its characteristic beta decay energy. Their isolated samples of ^{99}Tc produced only 2 to 3 decays per minute, which is close to the decay rate expected for ^{99}Tc if it were initially present in secular equilibrium with the ^{238}U. Given the minuscule amounts of ^{99}Tc present in this pitchblende, its near quantitative separation was a remarkable achievement. See references [82ALL/KEL, 82KUR] for detailed flow charts of the separation procedure.

In 1951 Moore [51MOO] reported three spectroscopic lines in the solar spectrum that were tentatively attributed by her to Tc II. As discussed by Kenna [62KEN], this identification has been disputed. Spectroscopic lines due to Tc I have been identified in many M, S, C and N-type stars, and mostly in "variable-type" stars [52MER, 77CHE, 82ALL/KEL]. However, there is disagreement whether ^{97}Tc [77CHE] or ^{99}Tc [93LAK/SÀF] forms in these stars.

Extremely low concentrations of ^{99}Tc can be found in the environment around the earth. Part of this technetium is a relic of atmospheric testing of nuclear weapons, part is from the low-activity level waste which is discharged in the ocean from a few nuclear reprocessing plants [87LIE/BAU], and part from accidental airborn releases from nuclear facilities. In aqueous systems under oxidising conditions most of the technetium is oxidised to TcO_4^- ions, which can be quite mobile.

Bishop, Beetham, and Cuff [89BIS/BEE] have reviewed published results for the uptake, excretion, and bioaccumulation of technetium by living organisms, Beasley and Lorz [86BEA/LOR] reviewed the biological behaviour of technetium in marine environments, and Seidel [82SEI] has summarised various medical aspects of technetium.

Various medical applications and use of radiopharmaceuticals of ^{99m}Tc have been reviewed by Seidel [82SEI]. Jurisson *et al*. [93JUR/BER] have reviewed the chemistry of many of these radiopharmaceuticals.

I.5 Review procedure and results

The object of this review is to provide a comprehensive literature survey of published chemical-thermodynamic data for technetium and its inorganic compounds and aqueous species; to provide an internally consistent recalculation of published thermodynamic data; and to assess the available thermodynamic data in order to provide a set of recommended values of Gibbs energies and enthalpies of formation along with entropies and heat capacities. Previous reviews are cited and provide a valuable source of literature references and critical assessments of earlier literature data. A number of guidelines for this reevaluation of primary literature data have been reported as part of the NEA-TDB project [98ÖST/WAN, 92GRE/WAN, 98WAN/ÖST, 98WAN/ÖST2, 98WAN]. Extracts from some of these are included in Chapter II and Appendices C and D of the present report.

The critically assessed thermodynamic data for technetium are summarised in Chapter III and are discussed and described in detail in Chapter V. Reported uncertainty limits represent the estimated 95% confidence limits. If an experimental thermodynamic quantity was reported along with its uncertainty in a publication, and the uncertainty was not otherwise identified, it was assumed to be an estimated one standard deviation uncertainty. These assessed thermodynamic values all refer to the reference temperature of 298.15 K and the standard pressure of 1 bar. For aqueous solutions the standard states are infinite dilution for enthalpies of dilution and apparent molar heat capacities, and for Gibbs energies the solute standard state is a hypothetical ideal solution with a mean molality of 1 mol $\cdot$ kg^{-1} and a mean molal activity coefficient equal to 1. For the thermodynamic modelling of technetium in a real system with non-zero ionic strength and/or a temperature different from 298.15 K, it is necessary, in general, to recalculate these standard state thermodynamic values to the actual non-standard state conditions. Unfortunately, there are very few experimental heat capacities for the compounds and aqueous species of technetium, so extrapolations of the data base to higher temperatures will require the estimation of heat capacities.

The quality of thermodynamic modelling calculations can be no better that the quality of the input data upon which they are based. That quality will depend not only on the uncertainties of the assessed thermodynamic properties, but will also depend on the completeness of the thermodynamic data base. It is important that the user of the technetium thermodynamic base, summarised in Chapter III, recognise that the data base may not be complete for all applications, and that some gaps are present. These gaps in the thermodynamic data are pointed out in Chapter V and are summarised in Section I.7 of the present chapter.

I.6 Previous reviews of the chemical or thermodynamic properties of technetium

This volume was written to provide a comprehensive and internally consistent chemical thermodynamic data base for technetium, and to examine its inorganic chemistry in detail. A number of earlier reviews are available which overlap with portions of the present review. In most cases, advances in the knowledge of the chemistry, electrochemistry, and thermodynamic properties of technetium have occurred since those reviews were published, which makes portions of those reviews out of date or which vitiates some of their conclusions or their assessed thermodynamic values. However, there is still much valuable information contained in these reviews, and many of them will now be mentioned. Some of these reviews cover aspects of the chemistry of technetium not covered in detail in the present review, and thus are valuable supplements to the present volume. However, much new information has been published since some of the earlier reviews appeared, which in some cases indicates the earlier chemical information was erroneous or makes the assessed thermodynamic information obsolete. Thus the reader is encouraged to read more recent publications in these areas.

There are two excellent reviews of the crystal structural data and unit cell parameters for inorganic and organometallic compounds and complexes of technetium [82BAN/MAZ, 87MEL/LIE]. The comprehensive review by Baldas [94BAL] extends this coverage to the beginning of 1993.

Among the earliest reviews of the chemistry of technetium are the books by Colton [65COL], Peacock [66PEA], Canterford and Colton [68CAN/COL], and Lavrukhina and Pozdnyakov [70LAV/POZ], and the book chapter by Kotegov, Pavlov, and Shvedov [68KOT/PAV]. These books also summarise thermodynamic and electrochemical data available at that time. Peacock's article in the book Comprehensive Inorganic Chemistry [73PEA] summarises the available vapour pressure data for technetium halides and oxohalides, including some from studies that have never been published. The report by Friedman [81FRI] summarises available data on the photochemical and electrochemical behaviour of aqueous solutions containing technetium salts and complexes. Spitsyn *et al*. [85SPI/KUZ] have reviewed the technetium cluster compounds. The excellent review article by Baldas [94BAL] contains an enormous amount of information about the inorganic and organometallic compounds and complexes of technetium and contains 685 literature references.

The Gmelin Handbook of Inorganic Chemistry Supplemental Volume 1, published in 1982, contains a considerable amount of information about technetium in addition to some of the topics covered in the present review. Other topics covered include the history of the search for technetium in nature, various aspects of the nuclear physics of technetium, and the applications of technetium in biology and in medicine. Various aspects of the environmental chemistry and biological chemistry of technetium were reviewed by Bishop, Beetham, and Cuff [89BIS/BEE] and its biological and medical aspects by Seidel [82SEI].

Several topical symposia in recent years have been devoted to technetium. For example, "The Topical Symposium on the Behaviour and Utilization of Technetium" was

held in Sendai, Japan, from March 18–29, 1993. Selected papers from this symposium were published in Volume 63 of Radiochimica Acta. The Tc-99 conference was held in Southampton, U. K., April 8–9, 1998. The proceedings of this meeting should be published sometime during 1999.

There are also a number of reviews devoted to the thermodynamic and/or electrochemical properties of technetium. The earliest reviews were by Latimer [52LAT] and Zoubov and Pourbaix [66ZOU/POU]. Relatively little thermodynamic data was available at the time they were written, and their estimated results for Tc^{2+} are rejected by this review since there is no credible evidence for the existence of this ion. More extensive reviews have been published since then by Magee and Cardwell [74MAG/CAR], Paquette, Reid, and Rosinger [80PAQ/REI], Rard [83RAR], Magee and Blutstein [85MAG/BLU], Zelverte [88ZEL], and Lemire and Garisto [89LEM/GAR]. Puigdomènech and Bruno [95PUI/BRU] have estimated the heat capacities and entropies for various aqueous ions and complexes and a few solid compounds of technetium. However, nearly all solubility data for $TcO_2 \cdot xH_2O$(s) were published after those reviews were written, as have a much more extensive emf study of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) redox couple and a direct determination of the enthalpy of formation of TcO_2(cr). Thus more thermodynamic data are available for the present review, which allowed a more accurate and more extensive data base to be produced for technetium.

I.7 Some gaps in our knowledge of the chemical and thermodynamic properties of technetium

Technetium can form compounds with a wide variety of valence states ranging up to +7. Its chemistry is quite complicated and, in many cases, is poorly understood. In Chapter V the chemical and thermodynamic properties of technetium are discussed in detail. There are some significant gaps in the available information. Below we summarise the most important information needed to improve the quality of the technetium thermodynamic data base for the safety assessment of nuclear waste disposal. We hope that some of the readers of this volume will help to provide this missing information.

1. There is a lack of experimental heat capacities for Tc(cr) above 15 K, which are needed for the direct determination of the entropies. However, the entropy of Tc(cr) is reasonably well established based on comparison to data for Re(cr) and from theoretical understanding of the dependence of the entropy of metals on their outer shell electronic configuration and other factors.

2. Of the anhydrous solid oxides, only TcO_2(cr) and Tc_2O_7(cr) are reasonably well characterised. There are reports of various red and black oxides, possibly TcO_3(s) and Tc_2O_5(s). The identity of these solid oxides needs to be determined. There is a need for heat capacities and thus entropies for TcO_2(cr) and Tc_2O_7(cr). An experimental entropy for Tc_2O_7(cr) would then allow the thermodynamic evaluation for $Tc_2O_7 \cdot H_2O$(s) to be refined.

Spectroscopic measurements for Tc_2O_7(g) need to be extended to determine the frequency of the lowest vibrational fundamental, which is needed to reduce the uncertainty of the statistical thermodynamic calculations. Existing vapour pressure measurements for Tc_2O_7(cr) are quite limited in temperature range and accuracy, and additional experimental measurements are needed to give a more accurate value of enthalpy of sublimation of Tc_2O_7(cr) and thus of the enthalpy of formation of Tc_2O_7(g). There are also significant inconsistencies between different determinations of the solubilities of TcO_2(cr) as a function of pH.

3. There are claims for the existence of a number of lower-valence hydrous oxides of technetium, of which the greatest amount of evidence is for a hydrous oxide of Tc(III). Additional evidence is needed to ascertain which of these purported hydrous oxides really exist, and attempts need to be made to characterise them thermodynamically.

4. The authors of several studies reported protonation constants for the formation of undissociated pertechnetic acid, $TcO_3(OH)$(aq) or $HTcO_4$(aq). Most of these studies were performed in acidic nitrate solutions, where the incomplete dissociation of nitric acid makes the analysis of these results highly uncertain, or in acidic chloride solutions at a single ionic strength. A better characterisation of this protonation constant is definitely needed.

5. There are almost no equilibrium constants determined for the formation of complexes between Tc(III) and Tc(IV), even with most of the common inorganic anions present in groundwater. The only available equilibrium constants of this type from which Gibbs energies of formation can be determined are hydroxide and mixed hydroxide/carbonate complexes of Tc(IV). A more detailed characterisation of the equilibria involving hydroxide and carbonate complexes of Tc(IV), especially at high pHs, and the determination of equilibrium constants for other inorganic complexes of Tc(III) and Tc(IV) are critically needed for the reliable geochemical modelling of solubility and speciation of dissolved technetium.

6. Low temperature heat capacities and entropies are available for TcF_6(cr, ortho.), TcF_6(cr, cubic), and TcF_6(l), as are vapour pressures from 256.83 to 324.82 K. An enthalpy of formation of TcF_6(cr, cubic) is required to complete the thermodynamic evaluation for this compound. This compound is very important because of its presence as a volatile impurity during the recovery of uranium from spent nuclear fuel, using gaseous diffusion of UF_6(g).

7. Either TcS_2(s) or Tc_2S_7(s) could potentially form as a solubility-limiting phase for technetium in groundwaters under very reducing conditions. Experimental thermodynamic data are required to replace the rather uncertain estimated values for these compounds.

Chapter II

Standards, Conventions, and Contents of the Tables[†]

This chapter outlines and lists the symbols, terminology and nomenclature, the units and conversion factors, the order of formulae, the standard conditions, and the fundamental physical constants used in this volume. They are derived from international standards and have been specially adjusted for the TDB publications.

II.1 Symbols, terminology and nomenclature

II.1.1 Abbreviations

Abbreviations are mainly used in tables where space is limited. Abbreviations for methods of measurement are kept to a maximum of three characters (except for composed symbols) and are listed in Table II.2.

Other abbreviations may also be used in tables, such as SHE for the standard hydrogen electrode or SCE for the saturated calomel electrode. The abbreviation NHE has been widely used for the "normal hydrogen electrode", which is by definition identical to the SHE. It should nevertheless be noted that NHE customarily refers to a standard state pressure of 1 atm, whereas SHE always refers to a standard state pressure of 0.1 MPa (1 bar) in this review.

II.1.2 Symbols and terminology

The symbols for physical and chemical quantities used in the TDB review follow the recommendations of the International Union of Pure and Applied Chemistry, IUPAC [79WHI, 88MIL/CVI]. They are summarised in Table II.1.

II.1.3 Chemical formulae and nomenclature

This review follows the recommendations made by IUPAC [71JEN, 77FER, 90LEI] on the nomenclature of inorganic compounds and complexes, except for the following items:

[†]The version of this chapter included here differs somewhat from those included in the other books in the series Chemical Thermodynamics [92GRE/FUG, 95SIL/BID].

i) The formulae of coordination compounds and complexes are not enclosed in square brackets [71JEN, Rule 7.21]. Exceptions are made in cases where square brackets are required to distinguish between coordinated and uncoordinated ligands.

ii) The prefixes "oxy-" and "hydroxy-" are retained if used in a general way, *e.g.*, "gaseous uranium oxyfluorides". For specific formula names, however, the IUPAC recommended citation [71JEN, Rule 6.42] is used, *e.g.*, "uranium(IV) difluoride oxide" for UF_2O(cr).

An IUPAC rule that is often not followed by many authors [71JEN, Rules 2.163 and 7.21] is recalled here: the order of arranging ligands in coordination compounds and complexes is the following: central atom first, followed by ionic ligands and then by the neutral ligands. If there is more than one ionic or neutral ligand, the alphabetical order of the symbols of the ligating atoms determines the sequence of the ligands. For example, $(UO_2)_2CO_3(OH)_3^-$ is standard, $(UO_2)_2(OH)_3CO_3^-$ is non-standard and is not used.

Abbreviations of names for organic ligands appear sometimes in formulae. Following the recommendations by IUPAC, lower case letters are used, and if necessary, the ligand abbreviation is enclosed within parentheses. Hydrogen atoms that can be replaced by the metal atom are shown in the abbreviation with an upper case "H", for example: H_3edta^-, Am(Hedta)(s) (where edta stands for ethylenediaminetetraacetate).

Table II.1: Symbols and terminology.

Symbols and terminology	
length	l
height	h
radius	r
diameter	d
volume	V
mass	m
density (mass divided by volume)	ρ
time	t
frequency	ν
wavelength	λ
internal transmittance (transmittance of the medium itself, disregarding boundary or container influence)	T
internal transmission density, (decadic absorbance): $\log_{10}(1/T)$	A
molar (decadic) absorption coefficient: $A/c_B l$	ϵ
relaxation time	τ
Avogadro constant	N_A

(Continued on next page)

Table II.1: (continued)

Symbols and terminology	
relative molecular mass of a substance[(a)]	M_r
thermodynamic temperature, absolute temperature	T
Celsius temperature	t
(molar) gas constant	R
Boltzmann constant	k
Faraday constant	F
(molar) entropy	S_m
(molar) heat capacity at constant pressure	$C_{p,\mathrm{m}}$
(molar) enthalpy	H_m
(molar) Gibbs energy	G_m
chemical potential of substance B	μ_B
pressure	p
partial pressure of substance B: $x_\mathrm{B}\,p$	p_B
fugacity of substance B	f_B
fugacity coefficient: $f_\mathrm{B}/p_\mathrm{B}$	$\gamma_{\mathrm{f,B}}$
amount of substance[(b)]	n
mole fraction of substance B: $n_\mathrm{B}/\sum_i n_i$	x_B
molarity or concentration of a solute substance B (amount of B divided by the volume of the solution)[(c)]	c_B, [B]
molality of a solute substance B (amount of B divided by the mass of the solvent)[(d)]	m_B
mean ionic molality[(e)], $m_\pm^{(\nu_+ + \nu_-)} = m_+^{\nu_+} m_-^{\nu_-}$	$m_\pm$
activity of substance B	a_B
activity coefficient, molality basis: $a_\mathrm{B}/m_\mathrm{B}$	γ_B
activity coefficient, concentration basis: $a_\mathrm{B}/c_\mathrm{B}$	y_B
mean ionic activity[(e)], $a_\pm^{(\nu_+ + \nu_-)} = a_\mathrm{B} = a_+^{\nu_+} a_-^{\nu_-}$	$a_\pm$
mean ionic activity coefficient[(e)], $\gamma_\pm^{(\nu_+ + \nu_-)} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}$	$\gamma_\pm$
osmotic coefficient, molality basis	ϕ
ionic strength: $I_m = \frac{1}{2}\sum_i m_i z_i^2$ or $I_c = \frac{1}{2}\sum_i c_i z_i^2$	I
SIT ion interaction coefficient between substance B_1 and substance B_2	$\varepsilon_{(\mathrm{B}_1,\mathrm{B}_2)}$
stoichiometric coefficient of substance B (negative for reactants, positive for products)	ν_B
general equation for a chemical reaction	$0 = \sum_\mathrm{B} \nu_\mathrm{B}\mathrm{B}$
equilibrium constant[(f)]	K
rate constant	k

(Continued on next page)

Table II.1: (continued)

Symbols and terminology	
Faraday constant	F
charge number of an ion B (positive for cations, negative for anions)	z_B
charge number of a cell reaction	n
electromotive force	E
$pH = -\log_{10}[a_{H^+}/(mol \cdot kg^{-1})]$	
electrolytic conductivity	κ
superscript for standard state[(g)]	$^\circ$

[(a)] The ratio of the average mass per formula unit of a substance to $\frac{1}{12}$ of the mass of an atom of nuclide ^{12}C.

[(b)] *cf.* Sections 1.2 and 3.6 of the IUPAC manual [79WHI].

[(c)] This quantity is called "amount-of-substance concentration" in the IUPAC manual [79WHI]. A solution with a concentration equal to $0.1\,mol \cdot dm^{-3}$ is called a 0.1 molar solution or a 0.1 M solution.

[(d)] A solution having a molality equal to $0.1\,mol \cdot kg^{-1}$ is called a 0.1 molal solution or a 0.1 m solution.

[(e)] For an electrolyte $N_{\nu_+}X_{\nu_-}$ which dissociates into $\nu_\pm (= \nu_+ + \nu_-)$ ions, in an aqueous solution with concentration m, the individual cationic molality and activity coefficient are $m_+ (= \nu_+ m)$ and $\gamma_+ (= a_+/m_+)$. A similar definition is used for the anionic symbols. Electrical neutrality requires that $\nu_+ z_+ = \nu_- z_-$.

[(f)] Special notations for equilibrium constants are outlined in Section II.1.6. In some cases, K_c is used to indicate a concentration constant in molar units, and K_m a constant in molal units.

[(g)] See Section II.3.1.

II.1.4 Phase designators

Chemical formulae may refer to different chemical species and are often required to be specified more clearly in order to avoid ambiguities. For example, UF_4 occurs as a gas, a solid, and an aqueous complex. The distinction between the different phases is made by phase designators that immediately follow the chemical formula and appear in parentheses. The only formulae that are not provided with a phase designator are aqueous ions. They are the only charged species in this review since charged gases are not considered. The use of the phase designators is described below.

- The designator (l) is used for pure liquid substances, *e.g.*, H_2O(l).
- The designator (aq) is used for undissociated, uncharged aqueous species, *e.g.*, $U(OH)_4$(aq), CO_2(aq). Since ionic gases are not considered in this review, all ions may be assumed to be aqueous and are not designed with (aq). If a chemical reaction refers to a medium other than H_2O (*e.g.*, D_2O, 90% ethanol/10% H_2O), then (aq) is replaced by a more explicit designator, *e.g.*, "(in D_2O)" or "(sln)". In the case of (sln), the composition of the solution is described in the text.

Table II.2: Abbreviations for experimental methods

aix	anion exchange
cal	calorimetry
chr	chromatography
cix	cation exchange
col	colorimetry
con	conductivity
cor	corrected
cou	coulometry
cry	cryoscopy
dis	distribution between two phases
em	electromigration
emf	electromotive force, not specified
gl	glass electrode
ise-X	ion selective electrode with ion X stated
ix	ion exchange
kin	rate of reaction
mvd	mole volume determination
nmr	nuclear magnetic resonance
pol	polarography
pot	potentiometry
prx	proton relaxation
qh	quinhydrone electrode
red	emf with redox electrode
rev	review
sp	spectrophotometry
sol	solubility
tc	transient conductivity
tls	thermal lensing spectrophotometry
vlt	voltammetry
?	method unknown to the reviewers

- The designator (sln) is used for substances in solution without specifying the actual equilibrium composition of the substance in the solution. Note the difference in the designation of H_2O in Eqs. (II.2) and (II.3). H_2O(l) in Reaction (II.2) indicates that H_2O is present as a pure liquid, *i.e.*, no solutes are present, whereas Reaction (II.3) involves a HCl solution, in which the thermodynamic properties of H_2O(sln) may not be the same as those of the pure liquid H_2O(l). In dilute solutions, however, this difference in the thermodynamic properties of H_2O can be neglected, and H_2O(sln) may be regarded as pure H_2O(l).

  Example:

$$\mathrm{UOCl_2(cr) + 2\,HBr(sln)} \rightleftharpoons \mathrm{UOBr_2(cr) + 2\,HCl(sln)} \quad \text{(II.1)}$$

$$\mathrm{UO_2Cl_2 \cdot 3H_2O(cr)} \rightleftharpoons \mathrm{UO_2Cl_2 \cdot H_2O(cr) + 2\,H_2O(l)} \quad \text{(II.2)}$$

$$\mathrm{UO_3(\gamma) + 2\,HCl(sln)} \rightleftharpoons \mathrm{UO_2Cl_2(cr) + H_2O(sln)} \quad \text{(II.3)}$$

- The designators (cr), (am), (vit), and (s) are used for solid substances. (cr) is used when it is known that the compound is crystalline, (am) when it is known that it is amorphous, and (vit) for glassy substances. Otherwise, (s) is used.

- In some cases, more than one crystalline form of the same chemical composition may exist. In such a case, the different forms are distinguished by separate designators that describe the forms more precisely. If the crystal has a mineral name, the designator (cr) is replaced by the first four characters of the mineral name in parentheses, *e.g.*, SiO_2(quar) for quartz and SiO_2(chal) for chalcedony. If there is no mineral name, the designator (cr) is replaced by a Greek letter preceding the formula and indicating the structural phase, *e.g.*, α-UF_5, β-UF_5.

Phase designators are also used in conjunction with thermodynamic symbols to define the state of aggregation of a compound a thermodynamic quantity refers to. The notation is in this case the same as outlined above. In an extended notation (*cf.* [82LAF]) the reference temperature is usually given in addition to the state of aggregation of the composition of a mixture.

Example:

$\Delta_f G^\circ_m$ (Na^+, aq, 298.15 K)	standard molar Gibbs energy of formation of aqueous Na^+ at 298.15 K
S°_m ($UO_2SO_4 \cdot 2.5H_2O$, cr, 298.15 K)	standard molar entropy of $UO_2SO_4 \cdot 2.5H_2O$(cr) at 298.15 K
$C^\circ_{p,m}$ (UO_3, α, 298.15 K)	standard molar heat capacity of α-UO_3 at 298.15 K
$\Delta_f H_m$(HF, sln, HF $\cdot$ 7.8H_2O)	enthalpy of formation of HF diluted 1:7.8 with water

Table II.3: Abbreviations used as subscripts of Δ to denote the type of chemical processes.

Subscript of Δ	Chemical process
at	separation of a substance into its constituent gaseous atoms (atomisation)
dehyd	elimination of water of hydration (dehydration)
dil	dilution of a solution
f	formation of a compound from its constituent elements
fus	melting (fusion) of a solid
hyd	addition of water of hydration to an unhydrated compound
mix	mixing of fluids
r	chemical reaction (general)
sol	process of dissolution
sub	sublimation (evaporation) of a solid
tr	transfer from one solution or liquid phase to another
trs	transition of one solid phase to another
vap	vaporisation (evaporation) of a liquid

II.1.5 Processes

Chemical processes are denoted by the operator Δ, written before the symbol for a property, as recommended by IUPAC [82LAF]. An exception to this rule is the equilibrium constant, *cf.* Section II.1.6. The nature of the process is denoted by annotation of the Δ, *e.g.*, the Gibbs energy of formation, $\Delta_f G_m$, the enthalpy of sublimation, $\Delta_{sub} H_m$, *etc*. The abbreviations of chemical processes are summarised in Table II.3.

The most frequently used symbols for processes are $\Delta_f G$ and $\Delta_f H$, the Gibbs energy and the enthalpy of formation of a compound or complex from the elements in their reference states (cf. Table II.6).

II.1.6 Equilibrium constants

The IUPAC has not explicitly defined the symbols and terminology for equilibrium constants of reactions in aqueous solution. The NEA has therefore adopted the conventions that have been used in the work *Stability constants of metal ion complexes* by Sillén and Martell [64SIL/MAR, 71SIL/MAR]. An outline is given in the paragraphs below. Note that, for some simple reactions, there may be different correct ways to index an equilibrium constant. It may sometimes be preferable to indicate the number of the reaction the data refer to, especially in cases where several ligands are discussed that might be confused. For example, for the equilibrium

$$m\,\mathrm{M} + q\,\mathrm{L} \quad \rightleftharpoons \quad \mathrm{M}_m\mathrm{L}_q \tag{II.4}$$

both $\beta_{q,m}$ and β(II.4) would be appropriate, and $\beta_{q,m}$(II.4) is accepted, too. Note that, in general, K is used for the consecutive or stepwise formation constant, and β is used for the cumulative or overall formation constant. In the following outline, charges are only given for actual chemical species, but are omitted for species containing general symbols (M, L).

II.1.6.1 Protonation of a ligand

$$\mathrm{H^+ + H_{r-1}L} \rightleftharpoons \mathrm{H_rL} \qquad K_{1,r} = \frac{[\mathrm{H_rL}]}{[\mathrm{H^+}][\mathrm{H_{r-1}L}]} \tag{II.5}$$

$$r\,\mathrm{H^+ + L} \rightleftharpoons \mathrm{H_rL} \qquad \beta_{1,r} = \frac{[\mathrm{H_rL}]}{[\mathrm{H^+}]^r[\mathrm{L}]} \tag{II.6}$$

This notation has been proposed and used by Sillén and Martell [64SIL/MAR], but it has been simplified later by the same authors [71SIL/MAR] from $K_{1,r}$ to K_r. This review retains, for the sake of consistency, *cf.* Eqs. (II.7) and (II.8), the older formulation of $K_{1,r}$.

For the addition of a ligand, the notation shown in Eq.(II.7) is used.

$$\mathrm{HL_{q-1} + L} \rightleftharpoons \mathrm{HL_q} \qquad K_q = \frac{[\mathrm{HL_q}]}{[\mathrm{HL_{q-1}}][\mathrm{L}]} \tag{II.7}$$

Eq. (II.8) refers to the overall formation constant of the species $\mathrm{H_rL_q}$.

$$r\,\mathrm{H^+} + q\,\mathrm{L} \rightleftharpoons \mathrm{H_rL_q} \qquad \beta_{q,r} = \frac{[\mathrm{H_rL_q}]}{[\mathrm{H^+}]^r[\mathrm{L}]^q} \tag{II.8}$$

In Eqs. (II.5), (II.6) and (II.8), the second subscript r can be omitted if $r = 1$, as shown in Eq. (II.7).

Example:

$$\mathrm{H^+ + PO_4^{3-}} \rightleftharpoons \mathrm{HPO_4^{2-}} \qquad \beta_{1,1} = \beta_1 = \frac{[\mathrm{HPO_4^{2-}}]}{[\mathrm{H^+}][\mathrm{PO_4^{3-}}]}$$

$$2\,\mathrm{H^+ + PO_4^{3-}} \rightleftharpoons \mathrm{H_2PO_4^-} \qquad \beta_{1,2} = \frac{[\mathrm{H_2PO_4^-}]}{[\mathrm{H^+}]^2[\mathrm{PO_4^{3-}}]}$$

II.1.6.2 Formation of metal ion complexes

$$\mathrm{ML_{q-1} + L} \rightleftharpoons \mathrm{ML_q} \qquad K_q = \frac{[\mathrm{ML_q}]}{[\mathrm{ML_{q-1}}][\mathrm{L}]} \tag{II.9}$$

$$\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{ML_q} \qquad \beta_q = \frac{[\mathrm{ML_q}]}{[\mathrm{M}][\mathrm{L}]^q} \tag{II.10}$$

For the addition of a metal ion, *i.e.*, the formation of polynuclear complexes, the following notation is used, analogous to Eq.(II.5):

$$\mathrm{M} + \mathrm{M}_{m-1}\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L} \qquad K_{1,m} = \frac{[\mathrm{M}_m\mathrm{L}]}{[\mathrm{M}][\mathrm{M}_{m-1}\mathrm{L}]} \tag{II.11}$$

Eq. (II.12) refers to the overall formation constant of a complex $\mathrm{M}_m\mathrm{L}_q$.

$$m\,\mathrm{M} + q\,\mathrm{L} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q \qquad \beta_{q,m} = \frac{[\mathrm{M}_m\mathrm{L}_q]}{[\mathrm{M}]^m[\mathrm{L}]^q} \tag{II.12}$$

The second index can be omitted if it is equal to 1, *i.e.*, $\beta_{q,m}$ becomes β_q if $m = 1$. The formation constants of mixed ligand complexes are not indexed. In this case, it is necessary to list the chemical reactions considered and to refer the constants to the corresponding reaction numbers.

It has sometimes been customary to use negative values for the indices of the protons to indicate complexation with hydroxide ions, OH^-. This practice is not adopted in this review. If OH^- occurs as a reactant in the notation of the equilibrium, it is treated like a normal ligand L, but in general formulae the index variable n is used instead of q. If $\mathrm{H_2O}$ occurs as a reactant to form hydroxide complexes, $\mathrm{H_2O}$ is considered as a protonated ligand, HL, so that the reaction is treated as described below in Eqs. (II.13) to (II.15) using n as the index variable. For convenience, no general form is used for the stepwise constants for the formation of the complex $\mathrm{M}_m\mathrm{L}_q\mathrm{H}_r$. In many experiments, the formation constants of metal ion complexes are determined by adding to a metal ion solution a ligand in its protonated form. The complex formation reactions thus involve a deprotonation reaction of the ligand. If this is the case, the equilibrium constant is supplied with an asterisk, as shown in Eqs. (II.13) and (II.14) for mononuclear and in Eq. (II.15) for polynuclear complexes.

$$\mathrm{ML}_{q-1} + \mathrm{HL} \rightleftharpoons \mathrm{ML}_q + \mathrm{H}^+ \qquad {}^*K_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]}{[\mathrm{ML}_{q-1}][\mathrm{HL}]} \tag{II.13}$$

$$\mathrm{M} + q\,\mathrm{HL} \rightleftharpoons \mathrm{ML}_q + q\,\mathrm{H}^+ \qquad {}^*\beta_q = \frac{[\mathrm{ML}_q][\mathrm{H}^+]^q}{[\mathrm{M}][\mathrm{HL}]^q} \tag{II.14}$$

$$m\,\mathrm{M} + q\,\mathrm{HL} \rightleftharpoons \mathrm{M}_m\mathrm{L}_q + q\,\mathrm{H}^+ \qquad {}^*\beta_{q,m} = \frac{[\mathrm{M}_m\mathrm{L}_q][\mathrm{H}^+]^q}{[\mathrm{M}]^m[\mathrm{HL}]^q} \tag{II.15}$$

Example:

$$\mathrm{UO_2^{2+}} + \mathrm{HF(aq)} \quad \rightleftharpoons \quad \mathrm{UO_2F^+} + \mathrm{H^+} \qquad {}^*K_1 = {}^*\beta_1 = \frac{[\mathrm{UO_2F^+}][\mathrm{H^+}]}{[\mathrm{UO_2^{2+}}][\mathrm{HF(aq)}]}$$

$$3\,\mathrm{UO_2^{2+}} + 5\,\mathrm{H_2O(l)} \quad \rightleftharpoons \quad (\mathrm{UO_2})_3(\mathrm{OH})_5^+ + 5\,\mathrm{H^+} \qquad {}^*\beta_{5,3} = \frac{[(\mathrm{UO_2})_3(\mathrm{OH})_5^+][\mathrm{H^+}]^5}{[\mathrm{UO_2^{2+}}]^3}$$

Note that an asterisk is only assigned to the formation constant if the protonated ligand that is added is deprotonated during the reaction. If a protonated ligand is added

and coordinated as such to the metal ion, the asterisk is to be omitted, as shown in Eq. (II.16).

$$\mathrm{M} + q\,\mathrm{H}_r\mathrm{L} \;\rightleftharpoons\; \mathrm{M}(\mathrm{H}_r\mathrm{L})_q \qquad \beta_q = \frac{[\mathrm{M}(\mathrm{H}_r\mathrm{L})_q]}{[\mathrm{M}][\mathrm{H}_r\mathrm{L}]^q} \tag{II.16}$$

Example:

$$\mathrm{UO_2^{2+}} + 3\,\mathrm{H_2PO_4^-} \;\rightleftharpoons\; \mathrm{UO_2(H_2PO_4)_3^-} \qquad \beta_3 = \frac{[\mathrm{UO_2(H_2PO_4)_3^-}]}{[\mathrm{UO_2^{2+}}][\mathrm{H_2PO_4^-}]^3}$$

II.1.6.3 Solubility constants

Conventionally, equilibrium constants involving a solid compound are denoted as "solubility constants" rather than as formation constants of the solid. An index "s" to the equilibrium constant indicates that the constant refers to a solubility process, as shown in Eqs. (II.17) to (II.19).

$$\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \;\rightleftharpoons\; a\,\mathrm{M} + b\,\mathrm{L} \qquad K_{\mathrm{s},0} = [\mathrm{M}]^a[\mathrm{L}]^b \tag{II.17}$$

$K_{\mathrm{s},0}$ is the conventional solubility product, and the subscript "0" indicates that the equilibrium reaction involves only uncomplexed aqueous species. If the solubility constant includes the formation of aqueous complexes, a notation analogous to that of Eq. (II.12) is used:

$$\begin{aligned} \frac{m}{a}\,\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) \quad &\rightleftharpoons \quad \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a} - q\right)\mathrm{L} \\ K_{\mathrm{s},q,m} &= [\mathrm{M}_m\mathrm{L}_q][\mathrm{L}]^{\left(\frac{mb}{a}-q\right)} \end{aligned} \tag{II.18}$$

Example:

$$\mathrm{UO_2F_2(cr)} \quad \rightleftharpoons \quad \mathrm{UO_2F^+ + F^-} \qquad K_{\mathrm{s},1,1} = K_{\mathrm{s},1} = [\mathrm{UO_2F^+}][\mathrm{F^-}]$$

Similarly, an asterisk is added to the solubility constant if it simultaneously involves a protonation equilibrium:

$$\begin{aligned} \frac{m}{a}\,\mathrm{M}_a\mathrm{L}_b(\mathrm{s}) + \left(\frac{mb}{a} - q\right)\mathrm{H^+} \quad &\rightleftharpoons \quad \mathrm{M}_m\mathrm{L}_q + \left(\frac{mb}{a} - q\right)\mathrm{HL} \\ {}^*K_{\mathrm{s},q,m} &= \frac{[\mathrm{M}_m\mathrm{L}_q][\mathrm{HL}]^{\left(\frac{mb}{a}-q\right)}}{[\mathrm{H^+}]^{\left(\frac{mb}{a}-q\right)}} \end{aligned} \tag{II.19}$$

Example:

$$\begin{aligned} \mathrm{U(HPO_4)_2 \cdot 4H_2O(cr) + H^+} \;&\rightleftharpoons\; \mathrm{UHPO_4^{2+} + H_2PO_4^- + 4\,H_2O(l)} \\ {}^*K_{\mathrm{s},1,1} \;=\; {}^*K_{\mathrm{s},1} \;&=\; \frac{[\mathrm{UHPO_4^{2+}}][\mathrm{H_2PO_4^-}]}{[\mathrm{H^+}]} \end{aligned}$$

II.1.6.4 Equilibria involving the addition of a gaseous ligand

A special notation is used for constants describing equilibria that involve the addition of a gaseous ligand, as outlined in Eq. (II.20).

$$\mathrm{ML}_{q-1} + \mathrm{L(g)} \rightleftharpoons \mathrm{ML}_q \qquad K_{\mathrm{p},q} = \frac{[\mathrm{ML}_q]}{[\mathrm{ML}_{q-1}]p_{\mathrm{L}}} \tag{II.20}$$

The subscript "p" can be combined with any other notations given above.

Example:

$$\mathrm{CO_2(g)} \rightleftharpoons \mathrm{CO_2(aq)} \qquad K_{\mathrm{p}} = \frac{[\mathrm{CO_2(aq)}]}{p_{\mathrm{CO_2}}}$$

$$3\,\mathrm{UO_2^{2+}} + 6\,\mathrm{CO_2(g)} + 6\,\mathrm{H_2O(l)} \rightleftharpoons (\mathrm{UO_2})_3(\mathrm{CO_3})_6^{6-} + 12\,\mathrm{H^+}$$

$${}^{*}\beta_{\mathrm{p},6,3} = \frac{[(\mathrm{UO_2})_3(\mathrm{CO_3})_6^{6-}][\mathrm{H^+}]^{12}}{[\mathrm{UO_2^{2+}}]^3 p_{\mathrm{CO_2}}^6}$$

$$\mathrm{UO_2CO_3(cr)} + \mathrm{CO_2(g)} + \mathrm{H_2O(l)} \rightleftharpoons \mathrm{UO_2(CO_3)_2^{2-}} + 2\,\mathrm{H^+}$$

$${}^{*}K_{\mathrm{p},s,2} = \frac{[\mathrm{UO_2(CO_3)_2^{2-}}][\mathrm{H^+}]^2}{p_{\mathrm{CO_2}}}$$

In cases where the subscripts become complicated, it is recommended that K or β be used with or without subscripts, but always followed by the equation number of the equilibrium to which it refers.

II.1.6.5 Redox equilibria

Redox reactions are usually quantified in terms of their electrode (half cell) potential, E, which is identical to the electromotive force (emf) of a galvanic cell in which the electrode on the left is the standard hydrogen electrode, SHE [2], in accordance with the "1953 Stockholm Convention" [88MIL/CVI]. Therefore, electrode potentials are given as reduction potentials relative to the standard hydrogen electrode, which acts as an electron donor. In the standard hydrogen electrode, $\mathrm{H_2(g)}$ is at unit fugacity (an ideal gas at unit pressure, 0.1 MPa), and $\mathrm{H^+}$ is at unit activity. The sign of the electrode potential, E, is that of the observed sign of its polarity when coupled with the standard hydrogen electrode. The electrode potential is related to the Gibbs energy change $\Delta_{\mathrm{r}}G_{\mathrm{m}}$ and the equilibrium constant K as outlined in Eq. (II.21).

$$E^\circ = -\frac{1}{nF}\Delta_{\mathrm{r}}G_{\mathrm{m}}^\circ = \frac{RT}{nF}\ln K^\circ \tag{II.21}$$

The symbol E° is used for the emf of a standard galvanic cell relative to the standard hydrogen electrode (all components in their standard state, *cf.* Section II.3.1, and with

[2] The definitions of SHE and NHE are given in Section II.1.1.

no liquid junction potential). Eq. (II.21) can then be written in terms of E°, $\Delta_r G^\circ_m$ and K°.

For example, for the hypothetical galvanic cell:

$$\mathrm{Pt} \;\Big|\; \mathrm{H_2(g}, p = 1\mathrm{bar}) \;\Big|\; \mathrm{HCl(aq}, a_\pm = 1) \;\Big\vdots\; \begin{matrix}\mathrm{Fe(ClO_4)_2(aq}, a'_\pm)\\ \mathrm{Fe(ClO_4)_3(aq}, a''_\pm)\end{matrix} \;\Big|\; \mathrm{Pt}, \qquad \text{(II.22)}$$

where "⋮" denotes a liquid junction and "|" a phase boundary, the cell reaction is:

$$\mathrm{Fe^{3+} + \tfrac{1}{2}H_2(g) \;\rightleftharpoons\; Fe^{2+} + H^+} \qquad \text{(II.23)}$$

For convenience Reaction (II.23) can be represented by half cell reactions, each involving an equal number of "electrons", as shown in the following equations

$$\mathrm{Fe^{3+} + e^- \;\rightleftharpoons\; Fe^{2+}} \qquad \text{(II.24)}$$

$$\mathrm{\tfrac{1}{2}H_2(g) \;\rightleftharpoons\; H^+ + e^-} \qquad \text{(II.25)}$$

where "$\mathrm{e^-}$" is a symbol devoid of any physical or chemical significance, and therefore its name, "electron", might be misleading but this inconvenience is compensated by its usefulness.

Equilibrium constants may be written for these half cell reactions in the following way:

$$K^\circ\text{(II.24)} = \frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}} \times a_{\mathrm{e^-}}} \qquad \text{(II.26)}$$

$$K^\circ\text{(II.25)} = \frac{a_{\mathrm{H^+}} \times a_{\mathrm{e^-}}}{\sqrt{f_{\mathrm{H_2}}}} = 1 \quad \text{(by definition)} \qquad \text{(II.27)}$$

In addition, $\Delta_r G^\circ_m$ (II.25) = $\Delta_r H^\circ_m$ (II.25) = $\Delta_r S^\circ_m$ (II.25) = 0 by definition, at all temperatures, and therefore $\Delta_r G^\circ_m$ (II.24) = $\Delta_r G^\circ_m$ (II.23).

The following equations describe the change in the Gibbs energy and redox potential of Reaction (II.23), if $p_{\mathrm{H_2}}$ and $a_{\mathrm{H^+}}$ are equal to unity (*cf.* Eq. (II.21)):

$$\Delta_r G_m\text{(II.23)} = \Delta_r G^\circ_m\text{(II.23)} + RT \ln\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right)$$

$$E\text{(II.23)} = E^\circ\text{(II.23)} - \frac{RT}{nF} \ln\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right) \qquad \text{(II.28)}$$

The "activity of electrons" in Eqs. (II.26) and (II.27) may be interpreted to represent the relative tendency for electrons to leave an aqueous solution. For the standard hydrogen electrode $a_{\mathrm{e^-}} = 1$ (by the convention expressed in Eq. (II.27)), while rearrangement of Eq. (II.26) for the half-cell containing the iron perchlorates in cell II.22 gives:

$$-\log_{10} a_{\mathrm{e^-}} = \log_{10} K^\circ\text{(II.24)} - \log_{10}\left(\frac{a_{\mathrm{Fe^{2+}}}}{a_{\mathrm{Fe^{3+}}}}\right)$$

and by the convention in Eq. (II.27):

$$-\log_{10} a_{e^-} \quad = \quad \log_{10} K^\circ(\text{II.23}) - \log_{10}\left(\frac{a_{Fe^{2+}}}{a_{Fe^{3+}}}\right) \qquad \text{(II.29)}$$

A comparison of Eqs. (II.28) and (II.29) taking into account Eq. (II.21) shows that for the right half-cell in II.22:

$$-\log_{10} a_{e^-} \quad = \quad \frac{F}{RT\ln(10)}\, E(\text{II.23}) \qquad \text{(II.30)}$$

The splitting of redox reactions into two half cell reactions by introducing the symbol "e^-", which according to Eq. II.30 is related to the standard electrode potential, is arbitrary but justified by the usefulness of the resulting equations. When calculating the equilibrium composition of a chemical system, both "e^-" and H^+ can be chosen as components and they can be treated numerically in a similar way: equilibrium constants, mass balance, *etc*. may be defined for both. However, while H^+ represents the hydrated proton in aqueous solution, "e^-" is void of chemical and physical significance, and its concentration must be set to zero during the calculations (arbitrary values, however, may be assigned to a_{e^-} which are then related to E by Eq. (II.30)).

In the literature on geochemical modelling of natural waters, it is customary to represent the "electron activity" of an aqueous solution with the symbol "pe" or "pε" ($= -\log_{10} a_{e^-}$) by analogy with pH ($= -\log_{10} a_{H^+}$), and the redox potential of an aqueous solution relative to the standard hydrogen electrode is usually denoted by either "Eh" or "E_H" (see for example [81STU/MOR, 82DRE, 84HOS, 86NOR/MUN]).

II.1.7 Order of formulae

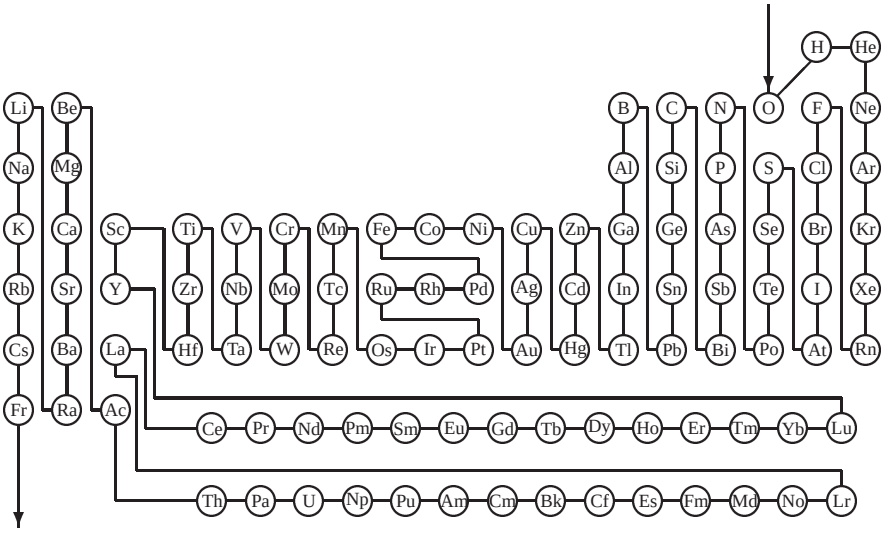
To be consistent with CODATA, the data tables are given in "Standard Order of Arrangement" [82WAG/EVA]. This scheme is presented in Figure II.1 below which shows the sequence of the ranks of the elements in this convention. The order follows the ranks of the elements.

For *e. g.* uranium, this means that, after elemental uranium and its monoatomic ions (*e.g.*, U^{4+}), the uranium compounds and complexes with oxygen would be listed, then those with hydrogen, then those with oxygen and hydrogen, and so on, with decreasing rank of the element and combinations of the elements. Within a class, increasing coefficients of the higher rank elements go before increasing coefficients of the lower rank elements. For example, in the U-O-F class of compounds and complexes, a typical sequence would be UOF_2(cr), UOF_4(cr), UOF_4(g), UO_2F(aq), UO_2F^+, UO_2F_2(aq), UO_2F_2(cr), UO_2F_2(g), $UO_2F_3^-$, $UO_2F_4^{2-}$, $U_2O_3F_6$(cr), *etc*. Formulae with identical stoichiometry are in alphabetical order of their designators.

II.1.8 Reference codes

The references cited in the review are ordered chronologically and alphabetically by the first two authors within each year, as described by CODATA [87GAR/PAR]. A

Figure II.1: Standard order of arrangement of the elements and compounds based on the periodic classification of the elements (from Ref. [82WAG/EVA]).



reference code is made up of the final two digits of the year of appearance (if the publication is not from the 20th century, the year will be put in full). The year is followed by the first three letters of the surnames of the first two authors, separated by a slash.

If there are multiple reference codes, a "2" will be added to the second one, a "3" to the third one, and so forth. Reference codes are always enclosed in square brackets.

II.2 Units and conversion factors

Thermodynamic data are given according to the *Système International d'unité* (SI units). The unit of energy is the joule. Some basic conversion factors, also for non-thermodynamic units, are given in Table II.4.

Since a large part of the NEA-TDB project deals with the thermodynamics of aqueous solutions, the units describing the amount of dissolved substance are used very frequently. For convenience, this review uses "M" as an abbreviation of "mol $\cdot$ dm^{-3}" for molarity, c, and, in Appendices C and D, "m" as an abbreviation of "mol $\cdot$ kg^{-1}" for molality, m. It is often necessary to convert concentration data from molarity to molality and vice versa. This conversion is used for the correction and extrapolation of equilibrium data to zero ionic strength by the specific ion interaction theory which works in molality units (*cf.* Appendix C). This conversion is made in the following way.

Table II.4: Unit conversion factors

To convert from (non-SI unit symbol)	to (SI unit symbol)	multiply by
ångström (Å)	metre (m)	1×10^{-10} (exactly)
standard atmosphere (atm)	pascal (Pa)	1.01325×10^5 (exactly)
bar (bar)	pascal (Pa)	1×10^5 (exactly)
thermochemical calorie (cal)	joule (J)	4.184 (exactly)
entropy unit (e.u. $\hat{=}$ cal $\cdot$ K^{-1} $\cdot$ mol^{-1})	J $\cdot$ K^{-1} $\cdot$ mol^{-1}	4.184 (exactly)

Molality is defined as m_B moles of substance B dissolved in 1000 grams of pure water. Molarity is defined as c_B moles of substance B dissolved in $(1000\rho - c_B M)$ grams of pure water, where ρ is the density of the solution in g·cm^{-3} and M the molar mass in g·mol^{-1}. From this it follows that

$$m_B = \frac{1000 c_B}{1000\rho - c_B M}$$

Baes and Mesmer [76BAE/MES, *p.*439] give a table with conversion factors (from molarity to molality) for nine electrolytes and various ionic strengths. Conversion factors at 298.15 K for twenty one electrolytes, calculated using the density equations reported by Söhnel and Novotný [85SÖH/NOV], are reported in Table II.5.

Example:

$$\begin{aligned} 1.00\ \text{M NaClO}_4 &\ \hat{=}\ 1.05\ \text{m NaClO}_4 \\ 1.00\ \text{M NaCl} &\ \hat{=}\ 1.02\ \text{m NaCl} \\ 4.00\ \text{M NaClO}_4 &\ \hat{=}\ 4.95\ \text{m NaClO}_4 \\ 6.00\ \text{M NaNO}_3 &\ \hat{=}\ 7.55\ \text{m NaNO}_3 \end{aligned}$$

It should be noted that equilibrium constants, unless they are dimensionless, need also to be converted if the concentration scale is changed from molarity to molality or vice versa. For a general equilibrium reaction, $0 = \sum_B \nu_B B$, the equilibrium constants can be expressed either in molarity or molality units, K_c or K_m, respectively:

$$\begin{aligned} \log_{10} K_c &= \sum_B \nu_B \log_{10} c_B \\ \log_{10} K_m &= \sum_B \nu_B \log_{10} m_B \end{aligned}$$

With $(m_B/c_B) = \varrho$, or $(\log_{10} m_B - \log_{10} c_B) = \log_{10} \varrho$, the relationship between K_c and K_m becomes very simple, as shown in Eq. (II.31).

$$\log_{10} K_m = \log_{10} K_c + \sum_B \nu_B \log_{10} \varrho \qquad \text{(II.31)}$$

Table II.5: Factors ϱ for the conversion of molarity, c_B, to molality, m_B, of a substance B, in various media at 298.15 K (calculated from densities in [85SÖH/NOV]).

	$\varrho = m_B/c_B$ (dm^3 of solution per kg of H_2O)							
c (M)	$HClO_4$	$NaClO_4$	$LiClO_4$	NH_4ClO_4	$Ba(ClO_4)_2$	HCl	NaCl	LiCl
0.10	1.0077	1.0075	1.0074	1.0091	1.0108	1.0048	1.0046	1.0049
0.25	1.0147	1.0145	1.0141	1.0186	1.0231	1.0076	1.0072	1.0078
0.50	1.0266	1.0265	1.0256	1.0351	1.0450	1.0123	1.0118	1.0127
0.75	1.0386	1.0388	1.0374	1.0523	1.0685	1.0172	1.0165	1.0177
1.00	1.0508	1.0515	1.0496	1.0703	1.0936	1.0222	1.0215	1.0228
1.50	1.0759	1.0780	1.0750	1.1086	1.1491	1.0324	1.0319	1.0333
2.00	1.1019	1.1062	1.1019		1.2125	1.0430	1.0429	1.0441
3.00	1.1571	1.1678	1.1605		1.3689	1.0654	1.0668	1.0666
4.00	1.2171	1.2374	1.2264			1.0893	1.0930	1.0904
5.00	1.2826	1.3167				1.1147	1.1218	1.1156
6.00	1.3547	1.4077				1.1418		1.1423
c (M)	KCl	NH_4Cl	$MgCl_2$	$CaCl_2$	NaBr	HNO_3	$NaNO_3$	$LiNO_3$
0.10	1.0057	1.0066	1.0049	1.0044	1.0054	1.0056	1.0058	1.0059
0.25	1.0099	1.0123	1.0080	1.0069	1.0090	1.0097	1.0102	1.0103
0.50	1.0172	1.0219	1.0135	1.0119	1.0154	1.0169	1.0177	1.0178
0.75	1.0248	1.0318	1.0195	1.0176	1.0220	1.0242	1.0256	1.0256
1.00	1.0326	1.0420	1.0258	1.0239	1.0287	1.0319	1.0338	1.0335
1.50	1.0489	1.0632	1.0393	1.0382	1.0428	1.0478	1.0510	1.0497
2.00	1.0662	1.0855	1.0540	1.0546	1.0576	1.0647	1.0692	1.0667
3.00	1.1037	1.1339	1.0867	1.0934	1.0893	1.1012	1.1090	1.1028
4.00	1.1453	1.1877	1.1241	1.1406	1.1240	1.1417	1.1534	1.1420
5.00		1.2477		1.1974	1.1619	1.1865	1.2030	1.1846
6.00					1.2033	1.2361	1.2585	1.2309
c (M)	NH_4NO_3	H_2SO_4	Na_2SO_4	$(NH_4)_2SO_4$	H_3PO_4	Na_2CO_3	K_2CO_3	NaSCN
0.10	1.0077	1.0064	1.0044	1.0082	1.0074	1.0027	1.0042	1.0069
0.25	1.0151	1.0116	1.0071	1.0166	1.0143	1.0030	1.0068	1.0130
0.50	1.0276	1.0209	1.0127	1.0319	1.0261	1.0043	1.0121	1.0234
0.75	1.0405	1.0305	1.0194	1.0486	1.0383	1.0065	1.0185	1.0342
1.00	1.0539	1.0406	1.0268	1.0665	1.0509	1.0094	1.0259	1.0453
1.50	1.0818	1.0619	1.0441	1.1062	1.0773	1.0170	1.0430	1.0686
2.00	1.1116	1.0848		1.1514	1.1055	1.0268	1.0632	1.0934
3.00	1.1769	1.1355		1.2610	1.1675		1.1130	1.1474
4.00	1.2512	1.1935		1.4037	1.2383		1.1764	1.2083
5.00	1.3365	1.2600			1.3194		1.2560	1.2773
6.00	1.4351	1.3365			1.4131			1.3557

$\sum_B \nu_B$ is the sum of the stoichiometric coefficients of the reaction, *cf.* Eq. (II.47), and the values of ϱ are the factors for the conversion of molarity to molality as tabulated in Table II.5 for several electrolyte media at 298.15 K. The differences between the values in Table II.5 and the values listed in the uranium NEA-TDB review [92GRE/FUG, *p*.23] are found at the highest concentrations, and are no larger than ± 0.003 dm^3/kg, reflecting the accuracy expected in this type of conversions. The uncertainty introduced by the use of Eq. (II.31) in the values of $\log_{10} K_m$ will be then no larger than $\pm 0.001 \sum_B \nu_B$.

II.3 Standard and reference conditions

II.3.1 Standard state

A precise definition of the term "standard state" has been given by IUPAC [82LAF]. The fact that only changes in thermodynamic parameters, but not their absolute values, can be determined experimentally, makes it important to have a well-defined standard state that forms a base line to which the effect of variations can be referred. The IUPAC [82LAF] definition of the standard state has been adopted in the NEA-TDB project. The standard state pressure, $p^\circ = 0.1$ MPa (1 bar), has therefore also been adopted, *cf.* Section II.3.2. The application of the standard state principle to pure substances and mixtures is summarised below. It should be noted that the standard state is always linked to a reference temperature, *cf.* Section II.3.3.

- The standard state for a gaseous substance, whether pure or in a gaseous mixture, is the pure substance at the standard state pressure and in a (hypothetical) state in which it exhibits ideal gas behaviour.
- The standard state for a pure liquid substance is (ordinarily) the pure liquid at the standard state pressure.
- The standard state for a pure solid substance is (ordinarily) the pure solid at the standard state pressure.
- The standard state for a solute B in a solution is a hypothetical liquid solution, at the standard state pressure, in which $m_B = m^\circ = 1\,\text{mol} \cdot \text{kg}^{-1}$, and in which the activity coefficient γ_B is unity.

It should be emphasised that the use of $^\circ$, *e.g.*, in $\Delta_f H^\circ_m$, implies that the compound in question is in the standard state and that the elements are in their reference states. The reference states of the elements at the reference temperature (*cf.* Section II.3.3) are listed in Table II.6.

II.3.2 Standard state pressure

The standard state pressure chosen for all selected data is 0.1 MPa (1 bar) as recommended by the International Union of Pure and Applied Chemistry IUPAC [82LAF].

Table II.6: Reference states for some elements at the reference temperature of 298.15 K and standard pressure of 0.1 MPa [82WAG/EVA, 89COX/WAG, 91DIN].

O_2	gaseous	Al	crystalline, cubic
H_2	gaseous	Zn	crystalline, hexagonal
He	gaseous	Cd	crystalline, hexagonal
Ne	gaseous	Hg	liquid
Ar	gaseous	Cu	crystalline, cubic
Kr	gaseous	Ag	crystalline, cubic
Xe	gaseous	Fe	crystalline, cubic, bcc
F_2	gaseous	Tc	crystalline, hexagonal
Cl_2	gaseous	V	crystalline, cubic
Br_2	liquid	Ti	crystalline, hexagonal
I_2	crystalline, orthorhombic	Am	crystalline, dhcp
S	crystalline, orthorhombic	Pu	crystalline, monoclinic
Se	crystalline, hexagonal (“black”)	Np	crystalline, orthorhombic
Te	crystalline, hexagonal	U	crystalline, orthorhombic
N_2	gaseous	Th	crystalline, cubic
P	crystalline, cubic (“white”)	Be	crystalline, hexagonal
As	crystalline, rhombohedral (“grey”)	Mg	crystalline, hexagonal
Sb	crystalline, rhombohedral	Ca	crystalline, cubic, fcc
Bi	crystalline, rhombohedral	Sr	crystalline, cubic, fcc
C	crystalline, hexagonal (graphite)	Ba	crystalline, cubic
Si	crystalline, cubic	Li	crystalline, cubic
Ge	crystalline, cubic	Na	crystalline, cubic
Sn	crystalline, tetragonal (“white”)	K	crystalline, cubic
Pb	crystalline, cubic	Rb	crystalline, cubic
B	β, crystalline, rhombohedral	Cs	crystalline, cubic

However, the majority of the thermodynamic data published in the scientific literature and used for the evaluations in this review, refer to the old standard state pressure of 1 “standard atmosphere” ($= 0.101325$ MPa). The difference between the thermodynamic data for the two standard state pressures is not large and lies in most cases within the uncertainty limits. It is nevertheless essential to make the corrections for the change in the standard state pressure in order to avoid inconsistencies and propagation of errors. In practice the parameters affected by the change between these two standard state pressures are the Gibbs energy and entropy changes of all processes that involve gaseous species. Consequently, changes occur also in the Gibbs energies of formation of species that consist of elements whose reference state is gaseous (H, O, F, Cl, N, and the noble gases). No other thermodynamic quantities are affected significantly. A large part of the following discussion has been taken from the NBS tables of chemical thermodynamic properties [82WAG/EVA], see also Freeman [84FRE].

The following expressions define the effect of pressure on the properties of all

substances:

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_p = V(1-\alpha T) \tag{II.32}$$

$$\left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p \tag{II.33}$$

$$\left(\frac{\partial S}{\partial p}\right)_T = -V\alpha = -\left(\frac{\partial V}{\partial T}\right)_p \tag{II.34}$$

$$\left(\frac{\partial G}{\partial p}\right)_T = V \tag{II.35}$$

$$\text{where} \qquad \alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \tag{II.36}$$

For ideal gases, $V = \frac{RT}{p}$ and $\alpha = \frac{R}{pV} = \frac{1}{T}$. The conversion equations listed below (Eqs. (II.37) to (II.44)) apply to the small pressure change from 1 atm to 1 bar (0.1 MPa). The quantities that refer to the old standard state pressure of 1 atm are assigned the superscript $^{(\mathrm{atm})}$ here, the ones that refer to the new standard state pressure of 1 bar the superscript $^{(\mathrm{bar})}$.

For all substances the change in the enthalpy of formation and the heat capacity is much smaller than the experimental accuracy and can be disregarded. This is exactly true for ideal gases.

$$\Delta_f H^{(\mathrm{bar})}(T) - \Delta_f H^{(\mathrm{atm})}(T) = 0 \tag{II.37}$$

$$C_p^{(\mathrm{bar})}(T) - C_p^{(\mathrm{atm})}(T) = 0 \tag{II.38}$$

For gaseous substances, the entropy difference is

$$\begin{aligned} S^{(\mathrm{bar})}(T) - S^{(\mathrm{atm})}(T) &= R\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= R\ln 1.01325 \\ &= 0.1094\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}. \end{aligned} \tag{II.39}$$

This is exactly true for ideal gases, as follows from Eq. (II.34) with $\alpha = \frac{R}{pV}$. The entropy change of a reaction or process is thus dependent on the number of moles of gases involved:

$$\begin{aligned} \Delta_r S^{(\mathrm{bar})} - \Delta_r S^{(\mathrm{atm})} &= \delta \times R\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= \delta \times 0.1094\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}}, \end{aligned} \tag{II.40}$$

where δ is the net increase in moles of gas in the process.

Similarly, the change in the Gibbs energy of a process between the two standard state pressures is

$$\begin{aligned}\Delta_r G^{(\mathrm{bar})} - \Delta_r G^{(\mathrm{atm})} &= -\delta \times RT \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= -\delta \times 0.03263\,\mathrm{kJ \cdot mol^{-1}} \text{ at } 298.15\,\mathrm{K}. \qquad \text{(II.41)}\end{aligned}$$

Eq. (II.41) applies also to $\Delta_f G^{(\mathrm{bar})} - \Delta_f G^{(\mathrm{atm})}$, since the Gibbs energy of formation describes the formation process of a compound or complex from the reference states of the elements involved:

$$\Delta_r G^{(\mathrm{bar})} - \Delta_r G^{(\mathrm{atm})} = -\delta \times 0.03263\,\mathrm{kJ \cdot mol^{-1}} \text{ at } 298.15\,\mathrm{K}. \qquad \text{(II.42)}$$

The change in the equilibrium constants and cell potentials with the change in the standard state pressure follows from the expression for Gibbs energy changes, Eq. (II.41):

$$\begin{aligned}\log_{10} K^{(\mathrm{bar})} - \log_{10} K^{(\mathrm{atm})} &= -\frac{\Delta_r G^{(\mathrm{bar})} - \Delta_r G^{(\mathrm{atm})}}{RT \ln 10} \\ &= \delta \times \frac{\ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)}{\ln 10} = \delta \times \log_{10}\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right) \\ &= \delta \times 0.005717 \qquad \text{(II.43)} \\ E^{(\mathrm{bar})} - E^{(\mathrm{atm})} &= -\frac{\Delta_r G^{(\mathrm{bar})} - \Delta_r G^{(\mathrm{atm})}}{nF} \\ &= \delta \times \frac{RT \ln\left(\frac{p^{(\mathrm{atm})}}{p^{(\mathrm{bar})}}\right)}{nF} \\ &= \delta \times \frac{0.0003382}{n}\,\mathrm{V} \text{ at } 298.15\,\mathrm{K}. \qquad \text{(II.44)}\end{aligned}$$

It should be noted that the standard potential of the hydrogen electrode is equal to 0.00 V exactly, by definition.

$$\mathrm{H^+ + e^-} \rightleftharpoons \tfrac{1}{2}\mathrm{H_2(g)} \qquad E^\circ \stackrel{\mathrm{def}}{=} 0.00\,\mathrm{V} \qquad \text{(II.45)}$$

This definition will not be changed, although a gaseous substance, $H_2(g)$, is involved in the process. The change in the potential with pressure for an electrode potential conventionally written as

$$\mathrm{Ag^+ + e^-} \rightleftharpoons \mathrm{Ag(cr)}$$

should thus be calculated from the balanced reaction that includes the hydrogen electrode,

$$\mathrm{Ag^+ + \tfrac{1}{2}H_2(g)} \rightleftharpoons \mathrm{Ag(cr) + H^+}.$$

Here $\delta = -0.5$. Hence, the contribution to δ from an electron in a half cell reaction is the same as the contribution of a gas molecule with the stoichiometric coefficient of 0.5. This leads to the same value of δ as the combination with the hydrogen half cell.

Example:

$Fe(cr) + 2\,H^+ \rightleftharpoons Fe^{2+} + H_2(g)$	$\delta = 1$	$E^{(bar)} - E^{(atm)} = 0.00017\,V$
$CO_2(g) \rightleftharpoons CO_2(aq)$	$\delta = -1$	$\log_{10} K^{(bar)} - \log_{10} K^{(atm)} = -0.0057$
$NH_3(g) + \frac{5}{4}O_2(g) \rightleftharpoons NO(g) + \frac{3}{2}H_2O(g)$	$\delta = 0.25$	$\Delta_r G^{(bar)} - \Delta_r G^{(atm)} = -0.008\,kJ \cdot mol^{-1}$
$\frac{1}{2}Cl_2(g) + 2\,O_2(g) + e^- \rightleftharpoons ClO_4^-$	$\delta = -3$	$\Delta_f G^{(bar)} - \Delta_f G^{(atm)} = 0.098\,kJ \cdot mol^{-1}$

II.3.3 Reference temperature

The definitions of standard states given in Section II.3 make no reference to fixed temperature. Hence, it is theoretically possible to have an infinite number of standard states of a substance as the temperature varies. It is, however, convenient to complete the definition of the standard state in a particular context by choosing a reference temperature. As recommended by IUPAC [82LAF], the reference temperature chosen in the NEA-TDB project is $T = 298.15$ K or $t = 25.00$°C. Where necessary for the discussion, values of experimentally measured temperatures are reported after conversion to the IPTS-68 [69COM]. The relation between the absolute temperature T (K, kelvin) and the Celsius temperature t (°C) is defined by $t = (T - T_0)$ where $T_0 = 273.15$ K.

II.4 Fundamental physical constants

The fundamental physical constants are taken from a publication by CODATA [86COD]. Those relevant to this review are listed in Table II.7.

II.5 Uncertainty estimates

One of the principal objectives of the NEA-TDB development effort is to provide an idea of the uncertainties associated with the data selected in the reviews. In general the uncertainties should define the range within which the corresponding data can be reproduced with a probability of 95%. In many cases, a full statistical treatment is limited or impossible due to the availability of only one or few data points. Appendix D describes in detail the procedures used for the assignment and treatment of uncertainties, as well as the propagation of errors and the standard rules for rounding.

II.6 The NEA-TDB system

A data base system has been developed at the NEA Data Bank that allows the storage of thermodynamic parameters for individual species as well as for reactions. The structure of the data base system allows consistent derivation of thermodynamic data

Table II.7: Fundamental physical constants. These values have been taken from CODATA [86COD]. The digits in parentheses are the one-standard-deviation uncertainty in the last digits of the given value.

Quantity	Symbol	Value	Units
speed of light in vacuum	c	299 792 458	$m \cdot s^{-1}$
permeability of vacuum	$\mu_\circ$	$4\pi \times 10^{-7}$	
		$= 12.566\,370\,614\ldots$	$10^{-7}\,N \cdot A^{-2}$
permittivity of vacuum	$\epsilon_\circ$	$1/\mu_\circ c^2$	
		$= 8.854\,187\,817\ldots$	$10^{-12}\,C^2 \cdot J^{-1} \cdot m^{-1}$
Planck constant	h	6.626 0755(40)	$10^{-34}\,J \cdot s$
elementary charge	e	1.602 177 33(49)	$10^{-19}\,C$
Avogadro constant	N_A	6.022 1367(36)	$10^{23}\,mol^{-1}$
Faraday constant, $N_A \times e$	F	96 485.309(29)	$C \cdot mol^{-1}$
molar gas constant	R	8.314 510(70)	$J \cdot K^{-1} \cdot mol^{-1}$
Boltzmann constant, R/N_A	k	1.380 658(12)	$10^{-23}\,J \cdot K^{-1}$
Non-SI units used with SI:			
electron volt, (e/C) J	eV	1.602 177 33(49)	10^{-19} J
atomic mass unit, $1u = m_u = \frac{1}{12}m(^{12}C)$	u	1.660 5402(10)	10^{-27} kg

for individual species from reaction data at standard conditions, as well as internal recalculations of data at standard conditions. If a selected value is changed, all the dependent values will be recalculated consistently. The maintenance of consistency of all the selected data, including their uncertainties (*cf.* Appendix D), is ensured by the software developed for this purpose at the NEA Data Bank. The literature sources of the data are also stored in the data base.

The following thermodynamic parameters, valid at the reference temperature of 298.15 K and at the standard pressure of 1 bar, are stored in the data base:

$\Delta_f G^\circ_m$	the standard molar Gibbs energy of formation from the elements in their reference state ($kJ \cdot mol^{-1}$)
$\Delta_f H^\circ_m$	the standard molar enthalpy of formation from the elements in their reference state ($kJ \cdot mol^{-1}$)
S°_m	the standard molar entropy ($J \cdot K^{-1} \cdot mol^{-1}$)
$C^\circ_{p,m}$	the standard molar heat capacity ($J \cdot K^{-1} \cdot mol^{-1}$)

For aqueous neutral species and ions, the values of $\Delta_f G^\circ_m$, $\Delta_f H^\circ_m$, S°_m and $C^\circ_{p,m}$ correspond to the standard partial molar quantities, and for individual aqueous ions they are relative quantities, defined with respect to the aqueous hydrogen ion, according to the convention [89COX/WAG] that $\Delta_f H^\circ_m(H^+, aq, T) = 0$, and that $S^\circ_m(H^+, aq, T) =$

0. Furthermore, for an *ionised solute* B containing any number of different cations and anions:

$$\begin{aligned}\Delta_f H^\circ_m(B_\pm, aq) &= \sum_+ \nu_+ \Delta_f H^\circ_m(\text{cation, aq}) + \sum_- \nu_- \Delta_f H^\circ_m(\text{anion, aq})\\ S^\circ_m(B_\pm, aq) &= \sum_+ \nu_+ S^\circ_m(\text{cation, aq}) + \sum_- \nu_- S^\circ_m(\text{anion, aq}).\end{aligned}$$

As the thermodynamic parameters vary as a function of temperature, provision is made for including the compilation of the coefficients of empirical temperature functions for these data, as well as the temperature ranges over which they are valid. In many cases the thermodynamic data measured or calculated at several temperatures were published for a particular species, rather than the deduced temperature functions. In these cases, a non-linear regression method is used in this review to obtain the most significant coefficients of the following empirical function:

$$\begin{aligned}F(T) &= a + b\times T + c\times T^2 + d\times T^{-1} + e\times T^{-2} + f\times \ln T + g\times T\ln T\\ &\quad + h\times\sqrt{T} + \frac{i}{\sqrt{T}} + j\times T^3 + k\times T^{-3}.\end{aligned} \tag{II.46}$$

Most temperature variations can be described with three or four parameters, a, b and e being the ones most frequently used. In the present review, only $C^\circ_{p,m}(T)$, *i.e.*, the thermal functions of the heat capacities of individual species, are considered and stored in the data base. They refer to the relation

$$C^\circ_{p,m}(T) = a + b\times T + c\times T^2 + d\times T^{-1} + e\times T^{-2}$$

and are listed in Tables III.3.

The pressure dependence of thermodynamic data has not been the subject of critical analysis in the present compilation. The reader interested in higher temperatures and pressures, or the pressure dependency of thermodynamic functions for geochemical applications, is referred to the specialised literature in this area, *e.g.*, [82HAM, 84MAR/MES, 88SHO/HEL, 88TAN/HEL, 89SHO/HEL, 89SHO/HEL2, 90MON, 91AND/CAS].

Selected standard thermodynamic data referring to chemical reactions are also compiled in the data base. A chemical reaction "r", involving reactants and products 'B", can be abbreviated as

$$0 = \sum_B \nu^r_B\, B \tag{II.47}$$

where the stoichiometric coefficients ν^r_B are positive for products, and negative for reactants. The reaction parameters considered in the NEA-TDB system include:

$\log_{10} K^\circ_r$	the equilibrium constant of the reaction, logarithmic	
$\Delta_r G^\circ_m$	the molar Gibbs energy of reaction	$(kJ\cdot mol^{-1})$
$\Delta_r H^\circ_m$	the molar enthalpy of reaction	$(kJ\cdot mol^{-1})$
$\Delta_r S^\circ_m$	the molar entropy of reaction	$(J\cdot K^{-1}\cdot mol^{-1})$
$\Delta_r C^\circ_{p,m}$	the molar heat capacity of reaction	$(J\cdot K^{-1}\cdot mol^{-1})$

The temperature functions of these data, if available, are stored according to Eq. (II.46).

The equilibrium constant, K_r°, is related to $\Delta_r G_m^\circ$ according to the following relation,

$$\log_{10} K_r^\circ = -\frac{\Delta_r G_m^\circ}{RT \ln(10)}$$

and can be calculated from the individual values of $\Delta_f G_m^\circ$ (B) (for example, those given in Tables III.1 and IV.1), according to

$$\log_{10} K_r^\circ = -\frac{1}{RT \ln(10)} \sum_B \nu_B^r \, \Delta_f G_m^\circ(B). \qquad \text{(II.48)}$$

II.7 Presentation of the selected data

The selected data are presented in Chapters III and IV. Unless otherwise indicated, they refer to standard conditions (*cf.* Section II.3) and 298.15 K (25.00°C) and are provided with an uncertainty which should correspond to the 95% confidence level (see Appendix D).

Chapter III contains a table of selected thermodynamic data for individual compounds and complexes of technetium (Table III.1), a table of selected reaction data (Table III.2) for reactions concerning technetium species, and a table containing selected thermal functions of the heat capacities of individual species of technetium (Table III.3). The selection of these data is discussed in Chapter V.

Chapter IV contains, for auxiliary compounds and complexes that do not contain technetium, a table of the thermodynamic data for individual species (Table IV.1) and a table of reaction data (Table IV.2). Most of these values are the CODATA Key Values [89COX/WAG]. The selection of the remaining auxiliary data is discussed in Chapter VI of the uranium review [92GRE/FUG].

All the selected data presented in Tables III.1, III.2, IV.1 and IV.2 are internally consistent. This consistency is maintained by the internal consistency verification and recalculation software developed at the NEA Data Bank in conjunction with the NEA-TDB data base system, *cf.* Section II.6. Therefore, when using the selected data for technetium species, the auxiliary data of Chapter IV must be used together with the data in Chapter III to ensure internal consistency of the data set.

It is important to note that Tables III.2 and IV.2 include only those species for which the primary selected data are reaction data. The formation data derived therefrom and listed in Table III.1 is obtained using auxiliary data, and their uncertainties are propagated accordingly. In order to maintain the uncertainties originally assigned to the selected data in this review, the user is advised to make direct use of the reaction data presented in Tables III.2 and IV.2, rather than taking the derived values in Tables III.1 and IV.1 to calculate the reaction data with Eq. (II.48). The later approach would imply a twofold propagation of the uncertainties and result in reaction data whose uncertainties would be considerably larger than those originally assigned.

The thermodynamic data in the selected set refer to a temperature of 298.15 K (25.00°C), but they can be recalculated to other temperatures if the corresponding data

(enthalpies, entropies, heat capacities) are available [97PUI/RAR]. For example, the temperature dependence of the standard reaction Gibbs energy as a function of the standard reaction entropy at the reference temperature ($T_0 = 298.15$ K), and of the heat capacity function is:

$$\begin{aligned}\Delta_r G^\circ_m(T) &= \Delta_r H^\circ_m(T_0) + \int_{T_0}^{T} \Delta_r C^\circ_{p,m} \mathrm{d}T \\ &\quad - T\left(\Delta_r S^\circ_m(T_0) + \int_{T_0}^{T} \frac{\Delta_r C^\circ_{p,m}}{T} \mathrm{d}T\right),\end{aligned}$$

and the temperature dependence of the standard equilibrium constant as a function of the standard reaction enthalpy and heat capacity is:

$$\begin{aligned}\log_{10} K^\circ(T) &= \log_{10} K^\circ(T_0) - \frac{\Delta_r H^\circ_m(T_0)}{R\ln(10)}\left(\frac{1}{T} - \frac{1}{T_0}\right) \\ &\quad - \frac{1}{RT\ln(10)} \int_{T_0}^{T} \Delta_r C^\circ_{p,m} \mathrm{d}T + \frac{1}{R\ln(10)} \int_{T_0}^{T} \frac{\Delta_r C^\circ_{p,m}}{T} \mathrm{d}T,\end{aligned}$$

where R is the gas constant (*cf.* Table II.7).

In the case of aqueous species, for which enthalpies of reaction are selected or can be calculated from the selected enthalpies of formation, but for which there are no selected heat capacities, it is in most cases possible to recalculate equilibrium constants to temperatures up to 100 to 150°C, with an additional uncertainty of perhaps about 1 to 2 logarithmic units, due to the disregard of the heat capacity contributions to the temperature correction. However, it is important to observe that "new" aqueous species, *i.e.*, species not present in significant amounts at 25°C and therefore not detected, may be significant at higher temperatures, see for example the work by Ciavatta, Iuliano and Porto [87CIA/IUL]. Additional high-temperature experiments may therefore be needed in order to ascertain that proper chemical models are used in the modelling of hydrothermal systems. For many species, experimental thermodynamic data are not available to allow a selection of parameters describing the temperature dependence of equilibrium constants and Gibbs energies of formation. The user may find information on various procedures to estimate the temperature dependence of these thermodynamic parameters in [97PUI/RAR].

Chapter III

Selected technetium data

This chapter presents the chemical thermodynamic data set for technetium species which has been selected in this review. Table III.1 contains the recommended thermodynamic data of the technetium compounds and complexes, Table III.2 the recommended thermodynamic data of chemical equilibrium reactions by which the technetium compounds and complexes are formed, and Table III.3 the temperature coefficients of the heat capacity data of Table III.1 where available. Table III.2 does not contain all conceivable reactions but only those for which primary data selections have been made in this review. These selected reaction data have been used, together with auxiliary data presented in Table IV.1, to derive the corresponding formation data in Table III.1. The uncertainties associated with the auxiliary data may in some cases be large, leading to comparatively large uncertainties in the so derived formation data. This is the main reason for including a table for reaction data (Table III.2), where the selected uncertainties are directly based on the experimental accuracies.

The species and reactions in Tables III.1, III.2 and III.3 appear in standard order of arrangement (*cf*. Fig. II.1).

The selected thermal functions of the heat capacities, listed in Table III.3, refer to the relation

$$C^{\circ}_{p,\mathrm{m}}(T) \quad = \quad a + b \times T + c \times T^2 + d \times T^{-1} + e \times T^{-2}. \qquad \text{(III.1)}$$

No references are given in these tables since the selected data are generally not directly attributable to a specific published source. A detailed discussion of the selection procedure is presented in Chapter V.

A warning: The addition of any other aqueous species to this internally consistent data base can result in a modified data set which is no longer rigorous and can lead to erroneous results. The situation is similar, to a lesser degree, with the addition of gases and solids.

It should also be noted that the data set presented in this Chapter may not be “complete” for all the conceivable systems and conditions. Gaps are pointed out in the various sections of Chapter V.

Table III.1: Selected thermodynamic data for technetium compounds and complexes. Selected thermodynamic functions for some Tc species are also given in Appendix B. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter V. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. It should be noted that insufficient auxiliary data are available in a number of cases to derive formation data from the reactions listed in Table III.2. The chemical formulae concerned by this constraint are marked with[(f)]. The data presented in this table are available on PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
Tc(cr)	0.000	0.000	32.500	24.900[(c)(d)]
			±0.700	±1.000
Tc(g)	630.709[(a)]	675.000[(b)]	181.052	20.795[(c)(d)]
	±25.001	±25.000	±0.010	±0.010
Tc(l)				
TcO(g)	357.492[(a)]	390.000	244.109	31.256[(e)]
	±57.001	±57.000	±0.600	±0.750
TcO^{2+}	> −116.801[(b)]			
TcO_2(cr)	−401.852[(a)]	−457.800	50.000	
	±11.762	±11.700	±4.000	
TcO_4^-	−637.408[(a)]	−729.400	199.600	−15.000
	±7.616	±7.600	±1.500	±8.000
TcO_4^{2-}	−575.761[(b)]			
	±8.880			
TcO_4^{3-}	−521.534[(b)]			
	±12.336			
Tc_2O_7(cr)	−950.284[(a)]	−1126.500	192.000	160.400[(c)(e)]
	±15.562	±14.900	±15.000	±15.000
Tc_2O_7(g)	−904.823[(a)]	−1008.100[(b)]	436.641	146.736[(e)]
	±16.462	±16.063	±12.000	±5.000
$TcO(OH)^+$	−345.379[(b)]			
	±9.009			
$TcO(OH)_2$(aq)	−568.249[(b)]			
	±8.845			
$TcO_2 \cdot 1.6H_2O$(s)	−758.481[(b)]			
	±8.372			
$TcO(OH)_3^-$	−743.172[(b)]			
	±9.135			

(Continued on next page)

Table III.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
$Tc_2O_7{\cdot}H_2O$(s)	−1194.300	−1414.146[b]	278.921[a]	
	±15.500	±14.905	±72.138	
TcF_6(cr, cubic)			253.520	157.840[c]
			±0.510	±0.320
TcF_6(g)			359.136	120.703
			±4.500	
TcO_3F(g)			306.879	77.261[c]
			±0.677	±0.308
$TcCl_6^{2-}$[f]				
$TcOCl_5^{2-}$[f]				
$TcO_2Cl_4^{3-}$[f]				
TcO_3Cl(g)			317.636	80.365[c]
			±0.797	±0.308
$TcBr_6^{2-}$				
TcS(g)	491.923[a]	549.000	255.990	34.474
	±65.001	±65.000	±1.000	±1.000
NH_4TcO_4(cr)	−722.000[b]			
	±7.632			
$(NH_4)_2TcCl_6$(cr)[f]				
$(NH_4)_2TcBr_6$(cr)[f]				
TcC(g)	765.600[a]	826.500	242.500	
	±40.250	±40.000	±15.000	
$TcCO_3(OH)_2$(aq)	−968.901[b]			
	±9.010			
$TcCO_3(OH)_3^-$	−1158.664[b]			
	±9.486			
$TlTcO_4$(cr)	−700.174[b]			
	±7.653			
$AgTcO_4$(cr)	−578.977[b]			
	±7.654			
$NaTcO_4{\cdot}4H_2O$(s)	−1843.412[b]			
	±7.622			
$KTcO_4$(cr)	−932.923[a]	−1035.100	164.780	123.300
	±7.604	±7.600	±0.330	±0.250
K_2TcCl_6(cr)[f]				
K_2TcBr_6(cr)[f]				

(Continued on next page)

Table III.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
Rb_2TcCl_6(cr)[f]				
Rb_2TcBr_6(cr)[f]				
$CsTcO_4$(cr)	−949.698[b] ±7.671			
Cs_2TcCl_6(cr)[f]				
Cs_2TcBr_6(cr)[f]				

[a] Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_f G^\circ_m = \Delta_f H^\circ_m - T \sum_i S^\circ_{m,i}$.
[b] Value calculated internally from reaction data (see Table III.2).
[c] Temperature coefficients of this function are listed in Table III.3.
[d] For this substance heat capacity values are given in Section V.1.
[e] For this compound heat capacity values are given in Section V.3.
[f] Only reaction data are selected for this compound, *cf.* Table III.2.

Table III.2: Selected thermodynamic data for reactions involving technetium compounds and complexes. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principal to the statistically defined 95% confidence interval. Values obtained from internal calculation, *cf.* footnote (a), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter V. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
Tc(g)	$Tc(cr) \rightleftharpoons Tc(g)$				
				675.000	
				±25.000	
TcO^{2+}	$2H^+ + TcO(OH)_2(aq) \rightleftharpoons 2H_2O(l) + TcO^{2+}$				
		< 4.000	−22.832		
TcO_4^{2-}	$TcO_4^- + e^- \rightleftharpoons TcO_4^{2-}$				
		−10.800[b]	61.647		
		±0.800	±4.566		
TcO_4^{3-}	$TcO_4^- + 2e^- \rightleftharpoons TcO_4^{3-}$				
		−20.300[b]	115.873		
		±1.700	±9.704		
$Tc_2O_7(g)$	$Tc_2O_7(cr) \rightleftharpoons Tc_2O_7(g)$				
				118.400	
				±6.000	
$TcO(OH)^+$	$H^+ + TcO(OH)_2(aq) \rightleftharpoons H_2O(l) + TcO(OH)^+$				
		2.500	−14.270		
		±0.300	±1.712		
$TcO(OH)_2(aq)$	$TcO_2{\cdot}1.6H_2O(s) \rightleftharpoons 0.60H_2O(l) + TcO(OH)_2(aq)$				
		−8.400	47.948		
		±0.500	±2.854		
$TcO_2{\cdot}1.6H_2O(s)$	$4H^+ + TcO_4^- + 3e^- \rightleftharpoons 0.40H_2O(l) + TcO_2{\cdot}1.6H_2O(s)$				
		37.829[b]	−215.930		
		±0.609	±3.476		
$TcO(OH)_3^-$	$H_2O(l) + TcO(OH)_2(aq) \rightleftharpoons H^+ + TcO(OH)_3^-$				
		−10.900	62.218		
		±0.400	±2.283		
$Tc_2O_7{\cdot}H_2O(s)$	$H_2O(g) + Tc_2O_7(cr) \rightleftharpoons Tc_2O_7{\cdot}H_2O(s)$				
				−45.820	
				±0.400	

(Continued on next page)

Table III.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
TcF_6(g)	TcF_6(cr, cubic) $\rightleftharpoons$ TcF_6(g)				
		$-0.535^{(c)}$	$3.055^{(a)}$	34.540	105.600
		±0.327	±1.868	±1.300	±4.500
$TcO_2Cl_4^{3-}$	$H_2O(l) + TcOCl_5^{2-} \rightleftharpoons Cl^- + 2H^+ + TcO_2Cl_4^{3-}$				
		−2.950	16.839		
		±0.150	±0.856		
NH_4TcO_4(cr)	$NH_4^+ + TcO_4^- \rightleftharpoons NH_4TcO_4$(cr)				
		0.910	−5.194		
		±0.070	±0.400		
$(NH_4)_2TcCl_6$(cr)	$2NH_4^+ + TcCl_6^{2-} \rightleftharpoons (NH_4)_2TcCl_6$(cr)				
		7.988	−45.596		
		±1.000	±5.708		
$(NH_4)_2TcBr_6$(cr)	$2NH_4^+ + TcBr_6^{2-} \rightleftharpoons (NH_4)_2TcBr_6$(cr)				
		6.680	−38.130		
		±1.000	±5.708		
$TcCO_3(OH)_2$(aq)	CO_2(g) + $TcO(OH)_2$(aq) $\rightleftharpoons$ $TcCO_3(OH)_2$(aq)				
		1.100	−6.279		
		±0.300	±1.712		
$TcCO_3(OH)_3^-$	$CO_2(g) + H_2O(l) + TcO(OH)_2(aq) \rightleftharpoons H^+ + TcCO_3(OH)_3^-$				
		−7.200	41.098		
		±0.600	±3.425		
$TlTcO_4$(cr)	$TcO_4^- + Tl^+ \rightleftharpoons TlTcO_4$(cr)				
		5.320	−30.367		
		±0.120	±0.685		
$AgTcO_4$(cr)	$Ag^+ + TcO_4^- \rightleftharpoons AgTcO_4$(cr)				
		3.270	−18.665		
		±0.130	±0.742		
$NaTcO_4{\cdot}4H_2O$(s)	$4H_2O(l) + Na^+ + TcO_4^- \rightleftharpoons NaTcO_4{\cdot}4H_2O$(s)				
		−0.790	4.509		
		±0.040	±0.228		
K_2TcCl_6(cr)	$2K^+ + TcCl_6^{2-} \rightleftharpoons K_2TcCl_6$(cr)				
		9.610	−54.854		
		±1.000	±5.708		
K_2TcBr_6(cr)	$2K^+ + TcBr_6^{2-} \rightleftharpoons K_2TcBr_6$(cr)				
		6.920	−39.500		
		±1.000	±5.708		
Rb_2TcCl_6(cr)	$2Rb^+ + TcCl_6^{2-} \rightleftharpoons Rb_2TcCl_6$(cr)				
		11.120	−63.473		
		±1.000	±5.708		
Rb_2TcBr_6(cr)	$2Rb^+ + TcBr_6^{2-} \rightleftharpoons Rb_2TcBr_6$(cr)				
		9.470	−54.055		
		±1.000	±5.708		

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Table III.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
$CsTcO_4$(cr)	$Cs^+ + TcO_4^- \rightleftharpoons CsTcO_4$(cr)				
		3.650	−20.834		
		±0.130	±0.742		
Cs_2TcCl_6(cr)	$2Cs^+ + TcCl_6^{2-} \rightleftharpoons Cs_2TcCl_6$(cr)				
		11.430	−65.243		
		±1.000	±5.708		
Cs_2TcBr_6(cr)	$2Cs^+ + TcBr_6^{2-} \rightleftharpoons Cs_2TcBr_6$(cr)				
		11.240	−64.158		
		±1.000	±5.708		

[a] Value calculated internally with the Gibbs-Helmholtz equation, $\Delta_r G^\circ_m = \Delta_r H^\circ_m - T\Delta_r S^\circ_m$.

[b] Value calculated from a selected standard potential.

[c] Value of $\log_{10} K^\circ$ calculated internally from $\Delta_r G^\circ_m$.

Table III.3: Selected temperature coefficients for heat capacities marked with [c] in Table III.1, according to the form $C^{\circ}_{p,\mathrm{m}}(T) = a + b\,T + c\,T^2 + e\,T^{-2}$. The functions are valid between the temperatures $T_{\min}$ and $T_{\max}$ (in K). Units are $\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

Compound	a	b	c	e	$T_{\min}$	$T_{\max}$
Tc(cr)	$2.5094{\cdot}10^{1}$	$4.3145{\cdot}10^{-3}$	$-2.7546{\cdot}10^{-7}$	$-1.3130{\cdot}10^{5}$	298	2430
Tc(g)	$2.49130{\cdot}10^{1}$	$-1.91834{\cdot}10^{-2}$	$2.512827{\cdot}10^{-5}$	$-5.61800{\cdot}10^{4}$	298	600
Tc_2O_7(cr)	$1.55{\cdot}10^{2}$	$8.6{\cdot}10^{-2}$		$-1.8{\cdot}10^{6}$	298	392
TcF_6(cr, cubic)	$7.2081{\cdot}10^{1}$	$2.87666{\cdot}10^{-1}$			268	311
TcO_3F(g)	$7.6120{\cdot}10^{1}$	$5.34274{\cdot}10^{-2}$	$-2.533931{\cdot}10^{-5}$	$-1.11446{\cdot}10^{6}$	298	1000
TcO_3Cl(g)	$8.0336{\cdot}10^{1}$	$4.63950{\cdot}10^{-2}$	$-2.200856{\cdot}10^{-5}$	$-1.05321{\cdot}10^{6}$	298	1000

Chapter IV

Selected auxiliary data

This chapter presents the chemical thermodynamic data for auxiliary compounds and complexes which are used within the NEA's TDB project. Auxiliary data used in the evaluation of the recommended technetium data in Table III.1 and III.2 are taken from Table IV.1 and IV.2. It is therefore essential to always use these auxiliary data in conjunction with the selected technetium data. The use of other auxiliary data can lead to inconsistencies and erroneous results.

The values in the Tables of this Chapter are either CODATA Key Values, taken from Ref. [89COX/WAG], or were evaluated within the NEA's TDB project, as described in Chapter VI of the uranium review [92GRE/FUG].

Table IV.1 contains the selected thermodynamic data of the auxiliary species and Table IV.2 the selected thermodynamic data of chemical reactions involving auxiliary species. The reason for listing both reaction data and entropies, enthalpies and Gibbs energies of formation is, as described in Chapter III, that uncertainties in reaction data are often smaller than the derived S°_m , $\Delta_f H^\circ_m$ and $\Delta_f G^\circ_m$, due to uncertainty accumulation during the calculations.

All data in Tables IV.1 and IV.2 refer to a temperature of 298.15 K, the standard state pressure of 0.1 MPa and, for aqueous species and reactions, to the infinite dilution reference state ($I = 0$).

The uncertainties listed below each reaction value in Table IV.2 are total uncertainties, and correspond mainly to the statistically defined 95% confidence interval. The uncertainties listed below each value in Table IV.1 have the following significance:

- for CODATA values from [89COX/WAG], the $\pm$ terms have the meaning: "it is probable, but not at all certain, that the true values of the thermodynamic quantities differ from the recommended values given in this report by no more than twice the $\pm$ terms attached to the recommended values".

- for values from [92GRE/FUG], the $\pm$ terms are derived from total uncertainties in the corresponding equilibrium constant of reaction (*cf.* Table IV.2), and from the $\pm$ terms listed for the necessary CODATA key values.

CODATA [89COX/WAG] values are available for CO_2(g), HCO_3^-, CO_3^{2-}, $H_2PO_4^-$ and HPO_4^{2-}. From the values given for $\Delta_f H^\circ_m$ and S°_m the values of $\Delta_f G^\circ_m$ and, consequently, all the relevant equilibrium constants and enthalpy changes can be calculated. The propagation of errors during this procedure, however, leads to uncertainties in the resulting equilibrium constants that are significantly higher than those obtained from experimental determination of the constants. Therefore, reaction data for CO_2(g),

HCO_3^-, CO_3^{2-} and $H_2PO_4^-$, which were absent from the corresponding Table IV.2 in [92GRE/FUG], are included in this volume to provide the user of selected data for technetium species (*cf.* Chapter III) with the data needed to obtain the lowest possible uncertainties on reaction properties.

Note that the values in Tables IV.1 and IV.2 may contain more digits than those listed in either [89COX/WAG] or in Chapter VI of [92GRE/FUG], because the data in the present chapter are retrieved directly from the computerised data base and rounded to three digits after the decimal point throughout.

Table IV.1: Selected thermodynamic data for auxiliary compounds and complexes, including the CODATA Key Values [89COX/WAG] of species not containing uranium, as well as other data that were evaluated in Chapter VI of the uranium review [92GRE/FUG]. All ionic species listed in this table are aqueous species. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a reference state or standard state of infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Values in **bold** typeface are CODATA Key Values and are taken directly from Ref. [89COX/WAG] without further evaluation. Values obtained from internal calculation, *cf.* footnotes (a) and (b), are rounded at the third digit after the decimal point and may therefore not be exactly identical to those given in Chapter VI of Ref. [92GRE/FUG]. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
O(g)	**231.743**[(a)]	**249.180**	**161.059**	**21.912**
	±0.100	**±0.100**	**±0.003**	**±0.001**
O_2(g)	**0.000**	**0.000**	**205.152**	**29.378**
			±0.005	**±0.003**
H(g)	**203.276**[(a)]	**217.998**	**114.717**	**20.786**
	±0.006	**±0.006**	**±0.002**	**±0.001**
H^+	**0.000**	**0.000**	**0.000**	**0.000**
H_2(g)	**0.000**	**0.000**	**130.680**	**28.836**
			±0.003	**±0.002**
OH^-	**−157.220**[(a)]	**−230.015**	**−10.900**	
	±0.072	**±0.040**	**±0.200**	
H_2O(g)	**−228.582**[(a)]	**−241.826**	**188.835**	**33.609**
	±0.040	**±0.040**	**±0.010**	**±0.030**
H_2O(l)	**−237.140**[(a)]	**−285.830**	**69.950**	**75.351**
	±0.041	**±0.040**	**±0.030**	**±0.080**
H_2O_2(aq)		−191.170[(c)]		
		±0.100		
He(g)	**0.000**	**0.000**	**126.153**	**20.786**
			±0.002	**±0.001**
Ne(g)	**0.000**	**0.000**	**146.328**	**20.786**
			±0.003	**±0.001**
Ar(g)	**0.000**	**0.000**	**154.846**	**20.786**
			±0.003	**±0.001**
Kr(g)	**0.000**	**0.000**	**164.085**	**20.786**
			±0.003	**±0.001**
Xe(g)	**0.000**	**0.000**	**169.685**	**20.786**
			±0.003	**±0.001**

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
F(g)	**62.280**[a]	**79.380**	**158.751**	**22.746**
	±0.300	**±0.300**	**±0.004**	**±0.002**
F^-	**−281.523**[a]	**−335.350**	**−13.800**	
	±0.692	**±0.650**	**±0.800**	
F_2(g)	**0.000**	**0.000**	**202.791**	**31.304**
			±0.005	**±0.002**
HF(aq)	−299.675[b]	−323.150[b]	88.000[a]	
	±0.702	±0.716	±3.362	
HF(g)	**−275.400**[a]	**−273.300**	**173.779**	**29.137**
	±0.700	**±0.700**	**±0.003**	**±0.002**
HF_2^-	−583.709[b]	−655.500[b]	92.683[a]	
	±1.200	±2.221	±8.469	
Cl(g)	**105.305**[a]	**121.301**	**165.190**	**21.838**
	±0.008	**±0.008**	**±0.004**	**±0.001**
Cl^-	**−131.217**[a]	**−167.080**	**56.600**	
	±0.117	**±0.100**	**±0.200**	
Cl_2(g)	**0.000**	**0.000**	**223.081**	**33.949**
			±0.010	**±0.002**
ClO^-	−37.669			
	±0.962			
ClO_2^-	10.250			
	±4.044			
ClO_3^-	−7.903[a]	−104.000	162.300	
	±1.342	±1.000	±3.000	
ClO_4^-	**−7.890**[a]	**−128.100**	**184.000**	
	±0.600	**±0.400**	**±1.500**	
HCl(g)	**−95.298**[a]	**−92.310**	**186.902**	**29.136**
	±0.100	**±0.100**	**±0.005**	**±0.002**
HClO(aq)	−80.023[b]			
	±0.613			
$HClO_2$(aq)	−0.938[b]			
	±4.043			
Br(g)	**82.379**[a]	**111.870**	**175.018**	**20.786**
	±0.128	**±0.120**	**±0.004**	**±0.001**
Br^-	**−103.850**[a]	**−121.410**	**82.550**	
	±0.167	**±0.150**	**±0.200**	
Br_2(aq)	4.900			
	±1.000			
Br_2(g)	**3.105**[a]	**30.910**	**245.468**	**36.057**
	±0.142	**±0.110**	**±0.005**	**±0.002**
Br_2(l)	**0.000**	**0.000**	**152.210**	
			±0.300	
BrO^-	−32.095[b]			
	±1.537			

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
BrO_3^-	19.070[(a)]	−66.700	161.500	
	±0.634	±0.500	±1.300	
HBr(g)	**−53.361**[(a)]	**−36.290**	**198.700**	**29.141**
	±0.166	**±0.160**	**±0.004**	**±0.003**
HBrO(aq)	−81.356[(b)]			
	±1.527			
I(g)	**70.172**[(a)]	**106.760**	**180.787**	**20.786**
	±0.060	**±0.040**	**±0.004**	**±0.001**
I^-	**−51.724**[(a)]	**−56.780**	**106.450**	
	±0.112	**±0.050**	**±0.300**	
I_2(cr)	**0.000**	**0.000**	**116.140**	
			±0.300	
I_2(g)	**19.323**[(a)]	**62.420**	**260.687**	**36.888**
	±0.120	**±0.080**	**±0.005**	**±0.002**
IO_3^-	−126.338[(a)]	−219.700	118.000	
	±0.779	±0.500	±2.000	
HI(g)	**1.700**[(a)]	**26.500**	**206.590**	**29.157**
	±0.110	**±0.100**	**±0.004**	**±0.003**
HIO_3(aq)	−130.836[(b)]			
	±0.797			
S(cr)	**0.000**	**0.000**	**32.054**	**22.750**
			±0.050	**±0.050**
S(g)	**236.689**[(a)]	**277.170**	**167.829**	**23.674**
	±0.151	**±0.150**	**±0.006**	**±0.001**
S^{2-}	120.695[(b)]			
	±11.610			
S_2(g)	**79.686**[(a)]	**128.600**	**228.167**	**32.505**
	±0.301	**±0.300**	**±0.010**	**±0.010**
SO_2(g)	**−300.095**[(a)]	**−296.810**	**248.223**	**39.842**
	±0.201	**±0.200**	**±0.050**	**±0.020**
SO_3^{2-}	−487.472[(b)]			
	±4.020			
$S_2O_3^{2-}$	−519.291[(b)]			
	±11.345			
SO_4^{2-}	**−744.004**[(a)]	**−909.340**	**18.500**	
	±0.418	**±0.400**	**±0.400**	
HS^-	**12.243**[(a)]	**−16.300**	**67.000**	
	±2.115	**±1.500**	**±5.000**	
H_2S(aq)	**−27.648**[(a)]	**−38.600**	**126.000**	
	±2.115	**±1.500**	**±5.000**	
H_2S(g)	**−33.443**[(a)]	**−20.600**	**205.810**	**34.248**
	±0.500	**±0.500**	**±0.050**	**±0.010**
HSO_3^-	−528.684[(b)]			
	±4.046			

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
$HS_2O_3^-$	−528.366[b]			
	±11.377			
H_2SO_3(aq)	−539.187[b]			
	±4.072			
HSO_4^-	**−755.315[a]**	**−886.900**	**131.700**	
	±1.342	**±1.000**	**±3.000**	
Se(cr)	0.000	0.000	42.270	25.030
			±0.050	±0.050
SeO_2(cr)		−225.100		
		±2.100		
SeO_3^{2-}	−361.597[b]			
	±1.473			
$HSeO_3^-$	−409.544[b]			
	±1.358			
H_2SeO_3(aq)	−425.527[b]			
	±0.736			
Te(cr)	0.000	0.000	49.221	25.550
			±0.050	±0.100
N(g)	**455.537[a]**	**472.680**	**153.301**	**20.786**
	±0.400	**±0.400**	**±0.003**	**±0.001**
N_2(g)	**0.000**	**0.000**	**191.609**	**29.124**
			±0.004	**±0.001**
N_3^-	348.200	275.140	107.710[a]	
	±2.000	±1.000	±7.500	
NO_3^-	**−110.794[a]**	**−206.850**	**146.700**	
	±0.417	**±0.400**	**±0.400**	
HN_3(aq)	321.372[b]	260.140[b]	147.381[b]	
	±2.051	±10.050	±34.403	
NH_3(aq)	−26.673[b]	−81.170[b]	109.040[b]	
	±0.305	±0.326	±0.913	
NH_3(g)	**−16.407[a]**	**−45.940**	**192.770**	**35.630**
	±0.350	**±0.350**	**±0.050**	**±0.005**
NH_4^+	**−79.398[a]**	**−133.260**	**111.170**	
	±0.278	**±0.250**	**±0.400**	
P(am)		−7.500		
		±2.000		
P(cr)	**0.000**	**0.000**	**41.090**	**23.824**
			±0.250	**±0.200**
P(g)	**280.093[a]**	**316.500**	**163.199**	**20.786**
	±1.003	**±1.000**	**±0.003**	**±0.001**
P_2(g)	**103.469[a]**	**144.000**	**218.123**	**32.032**
	±2.006	**±2.000**	**±0.004**	**±0.002**
P_4(g)	**24.419[a]**	**58.900**	**280.010**	**67.081**
	±0.448	**±0.300**	**±0.500**	**±1.500**

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
PO_4^{3-}	−1025.491[b]	−1284.400[b]	−220.970[b]	
	±1.576	±4.085	±12.846	
$P_2O_7^{4-}$	−1935.503[b]			
	±4.563			
HPO_4^{2-}	**−1095.985[a]**	**−1299.000**	**−33.500**	
	±1.567	**±1.500**	**±1.500**	
$H_2PO_4^-$	**−1137.152[a]**	**−1302.600**	**92.500**	
	±1.567	**±1.500**	**±1.500**	
H_3PO_4(aq)	−1149.367[b]	−1294.120[b]	161.912[b]	
	±1.576	±1.616	±2.575	
$HP_2O_7^{3-}$	−1989.158[b]			
	±4.482			
$H_2P_2O_7^{2-}$	−2027.117[b]			
	±4.445			
$H_3P_2O_7^-$	−2039.960[b]			
	±4.362			
$H_4P_2O_7$(aq)	−2045.668[b]	−2280.210[b]	274.919[b]	
	±3.299	±3.383	±6.954	
As(cr)	0.000	0.000	35.100	24.640
			±0.600	±0.500
AsO_2^-	−350.022[a]	−429.030	40.600	
	±4.008	±4.000	±0.600	
AsO_4^{3-}	−648.360[a]	−888.140	−162.800	
	±4.008	±4.000	±0.600	
As_2O_5(cr)	−782.449[a]	−924.870	105.400	116.520
	±8.016	±8.000	±1.200	±0.800
As_4O_6(cubi)	−1152.445[a]	−1313.940	214.200	191.290
	±16.032	±16.000	±2.400	±0.800
As_4O_6(mono)	−1154.008[a]	−1309.600	234.000	
	±16.041	±16.000	±3.000	
$HAsO_2$(aq)	−402.925[a]	−456.500	125.900	
	±4.008	±4.000	±0.600	
$H_2AsO_3^-$	−587.078[a]	−714.790	110.500	
	±4.008	±4.000	±0.600	
H_3AsO_3(aq)	−639.681[a]	−742.200	195.000	
	±4.015	±4.000	±1.000	
$HAsO_4^{2-}$	−714.592[a]	−906.340	−1.700	
	±4.008	±4.000	±0.600	
$H_2AsO_4^-$	−753.203[a]	−909.560	117.000	
	±4.015	±4.000	±1.000	
H_3AsO_4(aq)	−766.119[a]	−902.500	184.000	
	±4.015	±4.000	±1.000	
$(As_2O_5)_3{\cdot}5H_2O$(cr)		−4248.400		
		±24.000		

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
Sb(cr)	0.000	0.000	45.520	25.260
			±0.210	±0.200
C(cr)	**0.000**	**0.000**	**5.740**	**8.517**
			±0.100	**±0.080**
C(g)	**671.254**[a]	**716.680**	**158.100**	**20.839**
	±0.451	**±0.450**	**±0.003**	**±0.001**
CO(g)	**−137.168**[a]	**−110.530**	**197.660**	**29.141**
	±0.173	**±0.170**	**±0.004**	**±0.002**
CO_2(aq)	**−385.970**[a]	**−413.260**	**119.360**	
	±0.270	**±0.200**	**±0.600**	
CO_2(g)	**−394.373**[a]	**−393.510**	**213.785**	**37.135**
	±0.133	**±0.130**	**±0.010**	**±0.002**
CO_3^{2-}	**−527.900**[a]	**−675.230**	**−50.000**	
	±0.390	**±0.250**	**±1.000**	
HCO_3^-	**−586.845**[a]	**−689.930**	**98.400**	
	±0.251	**±0.200**	**±0.500**	
SCN^-	92.700	76.400	144.268[a]	
	±4.000	±4.000	±18.974	
Si(cr)	**0.000**	**0.000**	**18.810**	**19.789**
			±0.080	**±0.030**
Si(g)	**405.525**[a]	**450.000**	**167.981**	**22.251**
	±8.000	**±8.000**	**±0.004**	**±0.001**
SiO_2(quar)	**−856.287**[a]	**−910.700**	**41.460**	**44.602**
	±1.002	**±1.000**	**±0.200**	**±0.300**
$SiO_2(OH)_2^{2-}$	−1175.651[b]	−1381.960[b]	−1.488[b]	
	±1.265	±15.330	±51.592	
$SiO(OH)_3^-$	−1251.740[b]	−1431.360[b]	88.024[b]	
	±1.162	±3.743	±13.144	
$Si(OH)_4$(aq)	−1307.735[b]	−1456.960[b]	189.973[a]	
	±1.156	±3.163	±11.296	
$Si_2O_3(OH)_4^{2-}$	−2269.878[b]			
	±2.878			
$Si_2O_2(OH)_5^-$	−2332.096[b]			
	±2.878			
$Si_3O_6(OH)_3^{3-}$	−3048.536[b]			
	±3.870			
$Si_3O_5(OH)_5^{3-}$	−3291.955[b]			
	±3.869			
$Si_4O_8(OH)_4^{4-}$	−4075.179[b]			
	±5.437			
$Si_4O_7(OH)_5^{3-}$	−4136.826[b]			
	±4.934			
SiF_4(g)	**−1572.772**[a]	**−1615.000**	**282.760**	**73.622**
	±0.814	**±0.800**	**±0.500**	**±0.500**

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Ge(cr)	**0.000**	**0.000**	**31.090**	**23.222**
			±0.150	**±0.100**
Ge(g)	**331.209**[a]	**372.000**	**167.904**	**30.733**
	±3.000	**±3.000**	**±0.005**	**±0.001**
GeO_2(tetr)	**−521.404**[a]	**−580.000**	**39.710**	**50.166**
	±1.002	**±1.000**	**±0.150**	**±0.300**
GeF_4(g)	**−1150.018**[a]	**−1190.200**	**301.900**	**81.602**
	±0.584	**±0.500**	**±1.000**	**±1.000**
Sn(cr)	**0.000**	**0.000**	**51.180**	**27.112**
			±0.080	**±0.030**
Sn(g)	**266.223**[a]	**301.200**	**168.492**	**21.259**
	±1.500	**±1.500**	**±0.004**	**±0.001**
Sn^{2+}	**−27.624**[a]	**−8.900**	**−16.700**	
	±1.557	**±1.000**	**±4.000**	
SnO(tetr)	**−251.913**[a]	**−280.710**	**57.170**	**47.783**
	±0.220	**±0.200**	**±0.300**	**±0.300**
SnO_2(cass)	**−515.826**[a]	**−577.630**	**49.040**	**53.219**
	±0.204	**±0.200**	**±0.100**	**±0.200**
Pb(cr)	**0.000**	**0.000**	**64.800**	**26.650**
			±0.300	**±0.100**
Pb(g)	**162.232**[a]	**195.200**	**175.375**	**20.786**
	±0.805	**±0.800**	**±0.005**	**±0.001**
Pb^{2+}	**−24.238**[a]	**0.920**	**18.500**	
	±0.399	**±0.250**	**±1.000**	
$PbSO_4$(cr)	**−813.036**[a]	**−919.970**	**148.500**	
	±0.447	**±0.400**	**±0.600**	
B(cr)	**0.000**	**0.000**	**5.900**	**11.087**
			±0.080	**±0.100**
B(g)	**521.012**[a]	**565.000**	**153.436**	**20.796**
	±5.000	**±5.000**	**±0.015**	**±0.005**
B_2O_3(cr)	**−1194.324**[a]	**−1273.500**	**53.970**	**62.761**
	±1.404	**±1.400**	**±0.300**	**±0.300**
$B(OH)_3$(aq)	**−969.268**[a]	**−1072.800**	**162.400**	
	±0.820	**±0.800**	**±0.600**	
$B(OH)_3$(cr)	**−969.667**[a]	**−1094.800**	**89.950**	**86.060**
	±0.820	**±0.800**	**±0.600**	**±0.400**
BF_3(g)	**−1119.403**[a]	**−1136.000**	**254.420**	**50.463**
	±0.803	**±0.800**	**±0.200**	**±0.100**
Al(cr)	**0.000**	**0.000**	**28.300**	**24.200**
			±0.100	**±0.070**
Al(g)	**289.376**[a]	**330.000**	**164.554**	**21.391**
	±4.000	**±4.000**	**±0.004**	**±0.001**
Al^{3+}	**−491.507**[a]	**−538.400**	**−325.000**	
	±3.338	**±1.500**	**±10.000**	

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
Al_2O_3(coru)	**−1582.257**[a]	**−1675.700**	**50.920**	**79.033**
	±1.302	**±1.300**	**±0.100**	**±0.200**
AlF_3(cr)	**−1431.096**[a]	**−1510.400**	**66.500**	**75.122**
	±1.309	**±1.300**	**±0.500**	**±0.400**
Tl^+	−32.400			
	±0.300			
Zn(cr)	**0.000**	**0.000**	**41.630**	**25.390**
			±0.150	**±0.040**
Zn(g)	**94.813**[a]	**130.400**	**160.990**	**20.786**
	±0.402	**±0.400**	**±0.004**	**±0.001**
Zn^{2+}	**−147.203**[a]	**−153.390**	**−109.800**	
	±0.254	**±0.200**	**±0.500**	
ZnO(cr)	**−320.479**[a]	**−350.460**	**43.650**	
	±0.299	**±0.270**	**±0.400**	
Cd(cr)	**0.000**	**0.000**	**51.800**	**26.020**
			±0.150	**±0.040**
Cd(g)	**77.230**[a]	**111.800**	**167.749**	**20.786**
	±0.205	**±0.200**	**±0.004**	**±0.001**
Cd^{2+}	**−77.733**[a]	**−75.920**	**−72.800**	
	±0.750	**±0.600**	**±1.500**	
CdO(cr)	**−228.661**[a]	**−258.350**	**54.800**	
	±0.602	**±0.400**	**±1.500**	
$CdSO_4 \cdot 2.667H_2O$(cr)	**−1464.959**[a]	**−1729.300**	**229.650**	
	±0.810	**±0.800**	**±0.400**	
Hg(g)	**31.842**[a]	**61.380**	**174.971**	**20.786**
	±0.054	**±0.040**	**±0.005**	**±0.001**
Hg(l)	**0.000**	**0.000**	**75.900**	
			±0.120	
Hg^{2+}	**164.667**[a]	**170.210**	**−36.190**	
	±0.313	**±0.200**	**±0.800**	
Hg_2^{2+}	**153.567**[a]	**166.870**	**65.740**	
	±0.559	**±0.500**	**±0.800**	
HgO(mont)	**−58.523**[a]	**−90.790**	**70.250**	
	±0.154	**±0.120**	**±0.300**	
Hg_2Cl_2(cr)	**−210.725**[a]	**−265.370**	**191.600**	
	±0.471	**±0.400**	**±0.800**	
Hg_2SO_4(cr)	**−625.780**[a]	**−743.090**	**200.700**	
	±0.411	**±0.400**	**±0.200**	
Cu(cr)	**0.000**	**0.000**	**33.150**	**24.440**
			±0.080	**±0.050**
Cu(g)	**297.672**[a]	**337.400**	**166.398**	**20.786**
	±1.200	**±1.200**	**±0.004**	**±0.001**
Cu^{2+}	**65.040**[a]	**64.900**	**−98.000**	
	±1.557	**±1.000**	**±4.000**	

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
$CuSO_4$(cr)	**−662.185**[a]	**−771.400**	**109.200**	
	±1.206	**±1.200**	**±0.400**	
Ag(cr)	**0.000**	**0.000**	**42.550**	**25.350**
			±0.200	**±0.100**
Ag(g)	**246.007**[a]	**284.900**	**172.997**	**20.786**
	±0.802	**±0.800**	**±0.004**	**±0.001**
Ag^+	**77.096**[a]	**105.790**	**73.450**	
	±0.156	**±0.080**	**±0.400**	
AgCl(cr)	**−109.765**[a]	**−127.010**	**96.250**	
	±0.098	**±0.050**	**±0.200**	
Ti(cr)	**0.000**	**0.000**	**30.720**	**25.060**
			±0.100	**±0.080**
Ti(g)	**428.403**[a]	**473.000**	**180.298**	**24.430**
	±3.000	**±3.000**	**±0.010**	**±0.030**
TiO_2(ruti)	**−888.767**[a]	**−944.000**	**50.620**	**55.080**
	±0.806	**±0.800**	**±0.300**	**±0.300**
$TiCl_4$(g)	**−726.324**[a]	**−763.200**	**353.200**	**95.408**
	±3.229	**±3.000**	**±4.000**	**±1.000**
Th(cr)	**0.000**	**0.000**	**51.800**	**26.230**
			±0.500	**±0.050**
Th(g)	**560.745**[a]	**602.000**	**190.170**	**20.789**
	±6.002	**±6.000**	**±0.050**	**±0.100**
ThO_2(cr)	**−1169.238**[a]	**−1226.400**	**65.230**	
	±3.504	**±3.500**	**±0.200**	
Be(cr)	**0.000**	**0.000**	**9.500**	**16.443**
			±0.080	**±0.060**
Be(g)	**286.202**[a]	**324.000**	**136.275**	**20.786**
	±5.000	**±5.000**	**±0.003**	**±0.001**
BeO(brom)	**−580.090**[a]	**−609.400**	**13.770**	**25.565**
	±2.500	**±2.500**	**±0.040**	**±0.100**
Mg(cr)	**0.000**	**0.000**	**32.670**	**24.869**
			±0.100	**±0.020**
Mg(g)	**112.521**[a]	**147.100**	**148.648**	**20.786**
	±0.801	**±0.800**	**±0.003**	**±0.001**
Mg^{2+}	**−455.375**[a]	**−467.000**	**−137.000**	
	±1.335	**±0.600**	**±4.000**	
MgO(cr)	**−569.312**[a]	**−601.600**	**26.950**	**37.237**
	±0.305	**±0.300**	**±0.150**	**±0.200**
MgF_2(cr)	**−1071.051**[a]	**−1124.200**	**57.200**	**61.512**
	±1.210	**±1.200**	**±0.500**	**±0.300**
Ca(cr)	**0.000**	**0.000**	**41.590**	**25.929**
			±0.400	**±0.300**
Ca(g)	**144.021**[a]	**177.800**	**154.887**	**20.786**
	±0.809	**±0.800**	**±0.004**	**±0.001**

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_f H^\circ_m$ ($kJ \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)
Ca^{2+}	**−552.806**[a]	**−543.000**	**−56.200**	
	±1.050	**±1.000**	**±1.000**	
CaO(cr)	**−603.296**[a]	**−634.920**	**38.100**	**42.049**
	±0.916	**±0.900**	**±0.400**	**±0.400**
Sr(cr)	0.000	0.000	55.700	
			±0.210	
Sr^{2+}	−563.864[a]	−550.900	−31.500	
	±0.781	±0.500	±2.000	
SrO(cr)	−559.939[a]	−590.600	55.440	
	±0.914	±0.900	±0.500	
$SrCl_2$(cr)	−784.974[a]	−833.850	114.850	
	±0.714	±0.700	±0.420	
$Sr(NO_3)_2$(cr)	−783.146[a]	−982.360	194.600	
	±1.018	±0.800	±2.100	
Ba(cr)	0.000	0.000	62.420	
			±0.840	
Ba^{2+}	−557.656[a]	−534.800	8.400	
	±2.582	±2.500	±2.000	
BaO(cr)	−520.394[a]	−548.100	72.070	
	±2.515	±2.500	±0.380	
$BaCl_2$(cr)	−806.953[a]	−855.200	123.680	
	±2.514	±2.500	±0.250	
Li(cr)	**0.000**	**0.000**	**29.120**	**24.860**
			±0.200	**±0.200**
Li(g)	**126.604**[a]	**159.300**	**138.782**	**20.786**
	±1.002	**±1.000**	**±0.010**	**±0.001**
Li^+	**−292.918**[a]	**−278.470**	**12.240**	
	±0.109	**±0.080**	**±0.150**	
Na(cr)	**0.000**	**0.000**	**51.300**	**28.230**
			±0.200	**±0.200**
Na(g)	**76.964**[a]	**107.500**	**153.718**	**20.786**
	±0.703	**±0.700**	**±0.003**	**±0.001**
Na^+	**−261.953**[a]	**−240.340**	**58.450**	
	±0.096	**±0.060**	**±0.150**	
K(cr)	**0.000**	**0.000**	**64.680**	**29.600**
			±0.200	**±0.100**
K(g)	**60.479**[a]	**89.000**	**160.341**	**20.786**
	±0.802	**±0.800**	**±0.003**	**±0.001**
K^+	**−282.510**[a]	**−252.140**	**101.200**	
	±0.116	**±0.080**	**±0.200**	
Rb(cr)	**0.000**	**0.000**	**76.780**	**31.060**
			±0.300	**±0.100**
Rb(g)	**53.078**[a]	**80.900**	**170.094**	**20.786**
	±0.805	**±0.800**	**±0.003**	**±0.001**

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Table IV.1: (continued)

Compound	$\Delta_f G^\circ_m$ (kJ · mol^{-1})	$\Delta_f H^\circ_m$ (kJ · mol^{-1})	S°_m (J · K^{-1} · mol^{-1})	$C^\circ_{p,m}$ (J · K^{-1} · mol^{-1})
Rb^+	**−284.009**[a]	**−251.120**	**121.750**	
	±0.153	**±0.100**	**±0.250**	
Cs(cr)	**0.000**	**0.000**	**85.230**	**32.210**
			±0.400	**±0.200**
Cs(g)	**49.556**[a]	**76.500**	**175.601**	**20.786**
	±1.007	**±1.000**	**±0.003**	**±0.001**
Cs^+	**−291.456**[a]	**−258.000**	**132.100**	
	±0.535	**±0.500**	**±0.500**	

[a] Value calculated internally with the equation $\Delta_f G^\circ_m = \Delta_f H^\circ_m - T\,\Delta_f S^\circ_m$.
[b] Value calculated internally from reaction data (see Table IV.2).
[c] From [82WAG/EVA], uncertainty estimated in the uranium review [92GRE/FUG].
[d] Orthorhombic.
[e] P(cr) refers to white, crystalline (cubic) phosphorus and is the reference state for the element phosphorus. P(am) refers to red, amorphous phosphorus.
[f] Cubic.
[g] Monoclinic.
[h] α-Quartz.
[i] Tetragonal.
[j] Cassiterite, tetragonal.
[k] Corundum.
[l] Montroydite, red.
[m] Rutile.
[n] Bromellite.

Table IV.2: Selected thermodynamic data for reactions involving auxiliary compounds and complexes used in the evaluation of thermodynamic data for the NEA TDB Project data. All ionic species listed in this table are aqueous species. The selection of these data is described in Chapter VI of the uranium review [92GRE/FUG]. Unless noted otherwise, all data refer to 298.15 K and a pressure of 0.1 MPa and, for aqueous species, a reference state or standard state of infinite dilution ($I = 0$). The uncertainties listed below each value represent total uncertainties and correspond in principle to the statistically defined 95% confidence interval. Systematically, all the values are presented with three digits after the decimal point, regardless of the significance of these digits. The data presented in this table are available on PC diskettes or other computer media from the OECD Nuclear Energy Agency.

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
HF(aq)	$F^- + H^+ \rightleftharpoons HF(aq)$				
		3.180	−18.152	12.200	101.800[a]
		±0.020	±0.114	±0.300	±1.077
HF_2^-	$F^- + HF(aq) \rightleftharpoons HF_2^-$				
		0.440	−2.512	3.000	18.486[a]
		±0.120	±0.685	±2.000	±7.091
ClO^-	$HClO(aq) \rightleftharpoons ClO^- + H^+$				
		−7.420	42.354	19.000	−78.329[a]
		±0.130	±0.742	±9.000	±30.289
ClO_2^-	$HClO_2(aq) \rightleftharpoons ClO_2^- + H^+$				
		−1.960	11.188		
		±0.020	±0.114		
HClO(aq)	$Cl_2(g) + H_2O(l) \rightleftharpoons Cl^- + H^+ + HClO(aq)$				
		−4.537[c]	25.900		
		±0.105	±0.600		
$HClO_2(aq)$	$H_2O(l) + HClO(aq) \rightleftharpoons 2H^+ + HClO_2(aq) + 2e^-$				
		−55.400[b]	316.226		
		±0.700	±3.996		
BrO^-	$HBrO(aq) \rightleftharpoons BrO^- + H^+$				
		−8.630	49.260	30.000	−64.600[a]
		±0.030	±0.171	±3.000	±10.078
HBrO(aq)	$Br_2(aq) + H_2O(l) \rightleftharpoons Br^- + H^+ + HBrO(aq)$				
		−8.240	47.034		
		±0.200	±1.142		
$HIO_3(aq)$	$H^+ + IO_3^- \rightleftharpoons HIO_3(aq)$				
		0.788	−4.498		
		±0.029	±0.166		
S^{2-}	$HS^- \rightleftharpoons H^+ + S^{2-}$				
		−19.000	108.453		
		±2.000	±11.416		

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Table IV.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
SO_3^{2-}	$H_2O(l) + SO_4^{2-} + 2e^- \rightleftharpoons 2OH^- + SO_3^{2-}$				
		-31.400[b]	179.233		
		± 0.700	± 3.996		
$S_2O_3^{2-}$	$3H_2O(l) + 2SO_3^{2-} + 4e^- \rightleftharpoons 6OH^- + S_2O_3^{2-}$				
		-39.200[b]	223.755		
		± 1.400	± 7.991		
$H_2S(aq)$	$H_2S(aq) \rightleftharpoons H^+ + HS^-$				
		-6.990	39.899		
		± 0.170	± 0.970		
HSO_3^-	$H^+ + SO_3^{2-} \rightleftharpoons HSO_3^-$				
		7.220	-41.212	66.000	359.591[a]
		± 0.080	± 0.457	± 30.000	± 100.632
$HS_2O_3^-$	$H^+ + S_2O_3^{2-} \rightleftharpoons HS_2O_3^-$				
		1.590	-9.076		
		± 0.150	± 0.856		
$H_2SO_3(aq)$	$H^+ + HSO_3^- \rightleftharpoons H_2SO_3(aq)$				
		1.840	-10.503	16.000	88.891[a]
		± 0.080	± 0.457	± 5.000	± 16.840
HSO_4^-	$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^-$				
		1.980	-11.302		
		± 0.050	± 0.285		
SeO_3^{2-}	$HSeO_3^- \rightleftharpoons H^+ + SeO_3^{2-}$				
		-8.400	47.948	-5.020	-177.654[a]
		± 0.100	± 0.571	± 0.500	± 2.545
$H_2Se(aq)$	$H^+ + HSe^- \rightleftharpoons H_2Se(aq)$				
		3.800	-21.691		
		± 0.300	± 1.712		
$HSeO_3^-$	$H_2SeO_3(aq) \rightleftharpoons H^+ + HSeO_3^-$				
		-2.800	15.983	-7.070	-77.319[a]
		± 0.200	± 1.142	± 0.500	± 4.180
$H_2SeO_3(aq)$	$3H_2O(l) + 2I_2(cr) + Se(cr) \rightleftharpoons 4H^+ + H_2SeO_3(aq) + 4I^-$				
		-13.840	78.999		
		± 0.100	± 0.571		
$HSeO_4^-$	$H^+ + SeO_4^{2-} \rightleftharpoons HSeO_4^-$				
		1.800	-10.274	23.800	114.286[a]
		± 0.140	± 0.799	± 5.000	± 16.983
$HN_3(aq)$	$H^+ + N_3^- \rightleftharpoons HN_3(aq)$				
		4.700	-26.828	-15.000	39.671[a]
		± 0.080	± 0.457	± 10.000	± 33.575
$NH_3(aq)$	$NH_4^+ \rightleftharpoons H^+ + NH_3(aq)$				
		-9.237	52.725	52.090	-2.130[a]
		± 0.022	± 0.126	± 0.210	± 0.821

(Continued on next page)

Table IV.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
$HNO_2(aq)$	$H^+ + NO_2^- \rightleftharpoons HNO_2(aq)$				
		3.210	−18.323	−11.400	23.219[a]
		±0.160	±0.913	±3.000	±10.518
PO_4^{3-}	$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$				
		−12.350	70.494	14.600	−187.470[a]
		±0.030	±0.171	±3.800	±12.758
$P_2O_7^{4-}$	$HP_2O_7^{3-} \rightleftharpoons H^+ + P_2O_7^{4-}$				
		−9.400	53.656		
		±0.150	±0.856		
$H_2PO_4^-$	$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$				
		7.212	−41.166	−3.600	125.998[a]
		±0.013	±0.074	±1.000	±3.363
$H_3PO_4(aq)$	$H^+ + H_2PO_4^- \rightleftharpoons H_3PO_4(aq)$				
		2.140	−12.215	8.480	69.412[a]
		±0.030	±0.171	±0.600	±2.093
$HP_2O_7^{3-}$	$H_2P_2O_7^{2-} \rightleftharpoons H^+ + HP_2O_7^{3-}$				
		−6.650	37.958		
		±0.100	±0.571		
$H_2P_2O_7^{2-}$	$H_3P_2O_7^- \rightleftharpoons H^+ + H_2P_2O_7^{2-}$				
		−2.250	12.843		
		±0.150	±0.856		
$H_3P_2O_7^-$	$H_4P_2O_7(aq) \rightleftharpoons H^+ + H_3P_2O_7^-$				
		−1.000	5.708		
		±0.500	±2.854		
$H_4P_2O_7(aq)$	$2H_3PO_4(aq) \rightleftharpoons H_2O(l) + H_4P_2O_7(aq)$				
		−2.790	15.925	22.200	21.045[a]
		±0.170	±0.970	±1.000	±4.674
$CO_2(aq)$	$H^+ + HCO_3^- \rightleftharpoons CO_2(aq) + H_2O(l)$				
		6.354	−36.269		
		±0.020	±0.114		
$CO_2(g)$	$CO_2(aq) \rightleftharpoons CO_2(g)$				
		1.472	−8.402		
		±0.020	±0.114		
HCO_3^-	$CO_3^{2-} + H^+ \rightleftharpoons HCO_3^-$				
		10.329	−58.958		
		±0.020	±0.114		
$SiO_2(OH)_2^{2-}$	$Si(OH)_4(aq) \rightleftharpoons 2H^+ + SiO_2(OH)_2^{2-}$				
		−23.140	132.084	75.000	−191.461[a]
		±0.090	±0.514	±15.000	±50.340
$SiO(OH)_3^-$	$Si(OH)_4(aq) \rightleftharpoons H^+ + SiO(OH)_3^-$				
		−9.810	55.996	25.600	−101.948[a]
		±0.020	±0.114	±2.000	±6.719

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Table IV.2: (continued)

Species	Reaction	$\log_{10} K^\circ$	$\Delta_r G^\circ_m$ (kJ · mol^{-1})	$\Delta_r H^\circ_m$ (kJ · mol^{-1})	$\Delta_r S^\circ_m$ (J · K^{-1} · mol^{-1})
$Si(OH)_4(aq)$	$2H_2O(l) + SiO_2(quar) \rightleftharpoons Si(OH)_4(aq)$				
		-4.000	22.832	25.400	8.613[a]
		± 0.100	± 0.571	± 3.000	± 10.243
$Si_2O_3(OH)_4^{2-}$	$2Si(OH)_4(aq) \rightleftharpoons 2H^+ + H_2O(l) + Si_2O_3(OH)_4^{2-}$				
		-19.000	108.453		
		± 0.300	± 1.712		
$Si_2O_2(OH)_5^-$	$2Si(OH)_4(aq) \rightleftharpoons H^+ + H_2O(l) + Si_2O_2(OH)_5^-$				
		-8.100	46.235		
		± 0.300	± 1.712		
$Si_3O_6(OH)_3^{3-}$	$3Si(OH)_4(aq) \rightleftharpoons 3H^+ + 3H_2O(l) + Si_3O_6(OH)_3^{3-}$				
		-28.600	163.250		
		± 0.300	± 1.712		
$Si_3O_5(OH)_5^{3-}$	$3Si(OH)_4(aq) \rightleftharpoons 3H^+ + 2H_2O(l) + Si_3O_5(OH)_5^{3-}$				
		-27.500	156.971		
		± 0.300	± 1.712		
$Si_4O_8(OH)_4^{4-}$	$4Si(OH)_4(aq) \rightleftharpoons 4H^+ + 4H_2O(l) + Si_4O_8(OH)_4^{4-}$				
		-36.300	207.202		
		± 0.500	± 2.854		
$Si_4O_7(OH)_5^{3-}$	$4Si(OH)_4(aq) \rightleftharpoons 3H^+ + 4H_2O(l) + Si_4O_7(OH)_5^{3-}$				
		-25.500	145.555		
		± 0.300	± 1.712		

[a] Value calculated internally with the equation $\Delta_r G^\circ_m = \Delta_r H^\circ_m - T\,\Delta_r S^\circ_m$.
[b] Value calculated from a selected standard potential.
[c] Value of $\log_{10} K^\circ$ calculated internally from $\Delta_r G^\circ_m$.

Chapter V

Discussion of data selection

V.1 Elemental technetium

V.1.1 Technetium metal

V.1.1.1 Crystal structure

Tc(cr) has the hcp structure with $Z = 2$ (space group $P6_3/mmc$) over the whole of its solid range. The crystal structure was first determined by Mooney [48MOO] using a 40 μg sample whose chemical provenance was not described. Her values of a and c and subsequent determinations are summarised in Table V.1; the small differences are presumably due to different impurity levels. The recommended values are the average of all but two [48MOO, 75SPI/GRI] of these studies.

Prolonged reduction of samples of metal or oxide with H_2(g) around 1200 K [64MUL/WHI] or electron beam melting of the metal under vacuum [65BAK, 70GIO/SZK2] gave samples of technetium essentially free of oxide.

Marples and Koch [72MAR/KOC] reported that $a = b = (2.7364 \pm 0.0002) \times 10^{-10}$ m and $c = (4.3908 \pm 0.0002) \times 10^{-10}$ m at 4.2 K, and $a = 2.7407 \times 10^{-10}$ m and $c = 4.3980 \times 10^{-10}$ m at 298.15 K. The a/c ratio was almost independent of temperature. Measurements at various other temperatures (not reported) gave the thermal expansion coefficients $\alpha_a = 7.04 \times 10^{-6}$ K^{-1} and $\alpha_c = 7.06 \times 10^{-6}$ K^{-1} for 150 to 298 K.

Alekseyevskiy, Balakhovskiy and Kirillov [75ALE/BAL] found that the superconducting transition temperature of technetium decreased smoothly with pressure up to their maximum pressure of nearly 110 kbar. From this they deduced that technetium retained the same hcp structure over this pressure range.

V.1.1.2 Heat capacity and entropy

There are two experimental studies on the heat capacity of technetium, and a number of papers which present estimated thermal functions for the metal. Of the latter, all except three are derived more or less directly from the earliest estimate of Brewer [50BRE], as was pointed out by Fernández Guillermet and Grimvall [89FER/GRI]. Trainor and Brodsky [75TRA/BRO] studied the metal from 3 to 15 K, in relation to the superconducting transition at 7.86 K (the second highest for a pure element, after Nb), and approximate values of $C^\circ_{p,m}$ can be derived from the thermal diffusivity measurements by Spitsyn *et al.* [75SPI/ZIN], from 950 to 1500 K; these results (which have an uncer-

Table V.1: Crystal structure parameters for Tc(cr) around 298.15 K.

Lattice parameters ($\times 10^{10}$/ m)			
a	c	a/c	Reference
2.735 ± 0.002	4.388 ± 0.002	0.6233	[48MOO]
2.743 ± 0.002	4.400 ± 0.002	0.6234	[61LAM/DAR]
2.7415 ± 0.002	4.400 ± 0.002	0.6231	[64MUL/WHI]
2.7414	4.3997	0.6231	[65BAK]
2.740	4.398	0.6230	[62TRZ/RUD]
2.743	4.400	0.6234	[68KOC/LOV]
2.7407±0.0002	4.3980±0.0002	0.6232	[72MAR/KOC]
~2.73 [(a)]	~4.39 [(a)]	0.622	[75SPI/GRI]
2.740 ± 0.002	4.399 ± 0.004	0.6229	[70GIO/SZK2, 78GIO/MAT, 78STE/GIO, 85GIO]
2.7375	4.3950	0.6228	[80HAI/POT]
2.7409±0.0035	4.3987±0.0034	0.6231±0.0004	Average [(b)]

[(a)] Estimated from a plot given in that paper.
[(b)] Values recommended by the present review, (see text).

tainty of at least 5%) were presented only in the form of a small graph. The three recent methods of estimating the thermal functions of technetium all utilised some combination of lattice (C_L), dilatation (C_d), electronic (C_e) and vacancy (C_{vac}) contributions to the heat capacity or entropy.

Krikorian [88KRI] and Krikorian and Lai [89KRI/LAI] summed the first three terms

$$C_L = \mathrm{Deb}C_p(\theta/T)$$

where $\mathrm{Deb}C_p$(u) is the normal Debye function for heat capacity, and

$$\theta = \theta_0[1 - \exp(-20/T) + \exp(-26/T)]$$

with θ_0 = 375 K

$$C_d = 3.42 \times 10^{-6} C_L T^{4/3}$$

$$C_e = 3.2426 \times 10^{-3}[1 - \exp(-20/T)] + 4.5187 \times 10^{-3} \exp(-26/T) \ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

where the values of some of the coefficients are given to more significant figures [88KRI] than are in the published report [89KRI/LAI].

The terms for the temperature variation of the Debye temperature θ and the electronic specific heat are arbitrary expressions which have been shown to represent satisfactorily the behaviour of most metals [89KRI/LAI]. The justification of the choice of θ_0 = 375 K for Tc was not discussed.

Powers [91POW] added a further contribution C_{vac} from thermally induced vacancies to the heat capacity, (*cf.* Appendix A)

Fernández Guillermet and Grimvall [89FER/GRI] adopted a slightly different approach, in which the entropy was considered to be the sum of vibrational and electronic terms. The vibrational contribution (including anharmonic and dilatation terms), S_{vib}, is related to an "entropy Debye temperature", θ^S, which is more satisfactory than other Debye temperatures for such estimations, since it gives a logarithmic average of the phonon frequencies. The electronic contribution was taken from an electronic heat capacity of Tc, but reduced by a factor of 1.68 from the value appropriate near 0 K, $C_e = (4.3 \times 10^{-3}\ T)$ J·K^{-1}·mol^{-1} [75TRA/BRO], to allow for the decrease in the electron-phonon enhancement above ~100 K [89FER/GRI]. Fernández Guillermet and Grimvall [89FER/GRI] showed that the temperature dependent "entropy Debye temperatures" for 5d transition elements are simply related to those of the corresponding 4d element. In fact, their relationship reduces to

$$\theta^S(\text{Tc, cr}, T) \quad = \quad (1.198 \pm 0.016)\, \theta^S(\text{Re, cr}, T) \qquad \text{(V.1)}$$

allowing the calculation of S_{vib}(Tc, cr, T). Addition of the electronic contribution then gives calculated values of S°_m (Tc, cr, T), and by differentiation, the heat capacity. Fernández Guillermet and Grimvall [89FER/GRI] based their calculations for technetium on values of S°_m (Re, cr, T) taken from Hultgren *et al.* [73HUL/DES], in which owing to lack of good experimental work, the thermal functions above 1400 K are given a high uncertainty. However, more precise and extensive data for the enthalpy of rhenium are now available from five recent studies. These have been analysed in the recent assessment of the thermodynamic properties of rhenium by Arblaster [96ARB]. The derived $C^\circ_{p,m}$ and thermal functions up to 300 K are close to those of Hultgren *et al.* [73HUL/DES] (since there are no new low temperature data), but are noticeably smaller above 1000 K. We have therefore repeated the calculations of Fernández Guillermet and Grimvall [89FER/GRI] using these latest assessed data for rhenium.

The calculated values of S°_m (T) are summarised in Table V.2; all the values at round temperature from 298.15 to 2430 K can be fitted with good precision to the expression:

$$\begin{aligned} S^\circ_m(\text{Tc, cr}, T) \quad = \quad & -112.482 + 25.0940 \ln T + 4.3145 \times 10^{-3} T \\ & -1.3773 \times 10^{-7} T^2 + 6.5650 \times 10^{4} T^{-2} \ \text{J·K}^{-1}\text{·mol}^{-1} \end{aligned}$$

for 298.15 K $\leq T \leq$ 2430 K with a maximum deviation of 0.026 J·K^{-1}·mol^{-1}.

The derived heat capacity expression is thus

$$\begin{aligned} C^\circ_{p,m}(\text{Tc, cr}, T) \quad = \quad & 25.0940 + 4.3145 \times 10^{-3} T - 2.7546 \times 10^{-7} T^2 \\ & -1.3130 \times 10^{5} T^{-2} \ \text{J·K}^{-1}\text{·mol}^{-1} \end{aligned}$$

for 298.15 K $\leq T \leq$ 2430 K. Table V.3 compares the values of $C^\circ_{p,m}$ calculated from the four major independent estimation procedures [56STU/SIN, 88KRI, 89KRI/LAI, 91POW] and from the revised [89FER/GRI], discussed above, at a few round temperatures. Brewer [50BRE], in his original estimate, does not give values of $C^\circ_{p,m}$, but

Table V.2: Summary of calculations based on model of Fernández Guillermet and Grimvall [89FER/GRI] and S°_m (Re, T) from Arblaster [96ARB].

T (K)	S°_m(Re) ($J \cdot K^{-1} \cdot mol^{-1}$)	θ_{Re} (K)	θ_{Tc} (K)	S°_m(Tc) ($J \cdot K^{-1} \cdot mol^{-1}$)
298.15	36.482	272.738	326.241	32.506
500.00	49.757	268.572	321.258	45.827
1000.00	68.639	258.932	309.726	65.113
1500.00	80.312	251.104	300.363	77.237
2000.00	88.942	244.699	292.702	86.326
2400.00	94.651	239.746	286.777	92.403

Table V.3: Comparison of heat capacity and entropy estimates.

T (K)	[56STU/SIN]	Estimated [88KRI], [89KRI/LAI]	[91POW]	[89FER/GRI] Revised	Experimental [75SPI/ZIN]
		$C^\circ_{p,m}(T)$ / $J \cdot K^{-1} \cdot mol^{-1}$			
298.15	24.27	24.60	23.88	24.88	–
500	25.94	26.81	26.63	26.66	–
1000	30.12	30.09	30.05	29.00	28.3
1500	34.31	33.05	32.90	30.89	30.3
2000	38.49	36.03	35.85	32.59	–
2400	41.84	38.44	38.38	33.84	–
		S°_m (298.15 K)/ $J \cdot K^{-1} \cdot mol^{-1}$			
298.15	33.472	31.877	25.758	32.506	–

his values for the derived thermal functions (which are usually rounded to two or three significant digits) are close to those of [56STU/SIN].

The $C^\circ_{p,\mathrm{m}}$ values derived by Krikorian [88KRI] and Powers [91POW] up to 1500 K are close to the early, more empirical, estimates of Stull and Sinke [56STU/SIN], which are likely to reflect the earlier values for the heat capacity of rhenium; recent data suggest these latter are too high, particularly at temperatures above 1500 K. The estimates based on the methodology of [89FER/GRI], which reflect the lower $C^\circ_{p,\mathrm{m}}$ values for Re, are lower than these other estimates above 1000 K, but agree well within the uncertainties with the experimental values of Spitsyn *et al.* [75SPI/ZIN], although these latter data are not of high precision.

We prefer the values derived from the revised analysis of [89FER/GRI], since this has reasonably firm theoretical basis, uses a Debye temperature expression which gives a logarithmic average of the phonon frequencies, uses the most recent data for rhenium as a comparative basis, and the derived $C^\circ_{p,\mathrm{m}}$ values agree quite well with the very limited experimental data.

Estimated values of S°_m (Tc, cr, 298.15 K) are also included in Table V.3. The only strongly deviant estimate is that from [91POW], presumably resulting from the use of a constant Debye temperature appropriate to temperatures close to 0 K, (*cf.* Appendix A). We shall adopt the value from the revised [89FER/GRI] analysis, which is entirely consistent with the adopted $C^\circ_{p,\mathrm{m}}$ values. The derived values for Tc(cr) at and above 298.15 K can thus be summarised:

$$S^\circ_\mathrm{m}(\mathrm{Tc, cr, 298.15\ K}) = (32.5 \pm 0.7)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$C^\circ_{p,\mathrm{m}}(\mathrm{Tc, cr, 298.15\ K}) = (24.9 \pm 1.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$C^\circ_{p,\mathrm{m}}(\mathrm{Tc, cr}, T) = 25.0940 + 4.3145 \times 10^{-3}T - 2.7546 \times 10^{-7}T^2 - 1.3130 \times 10^{5}T^{-2}\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

for $298.15\ \mathrm{K} \leq T \leq 2430\ \mathrm{K}$.

The uncertainty in the entropy is based on the uncertainties in S°_m (Re, cr, 298.15 K) ($\pm 0.37\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$) and in the value of $\theta^\mathrm{S}(\mathrm{Tc})/\theta^\mathrm{S}(\mathrm{Re})$ (± 0.0016).

V.1.1.3 Fusion and liquid data

Fernández Guillermet and Grimvall [89FER/GRI], following Rard [83RAR], summarised the data on the melting point by Parker *et al.* [52PAR/CRE], Anderson *et al.* [60AND/BUC] and Behrens and Rinehart [80BEH/RIN]. Parker *et al.* used Pt, Al_2O_3, Nb and Ir as reference materials. When modern values [89FER/GRI] for the melting points of these materials are used, the corrected melting point for technetium becomes (2430 ± 30) K, in good agreement with the approximate value of (2435 ± 40) K suggested by Behrens and Rinehart, and a lower limit of (2427 ± 50) K, given by Anderson *et al.* [60AND/BUC]. This value of (2430 ± 30) K, selected by Fernández Guillermet and Grimvall [89FER/GRI] is accepted here.

Powers [91POW] has reviewed estimates of $\Delta_{fus}S^\circ_m/R = 1.16$ [66SCH], 1.56 [75GSC] and 1.11 [88XIA] (based on the simple relation $\Delta_{fus}H^\circ_m/R = 1.157(T_{fus} - 100)$) and has selected $\Delta_{fus}S^\circ_m/R = (1.14 \pm 0.03)$. This is appreciably smaller than the estimate by [89FER/GRI] which corresponds to $\Delta_{fus}S^\circ_m/R = (1.65 \pm 0.12)$, based on the convincing observation by Saunders, Miodownik and Dinsdale [88SAU/MIO] that $\Delta_{fus}S^\circ_m$ for metals of similar structure increases with T_{fus} and falls within a narrow scatter band. Powers [91POW] did not mention either of the papers by Saunders, Miodownik and Dinsdale [88SAU/MIO] or Fernández Guillermet and Grimvall [89FER/GRI].

For these reasons, we select the value from Fernández Guillermet and Grimvall [89FER/GRI]:

$$\Delta_{fus}S^\circ_m(T_{fus}) \quad = \quad (13.7 \pm 1.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

corresponding to

$$\Delta_{fus}H^\circ_m(T_{fus}) \quad = \quad (33291 \pm 2500)\ \text{J} \cdot \text{mol}^{-1}$$

An identical estimate of $\Delta_{fus}S^\circ_m = (13.7 \pm 1.0)\ \text{J·K}^{-1}\text{·mol}^{-1}$ was given by Kats and Chekhovskoi [79KAT/CHE]. None of the equations presented by these authors yields this value, and it appears to have been estimated from a plot of $\Delta_{fus}S^\circ_m$ as a function of T_{fus} for fcc metals, the same method used by Saunders, Miodownik and Dinsdale [88SAU/MIO] and adopted by Fernández Guillermet and Grimvall [89FER/GRI].

The values of $C^\circ_{p,m}$ (Tc, l), estimated by [91POW] from a set of complex assumptions modelling the liquid, increase from 45.49 $\text{J·K}^{-1}\text{·mol}^{-1}$ at T_{fus} to 49.91 $\text{J·K}^{-1}\text{·mol}^{-1}$ at 3500 K. In view of our rudimentary understanding of the behaviour of metallic liquids, it seems preferable to estimate the heat capacity directly. Fernández Guillermet and Grimvall [89FER/GRI] have suggested such an estimate, from the systematic trends of the neighbouring 4d transition elements, of a constant value of $(47 \pm 2)\ \text{J·K}^{-1}\text{·mol}^{-1}$, which, being close to the mean value of [91POW], we shall accept as selected value.

$$C^\circ_{p,m}(\text{Tc, l}, T) \quad = \quad (47 \pm 2)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

Thermal functions of Tc(cr) at temperatures below 298.15 K are estimated in Appendix B, which also includes a tabulation (Table B.1) of the thermal functions of Tc(cr,liq) up to 3000 K.

V.1.1.4 Other properties

Fernández Guillermet and Grimvall [89FER/GRI] summarised literature results for other properties of technetium metal. They recommended values for the elastic constants of technetium metal of $c_{11} = 433$ GPa, $c_{12} = c_{13} = 199$ GPa, $c_{44} = 117$ GPa and $c_{33} = 470$ GPa with uncertainties of about 3%, based on phonon dispersion curves. They also recommended values of the bulk modulus $B = 281$ GPa, shear modulus $G = 119$ GPa, Young's modulus $E = 314$ GPa, and Poisson number = 0.31.

Electrical resistivities have been reported up to about 2000 K [67KOC/LOV] and about 1400 K [75SPI/ZIN] and are in good agreement. These results were presented graphically, with only a few tabulated results given in Ref. [67KOC/LOV]. Thermal diffusivities (thermal conductivities) have been presented graphically up to about 848 K [65BAK] and to about 1173 K [98MIN/SER], and up to about 1820 K [75SPI/ZIN], with reasonable agreement in the overlap region, although the higher-temperature data do not form a good extrapolation of the lower temperature results. Nelson, Boyd and Smith [54NEL/BOY] tabulated magnetic susceptibilities for technetium metal from 78 to 402 K, and Spitsyn *et al.* [75SPI/ZIN] gave similar results graphically up to about 1425 K.

Technetium becomes superconducting below (7.86 ± 0.01) K [75TRA/BRO], which is the second highest at normal pressure (after Nb). This temperature, calculated from an analysis of the heat capacity as a function of temperature, is close to the value (7.77 K) given by Sekula *et al.* [67SEK/KER] from a magnetic study, but is somewhat higher than that reported for a less pure sample (7.46 K) by Kostorz and Mihailovich [71KOS/MIH]. Trainor and Brodsky also reported values for the electronic heat capacity coefficient $\gamma = (4.30 \pm 0.05)$ mJ $\cdot$ mol^{-1} $\cdot$ K^{-2}, Debye temperature $\theta^0 = (454 \pm 4)$ K, electron-phonon enhancement factor $\lambda = 0.65$ and a critical field $H_e(0\,K) = (1131 \pm 10)$ Oe.

V.1.1.5 Vaporisation behaviour

Krikorian, Carpenter and Newbury [69KRI/CAR] showed mass-spectrometically that Tc(g) is the only important species in the vapour. However, Miedema and Gingerich [79MIE/GIN] estimated the dissociation energy of Tc_2(g) to be about 330 kJ·mol^{-1} based on a correlation between enthalpies of vaporisation and dissociation energies, whereas Brewer and Winn [80BRE/WIN] estimated a value of 283 kJ·mol^{-1} based on valence band theory; both values are for 0 K. Since this species is therefore not important in vaporisation phenomena, even at 2000 K, it will not be considered any further.

V.1.2 Technetium mono-atomic gas

V.1.2.1 Heat capacity and entropy

Stull and Sinke [56STU/SIN], Poland, Green and Margrave [62POL/GRE] and Hultgren *et al.* [73HUL/DES] have all calculated the thermal functions of Tc(g) from the 79 energy levels (up to 45190 cm^{-1}) given by Moore [58MOO], based on spectroscopic work by Meggers and co-workers [50MEG/SCR, 51MEG] and the then unpublished results from Bozman and co-workers. Such calculations have here been extended to include the additional levels (totalling 255) given in [68BOZ/COR]. Since the configurations to which the new levels belong have not yet been determined (although the statistical weights are known), there is no sensible way that any of the procedures to cut off the energy levels contributing to the sum of the partition function [78DOW] can be applied. Similarly, we have not attempted to estimate any unidentified levels corresponding to any configuration. With the current list of energy levels about two thirds of

the 3316 observed lines of the spectrum of Tc(I) have been classified. Six of the 255 levels lie above the ionization limit of 58700 cm^{-1} [58MOO], but have been retained in the list since they will to a minor extent counterbalance some of the missing levels. The highest identified energy level is at 64785.90 cm^{-1}. The derived thermal functions of Tc(g) are given in Table B.2, (in Appendix B).

The differences from the earlier values with 79 levels are essentially negligible for practical purposes at all temperatures up to 2500 K and not large even at 6000 K.

The standard entropy (reference state pressure = 1 bar) for the ^{99}Tc isotope is

$$S^\circ_m(\text{Tc, g, 298.15 K}) \quad = \quad (181.052 \pm 0.010)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

and the heat capacity is

$$C^\circ_{p,m}(\text{Tc, g, 298.15 K}) \quad = \quad (20.795 \pm 0.010)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

In performing these statistical thermodynamic calculations for Tc(g) we have accepted the energy level assignments given by Meggers [51MEG] and Moore [58MOO], and which can also be found in more recent tabulations including the Handbook of Atomic Data [76FRA/KAR]. In these tabulations it was reported that the outer electronic configuration of atomic technetium in the ground state is $4s^2 4p^6 4d^5 5s^2$ with the term symbol $^6S_{5/2}$.

However, in a major monograph [73PEA] and the major inorganic chemistry textbook [88COT/WIL], the outer electronic configuration of Tc(g) was given as $4s^2 4p^6 4d^6 5s^1$, whereas in two other publications [77SPI/KUZ, 82BUR/PEA] the two electronic configurations are given as alternative possibilities. The origin of these discrepant assignments appears to come from a misinterpretation of the paper of Kessler and Trees [53KES/TRE], along with some confusion between the nuclear and electronic spins of ^{99}Tc [77SPI/KUZ2, 82BUR/PEA]. In fact, Kessler and Trees [53KES/TRE] unambiguously stated that the ground state of ^{99}Tc was ^6S state, which is consistent wih a $4s^2 4p^2 4d^5 5s^2$ configuration, and we have accepted this configuration for our calculations. We have discussed this issue in more detail elsewhere [91RAR/RAN].

V.1.2.2 Enthalpy of formation

There are three studies of the vapour pressure of technetium. Krikorian, Carpenter and Newbury [69KRI/CAR] were the first to measure the vapour pressure, by comparison with that of molybdenum, essentially by a Langmuir technique. The metal was heated in a rhenium cell and the Tc^+(g) ion currents measured in a mass-spectrometer from around 1900 to 2300 K. These were converted to pressures using molybdenum as a reference material. No detailed pressures (or even an equation) were given in the paper, but a plot was given, together with derived second law and third law enthalpies of sublimation at 298.15 K, using given thermal functions of Tc(cr) and Tc(g). The calculated pressures of Tc depend on, amongst other things, the estimated ratio of ionisation cross-sections of Tc and Mo; those given by Mann [67MAN] were used. Since these are neighbouring elements, this ratio was estimated to be uncertain only by about 20%, contributing an uncertainty of ~3.3 kJ·mol^{-1} to the value of $\Delta_f H^\circ_m$(Tc, g, 298.15 K) [69KRI/CAR].

There is a large discrepancy in the second and third law values of $\Delta_f H^\circ_m$(Tc, g, 298.15 K) from this study. Two second law values, themselves disparate, were given: one from a direct calculation from the variation of $\log_{10}(IT)$ with temperature, where I denotes the ion current, and a second after referring the calculated intensities to those of molybdenum. Table V.4 gives these values, recalculated with our selected thermal functions and corrected for a small change in $\Delta_f H^\circ_m$(Mo, g, 298.15 K) from the value of (659.0 ± 1.7) kJ·mol^{-1} used by [69KRI/CAR] to (657.6 ± 4.0) kJ·mol^{-1} given in the latest assessment [82GLU/GUR]. The large difference between either of the second and the third law enthalpies implies that the entropy of sublimation derived from the measurements is appreciably different from the calculated value, which cannot be greatly in error. Although the authors gave a detailed discussion of possible errors in their measurements, they did not discuss the possibility of dissolution of Tc in the Re substrate which is likely to increase with temperature, and thus give a temperature-dependent error. It may be noted that the derived enthalpies of sublimation of the other metals studied in this work (Mo, Nb and Ru) are generally higher than the accepted values, so this may also be true for Tc, perhaps because the thermodynamic activity of Tc was less than unity.

Behrens and Rinehart [80BEH/RIN] studied the vaporisation of Tc, contained in a TaC effusion cell, from 2051 to 2348 K mass-spectrometrically, using Ag and Au as standards, see Figure V.1. However, the experimental entropy of vaporisation (97.0 ± 2.9) J·K^{-1}·mol^{-1} is so much smaller than the calculated value ($\Delta_{sub}S^\circ_m(2200\ \text{K}) = 143.7$ J·K^{-1}·mol^{-1}), that it must be doubtful whether the measured pressures can correspond to a simple sublimation process, *cf.* Appendix A. The results of the normal second- and third-law analyses, using the selected thermal functions for Tc are shown in Table V.4.

Golubtsov *et al.* [84GOL/VEZ] have briefly reported an equation equivalent to

$$\log_{10}(p/\text{bar}) \quad = \quad -35700/T + 7.525$$

for the vapour pressure of Tc(cr) from 2041 to 2302 K, measured by target Knudsen effusion from a ^{99}Tc foil held in a tungsten cell with a tantalum holder. Their pressures are lower than those of [69KRI/CAR] and [80BEH/RIN] by factors of about 4 and 16 respectively as shown in Figure V.1. Since [84GOL/VEZ] do not report individual pressures, the principal check on their data is to compare their experimental entropy of vaporisation at the mean temperature of the experiments, $\Delta_{sub}S^\circ_m(2172\ \text{K, exp.}) = 144.06$ J·K^{-1}·mol^{-1} with the calculated value $\Delta_{sub}S^\circ_m$ (2172 K, calc.) $= 143.78$ J·K^{-1}·mol^{-1}. The excellent agreement gives confidence in the experimental study, despite the lack of detail in the report. The value of the pseudo third law value of $\Delta_{sub}H^\circ_m(298.15\ \text{K})$ obtained from six pressures calculated from their equation at round temperatures between 2050 and 2300 K, using our thermal functions, is (685.4 ± 0.02) kJ·mol^{-1} (the uncertainty is artificial), essentially the same as the second law value, corrected to 298.15 K, of (685.8 ± 8.4) kJ·mol^{-1}, where the uncertainty is that given by [84GOL/VEZ].

Table V.4 compares the results of these vaporisation studies. It also includes an estimate of the enthalpy of sublimation from the trends in the vaporisation behaviour of the 3d, 4d, 5d transition elements. As pointed out by [69KRI/CAR], the enthalpies

Figure V.1: Vapour pressure of Tc(cr).

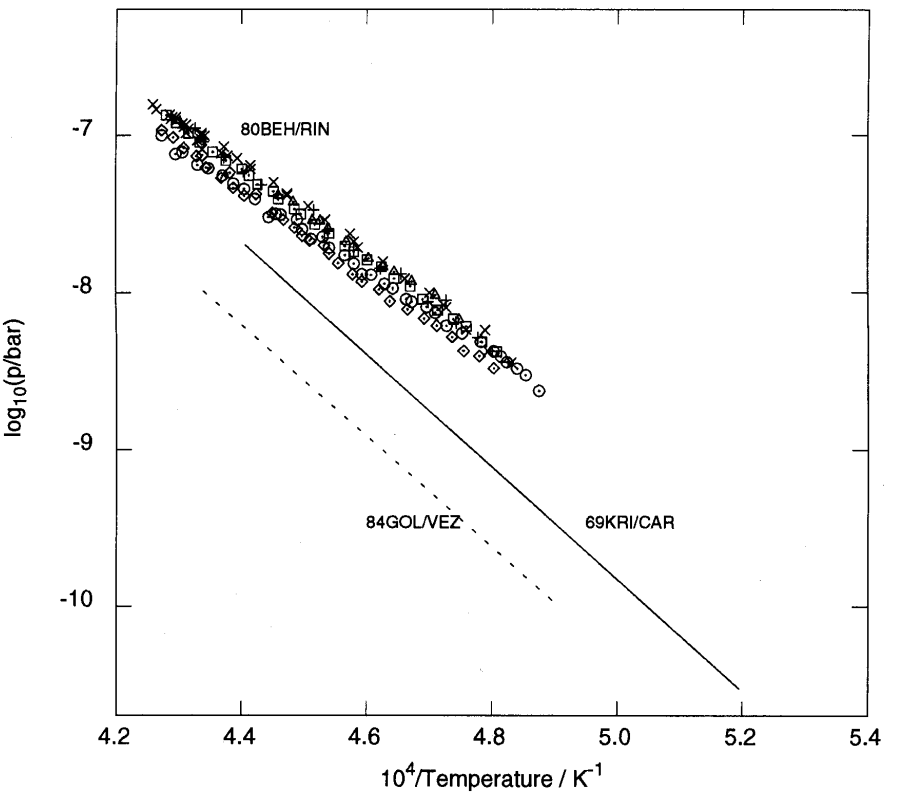


Table V.4: Comparison of $\Delta_{sub}H^{\circ}_{m}$(Tc, 298.15 K) values.

Reference	Method	$\Delta_{sub}H^{\circ}_{m}$(Tc, 298.15 K), kJ·mol^{-1}		Comments
		2nd law	3rd law	
[69KRI/CAR]	*cf.* Langmuir	764.0±31.4 712.2±18.8	665.9±5.9	Referenced to Mo
[80BEH/RIN]	Mass-spec. Knudsen	538.4±7.0	641.8±4.9	Reaction ?
[84GOL/VEZ]	Knudsen	685.8±8.4	685.4±?	
Estimated	3d, 4d, 5d trends		645 ± 20	

of sublimation of Mn and Re are each somewhat smaller than those of their immediate neighbours. If this trend occurs for the 4d elements, $\Delta_f H^{\circ}_{m}$(Tc, g, 298.15 K) would be expected to be slightly smaller than the values for Mo (657.6 ± 4.0 kJ·mol^{-1}) [82GLU/GUR] and Ru (649 ± 4 kJ·mol^{-1}) [95ARB], say (645 ± 20) kJ·mol^{-1}.

There will clearly be a large uncertainty in the value selected, given the unsatisfactory results from the two earlier studies. The big differences in the second and third law enthalpies of sublimation for the studies by Krikorian *et al*. [69KRI/CAR] and Behrens and Rinehart [80BEH/RIN] imply experimental entropies of sublimation which make it doubtful whether either of these studies refers to the simple sublimation of pure Tc. The latest work by [84GOL/VEZ], which with our thermal functions gives essentially identical second and third law enthalpies of sublimation, seems the most reliable study, but gives pressures appreciably lower than those predicted from trends in the transition metal series. The value selected is close to that of [84GOL/VEZ], but is biased to a slightly lower value to take account of the transition metal trends, and has been assigned asymmetrical uncertainty limits for the same reason.

$$\Delta_f H^{\circ}_{m}(\text{Tc, g, 298.15 K}) \quad = \quad (675^{+12}_{-40})\ \text{kJ·mol}^{-1}$$

When combined with the entropy values at 298.15 K, this gives

$$\Delta_f G^{\circ}_{m}(\text{Tc, g, 298.15 K}) \quad = \quad (630.7^{+12.0}_{-40.0})\ \text{kJ·mol}^{-1}$$

A more definitive study of the vapour pressure of the metal is clearly required.

V.1.3 Gaseous technetium ions

Data for the gaseous unipositive and uninegative ions are evaluated and tabulated in Appendix B (Section B.3).

V.2 Simple aqueous technetium ions of each oxidation state

Technetium has an extensive redox chemistry, and the most stable oxidation state in contact with air is pertechnetate(VII), TcO_4^-, in the entire pH range. TcO_4^- can therefore be used as a reference oxidation state. An aqueous system containing both TcO_4^- and a technetium species of a different oxidation state can be electrochemically characterised by measuring its potential against a reference electrode. Frequently used methods are potentiometry and polarography. Potentiometry is an appropriate method if the oxidation states involved have a sufficient stability under the conditions chosen. This is true, for example, for TcO_4^- and the hydrated Tc(IV) oxide which ensures a constant concentration of $TcO(OH)_2(aq)$, *cf.* Section V.3.2.5, affected only by changes of the activity coefficient with the composition of the aqueous solution. It is not difficult to prepare saturated Tc(IV) solutions as the solubility of $TcO_2 \cdot xH_2O(s)$ remains constant around 10^{-8} M from pH of about 2 to 10 and increases only outside this range reaching about 10^{-5} M in strong acid solution [91MEY/ARN2]. The redox couple $TcO_4^-/TcO_2 \cdot xH_2O(s)$ according to the reaction

$$TcO_4^- + 4H^+ + 3e^- \quad \rightleftharpoons \quad TcO_2 \cdot xH_2O(s) + (2-x)H_2O(l) \qquad \text{(V.2)}$$

is discussed in detail in Section V.2.1. The selected standard reduction potential and $\log_{10} K^\circ$ are reproduced in this section for completeness:

$$E^\circ(\text{V.2}, 298.15\ \text{K}) = (0.746 \pm 0.012)\ \text{V}$$
$$\log_{10} K^\circ(\text{V.2}, 298.15\ \text{K}) = 37.8 \pm 0.6$$

For equilibrium modelling purposes, however, the redox reactions are usually formulated between the reference species of each oxidation state. For Tc(IV) we recommend choosing $TcO(OH)_2(aq)$ as the reference species, because it is the major aqueous Tc(IV) species in non-complexing solutions between pH 2 and 10. The relevant half cell reaction is then

$$TcO_4^- + 4H^+ + 3e^- \quad \rightleftharpoons \quad TcO(OH)_2(aq) + H_2O(l) \qquad \text{(V.3)}$$

and the corresponding calculated standard reduction potential and $\log_{10} K^\circ$ values are:

$$E^\circ(\text{V.3}, 298.15\ \text{K}) = (0.579 \pm 0.016)\ \text{V}$$
$$\log_{10} K^\circ(\text{V.3}, 298.15\ \text{K}) = 29.4 \pm 0.8$$

Polarography or similar electrochemical methods using cathodic metals such as Hg are applied to investigate the reduction of TcO_4^- to oxidation states other than Tc(IV), because those show a lower stability. They are involved in secondary redox processes, *i.e.*,

they form as intermediate oxidation states along a redox reaction path. In such cases the potential $E_{1/2}$ is measured at which equal concentrations of the two involved oxidation states are present. In polarographic measurements the valency states of the reduced forms of the elements are calculated by use of the Ilkovic equation [52KOL/LIN]:

$$\frac{i_d}{c} = 607n\sqrt{D}\sqrt[3]{m^2}\sqrt[6]{\tau}$$

where i_d is the limiting diffusion current (μA), c the concentration (mM), n the change of charge (number of electrons), D the diffusion coefficient ($cm^2 \cdot s^{-1}$), m the flow rate of mercury ($mg \cdot s^{-1}$), and τ the drop time. The constant $\sqrt[3]{m^2}\sqrt[6]{\tau}$ can be determined experimentally. The reversibility of the wave is investigated by plotting E against $\log_{10}(i/(i_d - 1))$ and comparing the slope with the theoretical value of $0.059/n$. The half wave potential E is equal to the $E_{1/2}$ value for $i = i_d/2$ and corresponds to the standard potential *vs*. the used reference electrode (usually the saturated calomel electrode, SCE). A comparison of the $E_{1/2}$ values reported for the systems under discussion shows that the potential values (V) are given with only one or sometimes two digits after the decimal point. This shows the lower accuracy of the experimental data compared to those obtained by potentiometry. The diffusion potential arising from the contact of two solutions of different composition (reference electrode and investigated solution) is estimated to be lower than 0.01 V. However, because of the general use of the SCE, which contains 4.81 $mol \cdot kg^{-1}$ KCl at 298.15 K [81RAR/MIL], the use of certain background electrolytes, *e.g*., perchlorates, can lead to the precipitation of sparingly soluble salts, *e.g*., $KClO_4$(s), on the liquid junction frit and thus to erroneous E values. A serious complication in the investigation of the redox chemistry of technetium is the fact that the redox equilibria are frequently slow and therefore often overlapped by disproportionation and hydrolytic reactions. Unfortunately, it is hardly ever possible in the technetium system to distinguish between such overlapping processes.

In aqueous solution, and in the absence of complexing anions other than hydroxide, technetium can assume oxidation numbers from +VII to +III. All oxidation states have been characterised polarographically. In the following sections we discuss all these Tc redox equilibria. A recent Ph.D. thesis [97COU] contains extensive experiments on the redox behaviour of technetium, using 3D polarography, see discussion in Appendix A.

V.2.1 TcO_4^- and E° of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode

The enthalpy of formation of TcO_4^- can be calculated from the enthalpy of solution of Tc_2O_7(cr) according to the reaction

$$Tc_2O_7(cr) + H_2O(l) \rightleftharpoons 2TcO_4^- + 2H^+$$

cf. Section V.3.2.1.2.d, the enthalpy of formation of Tc_2O_7(cr), *cf*. Section V.3.2.1.2.a and the selected auxiliary data

$$\Delta_f H_m^\circ(TcO_4^-, aq, 298.15\ K) = -(729.4 \pm 7.6)\ kJ \cdot mol^{-1}$$

This is our recommended value. It is combined with the entropy value S°_m (TcO_4^-, aq, 298.15 K) = (199.6 ± 1.5) J·K^{-1}·mol^{-1}, *cf.* Section V.8.1.1.2, to yield

$$\Delta_f G^\circ_m(TcO_4^-, \text{aq}, 298.15\ \text{K}) \quad = \quad -(637.4 \pm 7.6)\ \text{kJ·mol}^{-1}$$

Values of various thermodynamic and transport properties of aqueous TcO_4^- are summarised in Table V.5. A reversible redox couple has been found to form between

Table V.5: Recommended values of thermodynamic and transport properties of TcO_4^- at 298.15 K.

property	value	units	discussed and selected in Section
$\Delta_f G^\circ_m$	−637.4±7.6	kJ·mol^{-1}	V.2.1
$\Delta_f H^\circ_m$	−729.4±7.6	kJ·mol^{-1}	V.2.1
S°_m	199.6±1.5	J·K^{-1}·mol^{-1}	V.8.1.1.2
$C^{\circ\,(a)}_{p,m}$	−15±8	J·K^{-1}·mol^{-1}	V.8.1.2.1
$\bar{V}^{\circ\,(a)}_2$	48.0±0.7	cm^3 · mol^{-1}	V.8.1.2.1
Λ°	55.4±0.5	S · cm^2 · equiv^{-1}	V.8.1.1.1
$D^{\circ\,(b)}$	(1.48±0.01)×10^{-5}	cm^2 · s^{-1}	V.8.1.1.1

(a) Temperatures derivatives are also available for $NaTcO_4$, see Section V.8.1.2.1 for details.
(b) Tracer diffusion coefficient.

TcO_4^- and $TcO_2 \cdot x H_2O$(s) at low pH values [53COB/SMI, 55CAR/SMI, 75LIE/MÜN, 88MEY/ARN, 89MEY/ARN, 91MEY/ARN]. We rewrite this redox reaction as Reaction (V.2)

$$TcO_4^- + 4H^+ + 3e^- \quad \rightleftharpoons \quad TcO_2 \cdot xH_2O(s) + (2 - x)H_2O(l)$$

Systematic studies on the redox potential of the pair $TcO_4^-/TcO_2 \cdot xH_2O$(s) were reported by Cobble, Smith and Boyd [53COB/SMI], Cartledge and Smith [55CAR/SMI], Liebscher and Münze [75LIE/MÜN] and Meyer and Arnold [91MEY/ARN]. Most of these studies are described in more detail in Appendix A.

In three of these emf studies [53COB/SMI, 55CAR/SMI, 75LIE/MÜN] the authors reported that the presence of O_2(g) caused the redox potential of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) half cell at low pH values to become more positive by up to 45 mV [55CAR/SMI], and upon removal of this O_2(g) the potential slowly decreased back to a steady-state value. Cobble [52COB] observed this same type of drift of emf to less positive values when N_2(g) was bubbled through a previously air-saturated solution, but only reported their measurements for air-saturated solutions. Cobble, Smith and Boyd [52COB, 53COB/SMI] reported observing a similar drift in emf for their alkaline solution measurements, which they attributed to absorption of CO_2(g) and, consequently, changes in pH.

The reversible effect of short-time oxygenation on the potential of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode [55CAR/SMI, 75LIE/MÜN] is very similar or identical to that observed for the calomel electrode [61HIL/IVE]. It is likely that both involve some type of "oxygen polarisation". In addition, we note that freshly prepared electrodes sometimes have different redox potentials than aged electrodes. These effects give rise to an observable drift to potentials generally for one day or less, and at longer times make a negligible contribution to the potentials. Thus both the effects of "oxygen polarisation" and aging can cause an initially erroneous reading for the redox potential, but should cause no inaccuracy in the potential measurement once a steady state or equilibrium value is reached. However, purging of solutions with an inert gas is required to reverse "oxygen polarisation".

A more prolonged contact of oxygenated solution with the $TcO_2 \cdot xH_2O$(s) electrode appears to cause an irreversible shift in the observed potential, and seems to be responsible for the higher E° values reported by Cobble, Smith and Boyd [52COB, 53COB/SMI]. It is well known that TcO_4^- is the predominant dissolved chemical form of technetium under oxidising conditions, whereas hydrolysed forms of Tc(IV) can predominate in reducing conditions [87LIE/BAU]. Even in nominally O_2(g)-free conditions, partial oxidation of dissolved Tc(IV) species and $TcO_2 \cdot xH_2O$(s) does occur (see Ref. [86MEY/ARN] in Appendix A).

At concentrations of TcO_4^- that are typically used in emf determinations, *i.e.*, 10^{-4} to 10^{-3} M, the contribution of TcO_4^- produced by oxidation of Tc(IV) relative to its total concentration will probably be small for experiments performed in the presence of an inert gas. However, Cobble, Smith and Boyd [53COB/SMI] performed their experiments in the presence of air; in that case the amount of TcO_4^- produced by oxidation should have been significantly larger. Inasmuch as Cobble, Smith and Boyd apparently did their corrections to E° using the concentrations of $HTcO_4$ added by them to the cells and not the actual equilibrium concentrations, their extrapolations to infinite dilution should be somewhat inaccurate and yield erroneously high values for E°. Consequently, their emf values are rejected and are not analysed further.

In addition to direct determinations of the emf of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) redox couple, there are several other types of experimental information that yield approximate values for the emf of redox couples involving $TcO_2 \cdot xH_2O$(s); see Refs. [45FLA/BLE, 65SPI/KUZ, 71CAR2, 87LIE/BAU] in Appendix A. Although those studies yield only approximate values for E°, they do corroborate values of the experimental E° values.

Cartledge [71CAR2] studied "corrosion" potentials for various redox couples involving technetium metal and lower-valence hydrous oxides of technetium: purportedly Tc(I) through Tc(IV). This study is discussed in detail in Appendix A. Because the identities of the various redox couples in this investigation were not determined directly, but depend on an assumed but experimentally-based value of $\Delta_f G_m^\circ(TcO_2 \cdot xH_2O, s, 298.15\ K)$, and on an assumed linear relation between the molar Gibbs energies of formation of the hydrous oxides and the valence of technetium in that hydrous oxide, they do not constitute independent determinations, and they are not utilised in this review.

Table V.6 gives a listing of the more reliable values for potentials involving the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode [55CAR/SMI, 75LIE/MÜN, 88MEY/ARN,

89MEY/ARN, 91MEY/ARN]. We note that for all of these studies the concentrations were reported in molar units, which need to be converted to molalities. In addition, the ionic strengths of the solutions need to be calculated, because they are required for the estimation of activity coefficient corrections for the TcO_4^- ion.

Densities are required to convert molarities to molalities, but they are not available for aqueous NH_4TcO_4, $KTcO_4$, or their mixtures with H_2SO_4 or HCl. However, the electrolyte concentrations used in these emf studies were fairly low, so the molarity-to-molality conversions can be estimated fairly accurately by the following procedure. At infinite dilution and 298.15 K their ratio is given by $m/c = 1/d^\circ = 1.00296\,\mathrm{dm^3 \cdot kg^{-1}}$, where $d^\circ = 0.997045\,\mathrm{kg \cdot dm^{-3}}$ is the density of pure water. Examination of the m/c values in Table II.5 indicates that for any given electrolyte and for concentrations up to several tenths molar, this ratio is accurately given by

$$m/c \approx 1.00296 + a I_c \tag{V.4}$$

Table II.5 contains a listing of values of the m/c ratios for various aqueous alkali metal chlorides, alkali metal nitrates, $LiClO_4$, $NaClO_4$, and alkaline earth perchlorates at 298.15 K. For those systems our calculated values of a range from 0.016 to 0.044 ($\mathrm{dm^6 \cdot kg^{-1} \cdot mol^{-1}}$), with an average of $a = (0.027 \pm 0.017)$ ($\mathrm{dm^6 \cdot kg^{-1} \cdot mol^{-1}}$). The reported values of I_c for the emf experiments are low enough that the last term in Eq. (V.4) is negligible or nearly negligible for the concentration region pertinent to these studies. Thus the chosen value of a is not important. Under this condition a common value of $a \approx 0.027$ ($\mathrm{dm^6 \cdot kg^{-1} \cdot mol^{-1}}$) will be accepted. Table V.6 contains the calculated molalities of TcO_4^- and the molal ionic strengths. In order to correct the experimental E values to standard conditions, we need to assume that the electrode reaction is reversible. That is, we need to assume that the emf values show a Nernstian response with changes in pH and TcO_4^- concentration.

Liebscher and Münze [75LIE/MÜN] reported that their $TcO_4^-/TcO_2 \cdot x H_2O$(s) electrode couple behaved reversibly as a function of pH for solutions containing 0.5×10^{-4} to 0.05 M H_2SO_4, but the TcO_4^- concentration was not varied enough in that study to provide a definitive check of reversible behaviour. Meyer *et al.* [88MEY/ARN, 89MEY/ARN, 91MEY/ARN] did a comparison of the pH and concentration dependence of E to the theoretical (Nernstian) slopes for their electrode reactions. At pH $\approx$ 2.3, the slope of dependence of E versus $\log_{10} a_{TcO_4^-}$ was reported by them to be $E/\Delta \log_{10} a_{TcO_4^-} = (0.0211 \pm 0.005)$ V, which is in reasonable agreement with the theoretical value of $(RT/3F)\ln 10 = 0.01972$ V.

Similarly, for concentrations of TcO_4^- around 10^{-4} M, their slope of potential plotted against pH was $E/\Delta\mathrm{pH} = -(0.0700 \pm 0.0024)$ V, but for 10^{-3} M TcO_4^- it was (-0.0773 ± 0.0023) V [88MEY/ARN, 89MEY/ARN, 91MEY/ARN]. This value at the higher concentration of TcO_4^- is very close to the theoretical reversible slope of $(4RT/3F)\ln 10 = -0.07888$ V. These slopes indicate that the $TcO_4^-/TcO_2 \cdot x H_2O$(s) couple behaves in a reversible manner at low pH values, at least for concentrations of TcO_4^- of 10^{-3} M and (presumably) higher. Thus the derived E° values yield valid thermodynamic results for $\Delta_f G_m^\circ$ of $TcO_2 \cdot x H_2O$(s).

Table V.6: Experimental values of redox potentials for the $TcO_4^-/TcO_2 \cdot xH_2O$(s) couple at 298.15 K and acidic pH values[(a)].

Solution composition	I_m (mol · kg^{-1})	$[TcO_4^-]$ (mol · kg^{-1})	pH	E[(b)] (V)	E°[(c)] (V)	Reference
$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO_2 \cdot xH_2O(s) + (2-x)H_2O(l)$						
1.00×10^{-3} M $KTcO_4$	1.00×10^{-3}	1.00×10^{-3}	6.65	> -0.091[(d)]	> 0.738	[55CAR/SMI]
1.16×10^{-3} M $KTcO_4$	2.60×10^{-3}	1.16×10^{-3}	3.10	0.198	0.745_9	
$+ 5 \times 10^{-4}$ M H_2SO_4				0.199	0.746_9	
1.66×10^{-3} M $KTcO_4$	6.91×10^{-3}	1.66×10^{-3}	2.49	0.250	0.746_9	
$+ 2.0 \times 10^{-3}$ M H_2SO_4				0.240	0.736_9	
				0.244	0.740_9	
$1.81_5 \times 10^{-3}$ M $KTcO_4$	7.07×10^{-3}	1.82×10^{-3}	2.49	0.244	0.740_2	
$+ 2.0 \times 10^{-3}$ M H_2SO_4						
$1.03_7 \times 10^{-3}$ M $KTcO_4$	5.56×10^{-3}	1.04×10^{-3}	2.69	0.223_5	0.740_2	
$+ 1.7 \times 10^{-3}$ M H_2SO_4						
				$0.742_6 \pm 0.08$[(e)]		
1.43×10^{-2} M NH_4TcO_4	$\sim 1.4 \times 10^{-2}$	1.43×10^{-2}	4.5	0.095	0.732_3[(g)]	[75LIE/MÜN]
$+H_2SO_4$[(f)]						
1.45×10^{-2} M NH_4TcO_4	$\sim 1.5 \times 10^{-2}$	1.45×10^{-2}	3.85	0.163	0.749_0[(g)]	
$+H_2SO_4$[(f)]						
1.40×10^{-2} M NH_4TcO_4	$\sim 1.6 \times 10^{-2}$	1.40×10^{-2}	2.90	0.262	0.773_4	
$+H_2SO_4$[(f)]						
1.25×10^{-2} M NH_4TcO_4	$\sim 3.5 \times 10^{-2}$	1.25×10^{-2}	1.85	0.340	0.769_9	
$+H_2SO_4$[(f)]						
1.14×10^{-2} M NH_4TcO_4	$\sim 1.5 \times 10^{-1}$	1.14×10^{-2}	1.05	0.403	0.771_6	
$+H_2SO_4$[(f)]						
				$0.771_6 \pm 0.003$[(h)]		

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Table V.6: (continued)

Solution composition	I_m (mol · kg^{-1})	[TcO_4^-] (mol · kg^{-1})	pH	$E^{(b)}$ (V)	$E^{\circ(c)}$ (V)	Reference
9.66×10^{-5} M NH_4TcO_4 + 5×10^{-3} M HCl	5.11×10^{-3}	9.69×10^{-5}	2.31	0.243[i]	0.750_0	[91MEY/ARN][j]
2.78×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	5.29×10^{-3}	2.79×10^{-4}	2.30	0.258[i]	0.755_2	
9.39×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	5.96×10^{-3}	9.42×10^{-4}	2.27	0.262[i]	0.746_4	
2.88×10^{-3} M NH_4TcO_4 + 5×10^{-3} M HCl	7.91×10^{-3}	2.89×10^{-3}	2.27	0.273[i]	0.747_9	
2.95×10^{-3} M NH_4TcO_4 + 5×10^{-3} M HCl	7.98×10^{-3}	2.96×10^{-3}	2.30	0.274[i]	0.751_1	
1.01×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	5.12×10^{-3}	1.01×10^{-4}	2.32	0.253[i]	0.760_4	
2.85×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	5.30×10^{-3}	2.86×10^{-4}	2.33	0.258[i]	0.757_3	
9.78×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	6.00×10^{-3}	9.81×10^{-4}	2.32	0.266[i]	0.754_0	
2.93×10^{-3} M NH_4TcO_4 + 5×10^{-3} M HCl	7.96×10^{-3}	2.94×10^{-3}	2.31	0.275[i]	0.752_9	
1.14×10^{-4} M NH_4TcO_4 + 1.00×10^{-4} M HCl	2.15×10^{-4}	1.14×10^{-4}	3.99	0.127[i]	0.764_6	
1.20×10^{-4} M NH_4TcO_4 + 3.92×10^{-4} M HCl	5.14×10^{-4}	1.20×10^{-4}	3.40	0.165[i]	0.755_7	
1.12×10^{-4} M NH_4TcO_4 + 1.66×10^{-3} M HCl	1.78×10^{-3}	1.12×10^{-4}	2.83	0.201[i]	0.747_5	

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Table V.6: (continued)

Solution composition	I_m (mol · kg^{-1})	[TcO_4^-] (mol · kg^{-1})	pH	$E^{(b)}$ (V)	$E^{\circ(c)}$ (V)	Reference
1.07×10^{-4} M NH_4TcO_4 + 5.61×10^{-3} M HCl	5.73×10^{-3}	1.07×10^{-4}	2.30	0.239[i]	0.744_4	
9.11×10^{-5} M NH_4TcO_4 + 1.64×10^{-2} M HCl	1.65×10^{-2}	9.14×10^{-5}	1.90	0.272[i]	0.747_6	
1.06×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	5.12×10^{-3}	1.06×10^{-4}	2.31	0.224[k]	0.730_2	[91MEY/ARN]
3.15×10^{-4} M NH_4TcO_4 + 5×10^{-3} M HCl	5.33×10^{-3}	3.16×10^{-4}	2.33	0.237[k]	0.735_5	
1.13×10^{-3} M NH_4TcO_4 + 5×10^{-3} M HCl	6.15×10^{-3}	1.13×10^{-3}	2.35	0.252[k]	0.741_2	
3.51×10^{-3} M NH_4TcO_4 + 5×10^{-3} M HCl	8.54×10^{-3}	3.52×10^{-3}	2.32	0.263[k]	0.740_2	
1.14×10^{-3} M NH_4TcO_4 + 1.00×10^{-4} M HCl	1.24×10^{-3}	1.14×10^{-3}	3.81	0.146[l]	0.749_9	
1.15×10^{-3} M NH_4TcO_4 + 1.97×10^{-4} M HCl	1.35×10^{-3}	1.15×10^{-3}	3.56	0.165[l]	0.749_1	
1.16×10^{-3} M NH_4TcO_4 + 7.82×10^{-4} M HCl	1.95×10^{-3}	1.16×10^{-3}	3.00	0.203[l]	0.742_9	
1.15×10^{-3} M NH_4TcO_4 + 3.32×10^{-3} M HCl	4.48×10^{-3}	1.15×10^{-3}	2.46	0.246[l]	0.743_6	
1.13×10^{-3} M NH_4TcO_4 + 1.27×10^{-2} M HCl	1.39×10^{-2}	1.13×10^{-3}	2.01	0.286[l]	0.748_6	
				$0.748_5 \pm 0.015$[m]		

[a] The temperatures at which these redox potentials were measured were 297 K [55CAR/SMI], (298.15 ± 0.2) K [75LIE/MÜN], and (298.15 ± 0.1) K [91MEY/ARN].

[b] These are reported emf values relative to the saturated calomel electrode.

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(footnotes continued)

[c] These are standard potentials relative to the standard hydrogen electrode. They were calculated from $E^\circ = E + E(\mathrm{SCE}) + E(\mathrm{LJP}) + 0.078880\,\mathrm{pH} - 0.019720\log_{10} a_{\mathrm{TcO_4^-}}$, were E(SCE) is the emf of the saturated calomel electrode and E(LJP) the estimated liquid junction potential. The value of $E(\mathrm{SCE}) + E(\mathrm{LJP}) = (0.2450 \pm 0.0001)$ V was taken from Table VI of Hills and Ives for an SCE in contact with a dilute acidic (non-buffered) solution [61HIL/IVE].

[d] This potential was still slowly ennobling; consequently it is not an equilibrium potential. Six different $\mathrm{TcO_4^-/TcO_2 \cdot \mathit{x}H_2O(s)}$ electrodes were used for the experiments of Cartledge and Smith [55CAR/SMI].

[e] Average of all of the calculated E° values except for the one at pH= 6.65.

[f] The concentrations of H_2SO_4 in these solutions were not reported by the authors, but they were estimated by this review from the reported pHs.

[g] The values of E° from this study exhibit a pH dependence in this pH region.

[h] Average of the calculated E° values at the three lowest pHs. Liebscher and Münze did not report the concentrations of H_2SO_4 added to their solutions; they were estimated by using the reported pHs of the solutions.

[i] These values were all based on use of a single electrode preparation.

[j] The values of Meyer *et al.* [91MEY/ARN] can also be found in Refs. [88MEY/ARN, 89MEY/ARN].

[k] Second electrode preparation.

[l] Third electrode preparation.

[m] The average of all their emf values is $E^\circ = (0.7485 \pm 0.015)$ V; for solutions with molalities $> 9 \times 10^{-4}\,\mathrm{mol \cdot kg^{-1}}$, $E^\circ = (0.747_3 \pm 0.009)$ V.

The standard potential of Reaction (V.2) is related to the experimental emf by the relation

$$\begin{aligned} E^\circ(\text{V.2}) &= E + (RT/3F)\ln(a_{H_2O}^{2-x}/(a_{TcO_4^-} \times a_{H^+}^4)) \\ &= E + (2-x)(RT/3F)\ln a_{H_2O} + (4RT/3F)(\ln 10)\text{pH} \\ &\quad - (RT/3F)\ln a_{TcO_4^-} \end{aligned} \tag{V.5}$$

where a_{H_2O} is the activity of water in the solution, $a_{TcO_4^-}$ the activity of the TcO_4^- ion, a_{H^+} the activity of the H^+ ion, and E the experimental emf relative to the standard hydrogen electrode. The solutions used for emf measurements are fairly dilute, and, except for solutions studied by Liebscher and Münze [75LIE/MÜN], the ionic strengths are $I_m \leq 8.5 \times 10^{-3}\text{mol} \cdot \text{kg}^{-1}$. At these concentrations $a_{H_2O} \geq 0.9995$. Assuming that $x = 1.6$ for the hydrated dioxides used in the emf studies, see Section V.3.2.5, at 298.15 K the value of $(2-x)(RT/3F)\ln a_{H_2O}$ falls between zero and -2×10^{-6} V. The correction to E°(V.2) for the variation of the water activity is thus about three orders of magnitude less than the precision of the experimental emf measurements and clearly can be neglected. The working form for Eq. (V.5) at 298.15 K thus becomes

$$E^\circ(\text{V.2}) = E + 0.078880\,\text{pH} - 0.019720\log_{10} a_{TcO_4^-}$$

To evaluate E°(V.2) requires values of the molality and ionic activity coefficients of the TcO_4^- ion. Although activity coefficients are available for aqueous solutions of $HTcO_4$ and $NaTcO_4$ at 298.15 K (see Appendix A under Ref. [91RAR/MIL]), experimental values are not available for the mixed electrolyte solutions used in the emf studies and they must therefore be estimated. The molality of the TcO_4^- ion may be equated to the stoichiometric molality of $KTcO_4$ [55CAR/SMI] or NH_4TcO_4 [75LIE/MÜN, 91MEY/ARN] used for preparation of the solutions. Some oxidation of $TcO_2 \cdot xH_2O$(s) to TcO_4^- is known to occur in deoxygenated solutions used for the solubility studies [89MEY/ARN, 91MEY/ARN2], and similar conditions were present for the emf measurements [55CAR/SMI, 75LIE/MÜN, 91MEY/ARN]. However, the observed concentrations of TcO_4^- from oxidation of Tc(IV) under similar experimental conditions were $\leq 4 \times 10^{-7}$ M [91MEY/ARN2], compared to concentrations of 9×10^{-5} to 1.4×10^{-2} M of TcO_4^- salts added in these solutions. The fractional contribution of this pertechnetate ion from oxidation to the total amount present is probably small enough that it can be neglected in the calculation of E°(V.2). The ionic strengths are low enough in the solutions used for emf studies that the activity coefficients of TcO_4^- may be estimated from the Debye-Hückel part of the specific ion interaction equation, which only requires a knowledge of the ionic strength of these solutions. The published emf measurements for the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode involved aqueous mixtures of $KTcO_4$ with H_2SO_4 [55CAR/SMI], of NH_4TcO_4 with H_2SO_4 [75LIE/MÜN], or of NH_4TcO_4 with HCl [91MEY/ARN]. The true ionic strengths of these solutions will be affected by the presence of ion pairs such as HSO_4^-, and will thus be affected by the amount of sulfuric acid present and possibly by other ionic association equilibria.

Solutions of ammonium salts contain NH_4^+ and NH_3(aq) in equilibrium. By using the critically reviewed data for these two species as given in the CODATA book of key values [89COX/WAG], we estimate that the fraction of the NH_4^+ ion that dissociates to form NH_3(aq) at the low pHs relevant to the emf studies will range from 10^{-8} to 10^{-5}. Clearly, the dissociation of NH_4^+ will have a negligible effect on the calculated ionic strength, and all of the ammonia in these solutions can be assumed to be present as NH_4^+.

The various values for the protonation constant of the TcO_4^- ion are discussed in Section V.3.1.2 and summarised in Table V.10. As noted there, all of the experimental values are suspect and may simply represent a misinterpretation of ionic media effects. A similar consideration applies to the alleged ion pair $KTcO_4$ as discussed in Section V.8.1.1.1. Test calculations were performed both assuming the absence of aqueous undissociated $HTcO_4$ [55CAR/SMI, 91MEY/ARN] and aqueous undissociated $KTcO_4$ [55CAR/SMI] and assuming their presence. The derived values of $E°$(V.2) are almost unaffected by the assumed speciation, $\Delta E°$(V.2) $\leq 10^{-4}$ V, which clearly is a negligible difference. Thus the possible formation of aqueous $HTcO_4$ and $KTcO_4$ was neglected in the calculation of ionic strengths of solutions.

Ion-pair association constants have been reported for aqueous KCl [79JOH/PYT], KSO_4^- [59DAV, 79JOH/PYT], and $NH_4SO_4^-$ [75REA], all at 298.15 K. These ion pairs are relatively weak and the reported values of the association constants highly uncertain, and their presence can be neglected in the calculation of ionic strengths and the analysis of thermodynamic data.

The only equilibrium that cannot be neglected for the calculation of ionic strengths is for incomplete dissociation of HSO_4^-. Detailed thermodynamic models have been presented for aqueous H_2SO_4 by Pitzer, Roy, and Silvester [77PIT/ROY] from 0 to 6 mol · kg^{-1} at 298.15 K and by Clegg, Rard, and Pitzer [94CLE/RAR] from 0 to 6.1 mol · kg^{-1} and 273.15 to 328.15 K. Both of these models are based on a dissociation constant of 0.0105 mol · kg^{-1} at 298.15 K which is equivalent to an association constant of $K_1^\circ = 95.24$ mol^{-1} · kg. This value is nearly identical to the value of $K_1^\circ = (95.5 \pm 11.0)$ mol^{-1} · kg used in the CODATA evaluation [89COX/WAG] and recommended by Grenthe *et al.* [92GRE/FUG]. Thus both of these treatments are compatible with the CODATA compilation. The thermodynamic model of Clegg, Rard, and Pitzer [94CLE/RAR] was obtained using a much larger data base than the model of Pitzer, Roy, and Silvester [77PIT/ROY] and should be slightly more accurate.

The thermodynamic model of Clegg, Rard, and Pitzer [94CLE/RAR] was used to calculate the pHs of the aqueous mixtures of $KTcO_4$[1] and H_2SO_4 used by Cartledge and Smith for their emf study [55CAR/SMI]. These modeling calculations predicted the pHs of the four mixture solutions to be 3.04, 2.48, 2.48, and 2.53, which compare quite well with the experimental pHs reported by Cartledge and Smith: 3.10, 2.49, 2.49, and 2.69, respectively. Since this model seems to be able to account fairly well for the thermodynamic properties of H_2SO_4 and its mixtures, it is used to calculate the ionic strengths of the solutions used by Cartledge and Smith.

[1] This $KTcO_4$ was assumed to be a non-interacting strong electrolyte that contributed to the total ionic strength of the solutions.

Liebscher and Münze [75LIE/MÜN] studied mixtures of NH_4TcO_4 with H_2SO_4 but neglected to report the concentrations of H_2SO_4 in the solutions. However, since the pHs of the solutions were given, this review used the model of Clegg, Rard, and Pitzer [94CLE/RAR] to estimate the molalities of H_2SO_4 and thus the total ionic strengths of these solutions.

Table V.6 gives a detailed listing of the solution compositions, ionic strengths, pHs, emfs, and derived $E°$(V.2) values for the three reanalysed data sets. Our recalculated values of $E°$(V.2) agree well with those reported by Meyer and Arnold [91MEY/ARN]. However, they are 3 to 4 mV higher than those reported by Liebscher and Münze [75LIE/MÜN] and 4 to 5 mV higher than those reported by Cartledge and Smith [55CAR/SMI]. Most of this difference arises because of different choices for the emf of the saturated calomel electrode.

Based on the above discussion, we consider the most reliable values of $E°$(V.2) to be the twelve values derived from the investigation of Meyer and Arnold [91MEY/ARN] for concentrations[2] of $TcO_4^- > 9 \times 10^{-4}$ M and the seven values from the investigation of Cartledge and Smith [55CAR/SMI] for solutions containing H_2SO_4. Our recommended value of $E°$(V.2) $= (0.745_6 \pm 0.009)$ V is obtained using equal weighting of these 19 values, but we increase this statistical uncertainty to ± 0.012 V because of possible small additional errors from use of estimated activity coefficient corrections and from possible incomplete correction for the liquid junction potentials. Thus the selected values are

$$\begin{aligned} E°(\text{V.2}, 298.15\ \text{K}) &= (0.746 \pm 0.012)\ \text{V} \\ \log_{10} K°(\text{V.2}, 298.15\ \text{K}) &= 37.8 \pm 0.6 \end{aligned}$$

Values of $E°$(V.2) derived from the study of Liebscher and Münze [75LIE/MÜN] show a slight but apparently systematic decrease with increasing pH, and tend to be higher that those obtained from the other two studies [55CAR/SMI, 91MEY/ARN]. Meyer and Arnold [91MEY/ARN] suggested that the higher $E°$(V.2) values obtained from the emfs in two studies [53COB/SMI, 75LIE/MÜN] may occur, in part, because of differences in hydration of the solid $TcO_2 \cdot xH_2O$(s) phase. At least in the first of these studies [53COB/SMI], the higher emfs more probably occurred because of the deleterious effect of oxygen on the redox potential of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode.

The Gibbs energy of formation of $TcO_2 \cdot xH_2O$(s) can be calculated once a value has been assigned for x. As discussed in Section V.3.2.5, $x \approx 1.6$ seems to be appropriate. Thus, using the selected value of $\Delta_f G°_m(TcO_4^-, \text{aq}, 298.15\ \text{K})$, and the CODATA [89COX/WAG] value of $\Delta_f G°_m(H_2O, \text{l}, 298.15\ \text{K})$, the recommended value

$$\Delta_f G°_m(TcO_2 \cdot 1.6H_2O, \text{s}, 298.15\ \text{K}) = -(758.5 \pm 8.4)\ \text{kJ·mol}^{-1}$$

is obtained.

[2] Solutions with lower concentrations of TcO_4^- have less reproducible emfs that change slowly with time, and are thus less precisely known.

V.2.2 TcO_4^{2-}

Several values have been published for the reduction potential of the half cell

$$TcO_4^- + e^- \rightarrow TcO_4^{2-} \quad \text{(V.6)}$$

in aqueous basic solutions, see Table V.7. Most reduction potentials were reported *vs.* the SCE, and we have converted them to refer to the normal hydrogen electrode, NHE, by using 0.2412 V for the potential of the SCE plus the liquid junction potential when the investigated solutions were not dilute [61HIL/IVE]. Hence, the potentials in this section all refer to the NHE. We have noticed that misunderstandings about reference electrodes have led to erroneous citations in the literature. For example, Zhdanov, Kuzina and Spitsyn [70ZHD/KUZ] erroneously quoted the $E_{1/2}$ potential of -1.15 V of [60COL/DAL] to refer to the "normal calomel electrode" instead of the SCE as given in the original paper. This misunderstanding, which causes a difference of 0.04 V in E, may be due to the fact that the authors [70ZHD/KUZ] themselves used a normal calomel electrode, which is supported by a corresponding footnote in a paper of the same group [70SPI/KUZ]. The same confusion is found in [70SPI/KUZ] where three values of the reduction potential of TcO_4^- in alkaline solution are compared ($E_{1/2} = -0.8$ V) without realising that two of them [62KUZ/ZHD, 65SPI/KUZ] referred to the normal calomel electrode, and the third [60MIL/KEL] to the SCE.

Table V.7: Experimental reduction potentials for Tc(VII)/Tc(VI) according to the half cell reaction: $TcO_4^- + e^- \rightleftharpoons TcO_4^{2-}$.

Method	Ionic medium	T (K)	$[TcO_4^-]$ (M)	$E^{(a)}$ (V)	Reference
amp[(b)]	1 M $Na(ClO_4, OH)$	298.15 ± 0.1	1.068×10^{-3}	-0.63 ± 0.05[(c)]	[69KIS/FEL]
pol	1 M Na_2SO_4	303-305	10^{-4}	-0.52 ± 0.05	[70ZHD/KUZ]
vlt[(d)]	0.12 M NaOH	298.15	1.7×10^{-3}	-0.61	[78DEU/HEI] [80HUR]
pol	0.1 M KOH	295-298	1.5×10^{-4}	-0.56 ± 0.05	[78RUS/CAS]
p-pol[(b)]	0.0075-0.018 M NaOH	298.15	2.77×10^{-5}	-0.64 ± 0.01	[87FOU/AIK]

(a) E has been converted when necessary to refer to the normal hydrogen electrode, NHE, by using 0.2412 V for the potential of the SCE plus the liquid junction potential. The conversion of the standard state pressure from 1 atm to 1 bar is negligible compared to experimental precision: $E^\circ_{(\text{bar})} = E^\circ_{(\text{atm})} - 0.0017$ V.

(b) amp = chronoamperometry, p-pol = pulse polarography.

(c) Value estimated from experimental curves by Rard [83RAR].

(d) High scan rates up to 100V/s were used.

As indicated above, several papers report $E_{1/2}$ values with only one digit, *e.g.*, -0.8 V *vs.* SCE [78RUS/CAS]. Conversion to refer to the NHE results in -0.56 V, pretending a higher precision. This could be avoided by providing the values with uncertainties.

As can be seen from Table V.7, the reported E values for the reduction of Tc(VII) to Tc(VI) rather consistently cluster around a potential of -0.6 V *vs.* NHE. Kissel and

Feldberg [69KIS/FEL], using chronoamperometry, have demonstrated that technetate ion, TcO_4^{2-}, is produced at the surface of the cathode when $\geq$ 0.005% gelatin was present in solution, and it then undergoes rapid disproportionation to Tc(VII) and Tc(V) according to the reaction

$$2TcO_4^{2-} \quad \rightarrow \quad TcO_4^- + Tc(V) \tag{V.7}$$

In this system gelatin seems to be the blocking agent for the disproportionation of TcO_4^{2-}, because in the absence of gelatin the production of technetate ion is bypassed, and the reaction observed is the two electron reduction

$$TcO_4^- + 2e^- \quad \rightarrow \quad Tc(V) \tag{V.8}$$

The ionic strength dependence of the rate constant of Reaction (V.7) confirms a two-fold charge of the reacting species. When solutions of 0.01-0.2 M $^{99}TcO_4^-$ in 0.1 M NaOH are irradiated with a electron beam under conditions designed to yield aqueous "e^-" [78DEU/HEI], the optical density of the aqueous "e^-" disappears according to a first order rate law both in the aqueous electron concentration and in $[TcO_4^-]$: $k_2(298.15\ K) = (2.48 \pm 0.05) \times 10^{10}\ dm^3 \cdot mol^{-1} \cdot s^{-1}$ Concomitant with the disappearance of electrons is the appearance of a new species presumed to be TcO_4^{2-} as shown by examination of the absorption spectra. It is stable for 10 ms and undergoes detectable chemical reaction within 50 ms. Hence, in aqueous alkaline media Tc(VI) is a viable oxidation state, which is potentially useful for the preparation of technetium radiopharmaceuticals [78DEU/HEI].

Because of this extremely rapid disproportionation of TcO_4^{2-} by Reaction (V.7), only the $2e^-$ reduction of TcO_4^- is observed using most traditional electrochemical techniques. The difficulty of studying the $1e^-$ reduction of TcO_4^- is further complicated by the nearly identical values of $E°$ (V.6, 298.15 K) and $E°$ (V.8, 298.15 K), which are the same within their uncertainty limits. Thus the most reliable techniques for determining the reversible potential of Reaction (V.6) are rapid scanning methods [78DEU/HEI, 80HUR, 87FOU/AIK] or studies using gelatin to kinetically block the disproportionation of TcO_4^{2-} [69KIS/FEL].

Two important contributions not listed in Table V.7 are those of Schwochau and Astheimer [74SCH/AST, 76AST/SCH]. They isolated tetramethylammonium technetate(VI) and measured its spectroscopic and magnetoscopic properties. When they dissolved $((CH_3)_4N)_2TcO_4(s)$ in neutral de-aerated water, they showed by dc-polarography that TcO_4^{2-} rapidly disproportionated into Tc(VII) and Tc(V). Founta, Aikens and Clark [87FOU/AIK] used normal pulse polarography to show a one-electron reduction to TcO_4^{2-} at pH = 11.05 and 11.85 and $I = 0.0075$ M. From measurements in the pH range 11.05 to 12.25 they showed that the upper limits of the ionic strength and the pulse width corresponding to Tc(VI) as the end product, are strongly interdependent. By using pulse radiolysis with electrons, TcO_4^{2-} has been produced in sufficient concentration to characterise its optical absorption spectrum in neutral and alkaline solutions [77PIK/KRY, 78DEU/HEI, 79KRY/PIK].

Electrochemical measurements of the redox potential using rapid scanning techniques [78DEU/HEI, 80HUR, 87FOU/AIK] for using gelatin to block the decomposition of TcO_4^{2-} [69KIS/FEL] yield more reliable values for the standard potential of

Reaction (V.7) than do more traditional electrochemical methods. Among the available reduction potentials according to Reaction (V.6), the value reported in [87FOU/AIK] is the most reliable one. The reproducibility is good, as is reflected in the low uncertainty given by the authors. Because of the low ionic strength used, this value can be considered, without corrections, as being representative at $I = 0$:

$$E^\circ(\text{V.6}, 298.15\ \text{K}) = -(0.64 \pm 0.03)\ \text{V}$$
$$\log_{10} K^\circ(\text{V.6}, 298.15\ \text{K}) = -10.8 \pm 0.5$$

Our uncertainty is estimated such that it includes possible systematic errors as well as considers the agreement among the other fairly reliable experimental values [69KIS/FEL, 78DEU/HEI, 80HUR]. However, because of the instability of TcO_4^{2-}, it is not meaningful to include this potential or the derived $\log_{10} K^\circ$ value in a thermodynamic database, without including the rate constant for the disproportionation of TcO_4^{2-} at the same time. In practice, Tc(VI) is only of potential relevance in the area of chemical syntheses, and in elucidating the stepwise redox behaviour of technetium.

It will never be a stable oxidation state in aqueous equilibrium systems.

V.2.3 Tc(V)

In 1968 Münze [68MÜN2] interpreted the pH-independent ac-polarographic wave at -0.57 V for the reduction of TcO_4^- in alkaline aqueous media as a reversible one-electron transfer to TcO_4^{2-}, followed by disproportionation of TcO_4^{2-} to TcO_4^- and Tc(V), hence an overall two-electron reduction:

$$TcO_4^- + 2e^- \rightarrow Tc(V) \qquad \text{(V.9)}$$

The Tc(V) produced by this reduction is highly unstable and disproportionates almost immediately. Consequently, the extent of hydrolysis of this Tc(V) is unknown. Experimental literature values are summarised in Table V.8.

Colton *et al.* [60COL/DAL] observed that in 0.1 M KOH the pertechnetate ion was reduced by a two-electron process followed by a one-electron process and resulting in Tc(IV). Miller, Kelley and Thomason [60MIL/KEL] obtained about the same values of E(V.9) in 0.1 M NaOH, alkaline KCl and NH_4Cl solutions, and a pH=10 borate buffer. Similarly, Astheimer and Schwochau [64AST/SCH] studied this reduction potential in 0.1 M, 0.5 M and 1 M NaOH and LiCl solutions. While the resulting potentials depended on ionic strength, they were essentially the same in NaOH and LiCl solutions of the same ionic strengths. Likewise, Bratu *et al.* [75BRA/BRA] obtained identical reduction potentials in 0.1 M KOH, NaOH or KCl, as well as in 1 M $NaClO_4$. However, documentation in that paper is not satisfactory, *cf.* Appendix A. Russel and Cash [78RUS/CAS] also found that the reduction potential of Reaction (V.9) was independent of pH. These studies indicate that no H^+ ions participate in the two-electron reduction of TcO_4^- at neutral and alkaline pHs. Hence, the primary reduced species can be formulated as Tc(V), according to Reaction (V.9). However, there is no direct

Table V.8: Experimental reduction potentials for Tc(VII)/Tc(V) according to the following half cell: $TcO_4^- + 2e^- \rightleftharpoons Tc(V)$.

Method	Ionic medium	T (K)	E[(a)] (V)	Reference
pol	0.1 M KOH	RT ?	-0.61 ± 0.01	[60COL/DAL]
pol	0.1 M NaOH, NH_4Cl, KCl	299.65	~ -0.56	[60MIL/KEL]
pol	pH = 10 (borate buffer)	299.65	-0.55	
pol	1 M $NaClO_4$ + KOH	298-299	-0.63[(b)]	[62KUZ/ZHD]
pol	0.1 M NaOH	298.15	-0.57	[64AST/SCH]
	0.5 M NaOH	298.15	-0.54	
	1 M NaOH	298.15	-0.52	
	0.1 M LiCl	298.15	-0.58	
	0.5 M LiCl	298.15	-0.54	
	1 M LiCl	298.15	-0.54	
pol	0.5 M $NaClO_4$ + 0.1 M NaOH	RT ?	-0.57	[68MÜN2]
amp[(c)]	1 M NaOH	298.15	-0.55[(d)]	[69KIS/FEL]
pol	0.1 M NaOH, KOH, KCl	RT ?	-0.64	[75BRA/BRA]
pol	1 M $NaClO_4$	RT ?	-0.56	
pol	0.05 M $(C_2H_5)_4NClO_4$	298.15	-0.60	[76AST/SCH]
pol	0.1 M KOH, pH = 13	295-298	-0.56[(d)]	[78RUS/CAS]
pol, vlt, cou	0.5 M KCl-NaOH, pH = 12	RT ?	-0.58[(e)]	[79GRA/DEV]
vlt	0.12 M KOH	RT?	-0.56[(e)]	[80HUR]

(a) E has been converted when necessary to refer to the normal hydrogen electrode, NHE, by using 0.2412 V for the potential of the SCE plus the liquid junction potential. The conversion of the standard state pressure from 1 atm to 1 bar is negligible compared to the experimental precision of the E values: $E^\circ_{(bar)} = E^\circ_{(atm)} - 0.0017$ V.

(b) If the authors used a "normal calomel electrode" instead of an SCE, *cf.* Appendix A, the potential *vs*. NHE would be -0.59 V.

(c) amp = chronoamperometry.

(d) The values vary from -0.54 to -0.61 V using pulse polarography and cyclic voltammetry.

(e) Value estimated from experimental curve by Rard [83RAR].

evidence that Tc(V) is the actual chemical species formed by electrochemical reduction of TcO_4^{2-} because the Tc(V) species is so unstable that it rapidly disproportionates to TcO_4^- and Tc(IV). Furthermore, no salts containing the Tc(V) anion have been isolated under such conditions.

It should be mentioned that the comparatively large scatter of the reported E values (as an illustration, for Reaction (V.9) a difference of 0.03 V in E corresponds to a difference of an order of magnitude in the equilibrium constant, K), see Table V.8, is mainly due to systematic errors from different measurements: (1) by using uncalibrated cells; (2) by not mentioning any effort to reduce the liquid junction potential; and (3) by reporting E values with only one or two digits after the decimal point, and thus implying an imprecision of at least 0.1 V or 0.01 V, respectively. Indeed, the values of $E = -0.56$ V in Table V.8 are all derived from reported half wave potentials of -0.8 V, and they therefore imply an uncertainty of $\pm(0.05 - 0.1)\ V$.

Since no new data for the redox potential of the pair TcO_4^-/Tc(V) have been published since the review of Rard [83RAR], his result is still valid. He fitted the data to the equation $E = E^\circ + A\sqrt{I}$ and obtained E°(V.9, 298.15 K) $= -(0.600 \pm 0.026)$ V, where the uncertainty corresponds to a standard deviation of 1σ. In the present review series, we prefer to use the SIT equation (*cf.* Appendix C) for ionic strength extrapolations. As did Rard, we consider the value reported in [62KUZ/ZHD] as an outlier, and we extrapolate the remaining E values of Table V.8 (with the exception of those of [75BRA/BRA], *cf.* Appendix A) to $I = 0$. Since all the potentials have already been converted to refer to the NHE, we have Δz^2(V.9) $= +8$, and hence[3] $E - 0.23664D = E^\circ - 0.02958\Delta\varepsilon I$. Figure V.2 shows that the consistency of the values is not very good. An unweighted linear regression of these values gives the same result as obtained by Rard [83RAR]:

$$\begin{aligned} E^\circ(\text{V.9}, 298.15\ \text{K}) &= -(0.60 \pm 0.05)\ \text{V} \\ \log_{10} K^\circ(\text{V.9}, 298.15\ \text{K}) &= -20.3 \pm 1.7 \end{aligned}$$

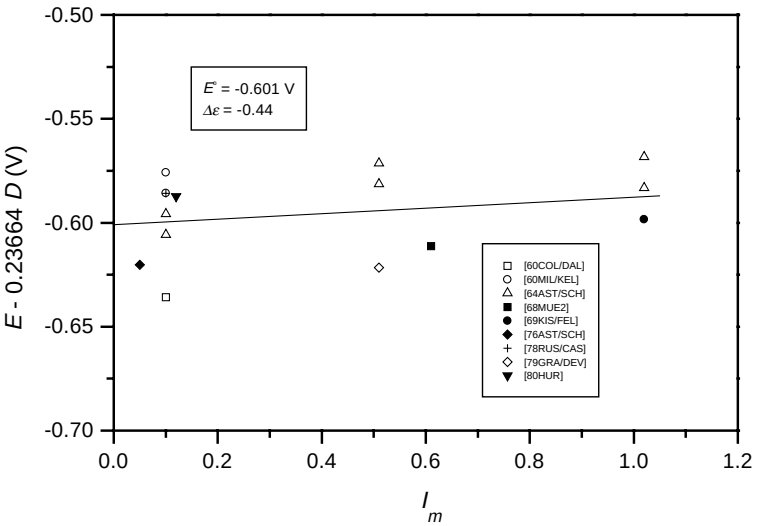
and from the slope of the straight line an ion interaction coefficient of $\Delta\varepsilon = -0.44\ \text{kg}\cdot\text{mol}^{-1}$ can be estimated. We estimate the uncertainty in the resulting standard potential to ± 0.05 V to reflect the significant scattering of the experimental points, *cf.* Figure V.2.

Note that Tc(V) is not a stable species as it decomposes further, and its consideration in chemical equilibrium calculations is thus not necessary (see also the discussion on the stability of TcO_4^{2-} above). Because of its instability, and because of the uncertainty about its degree of hydrolysis at neatral and alkaline pHs, no Gibbs energy of formation is recommended for Tc(V). The recommended values for E°(V.9, 298.15 K) and E°(V.6, 298.15 K) are indistinguishable within their experimental errors. Hence, whether a 1 e^- or 2 e^- reduction of TcO_4^- is observed by a particular technique depends on kinetic rather than thermodynamic factors.

The acid/base chemistry of Tc(V) is incompletely known.

[3] The coefficient of 0.02958 V corresponds to the conversion factor from $\log_{10} K$ to E (*i.e.*, $RT\ln(10)/nF$) for a two-electron transfer ($n = 2$) at 298.15 K.

Figure V.2: Unweighted extrapolation to $I = 0$ of experimental formal potential data for the half cell $TcO_4^- + 2e^- \rightleftharpoons Tc(V)$ in aqueous solutions containing various inert salts, *cf.* Table V.8. The straight line shows the result of the linear extrapolation. The resulting slope of about -0.013 V·kg·mol^{-1} corresponds to a $\Delta\varepsilon$ value of -0.44 kg·mol^{-1}, *cf.* Appendix C. The units of concentration reported in the various studies listed in Table V.8 were converted from mol·dm^{-3} to mol·kg^{-1}.



V.2.4 Tc(IV)

In contrast to Tc(VI) and Tc(V), Tc(IV) is a stable oxidation state. Tc(IV) is the most important oxidation state of technetium under reducing conditions. From the pH independence of the solubility of $TcO_2 \cdot xH_2O$(s), it is evident that an uncharged Tc(IV) species dominates in non-complexing solutions in the pH range $3 < pH < 10$. Possible chemical formulae of this uncharged Tc(IV) species are $Tc(OH)_4$(aq), $TcO(OH)_2$(aq) and TcO_2(aq). It is fairly well established today that a maximum of two protons can be forced upon the uncharged Tc(IV) complex in the pH range of aqueous solutions, *cf.* Section V.3.1.1. This leaves TcO^{2+} as an undissociable unit, and it is thus reasonable to follow the current practice and to use $TcO(OH)_2$(aq) as the reference formula of the uncharged Tc(IV) complex.

Due to the low solubility of TcO_2(s), the potentiometric redox measurements of the redox pair Tc(VII)/Tc(IV) have always been performed in the presence of $TcO_2 \cdot xH_2O$(s), and reduction potentials were thus expressed with respect to this solid, and not with respect to an aqueous Tc(IV) species. For convenience, we give here the redox potential of the half cell involving aqueous species only:

$$TcO_4^- + 4H^+ + 3e^- \rightleftharpoons TcO(OH)_2(aq) + H_2O(l) \qquad \text{(V.10)}$$

The corresponding standard reduction potential and $\log_{10} K^\circ$ values are calculated from the selected values in Sections V.2.1 and V.3.2.5:

$$\begin{aligned} E^\circ(\text{V.10}, 298.15\ \text{K}) &= (0.579 \pm 0.016)\ \text{V} \\ \log_{10} K^\circ(\text{V.10}, 298.15\ \text{K}) &= 29.4 \pm 0.8 \end{aligned}$$

The recommended thermodynamic data of $TcO(OH)_2$(aq) are selected and derived from solubility measurements of $TcO_2 \cdot 1.6H_2O$(s), *cf.* Section V.3.2.5. The formation constants of the protonation and deprotonation products of $TcO(OH)_2$(aq): TcO^{2+}, $TcO(OH)^+$ and $TcO(OH)_3^-$, are discussed and selected in Section V.3.1.1.

V.2.5 Tc^{3+}

The first polarographic reduction wave of TcO_4^- in acidic solution is strongly pH dependent and irreversible. At $pH < 4$ and in sulphate (0.25 M) and chloride (0.5 M) media, a $4e^-$ reduction to Tc(III) can be observed which becomes a $3e^-$ reduction at higher pH values: [63SAL/RUL, 78GRA/ROG, 78RUS/CAS]. The shift of $E_{1/2}$ with pH confirms, in both media, an approximately eighth power dependence on the hydrogen ion concentration, in accordance with the reaction

$$TcO_4^- + 8H^+ + 4e^- \longrightarrow Tc^{3+} + 4H_2O(l) \qquad \text{(V.11)}$$

Similar results were also obtained in 0.1 M $NaClO_4$ solutions [67RUL/PAC]. In some media, Tc(III) could be reoxidized at the electrode to Tc(IV) or Tc(V) [78RUS/CAS]. Contrary to earlier workers, Russel and Cash [78RUS/CAS] demonstrated the importance of the use of buffered solutions to prevent alkalinisation of the solution adjacent to

the electrode, as hydrogen ions are consumed in the reduction of pertechnetate. They measured a half-wave potential of $E_{1/2}$(V.11) $= -(0.10 \times \mathrm{pH})$ V *vs.* SCE in the range $0 < \mathrm{pH} < 7$. Concerning the reduction mechanism, Russel and Cash [78RUS/CAS] found support for a discharge reaction such as

$$\mathrm{HTcO_4 + e^- \longrightarrow HTcO_4^-} \tag{V.12}$$

preceded by a fast protonation reaction of pertechnetate ion, and followed by a series of fast reduction processes. In contrast, Pihlar [79PIH] proposed the reaction

$$\mathrm{TcO_4^- + 2H^+ + e^- \longrightarrow TcO_3(aq) + H_2O(l)} \tag{V.13}$$

to be the rate-determining step. However, the reduction of TcO_4^- to Tc^{3+} involves the stripping of four oxygen atoms, which is expected to involve several intermediate steps with slow kinetics. It thus seems that the reduction processes summarized by Eq. (V.11) are not completely understood.

As Rard [83RAR] indicated, Tc(III) solutions are also very prone to oxidation to Tc(IV) both electrochemically and by atmospheric oxygen [74MAG/CAR, 79GRA/DEV, 82PAQ/LIS]. In fact, reoxidation of Tc(III) to Tc(IV) can be done under rather gentle conditions. However, usually no clearly defined polarographic oxidation wave occurs for Tc(III) $\longrightarrow$ Tc(IV), because it is masked by the Hg oxidation wave in acidic solutions. Rard [83RAR] mentioned the possibility that Tc(III) and TcO_4^- may react to form $TcO_2 \cdot x H_2O$(s) [82RUS].

The radiopolarographic study of Grassi *et al.* [78GRA/ROG] provided the first quantitative evidence that Tc(III) reduction in acidic solution is a $3e^-$ reduction to Tc(0). The ratio of the diffusion currents of the first two polarographic diffusion-controlled reduction waves was 4/3. Since the first wave is a $4e^-$ reduction of TcO_4^- to Tc(III), the second reduction wave should consequently be a $3e^-$ reduction to Tc(0), assuming similar diffusion coefficients of the involved species. This measurement was made at $\mathrm{pH} = 2.83$, where the catalytic hydrogen current is low enough to allow the diffusion current and the half-wave potential to be measured for the second wave. It thus appears that Tc(III) is reduced to Tc(0) between -0.6 and -0.7 V (-0.9 V *vs.* SCE) in non-complexing media at pH values of 3 and lower. The lack of a pH dependence in the investigated pH range between 1 and 3 [78GRA/ROG] implies that unhydrolysed Tc(III) is involved in Reaction (V.14)

$$\mathrm{Tc^{3+} + 3e^- \rightleftharpoons Tc(in\ Hg)}, \tag{V.14}$$

but it is not known whether Tc(0) is present as small metallic particles in the Hg or as an insoluble Tc amalgam. The hydrolysis properties of Tc^{3+} are not known. On one hand, the homologue Mn^{3+} has been reported, based on spectroscopic measurements, to hydrolyse in concentrated strong acid [76BAE/MES], and a similar behaviour might be expected for Tc^{3+}. On the other hand, the acidities of Fe^{3+} and Cr^{3+} are much lower, which reduces the credibility of the Mn^{3+} analogy.

It cannot be excluded that the manganese solutions contained polymerized Mn^{3+} of some form instead of just a monomeric hydrolysis product. On this basis it is difficult to

predict the hydrolysis behaviour of Tc^{3+}. However, from the work of Grassi [77GRA] it seems clear that Tc(III) solutions can be prepared. Their investigation should give more information on the behaviour of this ion in aqueous solution.

Grassi [77GRA] carried out a coulometric reduction of 1.88×10^{-3} M TcO_4^- in 0.5 M (KCl + HCl) with starting pH = 2.27 which, at a final pH of about 3, had consumed only 3.4 protons instead of 8 as expected from Reaction (V.11) if unhydrolysed Tc^{3+} had been produced. This would mean that 4.6 protons had been liberated from each Tc^{3+} aqua ion, leading to negatively charged Tc(III) species in acidic solution. The fact that no such anionic species are found with Tc(IV) under similar conditions, makes the measurements of Grassi [77GRA] difficult to understand. An inclusion of possibly formed Tc(III) chloride complexes cannot help very much in explaining these results. As found elsewhere [78RUS/CAS], the limiting current of the second reduction wave was lower than expected for Reaction (V.14), which means that part of Tc(III) was lost or was unavailable for further reduction to Tc(0). Grassi [77GRA] stated that the loss of Tc(III) did not result from either poor solubility or reoxidation to Tc(IV) or TcO_4^- by atmospheric oxygen. Apparently, during the coulometric experiment a part of Tc(III) was transformed by an unknown reaction to an unidentified, electro-inactive species. Inconsistencies in the calculated predominance E_h-pH diagram using $E_{1/2}$ for Tc(III)/Tc(0) have already been mentioned by Rard [83RAR].

In contrast, the oxidation potentials for Tc(III) to Tc(IV) give more reasonable results. Grassi, Devynck and Trémillon [79GRA/DEV] studied the oxidation of Tc(III) to Tc(IV) in sulphate solution at pH values of 1.6, 2.0, 2.5 and 3.25. The oxidation was quasi-reversible and involved one electron and two protons, which they supposed corresponded to the following type of equilibrium:

$$TcO_2(aq) + 2H^+ + e^- \rightleftharpoons TcO^+ + H_2O(l) \qquad (V.15)$$

Because of the linear variation of $E_{1/2}$ in the corresponding pH range only one species of each oxidation state is involved, and they reported $E_{1/2}(V.15) = -0.319 + 0.1182 \times pH + 0.05911 \times \log_{10}[Tc(OH)_2^+]$. It is not clear why Grassi and coworkers did not discuss the following contradiction: they assumed that Tc(III) was involved as unhydrolysed aqua ion in Reaction (V.14), but as TcO^+ or $Tc(OH)_2^+$ in Reaction (V.15), both in the same pH region.

The half-wave potential for oxidation of Tc(III) in $NaHSO_4$-Na_2SO_4 changed linearly with pH, for pH about 1.6 to 3.0, and it was quasi-reversible [79GRA/DEV]. This potential can be used to relate the Gibbs energy of the reduction of aqueous Tc(IV) to Tc(III), provided 1) sulphate complexes are negligible or can be corrected for, and 2) an assumption is made as the hydrolysis state of Tc(IV). This redox reaction has the more general form

$$TcO_q(OH)_n^{4-2q-n} + 2H^+ + e^- \quad \rightleftharpoons \quad TcO_{q-1}(OH)_n^{5-2q-n} + H_2O(l) \qquad (V.16)$$

where ($q = 1$, $n = 0$), ($q = 1$, $n = 1$), and ($q = 1$, $n = 2$) are possible combinations, and the potential *vs.* NHE reported in [79GRA/DEV] was $E°$(V.16) = 0.319 V in 0.5 M $NaHSO_4$-Na_2SO_4 solutions.

The hydrolysis constants for Tc(IV) and the pH dependence of the solubilities (*cf.* Table V.9 and Table V.13 in Section V.3), indicate that more than one hydrolysed form

of Tc(IV) should be present at equilibrium in the pH range of 1.6 to 3.25. However, Reaction (V.15) was studied by Grassi, Devynck, and Trémillon [79GRA/DEV] over this pH range, was found to be quasi-reversible, and their emfs had the proper Nernstian slope for a one electron process involving the production of two protons per technetium. There are only two obvious ways to "explain" this seeming contradiction. 1) More than one hydrolysed form of Tc(III) and of Tc(IV) exist in these solutions. However, the hydrolysis constants have values such that there is essentially complete compensation when E° values are calculated from the experimental emfs, concentrations, and pHs, so that only single species each of Tc(III) and Tc(IV) appear to be present in this pH range. Such a complete compensation seems extremely unlikely. 2) An alternative possibility was suggested by Rard [83RAR], that the Tc(III) existed in aqueous solutions as unhydrolysed Tc^{3+} and thus polarographic oxidation initially produces TcO^{2+}. Furthermore, the lack of the pH dependence for the calculated E° for Reaction (V.15) in this pH range implies that further hydrolysis of TcO^{2+} to form $TcO(OH)^{+}$ or $TcO(OH)_2$(aq) would be too slow to be observed on the time scale of polarographic measurements.

We tentatively accept the value of $\Delta_f G^\circ_m(Tc^{3+}, aq, 298.15\ K) = (105.8 \pm 10.5)$ kJ·mol^{-1} derived by Rard [83RAR] from these emfs [79GRA/DEV], since including this value in the data base will allow the construction of fairly realistic potential-pH diagrams. However, this is not a unique solution to this dilemma, and future work may indicate that the Tc(III) is more hydrolysed than suggested by Rard. Thus this value of $\Delta_f G^\circ_m(Tc^{3+}, aq, 298.15\ K)$ is only provisional and is not a recommended value.

The oxidation of Tc(III) after coulometry can be done polarographically or using atmospheric oxygen; in both cases the formation of a sulphate complex, $[Tc(OH)_2(SO_4)_2]^{2-}$ is observed as already mentioned by Spitsyn *et al.* [76SPI/KUZ] (pH = 1.5). It appears that the rate of formation of this complex increases with decreasing pH, indicating that protons are involved. This could be due to the formation of the electro-inactive complex anticipated in the above discussion on the decrease of the Tc(III) reactivity, although Spitsyn *et al.* [76SPI/KUZ] obtained the complex at pH values near 0 (0.71 M H_2SO_4). Grassi [77GRA] did not include the sulphate complex in his discussion of the quasi-reversible oxidation of Tc(III) to Tc(IV) in 0.5 M ($NaHSO_4$ + Na_2SO_4). It was assumed that this reaction was too slow to exert an influence on the oxidation rate of Tc(III). This assumption is partly supported by the evolution of the voltammetric curves with pH, and by the fact that the slope of the curve $E_{1/2} = f(\text{pH})$ did not change [77GRA].

As a conclusion, the state-of-the-art is such that no data can be recommended on these systems, neither for any Tc(III) species, nor for any of the redox reactions connected with Tc(III).

V.2.6 Tc^{2+}

There is no experimental evidence for the existence of Tc^{2+} as a viable chemical species in aqueous solution. Although in some earlier reviews *e.g.*, [52LAT, 66ZOU/POU, 74MAG/CAR, 79ALL/KIG, 82JEN, 84KHA/WHI, 86BEA/LOR] estimated data for

Tc^{2+} were included, these are in conflict with the current knowledge of the redox chemistry of technetium. Values for the Gibbs energy of formation of Tc^{2+} in these databases are based directly or indirectly on Latimer's reported value [52LAT] of +0.4 V for the reduction potential

$$Tc^{2+} + 2e^- \rightleftharpoons Tc(s)$$

Latimer did not explain the source of this reduction potential, but it is probably an estimated value based on an analogy with the chemistry of manganese rather than an experimental value.

We concur with Rard [83RAR] that Tc^{2+} should not be included in a recommended thermodynamic data base for Tc.

V.3 Oxide, and hydrogen compounds and complexes

V.3.1 Aqueous species formed by hydrolysis and protonation reactions

V.3.1.1 The acid/base chemistry of Tc(IV)

The constants reported in the literature on Tc(IV) hydrolysis are summarised in Table V.9. The earliest measurements are by Gorski and Koch [69GOR/KOC]. Their measured electrophoretic mobilities at 18°C and $I = 0.1$ M KNO_3 suggest a species with charge +2 dominating at pH < 1.3, and a neutral one dominating at pH > 2.5. Although the shape of their curve of "mobility *vs.* pH", *cf.* Figure 2 of [69GOR/KOC], is not compatible with simple acid/base equilibria, the authors suggested that they correspond to the reactions

$$TcO^{2+} + H_2O(l) \rightleftharpoons TcO(OH)^+ + H^+ \qquad (V.17)$$

$$TcO(OH)^+ + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) + H^+ \qquad (V.18)$$

Their reported constants, $\log_{10}{}^{*}K$(V.17) $= -(1.37 \pm 0.04)$ and $\log_{10}{}^{*}K$(V.18) $= -(2.43 \pm 0.05)$, have been adopted in many subsequent publications and data bases, *e.g.*, [83RAR, 87CRO/EWA, 88PHI/HAL, 92PEA/BER]. However, due to several significant shortcomings, *cf.* Appendix A, these constants cannot be considered reliable. Guénnec and Guillaumont [73GUÉ/GUI] used solvent extraction and obtained only a rough estimate of $\log_{10}{}^{*}K$(V.18) ≈ -1, *cf.* Appendix A. The ion exchange experiments of Owunwanne, Marinsky and Blau [77OWU/MAR] suggested a species with charge +2 at pH $\leq$ 2, while Sundrehagen [79SUN] was not able to reproduce any of those results but, in contrast, proposed the formation of a dimer, $(TcO(OH)_2)_2(aq)$. However, the results of these experiments [79SUN] are difficult to evaluate and were not accepted in this review, *cf.* Appendix A.

Meyer *et al.* [91MEY/ARN2] were the first to measure and correct for the formation of TcO_4^- during the experiments. Their experiments are accepted in this review. Meyer *et al.* [91MEY/ARN2] did not make an independent evaluation of their solubility data at low pH, but rather adopted the values of [69GOR/KOC] in order to interpret

Table V.9: Experimental equilibrium data for the technetium(IV) hydroxide and hydroxide-carbonate system.

Method	Ionic Medium	t (°C)	$\log_{10}K^{(a)}$	Reference
$TcO^{2+} + H_2O(l) \rightleftharpoons TcO(OH)^+ + H^+$				
elp	0.1 M KNO_3	18	-1.37 ± 0.04	[69GOR/KOC]
sol	0.01 M (Na, H)Cl	25	> -1.5[(b)]	[91MEY/ARN2]
$TcO(OH)^+ + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) + H^+$				
elp	0.1 M KNO_3	18	-2.43 ± 0.05	[69GOR/KOC]
sp	0.2 M (H, Na)ClO_4	RT[(c)]	-2.03	[79SUN]
dis	var. $HClO_4$	RT[(c)]	-1	[73GUÉ/GUI]
sol	0.01 -1 M (Na, H)Cl	25	-2.5[(b)]	[91MEY/ARN2]
$TcO(OH)_2(aq) + H_2O(l) \rightleftharpoons TcO(OH)_3^- + H^+$				
pot	< 0.01 M	25	-10.89 ± 0.05[(d)]	[92ERI/NDA]
$2\ TcO(OH)_2(aq) \rightleftharpoons (TcO(OH)_2)_2(aq)$				
sp	0.2 M (H, Na)ClO_4	RT[(c)]	6.50 ± 0.04	[79SUN]
$TcO(OH)_2(aq) + CO_2(g) \rightleftharpoons TcCO_3(OH)_2(aq)$				
pot	< 0.01 M	25	1.08 ± 0.09[(d)]	[92ERI/NDA]
$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \rightleftharpoons TcCO_3(OH)_3^- + H^+$				
pot	< 0.01 M	25	-7.18 ± 0.09[(d)]	[92ERI/NDA]

(a) $\log_{10} K$ refers to the reactions indicated in the ionic medium and at the temperature given in the table.
(b) Estimated in this review.
(c) RT means room temperature.
(d) Recalculated to refer to the reactions indicated in this table.

their solubility curves. However, since they used HCl as inert electrolyte, their solubility at low pH (and, hence, high chloride concentration) may be erroneous because chloride and hydroxide-chloride complexes can be formed under these conditions, see for example [69KAN] and Section V.4. Unfortunately, quantitative information on the chloride-hydroxide system is insufficient to correct the data that were measured in chloride containing solutions.

Meyer *et al.* [91MEY/ARN2] performed solubility measurements for $TcO_2 \cdot xH_2O$(s) in aqueous 0.05 to 2.6 M NaCl solutions at pH=6.9 to 9.3 and observed no significant variation of the solubility with chloride concentration or pH. Since $TcO(OH)_2$(aq) is the predominant aqueous species at low ionic strengths for $3 < pH < 10$, the observed lack of a dependence of solubility with chloride concentration implies that this species persists even in chloride solutions. Thus chloride and mixed hydroxide-chloride complexes of Tc(IV) probably do not form in significant amounts for solutions with $pH > 3$.

In addition, the effect of the liquid junction potential at low pH is such that the real pH value is lower than indicated in [91MEY/ARN2]. Since both the chloride complexes and the liquid junction potential may, at low pH, have a significant effect on the solubility of $TcO_2 \cdot xH_2O$(s) or on the calculated pH, respectively, the existence of a species such as TcO^{2+} is not certain. The increased error in pH at large $[H^+]$ concentration is also indicated in the measurements using electrodeposited Tc(IV) oxide, in which case large differences in the solubility at low pH were observed, *cf.* Figure 5 of [91MEY/ARN2]. We therefore prefer to select a limiting value for the equilibrium constant of Reaction (V.17), $\log_{10}{}^{*}K$(V.17) > -1.5, and to use $TcO(OH)_2$(aq) as the main Tc(IV) species. The reactions are thus written as follows:

$$TcO(OH)_2(aq) + H^+ \rightleftharpoons TcO(OH)^+ + H_2O(l) \quad \text{(V.19)}$$

$$TcO(OH)_2(aq) + 2H^+ \rightleftharpoons TcO^{2+} + 2H_2O(l) \quad \text{(V.20)}$$

From the five solubility points of [91MEY/ARN2] between $pH = 0$ and $pH = 3$, the first two protonation constants of $TcO(OH)_2$(aq) are estimated based on the slopes of the solubility curve. The ionic strength dependence of Equilibrium (V.19) is negligible.

$$\log_{10}{}^{*}K^\circ(\text{V.19}, 298.15\ \text{K}) = 2.5 \pm 0.3$$

$$\log_{10}{}^{*}K^\circ(\text{V.20}, 298.15\ \text{K}) < 4$$

A better estimate of $\log_{10}{}^{*}K^\circ$(V.20) will only be possible on the basis of measurements in non-complexing solutions.

From these protonation constants and the Gibbs energy of formation of $TcO(OH)_2$(aq) selected in V.3.2.5.2, we obtain the following values:

$$\Delta_f G_m^\circ(TcO(OH)^+, \text{aq}, 298.15\ \text{K}) = -(345.4 \pm 9.0)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^\circ(TcO^{2+}, \text{aq}, 298.15\ \text{K}) > -116.8\ \text{kJ·mol}^{-1}$$

Nguyen-Trung, Palmer, and Giffaut [96NGU/PAL] also determined hydrolysis constants for Tc(IV) from variation of their solubilities as a function of pH. However, the resulting values of the hydrolysis constants were not listed in their extended abstract.

Eriksen *et al*. [92ERI/NDA] studied the solubility of $TcO_2 \cdot xH_2O$(s) in neutral to alkaline solutions without inert electrolyte and in the presence and absence of CO_2(g), and they found, in addition to two hydroxy-carbonate complexes, the formation of $TcO(OH)_3^-$:

$$TcO(OH)_2(aq) + H_2O(l) \quad \rightleftharpoons \quad TcO(OH)_3^- + H^+ \qquad \text{(V.21)}$$

with $\log_{10}{}^{*}K$(V.21) $= -(10.89 \pm 0.24)$. This value was obtained at low ionic strength ($I < 0.01$ M), and pertechnetate formed during the reaction was measured and corrected for. The activity correction term ($-2D$, D is the Debye-Hückel term, *cf*. Appendix C) is thus less than -0.1 in $\log_{10}{}^{*}K$(V.21), which means that $\log_{10}{}^{*}K^\circ$(V.21) will lie between -10.9 and -11.0. This value is accepted here, although the solubility of $TcO_2 \cdot xH_2O$(s) measured by Eriksen *et al*. [92ERI/NDA] between pH = 6 and 9 are somewhat higher than the one selected in this review. It should nevertheless be mentioned that the four points at high pH [92ERI/NDA] would suggest a slope of -0.5 rather than -1 due to Eq. (V.21). However, the few high pH data are insufficient to propose a more complex mechanism. More measurements at high pH are needed for this purpose. The uncertainty of the selected value is increased to ± 0.4 due to the fact that no independent confirmations are available and that no activity correction can be made:

$$\log_{10}{}^{*}K^\circ(\text{V.21}, 298.15\ \text{K}) \quad = \quad -10.9 \pm 0.4$$

The Gibbs energy of formation of $TcO(OH)_3^-$ derived from this constant is :

$$\Delta_f G_m^\circ(TcO(OH)_3^-, \text{aq}, 298.15\ \text{K}) \quad = \quad -(743.2 \pm 9.1)\ \text{kJ·mol}^{-1}$$

Burnett and Jobe [97BUR/JOB] pointed out that $TcO(OH)_3^-$ could possibly be partially co-exracted with TcO_4^- when liquid-liquid extraction is used to separate Tc(IV) from the TcO_4^- present in the solution phase obtained from solubility experiments for TcO_2(cr) or $TcO_2 \cdot xH_2O$(s). If this indeed happens, then the derived value of $\log_{10}{}^{*}K$(V.21) underestimates the concentration of $TcO(OH)_3^-$.

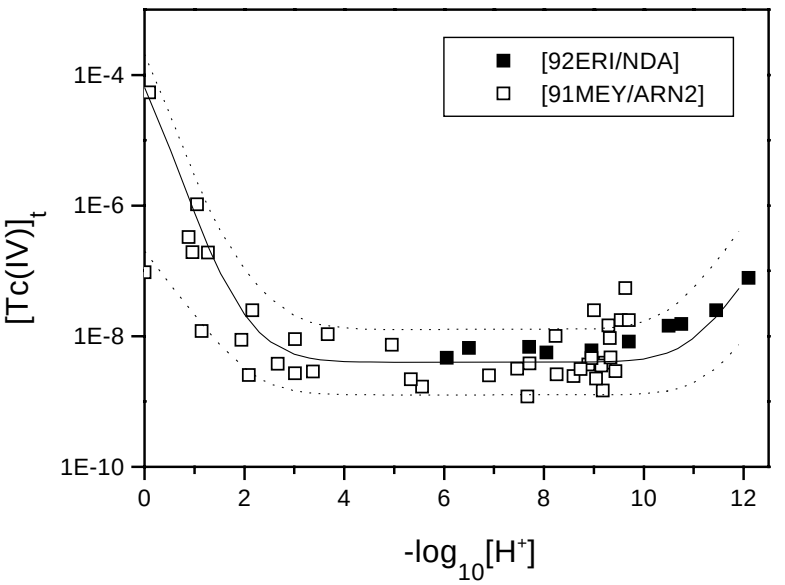
Lemire and co-workers [89LEM/GAR, 96LEM/JOB] included $\log_{10}{}^{*}K^\circ$(V.21) $= -9.0$ in their data base, based on the solubility curve presented in [88VIK/GAR]. This value is not compatible with the data in [91MEY/ARN2, 92ERI/NDA], *cf*. Appendix A.

The more recent solubility measurements of Nguyen-Trung, Palmer, and Giffaut [96NGU/PAL] are consistent with our selected data, see Appendix A, but they have not yet been published. Figure V.3 shows the experimental solubilities of hydrous Tc(IV) oxide from [91MEY/ARN2] and [92ERI/NDA], and the solubility curve of $TcO_2 \cdot 1.6H_2O$(s) calculated from our selected data, including uncertainty limits (dotted curves).

The various hydrolysed forms of Tc(IV) are denoted in this book as TcO^{2+}, $TcO(OH)^+$, $TcO(OH)_2$(aq) and $TcO(OH)_3^-$, which are the formulations used in most of the published studies of the hydrolysis equilibria involving Tc(IV) [69GOR/KOC, 73GUÉ/GUI, 79SUN, 91MEY/ARN, 92ERI/NDA]. These are the

simplest possible chemical formulae for the aqueous hydrolysed Tc(IV) species that are fully compatible with all of the available hydrolysis constant and solubility data. However, more realistic guesses can be made about the actual composition of the primary coordination spheres of Tc(IV) species, which are discussed in Section V.3.1.3.

Figure V.3: Solubility measurements of hydrous Tc(IV) oxide at 25°C from Refs. [91MEY/ARN2, 92ERI/NDA]. The full line represents the solubility of $TcO_2 \cdot 1.6H_2O$(s) as calculated with the selected equilibrium constants, and the dotted lines represent the limits of the uncertainty range.



V.3.1.2 The acid/base chemistry of other Tc oxidation states

V.3.1.2.1 The protonation of TcO_4^-

All aqueous solutions of inorganic acids contain some undissociated molecular acid, although the amounts that form vary considerably from system to system, and can be extremely small for strong acids. In the case of pertechnetic acid, the protonation reaction should be of the form

$$TcO_4^- + H^+ \quad \rightleftharpoons \quad HTcO_4(aq) \qquad \text{(V.22)}$$

The thermodynamic equilibrium constant for this reaction is given by

$$K^\circ(\text{V.22}) \quad = \quad K(\text{V.22})/(\gamma_{TcO_4^-} \times \gamma_{H^+})$$

Here we denote the concentration product as K(V.22), and we assume that $\gamma_{HTcO_4} = 1$ for the undissociated acid. By analogy to the chemically similar acid $HClO_4$, we expect $HTcO_4$ to be a fairly strong acid.

Attempts have been made to determine the dissociation constant of $HTcO_4$(aq) by potentiometric titration of its solutions with a base [52COB, 63RUL/HIR, 67RUL/PAC2]. The large variation of the obtained acidity constant with the initial concentration of the $HTcO_4$ being titrated [67RUL/PAC2] leaves no doubt that $HTcO_4$ is a too strong acid for this technique to be useful.

Values of the acidity constant of $HTcO_4$(aq) have also been determined by use of liquid-liquid distribution [83LIE/SIN, 84VIA/GER], anion-exchange [85BIB/WAL, 85NAK/LIE, 93KAW/OMO], and solubility [88GER/KRJ] measurements. These values are fairly concordant.

All results in those publications are in molar concentration units, K_c(V.22). Table (V.10) contains a summary of these values. Values that were originally reported as K_d or pK_d were converted into $\log_{10} K_c$(V.22) values. As can be seen from

Table V.10: Experimental equilibrium constant for the formation of $HTcO_4$

Method	Ionic medium	T (K)	$\log_{10} K_c$	Reference
$TcO_4^- + H^+ \rightleftharpoons HTcO_4$				
dis	0 to 7 M $(H,NH_4)NO_3$	293 − 333?	0.20	[83LIE/SIN]
dis	2 M NO_3^- ?	RT [a]	−0.26 [b]	[84VIA/GER]
aix	1.00 M $(H,Na)NO_3$	298±2	−0.386±0.151	[85BIB/WAL]
	2.00 M $(H,Na)NO_3$	298±2	−0.390±0.100	
	3.00 M $(H,Na)NO_3$	298±2	−0.389±0.148	
	4.00 M $(H,Na)NO_3$	298±2	−0.385±0.099	
	5.00 M $(H,Na)NO_3$	298±2	−0.381±0.194	
	6.00 M $(H,Na)NO_3$	298±2	−0.356±0.095	
aix	5 M (H,Li)Cl	293±1	0.033	[85NAK/LIE]
sol	0 to 3 M HNO_3	293.0	0.60±0.19	[88GER/KRJ]
aix	2.0 M (H,Na)Cl	293	0.602	[93KAW/OMO]
	2.0 M $(H,Na)NaNO_3$	293	0.398	[93KAW/OMO]

[a] RT means room temperature.
[b] Ref. [84VIA/GER] did not give any data. This value was supplied to us by Baron [91BAR].

Table V.10 nearly all of the determinations of K_c(V.22) involved the use of HNO_3 or its mixtures with various nitrate salts (NH_4NO_3, $LiNO_3$ or $NaNO_3$) to vary the ionic strength and acidity of the solutions. The determination of the values of acidity

constants from liquid-liquid distribution data or other experimental techniques is generally done at one or more constant ionic strengths on the molarity concentration scale. An assumption made in these calculations is that the activity coefficients of the acid being studied, in this case $HTcO_4$(aq), do not vary with the ratio of the other electrolytes provided that the ionic strength was held constant.

There is ample evidence that HNO_3 is partially associated in aqueous solutions to form the molecular acid HNO_3(aq). See for example, the degree of dissociation curves from Raman and NMR spectroscopy, Figures 2 and 3 of Young, Maranville and Smith [59YOU/MAR]. Most of the determinations of K_c(V.22) involved acidic nitrate solutions with stoichiometric ionic strengths ranging from 1 to 7 M. Aqueous solutions of pure HNO_3 contain about 1 or 2% of the undissociated acid at 1 M, about 18% at 5 M, and about 30% at 7 M. Thus the true ionic strengths of these solutions will be significantly lower than the stoichiometric ionic strengths used by the various authors in analyzing their data. In addition, the extent of formation of undissociated acid will vary with the ratio of HNO_3-to-MNO_3 used in the experiments at constant stoichiometric ionic strength, so the true ionic strengths of these solutions will not be constant. This invalidates the basic assumption used in deriving the values of K_c(V.22), *i.e.*, that the activity coefficients of H^+ and TcO_4^- are constant. It is thus quite likely that the resulting published values of K_c(V.22) are not meaningful and simply represent a misinterpretation of medium effects rather than the formation of aqueous $HTcO_4$(aq).

In view of the above discussion, we do not consider any of the reported values of K_c(V.22) to be reliable and consequently do not recommend a value for $\Delta_f G^\circ_m(HTcO_4, aq, 298.15\ K)$. Aqueous solutions of $HTcO_4$ are thus considered to be fully dissociated in this review.

V.3.1.2.2 The protonation of TcO_4^{2-}

Kryuchkov *et al*. [79KRY/PIK] have estimated the protonation constants of TcO_4^{2-}, based on pulse radiolysis at various pH values and variable ionic strength,

$$TcO_4^{2-} + H^+ \rightleftharpoons HTcO_4^- \quad \text{(V.23)}$$

$$HTcO_4^{2-} + H^+ \rightleftharpoons H_2TcO_4(aq) \quad \text{(V.24)}$$

obtaining $\log_{10} K_1$(V.23) $= (8.7 \pm 0.5)$ and $\log_{10} K_2$(V.24) ≤ 1. It is difficult to judge the quality of these values, but they are of no relevance in equilibrium systems due to the instability of Tc(VI), and they are therefore not selected in this review.

V.3.1.3 Possible formulations for the primary coordination spheres of Tc(IV) hydrolysed species

Thermodynamic data for the various aqueous hydrolysed forms of Tc(IV) are analysed in this book assuming their chemical formulae are TcO^{2+}, $TcO(OH)^+$, $TcO(OH)_2$(aq) and $TcO(OH)_3^-$. These are the simplest possible formulae for the observed species. However, since the available experimental measurements are incapable of distinguishing between oxides or hydroxides bound to the technetium atom, these same solution species could also be written as $Tc(OH)_2^{2+}$, $Tc(OH)_3^+$, $Tc(OH)_4$(aq), and $Tc(OH)_5^-$,

respectively, *e.g.* [96NGU/PAL]. Examination of the available structural information [82BAN/MAZ, 87MEL/LIE, 94BAL] for Tc(IV) complexes with singly charged inorganic ligands indicates that the majority of them contain hexacoordinated technetium. Thus another possible set of formulae for the primary coordination spheres of these same species are $Tc(OH)_2(OH_2)_4^{2+}$, $Tc(OH)_3(OH_2)_3^{+}$, $Tc(OH)_4(OH_2)_2$(aq), and $Tc(OH)_5(OH_2)^{-}$.

Consider the species with the double positive charge. Then,

$$\Delta_f G^\circ_m(Tc(OH)_2(OH_2)_4^{2+},\ aq,\ 298.15\,K) =$$
$$\Delta_f G^\circ_m(Tc(OH)_2^{2+},\ aq,\ 298.15\,K) \quad + \quad 4\Delta_f G^\circ_m(H_2O,\ l,\ 298.15\,K)$$
$$= \Delta_f G^\circ_m(TcO^{2+},\ aq,\ 298.15\,K) \quad + \quad 5\Delta_f G^\circ_m(H_2O,\ l,\ 298.15\,K).$$

Similar relations apply to the more hydrolysed forms of Tc(IV). In any thermodynamic reaction calculation, the different sets of formulations will give identical results, since the factors of $n\Delta_f G^\circ_m(H_2O, l, 298.15\,K)$ will appear on both sides of the reaction and thus exactly cancel. Consequently, it is irrelevant for thermodynamic calculations which of these three sets of formulae are assigned to the solution species. Following the usual practice in chemical thermodynamics, the simplest set of chemical formulae that reproduces the thermodynamic data is chosen here.

The possibility also exists that the correct formula for the Tc(IV) hydrolysed species may involve dimers or some other small polymer. However, there is presently no significant evidence for polymeric hydrolysed Tc(IV) ions. The available redox data for the Tc(IV)/Tc(III) couple gives no evidence for a species of intermediate average valence, such as Tc(4.5) or Tc(3.67), which would be expected to be observed if the solution species are dimeric or trimeric. Thus, the available data are fully consistent with the solution species being monomeric, although there are too few redox studies to provide a definitive conclusion about the monomeric/polymeric nature of Tc(IV) species.

V.3.2 Solid technetium oxides and their hydrates

V.3.2.1 Tc_2O_7(cr) and Tc_2O_7(l)

V.3.2.1.1 General properties

Combustion of metallic technetium with O_2(g) is the general method used to prepare Tc_2O_7(cr), but the product is often a mixture [52COB] and the reaction often incomplete [53COB/SMI, 67RUL/PAC2].

There are several reports that combustion of technetium metal by dry O_2(g) yielded Tc_2O_7(cr) [52BOY/COB, 53COB/SMI, 53SMI/COB, 69KRE]; in each case sublimation or vacuum distillation of Tc_2O_7(cr) was used to purify the Tc_2O_7(cr), but no mention was made of side products. The more detailed description of the reaction products [76GAY/HER, 77HER/BUS] leaves no doubt that the initial reaction produced a mixture of oxides. Both noted that the major product was yellow-coloured Tc_2O_7(cr), but smaller quantities of red to black material were present in the product before sublimation was used to purify the Tc_2O_7(cr).

There is little doubt that the yellow oxide produced by combustion of technetium metal is Tc_2O_7(cr). For example, Boyd *et al*. [52BOY/COB] reported that samples of this oxide dissolved in aqueous Ce(IV) did not undergo oxidation, and that the UV spectrum of a solution of this oxide was identical before and after treatment with alkaline H_2O_2(aq). This indicates that technetium was already present in its maximum oxidation state of Tc(VII).

Spitsyn *et al*. [88SPI/BUK] studied the kinetics of the oxidation of technetium in air from about 373 to 848 K, by observing weight changes on a microbalance. From about 598 to 798 K, the oxidation of technetium followed the linear rate law, $g = -kt$, where g is the rate of weight loss of sample due to formation of volatile oxide, t is the time, and k is the rate constant for oxidation. They found that their results for an air flow rate of 5.5 $dm^3 \cdot h^{-1}$ could be represented by the equation $\ln k = 21.6 - 1.1 \times 10^4\ T^{-1}$, for k in units of $\mu g \cdot cm^{-2} \cdot h^{-1}$, and the activation energy was reported to be about 90 $kJ{\cdot}mol^{-1}$. The condensate from this reaction was found to be Tc_2O_7(cr).

An X-ray diffraction study has been reported for thin, pale-yellow plates of Tc_2O_7(cr) produced by oxidation of technetium in O_2(g) followed by slow sublimation [69KRE], *cf*. Table V.11. The structure contained isolated molecules of Tc_2O_7 with tetrahedral coordination for the technetium. It is one of the few transition metal oxides with a molecular structure in the solid state. The Tc-O bond length is $(1.840 \pm 0.002) \times 10^{-10}$ m for the bridging oxygen, and the average length for terminal Tc-O bonds is 1.673×10^{-10} m.

Various properties have been reported for solid and liquid Tc_2O_7. It melted at 392.6 K [52BOY/COB], and extrapolation of published vapour pressures [53SMI/COB] by the present review to 1 atm pressure yields a boiling point of about 596 K. Vapour pressures were measured from 362.2 to 391.2 K for solid Tc_2O_7(cr), and from 393.3 to 529.4 K for liquid Tc_2O_7(l) [53SMI/COB]. Solid Tc_2O_7(cr) exhibited a slight temperature independent paramagnetism in the temperature range of 78 to 349 K [54NEL/BOY]. It is also quite hygroscopic [52BOY/COB, 69KRE, 77HER/BUS].

Raman spectra have been reported for solid Tc_2O_7(cr) at room temperature, for liquid Tc_2O_7(l) at 403 K, and for Tc_2O_7(g) vapour (see Section V.3.3) at 593 K [71SEL/FRI].

V.3.2.1.2 Thermodynamic data

V.3.2.1.2.a Enthalpy of formation and entropy of Tc_2O_7(cr)

There are two reported experimental values for the enthalpy of formation of Tc_2O_7(cr). Cobble, Smith and Boyd [53COB/SMI] reported $\Delta_f H^\circ_m = -(1113.4 \pm 10.9)$ $kJ{\cdot}mol^{-1}$ based on the combustion of technetium metal in an oxygen-bomb calorimeter, and Gayer, Herrell and Busey [76GAY/HER] reported $\Delta_f H^\circ_m = -(1127.6 \pm 7.9)$ $kJ{\cdot}mol^{-1}$ based on solution calorimetry.

The reported uncertainty limits are one standard deviation in the second study, and are presumed to be one standard deviation in the first although this was not stated. Gayer, Herrell and Busey attributed a lower accuracy to the value of Cobble, Smith and Boyd, in part because of the use of less pure metal, and in part because less than 20% of the measured energy change was due to combustion of the metal. They also noted that

Table V.11: Crystal structure parameters of binary oxides of technetium

Oxide	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
TcO_2(cr)	monoclinic[a]	$P2_1/c$		$a = 5.53$	[55MAG/AND]
				$b = 4.79$	
				$c = 5.53$	
	tetragonal[b]			$a = 4.753 \pm 0.010$	[65SPI/KUZ]
				$c = 2.840 \pm 0.010$	
	monoclinic[c]			$a = 5.55 \pm 0.02$	[69ROG/SHA]
				$b = 4.85 \pm 0.02$	
				$c = 5.62 \pm 0.02$	
	monoclinic[d]			$a = 5.52 \pm 0.04$	[87LIE/BAU2]
				$b = 4.99 \pm 0.10$	
				$c = 5.57 \pm 0.06$	
	monoclinic[e]	$P2_1/c$		$a = 5.6872 \pm 0.0012$	[99JOB/TAY]
				$b = 4.7635 \pm 0.0014$	
				$c = 5.9195 \pm 0.0012$	
TcO_q(cr)$(2 > q > 0)$	pseudo-cubic[f]			$a = 9.45$	[64MUL/WHI] [68MÜN]
Tc_2O_7(cr)	orthorhombic	Pbca	4	$a = 13.756 \pm 0.014$	[69KRE]
				$b = 7.439 \pm 0.008$	
				$c = 5.617 \pm 0.006$	

[a] From data of W.H. Zachariasen; $\beta \approx 120°$; MoO_2 type structure.

[b] Obviously misindexed with a tetragonal unit cell. Their $a = b$ dimension is similar to these for b in the other studies, and twice their c value is comparable to a and c given in the other studies.

[c] Derived by them from the powder pattern results reported by Muller, White and Roy [64MUL/WHI]; $\beta = (121.9 \pm 0.2)°$; possibly MoO_2 type.

[d] $\beta = (121.9 \pm 0.8)°$

[e] $\beta = (121.59 \pm 0.02)°$. This is the preferred set of unit cell parameters. See the discussion of [99JOB/TAY] in Appendix A for alternative sets of unit cell parameters, based on non-standard settings for the unit cell.

[f] Formed as a phase when Tc(cr) and TcO_2(cr) were heated together in sealed tubes.

if their own enthalpies of solution of Tc_2O_7(cr) into water were used instead of those of Cobble, Smith and Boyd, then the discrepancy between the two $\Delta_f H^\circ_m$ values would be reduced slightly. As mentioned in Section V.3.2.1.1, the combustion of technetium metal generally gives partial formation of lower oxides in addition to Tc_2O_7(cr). If any of these lower oxides also formed in Cobble, Smith and Boyd's calorimeter, they would give a less exothermic calculated value for $\Delta_f H^\circ_m$.

These two papers [53COB/SMI, 76GAY/HER] are discussed in more detail in Appendix A. From the first study [53COB/SMI], this review recalculates a value of $\Delta_f H^\circ_m(Tc_2O_7, cr, 298.15\ K) = -(1114 \pm 52)\ kJ{\cdot}mol^{-1}$, and from the second investigation [76GAY/HER] a value of $\Delta_f H^\circ_m(Tc_2O_7, cr, 298.15\ K) = -(1127.6 \pm 15.5)\ kJ{\cdot}mol^{-1}$.

The two values are compatible and we select the statistically weighted average,

$$\Delta_f H^\circ_m(Tc_2O_7, cr, 298.15\ K) = -(1126.5 \pm 14.9)\ kJ{\cdot}mol^{-1}$$

We note that there is some uncertainty about the correct numerical value of $\Delta_f H^\circ_m$ (HgO, cr, yellow, 298.15 K), which is needed for the recalculation of $\Delta_f H^\circ_m$ (Tc_2O_7, cr, 298.15 K) from the enthalpy of solution study of Gayer, Herrell and Busey [76GAY/HER]. If Vanderzee, Rodenburg and Berg [74VAN/ROD] are correct in that $\Delta_f H^\circ_m$ of the yellow and the red forms of HgO(cr) are identical, then the resulting $\Delta_f H^\circ_m(Tc_2O_7, cr, 298.15\ K)$ would be more negative by $2.6\ kJ{\cdot}mol^{-1}$; see the discussion of Ref. [76GAY/HER] in Appendix A.

There are no experimental data on the heat capacity of Tc_2O_7(cr), so no precise value of the standard entropy can be given. However, a reasonable estimate of the heat capacity of the heptoxide is to take values slightly smaller than those of Re_2O_7(cr) since technetium has a lower molar mass than rhenium and Tc_2O_7(cr) is molecular while Re_2O_7(cr) is polymeric in the solid state. With the values for Re_2O_7(cr) given by Stuve and Ferrante [76STU/FER], we suggest for Tc_2O_7(cr):

$$C^\circ_{p,m}(Tc_2O_7, cr, T) = 155.0 + 8.6 \times 10^{-2} T - 1.8 \times 10^6 T^{-2}\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

for $298.15\ K \leq T \leq 392.7\ K$, giving

$$C^\circ_{p,m}(Tc_2O_7, cr, 298.15\ K) = (160.4 \pm 15.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

A good estimate of the standard entropy of Tc_2O_7(cr) is obtained in Section V.3.2.1.2.c from an analysis of the vapour pressure data. As noted therein there is still an appreciable uncertainty in this value, but we shall adopt

$$S^\circ_m(Tc_2O_7, cr, 298.15\ K) = (192 \pm 15)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

We note the corresponding value for Re_2O_7(cr) is $(207.3 \pm 0.8)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, [76STU/FER].

The Gibbs energy of formation of Tc_2O_7(cr) is calculated from the selected enthalpy of formation and entropy values.

$$\Delta_f G^\circ_m(Tc_2O_7, cr, 298.15\ K) = -(950.3 \pm 15.5)\ kJ{\cdot}mol^{-1}$$

V.3.2.1.2.b Melting point and heat capacity of Tc_2O_7(l)

Boyd *et al.* [52BOY/COB] directly measured the melting point of Tc_2O_7(cr) to be (392.7±0.1) K, and the vapour pressure curves measured by Smith *et al.* [53SMI/COB] show a large change in slope very close to this temperature. Our final analysis of the vapour pressure data (see Section V.3.2.1.2.c) is quite consistent with this value, which we adopt. The heat capacity of the liquid is estimated to be somewhat smaller than that of Re_2O_7 (271.3 $J{\cdot}K^{-1}{\cdot}mol^{-1}$) [76STU/FER], and we adopt the estimated value:

$$C^\circ_{p,m}(Tc_2O_7, l, T) \quad = \quad (250 \pm 25)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

for 392.7 K $\leq T \leq$ 600 K.

The thermal functions for Tc_2O_7(cr, l) calculated from the estimated values are given in Table B.5 and the formation properties from Tc(cr) and O_2(g) are given in Table B.6 in Appendix B.

V.3.2.1.2.c Vapour pressures of Tc_2O_7(cr, l)

Cobble [52COB] and Smith *et al.* [53SMI/COB] suggested that Tc_2O_7(l) is stable up to its boiling point (ca. 600 K), although the evidence for this is not clear. Gibson [93GIB] found that Tc_2O_5(g) was present to a significant extent at 1223 K in the vapour over an unspecified solid technetium oxide in the presence of O_2(g). It thus seems probable that below its boiling point Tc_2O_7(l) vaporises essentially congruently, perhaps with a small decomposition to Tc_2O_5(g) and O_2(g) at higher temperatures. This possible minor decomposition has been neglected in the following analysis, since it probably lies within the uncertainty of the experimental data, and certainly within that of the assessed data at 298.15 K. Smith *et al.* [53SMI/COB] have measured the vapour pressures of solid and liquid Tc_2O_7 from 362.2 to 391.2 K and 393.3 to 529.4 K, respectively. They fitted their data initially to linear expressions which correspond to the equations:

$$\log_{10}(p/\text{bar}) \quad = \quad -7205/T + 15.404$$

for the solid and

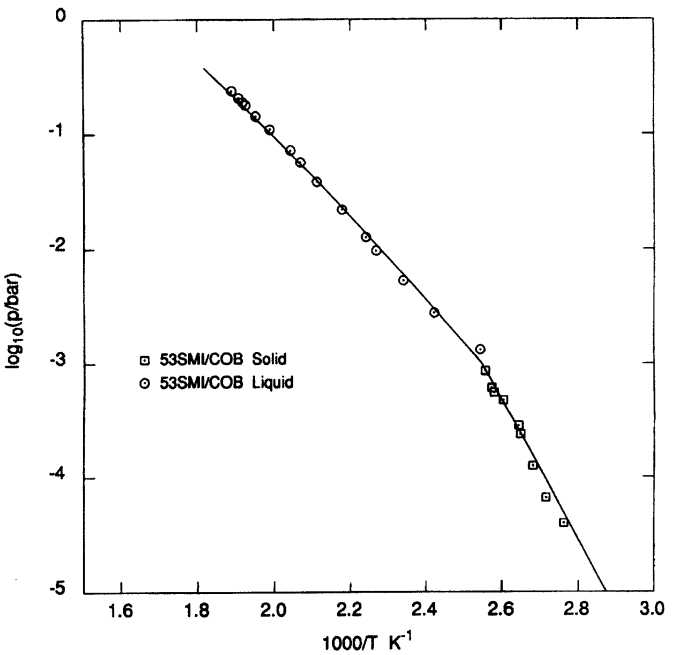
$$\log_{10}(p/\text{bar}) \quad = \quad -3571/T + 6.124$$

for the liquid, giving the following entropies of sublimation and vaporisation at the mean temperatures:

$$\Delta_{sub}S^\circ_m(376.7\ \text{K}) \quad = \quad 294.9\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$
$$\Delta_{vap}S^\circ_m(461.4\ \text{K}) \quad = \quad 117.2\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

The very big difference between these values is notable, implying a large entropy of fusion for Tc_2O_7. However, the vaporisation data for the solid are appreciably less reliable than those for the liquid, since they extend over a temperature range of only 29 K and were subject to corrections of 30 to 90% of the observed value. Moreover, as Smith *et al.* [53SMI/COB] realised, ΔC_p for the vaporisation will in fact be quite large, and the second-law analysis far from adequate. With the thermal functions for the

Figure V.4: Vapour pressure of Tc_2O_7.



gas and the estimated thermal functions for the condensed phases, a third-law analysis becomes possible, although the enthalpy of fusion is not known. However, as shown in Figure V.4, very good consistency of the vapour pressure data for the liquid is obtained with the following value for the entropy of the liquid at the melting point:

$$S^\circ_m(Tc_2O_7, l, 392.7\ K) = 350.58\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

and any reasonable combination of S°_m (Tc_2O_7, cr, 298.15 K) and $\Delta_{fus}S^\circ_m(Tc_2O_7$, 392.7 K) consistent with this value gives good agreement with the less precise vapour pressure data for the solid. We have chosen the combination

$$S^\circ_m(Tc_2O_7, cr, 298.15\ K) = (192.0 \pm 15.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$
$$\Delta_{fus}H^\circ_m(Tc_2O_7, 392.7\ K) = (44.0 \pm 6.0)\ kJ{\cdot}mol^{-1}$$

since these values are similar to those for Re_2O_7(cr). The simpler analysis by Smith and Cobble [53SMI/COB] using constant ΔC_p values for sublimation and vaporisation led to $\Delta_{fus}H^\circ_m(Tc_2O_7) = 47.6\ kJ{\cdot}mol^{-1}$.

The third-law analysis with our data gives

$$\Delta_{sub}H^\circ_m(Tc_2O_7, 298.15\ K) = (118.4 \pm 6.0)\ kJ{\cdot}mol^{-1}$$

where most of the uncertainty arises from that in the enthalpy of fusion. The last value, when combined with our selected value for $\Delta_fH^\circ_m$ (Tc_2O_7, cr, 298.15 K) gives finally

$$\Delta_fH^\circ_m(Tc_2O_7, g, 298.15\ K) = -(1008.1 \pm 16.1)\ kJ{\cdot}mol^{-1}$$

The calculated vapour pressure curve with the above values is given in Figure V.4, with the experimental values superimposed. The excellent agreement suggests that the current values provide a very reasonable representation of the data for Tc_2O_7(cr, l, g). Clearly, a more extensive vapour pressure study is required to improve the reliability of the enthalpy of vaporisation.

We may note in passing that a similar analysis has also been carried out on the vaporisation behaviour of Re_2O_7(cr, l), for which the data are much more extensive [96RAN]. Again the agreement with the vapour pressure data is excellent, giving good support to the analyses of the vibrational frequencies of these two heptoxides [96BEA/GIL] discussed in Section V.3.3.

V.3.2.1.2.d Enthalpy of solution of Tc_2O_7(cr)

The enthalpy of solution of Tc_2O_7(cr) into water has been reported in two studies [53COB/SMI, 76GAY/HER]. Cobble, Smith and Boyd [53COB/SMI] performed two determinations of this quantity, but they did not extrapolate their results to infinite dilution. In addition, they did not report their final dilution molarities, but instead just reported that the average of the two dilution molarities was 0.041 M. However, the actual molarities were given in Cobble's thesis [52COB]. Gayer, Herrell and Busey [76GAY/HER] reported the results of eleven enthalpy of solution experiments, with final dilution molarities of 3.20×10^{-4} to 8.64×10^{-4} M. They extrapolated their

enthalpies of solution results to infinite dilution by using the Debye-Hückel limiting law.

Both studies of the enthalpy of solution of Tc_2O_7(cr) into water [53COB/SMI, 76GAY/HER] reported their final dilution concentrations in molar units, and these need to be converted to mol · kg^{-1}. In the study of Gayer, Herrell and Busey, these concentrations are low enough that the ratio of *c/m* was equated to the density of pure water, 0.997045 g · cm^{-3}. Cobble, Smith and Boyd only reported their final concentration to two significant figures in the journal article, but three figures were given in Cobble's thesis [52COB]. The values from the thesis were used for recalculations. In both studies the values of $\Delta_{sol}H_m$ were reported to four significant figures. Gayer, Herrell and Busey did not report the molar mass for Tc_2O_7(cr) that was used for reporting their results, but if we assume they used up-to-date atomic masses at that time, there would be no significant change in $\Delta_{sol}H_m$. Cobble, Smith and Boyd reported that they used 99.00 g · mol^{-1} for ^{99}Tc [53COB/SMI], but the discussion in Cobble's thesis [52COB] indicated that 98.91 g · mol^{-1} was actually used; their $\Delta_{sol}H_m$ are corrected to the current value of 98.9063 g · mol^{-1}.

The enthalpies of solution also need to be extrapolated to infinite dilution. The solution reaction is

$$Tc_2O_7(cr) + H_2O(l) \rightleftharpoons 2H^+ + 2TcO_4^- \qquad (V.25)$$

for which the corrected enthalpy of solution is $\Delta_{sol}H^\circ_m = \Delta_{sol}H_m - 2L_\phi$. Here L_ϕ is the relative apparent molar enthalpy of $HTcO_4$ at the final dilution molality. The values of L_ϕ are unknown, but are approximated by equating them to values for $HClO_4$ [65PAR] which should be a good chemical model for $HTcO_4$. Table V.12 summarises the experimental values of $\Delta_{sol}H_m$ and the derived values of $\Delta_{sol}H^\circ_m$. The data of Cobble, Smith and Boyd [53COB/SMI] yield $\Delta_{sol}H^\circ_m$(V.25) $= -(48.99 \pm 0.96)$ kJ·mol^{-1}, whereas that of Gayer, Herrell and Busey yield $-(45.89 \pm 2.37)$ kJ·mol^{-1}. Although the results of Cobble, Smith and Boyd are more negative, the two sets of data do agree within their combined uncertainty limits. The precision of the results of Cobble, Smith and Boyd appears to be greater than that of Gayer, Herrell and Busey, but this is probably a computational artifact, because Cobble, Smith and Boyd did too few experiments to derive a meaningful standard deviation. In addition, the L_ϕ corrections are larger for the experiments of Cobble, Smith and Boyd, which adds to the uncertainty of their $\Delta_{sol}H^\circ_m$. The unweighted average of all the experimental studies yields our recommended value of

$$\Delta_{sol}H^\circ_m(\text{V.25}, 298.15\ \text{K}) = -(46.37 \pm 3.15)\ \text{kJ·mol}^{-1}$$

This value is used in deriving the standard enthalpy of formation of TcO_4^-, *cf.* Section V.2.1.

V.3.2.2 Tc_2O_7·x H_2O(s)

V.3.2.2.1 General properties, hydration number

Dilute aqueous solutions of pertechnetic acid, $HTcO_4$, are colourless. However, if such a solution is concentrated over concentrated H_2SO_4, it undergoes a sequence

Table V.12: Integral enthalpies of solution of solid Tc_2O_7(cr) according to Reaction V.25 in water at 298.15 K.

molality [a] ($mol \cdot kg^{-1}$)	$\Delta_{sol}H_m$ [b] $kJ \cdot mol^{-1}$	L_ϕ [c] $kJ \cdot mol^{-1}$	$\Delta_{sol}H_m - 2L_\phi$ $kJ \cdot mol^{-1}$	Reference
0.0450 [d]	−48.83	0.251	−49.33	[52COB, 53COB/SMI]
0.0370 [d]	−48.16	0.242	−49.64	[52COB, 53COB/SMI]
			−48.99 ± 0.96 (average)	
8.67×10^{-4} [e]	−45.38	0.054	−45.49	[76GAY/HER]
8.12×10^{-4} [e]	−44.82	0.052	−44.92	
7.43×10^{-4} [e]	−43.91	0.049	−44.01	
7.25×10^{-4} [e]	−47.27	0.049	−47.37	
6.34×10^{-4} [e]	−46.47	0.046	−46.56	
5.77×10^{-4} [e]	−45.63	0.044	−45.72	
5.52×10^{-4} [e]	−46.46	0.043	−46.55	
5.28×10^{-4} [e]	−47.21	0.042	−47.29	
4.71×10^{-4} [e]	−44.38	0.041	−44.46	
3.55×10^{-4} [e]	−45.01	0.036	−45.08	
3.21×10^{-4} [e]	−47.30	0.034	−47.37	
			−45.89 ± 2.37 (average)	
			−46.37 ± 3.15 (recommended value [f])	

[a] Final molality of solution of $HTcO_4$ by dissolution of solid Tc_2O_7(cr) in H_2O(l) at 298.15 K.

[b] Integral enthalpy of solution from dissolution of solid Tc_2O_7(cr) to form a solution at the given molality. The results of Cobble, Smith and Boyd [53COB/SMI] have been multiplied by (309.8084)(4.184)/(309.816) = 4.18390 to convert kcal to kJ and from their values of the molar mass to the current value.

[c] Relative apparent molar enthalpy of dilution as estimated from values for $HClO_4$. The negative of this quantity is equal to the enthalpy change from diluting the solution from given final molality to infinite dilution.

[d] Their concentration were reported in molar units (M). They were corrected for changes in molar mass and from litre to dm^3, and m/c ratio was estimated from that of $HClO_4$.

[e] Concentrations were reported in molar units; at these low concentration c/m is assumed to be equal to the density of water 0.997045 $g \cdot cm^{-3}$.

[f] Unweighted average of all of the experimental values.

of colour changes: first to yellow, then dark yellow, followed by red and then dark red [52BOY/COB]. Ultimately, long red-black crystals are precipitated. Chemical analyses of two samples of these crystals gave the empirical compositions $Tc_2O_7 \cdot 0.97H_2O$(s) and $Tc_2O_7 \cdot 1.03H_2O$(s). This compound is thus compatible with a formulation of either $Tc_2O_7 \cdot H_2O$(s) or $HTcO_4$(s). It is a very hygroscopic compound, and deliquesces in air to form a dark-red solution of $HTcO_4$. The colour change in highly concentrated solutions may be an indication of the presence of polynuclear technetium complexes or partial reduction to Tc(VI) (see Refs. [67RUL/PAC2, 78BOY] in Appendix A).

We conclude from two rather different types of information, decomposition pressures [53SMI/COB] and nuclear quadrupole coupling constants (QCC) [86SPI/TAR, 86TAR/PET], that the hydrous oxide of Tc(VII) could be the hydrated oxide of $Tc_2O_7 \cdot H_2O$(s), *cf.* the discussion of reference [86SPI/TAR] in Appendix A. However, recent experimental results from Guerman and his colleagues suggest rather that it has an ionic structure of uncertain composition, *cf.* the discussion of reference [98GUE] in Appendix A. For the purpose of thermodynamic calculations, we will formally assume this substance has the stoichiometric composition $Tc_2O_7 \cdot H_2O$(s).

V.3.2.2.2 Thermodynamic data

Smith, Cobble and Boyd [53SMI/COB] and Cobble [53COB] reported the results of vapour pressure measurements of $Tc_2O_7 \cdot H_2O$(s) from about 291.8 to 363.3 K, and for the saturated aqueous solution of $HTcO_4$ from about 312.9 to 363.6 K (Appendix A). The major vapour species was considered by them to be H_2O(g), based on the very low vapour pressure of Tc_2O_7(cr) in this temperature region. Thus the vaporisation reaction of $Tc_2O_7 \cdot H_2O$(s) is assumed to be:

$$Tc_2O_7 \cdot H_2O(s) \quad \rightleftharpoons \quad Tc_2O_7(cr) + H_2O(g). \tag{V.26}$$

The possible presence of species other than water in the vapour phase is discussed in Appendix A under reference [53SMI/COB]. As discussed in Appendix A, we represent the fugacities of H_2O(g) above $Tc_2O_7 \cdot H_2O$(s) by the least-squares equation

$$\ln f_w \quad = \quad (12.2686 \pm 0.1480) - (5510.44 \pm 48.65)/T \tag{V.27}$$

with a correlation coefficient of -0.99992. Vapour pressures for $Tc_2O_7 \cdot H_2O$(s) extend from 291.8 to 363.3 K, so the vapour pressure at 298.15 K can be accurately obtained by interpolation.

The incongruent vaporisation of $Tc_2O_7 \cdot H_2O$(s) is given by Reaction (V.26), for which there is a Gibbs energy of reaction $\Delta_r G_m$. However, the vapour pressure of a substance is an equilibrium property, so that $\Delta_r G_m = 0$ for a closed system. This gives rise to the relationship

$$\begin{aligned} \Delta_f G^\circ_m(Tc_2O_7 \cdot H_2O, s, 298.15\ K) \quad = \quad & \Delta_f G^\circ_m(Tc_2O_7, cr, 298.15\ K) \\ & + \Delta_f G^\circ_m(H_2O, g, 298.15\ K) + RT \ln f_w \end{aligned}$$

where $T = 298.15$ K.

From Eq. (V.27), $\ln f_w = -(6.2135 \pm 0.2203)$ at 298.15 K, which with the selected value of $\Delta_f G^\circ_m(Tc_2O_7, cr, 298.15\ K)$ (Section V.3.2.1.2) then yields

$$\Delta_f G^\circ_m(Tc_2O_7 \cdot H_2O, s, 298.15\ K) = -(1194.3 \pm 15.5)\ kJ{\cdot}mol^{-1}.$$

We can rewrite $\Delta_r G^\circ_m$ as $\Delta_r H^\circ_m - T\Delta_r S^\circ_m$. Thus, from Eq. (V.27), $\Delta_r H^\circ_m$(V.26) $= (5510.44 \pm 48.65)(10^{-3})R = (45.82 \pm 0.40)\ kJ{\cdot}mol^{-1}$. From this, and the selected values of $\Delta_f H^\circ_m(Tc_2O_7, cr, 298.15\ K)$ and $\Delta_f H^\circ_m(H_2O, g, 298.15\ K)$ the enthalpy of formation is derived.

$$\Delta_f H^\circ_m(Tc_2O_7 \cdot H_2O, s, 298.15\ K) = -(1414.2 \pm 14.9)\ kJ{\cdot}mol^{-1}$$

Combining these results with selected auxiliary data, the entropy is then obtained.

$$S^\circ_m(Tc_2O_7 \cdot H_2O, s, 298.15\ K) = (278.9 \pm 72.1)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

V.3.2.3 TcO_3(s)

V.3.2.3.1 General properties

There are a number of claims in the literature for the existence of solid or gaseous TcO_3, and many of these claims were made as part of interpretation of high-temperature gas chromatography experiments. These gas phase studies are discussed in Section V.3.3. Several reports have been made for TcO_3(s) also, but little of the evidence holds up to close scrutiny. Older claims for the existence of TcO_3(s) were discussed by Anders [59AND].

The chemistry of rhenium and technetium share some common features, and since ReO_3(s) is well known, it is not surprising that TcO_3(s) has also been claimed to form. Some information suggests that TcO_3(s) possibly has been prepared, but this is uncertain because the conditions for its synthesis are poorly defined and the oxide itself is poorly characterised. In addition, some reports of "pink oxides" may simply have been mixtures of black TcO_2(cr) dispersed in pertechnetate salts or Tc_2O_7(cr). For readers interested further in this topic, see discussion under Ref. [59AND] in Appendix A.

V.3.2.3.2 Thermodynamic data

There are several publications in which estimated values are given for S°_m, $\Delta_f H^\circ_m$, and/or $\Delta_f G^\circ_m$ of TcO_3(s). Most of these values [53COB/SMI, 66ZOU/POU, 80PAQ/REI, 85MAG/BLU] are identical or nearly identical, and are based upon the calculations of Cobble, Smith and Boyd [53COB/SMI]. Cobble, Smith and Boyd estimated that $\Delta_f H^\circ_m$ (TcO_3, cr, 298.15 K) $= -539.7\ kJ{\cdot}mol^{-1}$ from available values for $\Delta_f H^\circ_m$ of Tc_2O_7(cr), Re_2O_7(s), and ReO_3(s), by assuming that the differences between enthalpies of formation of the oxides with different stoichiometries are the same for rhenium and technetium. They similarly estimated that S°_m (TcO_3, s, 298.15 K) $= 72.4\ J{\cdot}K^{-1}{\cdot}mol^{-1}$, which then yields $\Delta_f G^\circ_m$ (TcO_3, s, 298.15 K) $= -461.0\ kJ{\cdot}mol^{-1}$.

Voitovich and Golovko [67VOI/GOL] gave tabulated values of $-[G^\circ_m(T) - H^\circ_m\ (298.15\ K)]/T$ from 298.15 to 1000 K for TcO_3(s). Their values yield $S^\circ_m =$

88.28 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for TcO_3(s) at 298.15 K, which is rather higher than the estimated value of 72.4 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ given by Cobble, Smith and Boyd [53COB/SMI]. The origin of the input for the estimated values of Voitovich and Golovko is unclear.

Migge [89MIG] noted that using the estimated thermodynamic values of Cobble, Smith and Boyd [53COB/SMI] gives the prediction that TcO_3(s) has a fairly wide stability field as a function of temperature and O_2(g) fugacity. Given the lack of clear cut direct evidence for TcO_3(s), a "stability" field of this size seemed unlikely to him. Migge preferred estimated values of $S^\circ_m = (71 \pm 6)$ $J{\cdot}K^{-1}{\cdot}mol^{-1}$ and $\Delta_f H^\circ_m = -524$ $kJ{\cdot}mol^{-1}$. These values were selected by him so that TcO_3(s) was required to disproportionate to TcO_2(cr) and to Tc_2O_7(l or g) above about 500 K.

Because the very existence of TcO_3(s) has not been established with certainty, we do not recommend any estimated thermodynamic values for it. Clearly, additional studies are desirable to provide chemical and thermodynamic characterisation of TcO_3(s).

V.3.2.4 TcO_2(cr)

V.3.2.4.1 General properties

The solid oxide TcO_2(cr) is well known. It can be prepared by thermal dehydration of $TcO_2 \cdot xH_2O$(s) at 573 K in vacuum [54NEL/BOY]; at high temperatures in air TcO_2(cr) should react with O_2(g) to form Tc_2O_7 instead. Thermal decomposition of NH_4TcO_4(cr) in an argon stream around 513 to 598 K has been used to prepare TcO_2(cr) [78SPI/KUZ, 78VIN/KON3], although temperatures of 973 K or higher in a N_2(g) stream are recommended [64MUL/WHI, 68MUL, 87LIE/BAU2] to ensure that complete decomposition takes place.

Similar experiments have recently been performed by Burnett *et al.* [95BUR/CAM]. They prepared TcO_2(cr) by thermal decomposition of purified NH_4TcO_4(cr) in an atmosphere of flowing ultra-high-purity N_2(g), (Appendix A). An X-ray diffraction study of a sample of their TcO_2(cr) gave the same peaks when it was freshly prepared and after it had been aged for one year in air, which implies that TcO_2(cr) is kinetically stable in air.

Extended X-ray absorption fine structure spectroscopy (EXAFS) measurements of TcO_2(cr), indicated that this solid has a distorted rutile structure with a Tc-Tc nearest neighbour distance of 2.61×10^{-10} m and a Tc-O distance of 1.98×10^{-10} m, [95ALM/BRY].

Unit cell parameters have been reported for TcO_2(cr) in four publications [55MAG/AND, 65SPI/KUZ, 69ROG/SHA, 87LIE/BAU2]. Even the three studies in better agreement [55MAG/AND, 69ROG/SHA, 87LIE/BAU2] show surprisingly large differences in the unit cell dimensions, *cf.* Table V.11. Such large variation suggests that the TcO_2(cr) samples may have been non-stoichiometric in some of the studies, either because the decomposition of NH_4TcO_4(cr) was not entirely complete, or that TcO_2(cr) has slightly variable composition and should be written as $TcO_{2\pm\delta}$(cr). In a most recent study [87LIE/BAU2] the TcO_2(cr) was annealed in a sealed quartz ampoule at 1133 K to yield well-crystallised material. However, the main cause of this variation appears to result from the peculiar dimensions of the unit cell as described in

the following two paragraphs.

Burnett *et al*. [95BUR/CAM] performed powder pattern X-ray diffraction for TcO_2(cr) but did not derive unit cell dimensions. However, they did note that their peak positions and relative intensities were in excellent agreement with those reported by Muller, White and Roy [64MUL/WHI] and analysed by Rogers *et al*. [69ROG/SHA]. Table V.11 contains structural results for all of the known binary oxides of technetium. Burnett *et al*. pointed out that crystals of the MoO_2 type metal dioxides have values of $a \approx c \approx 2b/\sqrt{3}$ and $\beta \approx 120°$, with nearly hexagonal symmetry. Under this condition there is clustering of peaks with "d" spacings around 1.7×10^{-10} m and around 2.4×10^{-10} m. Individual peaks thus can be easily incorrectly assigned, which results in errors in the unit cell dimensions.

The authors of reference [95BUR/CAM] have since analysed their X-ray diffraction patterns to yield the unit cell dimensions for TcO_2(cr) [99JOB/TAY], which are given in Table V.11. These are probably the most accurate unit cell parameters for TcO_2(cr). However, the pseudo-symmetric relation between the unit cell parameters make it difficult to obtain unique values because of multiple local minima in the least-squares analysis of the diffraction pattern positions. See the discussion of the selected reference [99JOB/TAY] in Appendix A.

TcO_2(cr) was described as black coloured [54NEL/BOY] or dark grey with a pink metallic lustre [78SPI/KUZ], and it sublimed in vacuum above 1173 K [54NEL/BOY] or in N_2(g) above 1223 K [64MUL/WHI]. Sasaki and Soga [81SAS/SOG] used band structure calculations to predict that TcO_2(cr) should be an electrical conductor at room temperature (conductance = 10 to 50 $S \cdot cm^{-1}$). These claims for the congruent sublimation of TcO_2 at 1173 and 1223 K [54NEL/BOY, 64MUL/WHI] are rather surprising, since we do not expect the vapour pressure of TcO_2(g) to be significant until much higher temperatures. However, modelling calculations using our evaluated thermodynamic data indicate that the observed transport of TcO_2 most probably resulted from the incongruent vaporisation process

$$\frac{7}{2}TcO_2(cr) \rightleftharpoons \frac{3}{2}Tc(s) + Tc_2O_7(g)$$

rather than as the congruent sublimation of TcO_2(g). Upon reaching the cooler regions of the reaction vessel, the Tc_2O_7(g) decomposed to form the observed deposits of TcO_2(cr). A similar high temperature vaporisation reaction was also observed for ReO_2(cr) [68BAT/GUN, 71FRA/KLE], although the reaction is not quantitative for that system because of partial formation of ReO_3.

Muller, White and Roy [64MUL/WHI, 68MUL] described an attempt to prepare a lower oxide of technetium by reducing TcO_2(cr) in a carbon monoxide-carbon dioxide mixture at elevated temperatures, with O_2(g) partial pressures at 4.2×10^{-11} and 4×10^{-21} bar. Reaction mixtures heated to 873 and to 1228 K formed technetium metal, without any intermediate oxide phase being produced. As an alternative approach for producing lower oxides of technetium, they [64MUL/WHI, 68MUL] reacted technetium metal and TcO_2(cr) in a closed platinum capsule. Samples of TcO_2(cr) and Tc(cr) corresponding to "$TcO_{0.51}$", "$TcO_{0.99}$", "$TcO_{1.12}$", and "$TcO_{1.20}$" yielded a mixture to TcO_2(cr) and a new phase after being heated [64MUL/WHI, 68MUL].

This new phase was also produced by reaction of a mixture corresponding to the composition $TcO_{0.10}$ that was heated to 1523 K in a silica tube, so the presence of platinum was not required for its formation. Assuming that this phase was a lower oxide, it could have been TcO, Tc_2O_3, or a mixed valence oxide. One unindexable diffraction peak in the X-ray pattern of the pseudocubic phase varied from sample to sample, and this may indicate the presence of a second lower oxide.

V.3.2.4.2 Thermodynamic data

Several estimated values for $\Delta_f G^\circ_m$ of TcO_2(cr) at 298.15 K ranging from -358.8 kJ·mol^{-1} [71CAR2] to -382.2 kJ·mol^{-1} [53COB/SMI] have been reported [55CAR/SMI, 66ZOU/POU, 80PAQ/REI, 85MAG/BLU, 86MAG]. In addition, several reports [53COB/SMI, 80PAQ/REI, 85MAG/BLU, 91LEM/SAL] contain values of S°_m and (in some cases) $\Delta_f H^\circ_m$ for TcO_2(cr), and Voitovich and Golovko [67VOI/GOL] tabulated values of $-[G^\circ_m(T) - H^\circ_m(298.15\ K)]/T$ from 298 to 2000 K.

The reported values of S°_m for TcO_2(cr) were all obtained from estimation schemes, and values of $\Delta_f H^\circ_m$ were then calculated from $\Delta_f S^\circ_m$ and estimated $\Delta_f G^\circ_m$. Thus they are not experimentally based values. Furthermore, all of those reported $\Delta_f G^\circ_m$ values for TcO_2(cr) are based either directly or indirectly upon the emf measurements of Cobble, Smith and Boyd [53COB/SMI], Cartledge and Smith [55CAR/SMI], or Cartledge [71CAR2]. However, the redox potentials reported in those studies were for the $TcO_4^-/TcO_2 \cdot xH_2O$(s) or $TcO_2 \cdot xH_2O$(s)/Tc(cr) redox couples, and actually yield $\Delta_f G^\circ_m$ of $TcO_2 \cdot xH_2O$(s) and not of TcO_2(cr).

All of the values of $\Delta_f G^\circ_m$ of TcO_2(cr) in those studies were derived by formally treating $TcO_2 \cdot xH_2O$(s) as being unhydrated. That is, for the hydration reaction:

$$TcO_2(cr) + xH_2O \quad \rightleftharpoons \quad TcO_2 \cdot xH_2O(s)$$

the value of $\Delta_{hyd} G^\circ_m$ was formally assigned a value of zero. This is equivalent to assuming that both TcO_2(cr) and $TcO_2 \cdot xH_2O$(s) have equal thermodynamic stability at 298.15 K.

There are several studies in which attempts were made to measure solubilities that could be used to calculate $\Delta_f G^\circ_m$ of TcO_2(cr), *cf.* Appendix A [80PAQ/REI, 87LIE/BAU2, 88VIK/GAR, 96NGU/PAL, 97BUR/JOB]. The reported solubilities at most pHs span about three orders of magnitude. Some of these studies found the solubility of TcO_2(cr) to be lower than that of $TcO_2 \cdot xH_2O$(s) whereas others found it to be higher. Generally, amorphous or poorly crystalline hydrous oxides are more soluble than their corresponding anhydrous crystalline oxides. In addition, there is no way to be sure whether the surface layer of the TcO_2(cr) remained unhydrated during the solubility experiments, and thus whether the observed solubilities are actually for a partially hydrated dioxide. Because of these uncertainties, we base our evaluation of the thermodynamic properties of TcO_2(cr) on the calorimetric measurements of Burnett *et al.* [95BUR/CAM] where the solid phase was well characterised.

Burnett *et al.* [95BUR/CAM] have measured the enthalpy of solution of TcO_2(cr). The average of their 17 dissolution enthalpy measurements according to the dissolution

reaction

$$TcO_2(cr) + 3Ce(ClO_4)_4(sln) + 2H_2O(l) \quad \rightleftharpoons \quad HTcO_4(sln) + 3Ce(ClO_4)_3(sln) + 3HClO_4(sln) \qquad (V.28)$$

is selected here: $\Delta_{sol}H_m(V.28) = -(138.5 \pm 11.3)$ kJ·mol^{-1}, *cf.* Appendix A. Taking enthalpy values for auxiliary reactions from Gayer, Herrell, and Busey [76GAY/HER], gives the selected value

$$\Delta_f H^\circ_m(TcO_2, cr, 298.15\ K) \quad = \quad -(457.8 \pm 11.7)\ kJ{\cdot}mol^{-1}.$$

There is a lack of published heat capacities for TcO_2(cr), and therefore a lack of an experimental value of S°_m (TcO_2, cr, 298.15 K). However, the published literature abounds with estimated values, *e.g.*, 62.3 J·K^{-1}·mol^{-1} [53COB/SMI], 62 J·K^{-1}·mol^{-1} [80PAQ/REI], 63 J·K^{-1}·mol^{-1} [85MAG/BLU], and 54.5 J·K^{-1}·mol^{-1} [91LEM/SAL, 95BUR/CAM], all of which were based on Latimer's rule with different assumptions about atomic contributions. Burnett *et al.* [95BUR/CAM] have cited experimental standard entropy values for the transition metal dioxides CrO_2(cr), MoO_2(cr), WO_2(cr), MnO_2(cr), and ReO_2(cr) that range from 46.3 to 54 J·K^{-1}·mol^{-1} with an average of 50.3 J·K^{-1}·mol^{-1}. This review considers the standard entropy values for the structurally similar transition metal dioxides to be a better approximation than Latimer's rule values for the standard entropy of TcO_2(cr), and selects an estimated value of

$$S^\circ_m(TcO_2, cr, 298.15\ K) \quad = \quad (50 \pm 4)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

for thermodynamic calculations. Combining this value with the selected value of $\Delta_f H^\circ_m$ yields

$$\Delta_f G^\circ_m(TcO_2, cr, 298.15\ K) \quad = \quad -(401.8 \pm 11.8)\ kJ{\cdot}mol^{-1}$$

V.3.2.5 $TcO_2{\cdot}xH_2O$(s)

V.3.2.5.1 General properties, hydration number

There is considerable information about the hydrous oxides of Tc(IV). The reported methods of preparation include chemical reduction of TcO_4^- solutions, hydrolysis of Tc(IV) salts, electrolytic reduction of TcO_4^- (both polarographic reduction and cathodic deposition), and radiolysis of TcO_4^- solutions.

Cobble, Smith and Boyd [53COB/SMI], Nelson, Boyd and Smith [54NEL/BOY], and Pilkington [90PIL] reduced TcO_4^- with zinc metal in the presence of HCl. A second chemical method for preparing hydrous oxides of Tc(IV) involves reduction of TcO_4^- with Sn(II) in the presence of $HClO_4$ [77OWU/MAR]. The third method for the chemical reduction of TcO_4^- is to use hydrazine in aqueous $HClO_4$ [69GOR/KOC], in water [86MEY/ARN, 87MEY/ARN], or in 0.01 M HCl [79SUN].

Lefort [63LEF] reported that radiolysis of aqueous TcO_4^- with gamma rays in 0.05 and 0.5 M H_2SO_4 caused TcO_4^- to be reduced to Tc(IV). If the concentration of Tc(IV) exceeded 5×10^{-4} M, then a hydrous oxide of Tc(IV) was precipitated.

A number of studies have been reported in which a hydrous oxide of Tc(IV) was prepared by polarographic, coulometric, or voltammetric reduction of TcO_4^- from aqueous solution [63LEF, 63SAL/RUL, 68MÜN2, 74MAZ/MAG, 79GRA/DEV, 82PAQ/LIS]. Both acidic and basic solutions were investigated.

The colour of the hydrous oxide or oxides of Tc(IV) has been described as being black [53COB/SMI, 54NEL/BOY, 63LEF, 63SAL/RUL, 67RUL/PAC2, 75BES/COS, 79SUN, 86MEY/ARN, 90PIL], brownish-black [71CAR2, 74MAZ/MAG], or brown to dark brown [55CAR/SMI, 67RUL/PAC2, 75BES/COS, 76SPI/KUZ]. These colour differences may be due to minor differences in chemistry such as different amounts of water of hydration or state of crystallinity (or lack of crystallinity), or may simply be due to differences in particle size.

The chemical formulae proposed for this hydrous oxide range from TcO_2(cr) to $TcO_2 \cdot xH_2O$(s), $TcO(OH)_2$(s) and $Tc(OH)_4$(s). In many studies the solid phase was not directly characterised but, in a few cases, some partial characterisation was reported.

Meyer *et al.* [89MEY/ARN, 91MEY/ARN2] measured the values of x in $TcO_2 \cdot xH_2O$(s) for several solids precipitated from acidic and basic solutions. Large variations from $x = 0.44$ to $x = 4.22$ were obtained from acidic deposition, and values from $x = 1.38$ to $x = 1.81$ were obtained from basic deposition. Meyer *et al.* [89MEY/ARN, 91MEY/ARN2] recommended $x = (1.63 \pm 0.28)$, which is compatible with $x = 1.6$ proposed earlier by Nelson, Boyd and Smith [54NEL/BOY]. Rard [83RAR] in his review selected $x = 2$, and other authors, *e.g.* [92ERI/NDA], left the hydration number as a variable or simply called the solid "hydrated TcO_2(s)".

A more recent characterisation of a freshly prepared "amorphous TcO_2" by Burnett *et al.* [95BUR/CAM] yielded a rather lower hydration number of $x \sim 0.46$. Their samples of this substance were prepared by hydrolysis of aqueous solutions of $(NH_4)_2TcCl_6$ or $(NH_4)_2TcBr_6$ with excess NaOH in an atmosphere of purified N_2(g), followed by washing of the precipitate. They characterised this substance by oxidation with Ce(IV), by determination of the mass fraction of Tc in the precipitate, and by determining the mass fraction of water using Karl Fischer reagent. Their analyses indicated that part of the technetium in their "amorphous TcO_2" was actually in a higher oxidation state than Tc(IV). Thus samples of "amorphous TcO_2" prepared in this manner are probably not chemically equivalent to samples of $TcO_2 \cdot xH_2O$(s) prepared by other methods such as reduction of TcO_4^- electrolytically or chemically with hydrazine.

Meyer *et al.* [89MEY/ARN] determined the hydration number of their hydrous oxides from the mass of electrodeposited material after some drying, followed by determination of the amount of ^{99}Tc present in each deposit of hydrous oxide by liquid scintillation counting of the solution obtained by stripping of the electrode with nitric acid. Similarly, Nelson, Boyd and Smith [54NEL/BOY] determined the molar mass of weighed samples of their hydrous oxide by oxidation with Ce(IV). Both determinations involved the assumption that all of the technetium in the hydrous oxides was present as Tc(IV), which was not verified. Thus the characterisation of these hydrous oxides was incomplete.

Hydrous oxides of technetium used for emf measurements involving the $TcO_4^-/TcO_2 \cdot xH_2O$ electrode, see Section V.2.1, were prepared by electrodeposition [55CAR/SMI, 75LIE/MÜN, 88MEY/ARN, 89MEY/ARN, 91MEY/ARN] and, under

such reducing preparation conditions, the resulting hydrous oxides are likely to contain all or mostly Tc(IV). However, solubility measurements for the hydrous oxide(s) require equilibration periods of at least several days to reach steady state concentrations of Tc(IV), *e.g.* [89MEY/ARN], during which time chemical changes could be occurring in the solid hydrous oxide. Because of the lack of definitive information, it is assumed for our thermodynamic calculations that these hydrous oxides contain exclusively Tc(IV).

In view of these differences, and since the exact value of x is of no importance in aqueous chemistry, a notation such as TcO_2(s, hyd) for this compound would not be unreasonable. However, in order to visibly indicate in the chemical formula that the solid phase in question is hydrated, we prefer to use the formula $TcO_2 \cdot 1.6H_2O$(s) as 1.6 seems to be a reasonable average hydration number in spite of possible larger variations.

V.3.2.5.2 Thermodynamic data

Experimental studies of the solubility of $TcO_2 \cdot xH_2O$(s) are summarised in Table V.13, and the papers are described in Appendix A. As can be seen, the solubility of ^{99}Tc(IV) is quite low, and quantitative determinations of some accuracy are possible due to the β-activity of ^{99}Tc. The values obtained show strong increase of the solubility in acidic solutions and a less marked increase in basic solutions. Among the inert salts used is NaCl, in spite of the fact that Cl^- forms complexes with Tc(IV). As discussed in section V.3.1.1, the formation of chloride or mixed hydroxide-chloride complexes of Tc(IV) is a potential concern only at low pH where pH < 3.

Lefort [63LEF] found a high solubility of $TcO_2 \cdot xH_2O$(s) at low pH. Other Tc solubility studies are also briefly described in Appendix A [88VIK/GAR, 89GUP/ATK, 90PIL]. The most reliable published solubility studies of $TcO_2 \cdot xH_2O$(s) have been published by Meyer *et al*. [91MEY/ARN2] and by Eriksen *et al*. [92ERI/NDA]. In both studies, pertechnetate was present in the solutions and was measured and corrected for, *cf*. Appendix A.

This correction is important, because the amount of TcO_4^- is significant even at low partial pressures of oxygen (less than 1 ppm and 0.5 ppm, respectively, in the two studies), leading to a ratio of Tc(VII)/Tc(IV) in the range of 10 to more than 200. Earlier studiesare in general not reliable due to failure to determine the pertechnetate concentrations in the equilibrated solutions. The largest number of reliable solubility data in near-neutral solutions were published by Meyer *et al*. [91MEY/ARN2]. The solubilities from dissolution experiments of 2 to 3 weeks equilibration time consistently lie between 10^{-9} and 10^{-8} M. Eriksen *et al*. [92ERI/NDA] reported five measurements between pH 6 and 9 with an average solubility of 6×10^{-9} M but without indicating the temperature. The experimental values of this study are tabulated in [93ERI/NDA]. The average of 19 solubility measurements of Meyer *et al*. *cf*. Tables 1, 2 and 3 of [91MEY/ARN2], in NaCl solutions between pH 5 and 9.5, which results in $(3.6 \pm 2.1) \times 10^{-9}$ M. The uncertainty is 1σ. The relevant reaction for the solubility measurements is

Table V.13: Summary of experimental data on the solubility of $TcO_2 \cdot xH_2O$(s) and TcO_2(cr).

Method of preparation of $TcO_2 \cdot xH_2O$(s) or TcO_2(cr)	Ionic medium	T (K)	[Tc][a] (M)	Reference
el. dep. Pt[b]	0.05 and 0.5 M H_2SO_4	RT[c]	5×10^{-4}	[63LEF]
$TcO_2 \cdot xH_2O$(s)[d]	acidic Tc(IV) solution + NaOH, pH 6 – 12	298	10^{-9}[e]	[88VIK/GAR]
TcO_2(cr)[d]	acidic Tc(IV) solution + NaOH, pH 4 – 11	298	10^{-8}[e]	
el. dep. Pt [b]	sat. $Ca(OH)_2$ and redox, pH = 12.5	RT[c]	$10^{-8} - 10^{-7}$	[89GUP/ATK]
TcO_4^- + Zn in acidic solution	cement equilibrated waters, pH 8 – 13, redox	RT[c]	$2 \times 10^{-8} - 2 \times 10^{-7}$	[90PIL]
el. dep. Pt [b] in basic and acidic solution	0.01 M NaCl, and 0.05 – 2.6 M NaCl	298	$(3.6 \pm 4.2) \times 10^{-9}$[f]	[91MEY/ARN2]
el. dep. Pt [b] in neutral solution	no inert salt	RT[c]	$(6.8 \pm 0.8) \times 10^{-9}$[g]	[92ERI/NDA] [93ERI/NDA]
TcO_4^- reduction with hydrazine	0.1 M NaCl pH 1–13	298	10^{-8}[h]	[96NGU/PAL]
dehydration of hydrous oxide	0.1 M NaCl pH 1–13	298	$10^{-8.5}$[h]	[96NGU/PAL]

[a] In references [91MEY/ARN2, 92ERI/NDA, 93ERI/NDA, 96NGU/PAL] and, presumably, reference [88VIK/GAR], the equilibrated solutions were extracted to remove TcO_4^-, so these concentrations are total concentrations of the Tc(IV)species. In the other studies [63LEF, 89GUP/ATK, 90PIL] the TcO_4^- was not removed, so these concentrations are the total concentrations of Tc(IV) plus TcO_4^-.

[b] Electrodeposition on Pt electrode.

[c] RT means room temperature.

[d] $TcO_2 \cdot xH_2O$(s) was freshly precipitated, and TcO_2(cr) was obtained by thermal decomposition of ammonium pertechnetate.

[e] These are minimum values of the solubility curves and correspond to pH 7 – 9 for $TcO_2 \cdot xH_2O$(s) and pH 6 – 8 for TcO_2(cr), respectively.

[f] Average of 19 values between pH 5 and 9.5, calculated in this review. The uncertainty is 2σ.

[g] The uncertainty is 1σ as given by the authors.

[h] The solubility minimum occurs at about 10^{-8} M for $TcO_2 \cdot xH_2O$(s) and about $10^{-8.5}$ M for TcO_2(cr), both for the range of pH=3 to 10.

$$TcO_2 \cdot 1.6H_2O(s) \quad \rightleftharpoons \quad TcO(OH)_2(aq) + 0.6H_2O(l) \qquad \text{(V.29)}$$

Since the ionic strength dependence of Eq. (V.29) should be negligible, the selected equilibrium constant at $I = 0$ with uncertainty converted to 95% confidence limits, is

$$\log_{10} K_s^\circ(\text{V.29}, 298.15\ \text{K}) \quad = \quad -8.4 \pm 0.5$$

From this solubility constant, and using our selected value of $\Delta_f G_m^\circ$

$$\Delta_f G_m^\circ(TcO_2 \cdot 1.6H_2O, \text{s}, 298.15\ \text{K}) \quad = \quad -(758.5 \pm 8.4)\ \text{kJ·mol}^{-1}$$

cf. Section V.2.1, we derive our selected Gibbs energy of formation for the uncharged Tc(IV) hydrolysis species:

$$\Delta_f G_m^\circ(TcO(OH)_2,\ \text{aq},\ 298.15\ \text{K}) = -(568.2 \pm 8.8)\ \text{kJ·mol}^{-1}$$

Meyer *et al.* [91MEY/ARN2] found that solubilities of $TcO_2 \cdot xH_2O$(s) were essentially identical for different samples prepared by reduction of TcO_4^- from acidic solutions both by electrolysis and by chemical reduction with hydrazine. Thus these two methods yield an identical product from a thermodynamic viewpoint. However, they found that samples of $TcO_2 \cdot xH_2O$(s) that were prepared by electrodeposition of TcO_4^- from an alkaline solution of 0.01 M NH_3(aq) had somewhat lower solubilities at any particular pH, and therefore differ chemically in some subtle manner from samples prepared from acidic solutions.

Nguyen-Trung *et al.* [96NGU/PAL] have also performed solubility experiments for $TcO_2 \cdot xH_2O$(s) prepared by reduction of TcO_4^- with hydrazine. At the time this section was written, we did not have access to their actual experimental solubilities and thus a detailed comparison is not possible. However, their extended abstract, *cf.* Appendix A, indicates that their solubilities for the pH range of 3 to 10 are about 10^{-8} mol·dm^{-3}. Although this is slightly higher than our assessed value, it falls within our assigned uncertainty limits.

Solubilities of $TcO_2 \cdot xH_2O$(s) at alkaline pHs have been reported for cement equilibrated or simulated cement equilibrated waters [89GUP/ATK, 90PIL]. Dissolved technetium concentrations from those two studies were generally higher than those obtained from the fairly concordant solubility studies just discussed [91MEY/ARN2, 92ERI/NDA, 93ERI/NDA, 96NGU/PAL]. No attempts were made to distinguish between the amount of total dissolved technetium present and the fractions present as Tc(IV) and TcO_4^- in these two studies [89GUP/ATK, 90PIL], and thus they provide insufficient information to calculate values of $\log_{10} K_s^\circ$(V.29, 298.15 K).

Kunze *et al.* [96KUN/NEC] have investigated the concentration of dissolved Tc(IV) present in solutions of TcO_4^- being reduced to $TcO_2 \cdot xH_2O$(s) by Fe(cr) or FeO(cr). Their measured concentrations of technetium were generally higher than those recommended here, both in dilute solutions and in concentrated chloride brines, but the Tc(IV) concentrations gradually decreased with time to reach values of $(1\text{–}7)\times10^{-8}$ mol·dm^{-3} after about 250 to 490 days. These solubilities are

approaching those reported for $TcO_2 \cdot xH_2O$(s) samples prepared by other methods [91MEY/ARN2, 92ERI/NDA, 93ERI/NDA, 96NGU/PAL], which suggest the solid phases in these studies are either chemically identical or close to becoming so.

We can also calculate an approximate value for $\Delta_f G^\circ_m$ of TcO_2(cr), by using the E° values as if the solid phase were TcO_2(cr) rather than $TcO_2 \cdot xH_2O$(s). This assumption yields $\Delta_f G^\circ_m$ (TcO_2, cr, 298.15 K)= -379 kJ·mol^{-1}. This value is considerably different that the experimentally-based value of $\Delta_f G^\circ_m(TcO_2, \text{cr}, 298.15\ \text{K}) = (-401.8_5 \pm 11.7)$ kJ·mol^{-1} derived in Section V.3.2.4. As noted by Burnett *et al*. [95BUR/CAM], this experimentally-based value predicts that TcO_2(cr) should be stable over a wider range of values of Eh than is predicted from the value of $\Delta_f G^\circ_m$ estimated from that of the hydrous oxide.

Burnett *et al*. [95BUR/CAM] performed experiments for the enthalpy of (oxidative) dissolution of samples of hydrated oxide corresponding to the empirical composition $TcO_2 \cdot 0.46H_2O$(s). As noted by the authors of that study, the resulting value of $\Delta_f H^\circ_m(TcO_2 \cdot 0.46H_2O, \text{s}, 298.15\ \text{K})$ yields an unrealistic value for the enthalpy of dehydration of $TcO_2 \cdot 0.46H_2O$(s). Their "$TcO_2 \cdot 0.46H_2O$(s)" was prepared by hydrolytic precipitation from aqueous solutions of $(NH_4)_2TcCl_6$ and $(NH_4)_2TcBr_6$ and contained significant amounts of technetium in an oxidation state higher than +4. Given the uncertainty in the exact chemical composition of this "$TcO_2 \cdot 0.46H_2O$(s)" and following the recommendation of Burnett *et al*. we do not analyse these results.

The value of $\Delta_f G^\circ_m(TcO_2 \cdot 1.6H_2O, \text{s}, 298.15\ \text{K})$ obtained in this section could be combined with $\Delta_f G^\circ_m(TcO_2, \text{cr}, 298.15\ \text{K})$ of Section V.3.2.4.2 and the CODATA value of $\Delta_f G^\circ_m(H_2O, \text{l}, 298.15\ \text{K})$ to yield a value of the Gibbs energy of hydration of TcO_2(cr). The Gibbs energies of formation of the first two of these compounds are quite uncertain, and the standard propagation of error calculation implies that the derived value of $\Delta_{hyd}G^\circ_m = 22.7$ kJ·mol^{-1} is uncertain by ± 14.5 kJ·mol^{-1}. However, since the experimental Gibbs energies of formation of TcO_2(cr) and $TcO_2 \cdot 1.6H_2O$(s) are completely independent of each other, it is perhaps more realistic to take the sum of the uncertainties ± 20.2 kJ·mol^{-1}to be the actual uncertainty for this calculated value of $\Delta_{hyd}G^\circ_m$. Obviously, the uncertainty in this value of $\Delta_{hyd}G^\circ_m$ is so large as to make this calculation meaningless.

Because of their large relative uncertainties, values of the assessed thermodynamic properties of TcO_2(cr) and $TcO_2 \cdot 1.6H_2O$(s) should not both be used in the same thermodynamic calculation. The thermodynamic data for $TcO_2 \cdot 1.6H_2O$(s) and the aqueous species are thermodynamically consistent, and thus it is the appropriate substance to include in aqueous solubility calculations. In contrast, if the Tc(cr) + O_2(g) system were being modeled, then thermodynamic data for anhydrous TcO_2(cr) would be more appropriate.

V.3.2.6 Lower valence hydrous Tc oxides and mixed valence Tc oxides

The preparation of several lower valence and mixed valence hydrous oxides has been claimed. In one case, "$Tc_4O_5 \cdot xH_2O$(s)" was prepared as a bulk phase [80SPI/KUZ]. Cartledge [71CAR2, 71CAR] has claimed a number of compounds but only as surface films on technetium metal. The existence of these compounds is not proven, *cf*.

Appendix A [71CAR2, 80SPI/KUZ]. As discussed there under reference [71CAR2], it is impossible to unambiguously assign the observed redox potentials to any definite redox reaction, and thus no valid Gibbs energies of formation can be calculated for the proposed lower valence hydrous oxides.

Further compounds such as "Tc_2O_3(s)" and "$Tc(OH)_3$(s)" [63SAL/RUL] were postulated without characterisation, *cf.* Appendix A. Mazzocchin *et al.* [74MAZ/MAG] reported convincing evidence for a Tc(III) hydrous oxide (Appendix A). These studies leave no doubt that electrolytic reduction of TcO_4^- in acidic solutions can give soluble Tc(III), and that a hydrous oxide of Tc(III) precipitates if the technetium concentration is high enough. However, both Tc(III) solutions and the hydrous oxide of Tc(III) are quite unstable with regard to disproportionation if the pH is increased to above 3 or 4 [79GRA/DEV, 82PAQ/LIS].

These Tc(III) ions and hydrous oxides are also sensitive to oxidation to Tc(IV) by O_2(g) in air. This Tc(III) hydrous oxide should formally be written as Tc_2O_3(s, hyd), for lack of any information about its true chemical nature.

V.3.3 Gaseous technetium oxides

V.3.3.1 Summary of Tc oxide system

There is no doubt that Tc_2O_7(l) vaporises essentially congruently, because the condensate from its sublimation is still Tc_2O_7(g) (*cf.* Section V.3.2.1). Further support from this comes from measurements of the Raman spectrum of Tc_2O_7(g) at 593 K [71SEL/FRI]. The observed Raman spectrum is very similar to that for liquid Tc_2O_7(l). Other studies of interest are also described in Appendix A [52SIT/BAL, 74BAR, 78STE/BÄC, 92SIN, 93GIB].

There are several reports of the observation of TcO_3(g) in the vapour phase but, in reality, those studies only provided evidence for the existence of one or more oxides that are volatile at high temperatures, without determining which oxides or oxide they were [51FRI/JAF, 75EIC, 75EIC/DOM]. Therefore, no direct evidence for the existence of TcO_3(g) was given.

Mass spectrometric measurements have been reported for NH_4TcO_4 and and uncharacterised oxide of technetium, and the resulting gas phase ions produced by fragmentation give some indication about molecular oxides that might form in the vapour at high temperatures [82SCH/HOL, 93GIB] (*cf.* Ref. [52SIT/BAL] in Appendix A). With consideration being given to the various ions observed by mass spectrometry, and given the proper temperature and oxygen fugacity conditions, it may be possible to form any of the following gas phase molecular oxides: Tc_2O_7(g) (well known), Tc_2O_6(g), Tc_2O_5(g), Tc_2O_4(g), TcO_3(g), TcO_2(g), and TcO(g). In the presence of water vapour, both TcO_3OH(g) and $TcO_2(OH)_3$(g) have also been reported [93GIB]. High temperatures might be required to produce some of them.

The only experimental thermodynamic data available for the gaseous technetium oxides are the vapour pressure measurements for Tc_2O_7(cr, l) considered in Section V.3.2.1.2.c, but a number of estimates have been made as discussed below. There are two published sets of ideal gas statistical thermodynamic calculations for gas phase

oxides of technetium. Brewer and Rosenblatt [61BRE/ROS] reported estimated values of $-[G^\circ_m(T) - H^\circ_m(298.15\ K)]/T$ for TcO_2(g) from 298.15 to 3000 K, along with $H^\circ_m(298.15\ K) - H^\circ_m(0\ K)$ and an estimated value of $\Delta_r H^\circ_m$ for the dissociation of TcO_2(g) to Tc(g) and O(g). Schick [66SCH] gave detailed calculations of $C^\circ_{p,m}(T)$, $S^\circ_m(T)$, $H^\circ_m(T) - H^\circ_m(298.15\ K)$, and $-[G^\circ_m(T) - H^\circ_m(298.15\ K)]/T$ for TcO(g), by using molecular parameters for TcO(g) that were estimated by comparison with values for neighbouring elements in the periodic table. Schick [66SCH] similarly estimated a value for $\Delta_f H^\circ_m$ (TcO, g, 298.15 K) by comparison with values for neighbouring elements, and then used this value to estimate $\Delta_f G^\circ_m$ as a function of temperature. The thermodynamic properties of TcO(g) were tabulated by him from 298.15 to 6000 K. Above about 1000 K, however, these values should decrease in reliability due to the neglect of possible contributions of higher electronic levels in the statistical thermodynamic calculations.

Brewer and Rosenblatt's [61BRE/ROS] tabulated values give S°_m (298.15 K) = 262.8 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for TcO_2(g), and Schick [66SCH] gave 240.74 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for TcO(g).

V.3.3.2 TcO(g)

There are no definitive measurements on the spectrum of TcO(g), from which its molecular parameters can be derived, but various values of these appear in the literature, (see Tables B.7 and B.8 in Appendix B).

The ground state of the TcO(g) molecule was taken to be $^6\Sigma^+$, by comparison with MnO(g) [79HUB/HER], and as predicted by Langhoff *et al.* [89LAN/BAU]. Values for five higher electronic states were calculated by the same authors, by two different approximations for the $^6\Pi$ state. We have adopted the parameters for these states, *cf.* Table V.14, where the term values for the three highest states given have been rounded, bearing in mind the difference in the two estimates for the $^6\Pi$ state.

Table V.14: Calculated molecular parameters for TcO(g).

State	Term value (cm^{-1})	Statistical weight	ω (cm^{-1})	r $\times 10^{10}$ (m)
$^6\Sigma$	0	6	900	1.780
$^4\Pi$	9367	8	875	1.725
$^4\Delta$	11713	8	825	1.755
$^6\Pi$	13300	12	660	1.837
$^4\Pi$	20500	8	788	1.763
$^6\Sigma$	21500	6	833	1.815

Statistical thermodynamic calculations have been made using the molecular parameters (*cf.* Table V.14) for the ^{99}TcO(g) isotopic species. In order to estimate the uncertainties in the derived thermal functions, these calculations were repeated with the extreme combinations of the values for ω, the fundamental vibration wave number

and r, the interatomic distance in the ground state, from the uncertainties in the selected values. The calculated thermal functions are given in detail in Table B.9 (Appendix B). The values at 298.15 K are:

$$S^\circ_m(\text{TcO, g, 298.15 K}) = (244.109 \pm 0.600)\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$C^\circ_{p,m}(\text{TcO, g, 298.15 K}) = (31.256 \pm 0.750)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

Uncertainties in the calculated parameters for the five excited states which have been included, and the undoubted presence of other excited states, will add an appreciable uncertainty, particularly to $C^\circ_{p,m}$, above 1500 K.

There are no experimental thermodynamic data from which the enthalpy of formation can be derived, but there are values based on approximate calculations [89LAN/BAU], and a number of estimates. In their *ab initio* calculations, Langhoff *et al*. [89LAN/BAU] also estimated the dissociation energy. The uncorrected value is D_0(TcO, g) = 3.55 eV (342.5 kJ·mol^{-1}). However, their calculational method is known not to give very accurate values of D_0, and this value has been increased by the same ratio of D_0(exp.)/D_0(calc.) for MoO(g) as suggested by these authors. We take D_0(exp.)(MoO, g) to be (556 ± 21) kJ·mol^{-1} from the assessment of Pedley and Marshall [83PED/MAR] discussed below, which with D_0(calc.)(MoO, g)= 389.8 kJ·mol^{-1} from Langhoff *et al*. [89LAN/BAU] gives a correction factor of 1.426 and a corrected D_0(TcO, g) = (489 ± 30) kJ·mol^{-1}. Schick [66SCH] and Pedley and Marshall [83PED/MAR] have both estimated D_0(TcO, g) from the dissociation energies of the neighbouring transition elements. Schick's value can be inferred to be 527 kJ·mol^{-1} (with an (unknown) uncertainty of at least 21 kJ·mol^{-1}), while that from Pedley and Marshall, based on more recent data for the neighbouring metal monoxide gases, is (544 ± 84) kJ·mol^{-1}. The suggested value is D_0(TcO, g)= (530 ± 50) kJ·mol^{-1}, which after correction to 298.15 K with our selected value for $\Delta_f H^\circ_m$(Tc, g, 298.15 K) and the well-defined value of (249.18 ± 0.100) kJ·mol^{-1} for $\Delta_f H^\circ_m$(O, g, 298.15 K) [89COX/WAG] gives finally

$$\Delta_f H^\circ_m(\text{TcO, g, 298.15 K}) = (390^{+51}_{-64})\ \text{kJ·mol}^{-1}$$

The statistical thermodynamic value of S°_m (TcO, g, 298.15 K) yields a standard entropy of formation of $\Delta_f S^\circ_m$(TcO, g, 298.15 K) = (109.033 ± 0.922) J·K^{-1}·mol^{-1}. Combining this value with the standard enthalpy of formation then yields:

$$\Delta_f G^\circ_m(\text{TcO, g, 298.15 K}) = (357.5^{+51.0}_{-64.0})\ \text{kJ·mol}^{-1}$$

V.3.3.3 Tc_2O_7(g)

The thermal functions of Tc_2O_7(g) are derived from the analysis, partly estimated, of the structure and vibration frequencies of Tc_2O_7(g) by Beattie and Gilson [96BEA/GIL] from the observed Raman spectra [71SEL/FRI] and by comparisons with Re_2O_7(g), for which new spectroscopic measurements have been made [96BEA/GIL]. Since the detailed analysis for Tc_2O_7(g) which appeared in a preprint

of [96BEA/GIL] obtained by the reviewers did not appear in the published article [96BEA/GIL], we present an extended summary here.

The solid M_2O_7(cr) heptoxides (M = Mn, Tc, Re) have been studied, by other workers, using X-ray single crystal diffraction techniques. Mn_2O_7(cr) (which melts at 279.1 K) is molecular with exact C_{2v} symmetry with an Mn-O-Mn bond angle of 120.7° [88DRO/KRE]. (This structure can be obtained from the "linear" eclipsed Mn_2O_7 by bending the Mn-O-Mn link). Crystalline Tc_2O_7(cr) is also molecular [69KRE/MÜL] , but with C_i symmetry with linear Tc-O-Tc bonds, the length of the bridging Tc-O bond being $= 1.840 \times 10^{-10}$ m. The terminal Tc-O bonds vary from (1.649 to 1.695) $\times 10^{-10}$ m, 1.673×10^{-10} m, being the average value. If all the Tc-O bonds were made equivalent, the molecule would have D_{3d} symmetry, with the staggered configuration. By contrast, solid Re_2O_7(cr) has a polymeric structure [69KRE/MÜL], in which strongly distorted ReO_6 octahedra and fairly regular ReO_4 tetrahedra are connected through corners to form double layers. The average Re-O-Re angle is about 150°.

As a thin film, or when isolated in argon or nitrogen matrices, Mn_2O_7 was estimated to have a bond angle of 150 - 160° [83LEV/OGD], and a recent electron diffraction study of molecular Re_2O_7 in the vapour at 503 K [92KIP/HER] indicates an Re-O-Re bond angle of 143.6°, with the ReO_3 groups offset by 31°, thus reducing O-O repulsions in the different ReO_3 groups.

The calculated Raman spectrum of Tc_2O_7(g) assuming a structure identical to that of gaseous Re_2O_7(g) closely resembles the experimental data of Selig and Fried [71SEL/FRI], in terms of both frequencies and intensities. This is not true if the linear Tc-O-Tc structure is adopted. Thus although the spectroscopic data may not unambiguously distinguish between a bent and "linear" species, the evidence for non-linearity is compelling.

The "bent to linear to bent" sequence found in the diffraction experiments of the solids, on passing from Mn to Re, is most likely to be attributable to packing effects in the solids. We therefore assume that Tc_2O_7(g) has a non-linear Tc-O-Tc link, and adopt a molecule with precisely the same dimensions as derived for Re_2O_7(g) from the electron diffraction study [92KIP/HER]. This is a justificable assumption since Selig and Fried [71SEL/FRI] showed that the two molecules had nearly identical gas phase Raman spectra. This structure has C_2 symmetry, Tc-O(bridging) $= 1.892 \times 10^{-10}$ m, Tc-O(terminal) $= 1.708 \times 10^{-10}$ m, a Tc-O-Tc angle of 143.6°, O(bridging)-Tc-O(terminal) of 110.2°, and 31° twist of the TcO_3 unit. A force-field model has been developed for Re_2O_7(g) [96BEA/GIL], and replacement of the mass of Re by that of Tc led to a first set of frequencies for Tc_2O_7(g). The terminal stretching force constant and the corresponding interaction term, plus the interaction between the terminal-stretch and the bridge-stretch were first adjusted manually from the ratios of the squares of the appropriate observed Raman frequencies [71SEL/FRI]. A series of least-square fits was then obtained by relaxing the force constants in selected batches. Finally, in the 340 - 360 cm^{-1} region, calculated Raman intensities were used to match the observed Raman envelope. These Raman intensities were calculated using a combination of bond and atom polarisabilities.

The results of these calculations are given in Table B.10 (Appendix B), which

includes a comparison with the experimental Raman data [71SEL/FRI]; the infrared spectrum of Tc_2O_7(g) has not been reported.

The symmetric torsional mode was reasonably assigned as approximately coincident with the low frequency deformation at 60 cm^{-1}; with this, the anti-symmetric torsion is calculated to be at 38 cm^{-1}. However, these low frequency modes are open to serious question and represent no more than intelligent guesses. It is seen that there is good-to-excellent agreement with the experimental frequencies both as regard position, intensity and polarisation. The frequencies selected for the thermodynamic analysis are highlighted (see Table B.10); these are the experimental frequencies from [71SEL/FRI] where available, otherwise the calculated values.

The ideal gas thermal functions calculated with the data discussed above are given in Table B.11 (Appendix B). The symmetry number has been taken to be 2, consistent with C_2 symmetry.

To ascertain the effect of the uncertainties in the vibration frequencies, calculations were also made with increased and decreased values of the frequencies, from which it was concluded that realistic uncertainties in S°_m (298.15 K) and $C^\circ_{p,m}$ (298.15 K) for Tc_2O_7(g) are less than 12 and 5 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ respectively. For these comparisons, the eight frequencies for which experimental confirmation is available were varied by $\pm 2\%$; the remaining eleven frequencies above 60 cm^{-1} were varied by $\pm 10\%$, and the two lowest frequencies, which are more uncertain, by $\pm 50\%$. Thus, our selected values are

$$S^\circ_m(Tc_2O_7, g, 298.15\ K) = (436.64 \pm 12.00)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$
$$C^\circ_{p,m}(Tc_2O_7, g, 298.15\ K) = (146.7 \pm 5.0)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

With the help of the enthalpy of formation selected in Section V.3.2.1.2.c,

$$\Delta_f H^\circ_m(Tc_2O_7, g, 298.15\ K) = -(1008.1 \pm 16.1)\ kJ{\cdot}mol^{-1}$$

we can derive the Gibbs energy of formation

$$\Delta_f G^\circ_m(Tc_2O_7, g, 298.15\ K) = -(904.8 \pm 16.4)\ kJ{\cdot}mol^{-1}$$

V.3.4 Technetium hydrides

V.3.4.1 Solid technetium hydrides

V.3.4.1.1 Binary hydrides

Metallic technetium shows little tendency to react with H_2(g) under conditions of ambient temperature and pressure. However, in 1979, Spitsyn *et al.* [79SPI/PON] reported the synthesis of $TcH_{(0.73\pm0.05)}$(cr) by direct reaction using H_2(g) pressures of up to 19 kbar at 573 K. It formed a single phase with a hexagonal lattice with $a = (2.805 \pm 0.02) \times 10^{-10}$ m and $c = (4.455 \pm 0.02) \times 10^{-10}$ m. At room temperature and one atmosphere pressure it took several months for this hydride to spontaneously decompose, and it was kinetically stable during isothermal annealings up to

about 470 K. However, with continuous heating under open conditions it decomposed almost completely back to the metal and H_2(g) by 570 K.

Spitsyn *et al.* [81SPI/ANT] varied the H_2(g) pressures from low pressures to about 22 kbar at 573 K and studied the Tc-H_2 isotherm. Below about 1 kbar, Sieverts's law was observed for dissolution of hydrogen; that is, TcH_m(cr) formed with $m \propto \sqrt{p_{H_2}}$. The formation of material with the approximate composition $TcH_{0.5}$(s), and the $TcH_{0.78}$(s) was reported.

Samples of $TcH_{0.45}$(cr) and $TcH_{0.69}$(cr) were later studied by neutron diffraction [84GLA/IRO, 85SHI/GLA]. Both hydrides were indexed for hexagonal cells with

- $a = (2.801 \pm 0.004) \times 10^{-10}$ m and $c = (4.454 \pm 0.010) \times 10^{-10}$ m for $TcH_{0.45}$(cr),
- $a = (2.838 \pm 0.004) \times 10^{-10}$ m and $c = (4.465 \pm 0.010) \times 10^{-10}$ m for $TcH_{0.69}$(cr).

Three unexpected diffraction peaks were observed for $TcH_{0.45}$(cr), which the authors interpreted as evidence for a superstructure. They concluded that hydrogen atoms occupied octahedral intersticies in the technetium lattice.

Antonov *et al.* [89ANT/BEL] similarly prepared samples of TcH_m(s) with $m =$ 0.26, 0.385, 0.485, and 0.765. Magnetic susceptibilities were measured as a function of temperature, and the experimental results were used to estimate critical temperatures for superconductivity as a function of the H/Tc mole ratio.

Zakharov *et al.* [91ZAK/BAG] studied the electrolytic reduction of aqueous NH_4TcO_4 at pH = 1 on to a nickel substrate at current densities of 7 and 12 $A \cdot dm^{-2}$. The electrode deposits were examined by X-ray diffraction and were reported to be $TcH_{\leq 0.27}$(s), *cf.* Appendix A.

There are no experimental thermodynamic data for TcH_m(s). However, Bouten and Miedema [80BOU/MIE] estimated that $\Delta_f H^\circ_m$ ($Tc_{0.5}H_{0.5}$, s) $= +9$ kJ·mol^{-1}. This positive value indicates that it should spontaneously decompose at 1 bar pressure, as is observed to happen.

V.3.4.1.2 Ternary hydrides

Floss and Grosse [60FLO/GRO] reduced TcO_4^- along with a NH_4ReO_4 carrier using potassium in ethylenediamine, to yield the ternary hydride $KReH_4 \cdot 2H_2O$(s). The technetium co-crystallised in the rhenium hydride, presumably as K(Re, Tc)$H_4 \cdot 2H_2O$(s). This material could be dissolved in cold aqueous 2 M KOH with slow decomposition, but when it was added to dilute HCl the decomposition was rapid.

Ginsburg [64GIN] repeated this preparation in an ethylenediamine-ethanol mixture but used carrier free NH_4TcO_4. The resulting crystals were hexagonal with $a = 9.64 \times 10^{-10}$ m and $c = 5.56 \times 10^{-10}$ m, and they were shown to be isostructural with K_2ReH_9(cr). Thus, the technetium compound was probably K_2TcH_9(cr). Small quantities of K_2TcH_9(cr) could be dissolved in 20 to 50 mass-% aqueous KOH without excessive decomposition, but decomposition was rapid when >0.05% K_2TcH_9(cr) was added.

No thermodynamic data are available, but K_2TcH_9(cr) decomposes under normal environmental conditions.

V.3.4.2 Gaseous technetium hydrides

Mastryukov [72MAS] estimated that the bond dissociation energy for TcH(g) was 198 to 243 kJ·mol^{-1} based on correlations for hydrides of other elements. A value of 188 kJ·mol^{-1} was estimated by Langhoff *et al.* [87LAN/PET] from quantum mechanical calculations using the coupled pair functional method with relativistic effective core potentials, and 168 kJ·mol^{-1} by using the singles-plus-doubles configuration interaction method. No experimental value is available for comparison. They concluded that the ground state was most likely to be $^5\Sigma^+$, and the bond length was (1.85 to 1.86) $\times 10^{-10}$ m.

Wang and Balasubramanian [89WAN/BAL] performed quantum mechanical calculations for TcH(g) by using the state-averaged complete active space self-consistent field (CASSCF), first-order configuration interaction (FOCI), and multireference single plus double configuration interaction (MRSDCI) methodologies, and spin-orbit effects were accounted for using the relativistic configuration interaction (RCI) method. The ground state of TcH(g) was predicted to be of $^7\Sigma^+$ symmetry with an atomic distance of 1.75 $\times$ 10^{-10} m and a dissociation energy of 254 kJ·mol^{-1}, which is somewhat higher than most of the other estimates noted above.

Balasubramanian and Wang [89BAL/WAN] performed similar quantum mechanical calculations for TcH_2(g) using the same methodologies as used by them for TcH(g). The ground state for TcH_2(g) was predicted to be a linear $^6\Sigma_g^+$ state with Tc−H distances of (1.745 to 1.766) $\times$ 10^{-10} m, and it was 74.5 kJ·mol^{-1} more stable than the ground states of the elements Tc(cr)(^{6}S) and H_2(g).

V.4 Group 17 (halogen) compounds and complexes

V.4.1 Fluorine compounds and complexes

V.4.1.1 Aqueous technetium fluorides

There are few studies in the literature on technetium complexation with fluoride anions. Only the Tc(IV) TcF_6^{2-} complex has been identified [63SCH/HER, 65JØR/SCH], but no thermodynamic data are available. This species is also briefly discussed in Section V.4.2.1.1.

V.4.1.2 Solid technetium fluorides

V.4.1.2.1 Binary technetium fluorides

V.4.1.2.1.a TcF_6(cr)

Selig, Chernick and Malm [61SEL/CHE] reported that direct reaction of powdered technetium metal and F_2(g) for two hours at 673 K produced the volatile solid TcF_6(cr)

in greater than 90% yield. This chemical formula was deduced from the number of moles of F_2(g) consumed per mole of technetium, and chemical analyses indicated 5.8 F per Tc. Solid TcF_6(cr) was golden-yellow at room temperature and underwent a solid-solid transition around 270 K, it had a vibrational fundamental at 745 cm^{-1}, and it was hydrolysed and disproportionated by aqueous NaOH to form $TcO_2 \cdot xH_2O$(s) and TcO_4^-. The TcF_6(cr) melted around 306 K.

Siegel and Northrop [66SIE/NOR] reported an X-ray structural determination for both solid modifications of TcF_6(cr):

- TcF_6(cr, cubic), the high-temperature form. It was cubic with $a = (6.16 \pm 0.06) \times 10^{-10}$ m and $Z = 2$ at 283 K.
- TcF_6(cr, ortho.), the low-temperature form. It was probably orthorhombic, with $a = 9.55 \times 10^{-10}$ m, $b = 8.74 \times 10^{-10}$ m, $c = 5.02 \times 10^{-10}$ m and $Z = 4$ at 254 K.

They revised the earlier reported melting temperature [61SEL/CHE] to 310.2 K and the solid-solid transition temperature to 267.9 K.

The solubility of TcF_6(cr) in anhydrous HF was reported to be 0.89 mol·kg^{-1} at room temperature [67FRL/SEL] but no experimental details were given.

Selig and Malm [62SEL/MAL] reported vapour pressures of the low-temperature solid of TcF_6 (cr, ortho.) from 256.83 to 267.68 K, for the high-temperature TcF_6(cr, cubic) from 268.32 to 310.03 K, and for the liquid from 311.11 to 324.82 K.Their reported least-squares equations are equivalent to

$$\ln p/\text{bar}\ (TcF_6,\ \text{cr},\ \text{ortho.}) = 88.0741 - 8208.3T^{-1} - 10.787 \ln T \quad \text{(V.30)}$$

$$\ln p/\text{bar}\ (TcF_6,\ \text{cr},\ \text{cubic}) = 28.6883 - 5015.0T^{-1} - 2.295 \ln T \quad \text{(V.31)}$$

$$\ln p/\text{bar}\ (TcF_6,\ \text{liq}) = 50.5040 - 5537.5T^{-1} - 5.8036 \ln T \quad \text{(V.32)}$$

These equations yield an enthalpy of fusion of 4.7 kJ · mol^{-1} at the fusion temperature 310.55 K, an enthalpy of sublimation for TcF_6(cr, ortho.) of 44.2 kJ·mol^{-1} at 267.9 K, and an enthalpy of sublimation for TcF_6(cr, cubic) of 36.6 kJ · mol^{-1} at 267.9 K. No uncertainties were given for the least-squares parameters of these equations, but the typical deviations between experimental and least-squares values are around 1×10^{-4} bar for $T < 274$ K, from (3 to 7)$\times 10^{-4}$ bar up to about 305 K, and about (1.0 to 1.5)$\times 10^{-3}$ bar at higher temperatures. The difference between the enthalpies of sublimation of the two solid forms leads to an enthalpy of transition of 7.6 kJ · mol^{-1} without any correction for differences in heat capacity.

A careful and detailed calorimetric study was made by Osborne *et al.* [78OSB/SCH] for both solid forms and for liquid $^{99}TcF_6$. They measured heat capacities from 5.809 to 347.937 K by a combination of isoperibolic and adiabatic calorimetry, the enthalpy of transition between the two solid phases, the enthalpy

of fusion of TcF_6(cr, cubic), and the transition and melting temperatures. These enthalpies of phase transitions are more precise and should be more accurate that their earlier results from vapour pressure measurements, and they are accepted by us. Table V.15 contains their derived results at selected temperatures. Correction of their values from 1 atm to 1 bar was not necessary because these corrections are smaller than the experimental precision. In addition, adjustment of their molecular mass of 212.8968 g · mol^{-1} to the current value of 212.8967 g · mol^{-1} yields negligible corrections of 0.00005% for thermodynamic values. These authors estimated that their values of $C^\circ_{p,m}$, S°_m , $[H^\circ_m(T) - H^\circ_m(0\ K)]$ and $[G^\circ_m(T) - H^\circ_m(0\ K)]$ were uncertain by 0.1% above 25 K and by up to 1% at lower temperatures. This review doubles these uncertainties to 0.2% and 2%, respectively, for 95% confidence limits.

The recommended thermodynamic values at 298.15 K are:

$$S^\circ_m(TcF_6, cr,\ cubic,\ 298.15\ K) = (253.52 \pm 0.51)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$
$$C^\circ_{p,m}(TcF_6, cr,\ cubic,\ 298.15\ K) = (157.84 \pm 0.32)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

The earlier value of the enthalpy of fusion of TcF_6(cr, cubic) from vapour pressure measurements reported by Selig and Malm [62SEL/MAL], 4.7 kJ · mol^{-1}, is less precisely but in very good agreement with the direct calorimetry value of (4.6189 ± 0.0031) kJ·mol^{-1} [78OSB/SCH]. Similarly, the enthalpy of transition of TcF_6(cr, ortho.) to TcF_6(cr, cubic) of 7.6 kJ · mol^{-1} from their vapour pressure measurements is in reasonably good agreement with (8.0249 ± 0.0098) kJ·mol^{-1} from direct calorimetry. The more precise direct calorimetry values are accepted. Their recommended melting temperature was (311.136 ± 0.098) K and transition temperature was (286.335 ± 0.004) K, both at 1 atm pressure.

The $\Delta_{sub}H^\circ_m(TcF_6, cr\ cubic)$, $\Delta_{sub}G^\circ_m(TcF_6, cr\ cubic)$ and $\Delta_{sub}S^\circ_m(TcF_6, cr\ cubic)$ are discussed in Section V.4.1.3.1.

V.4.1.2.1.b TcF_5(cr)

TcF_5(cr) was found as a byproduct of fluoridation of technetium by Edwards, Hugill and Peacock [63EDW/HUG]. This solid melted at 323 K, and it began to decompose in glass at 333 K (possibly by reaction with oxygen from the silica). This TcF_5(cr) crystallised in an orthorhombic space group with $a = 7.6 \times 10^{-10}$ m, $b = 5.8 \times 10^{-10}$ m, and $c = 16.6 \times 10^{-10}$ m, and it was isostructural with CrF_5(cr).

TcF_5(cr) was later prepared in quantitative yield by reduction of TcF_6(s) with I_2(g) in IF_5 [76BIN/SEL]. Solid TcF_5(cr) had a magnetic moment of 3.00 B.M. Supercooled liquid TcF_5(l) at 298.15 K had vibrational bands at 749 and 693 cm^{-1} (both are intense and polarised), with weaker bands at 669, 282, 225, and 139 cm^{-1}. The vibrational fundamentals were not identified. Solid TcF_5(cr) at 223 K had three strong vibrational bands at 698, 750, and 775 cm^{-1}. No thermodynamic data have been reported.

V.4.1.2.2 Ternary technetium fluorides

V.4.1.2.2.a M_2TcF_6(cr) (M = K, Rb) and their hydrates

A number of double metal halides have been reported for technetium. Early data for them have been summarised by Colton [65COL] and Peacock [66PEA].

Table V.15: Thermodynamic properties of solid and liquid TcF_6.[(a)]

T (K)	$C^\circ_{p,m}$ ($J\cdot K^{-1}\cdot mol^{-1}$)	S°_m ($J\cdot K^{-1}\cdot mol^{-1}$)	$[H^\circ_m(T) - H^\circ_m(0\,K)]$ ($kJ\cdot mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(0\,K)]/T$ ($J\cdot K^{-1}\cdot mol^{-1}$)
			cr, orthorhombic	
0	0.000	0.000	0.00000	–
20	18.117	13.463	0.12765	7.080
40	41.539	34.091	0.74992	15.343
50	49.625	44.243	1.20636	20.116
60	57.261	53.970	1.74102	24.953
80	71.656	72.446	3.03244	34.541
100	84.381	89.838	4.5959	43.878
120	95.551	106.23	6.3972	52.917
140	105.73	121.73	8.4116	61.650
160	114.97	136.46	10.620	70.089
180	123.77	150.52	13.008	78.250
200	132.35	164.00	15.569	86.155
220	141.06	177.02	18.303	93.827
240	150.23	189.68	21.214	101.29
260	163.38	202.18	24.338	108.57
268.335	170.15	207.44	25.729	111.56
			cr, cubic	
268.335	149.27	237.35	33.754	111.56
280	152.62	243.77	35.514	116.93
298.15	157.84	253.52	38.331	124.95
300	158.38	254.50	38.624	125.75
311.136	161.58	260.33	40.405	130.46
			Liquid	
311.136	172.65	275.17	45.024	130.46
320	173.97	280.04	46.561	134.54
340	176.94	290.67	50.070	143.41
350	178.43	295.83	51.846	147.69

(a) Transition enthalpy from TcF_6(cr, ortho.) to TcF_6(cr, cubic) is $(8.0249 \pm 0.0098)\ kJ\cdot mol^{-1}$ at the transition temperature of 268.335 K. The enthalpy of fusion is $(4.6189 \pm 0.0031)\ kJ\cdot mol^{-1}$ at the melting temperature of (311.14 ± 0.10) K. Values of $C^\circ_{p,m}$, S°_m, $[H^\circ_m(T) - H^\circ_m(0\,K)]$, and $[G^\circ_m(T) - H^\circ_m(0\,K)]$ and are uncertain by 0.2% above 25 K, and by up to 2% at lower temperatures. The temperature scale used for these heat capacity measurements was not identified, but we presume that it was the International Practical Temperature Scale of 1968 (IPTS-68). Thermodynamic values were not corrected to the most recent temperature scale (ITS-90) because any resulting changes for the various thermodynamic properties would be significantly less than their corresponding experimental uncertainties.

Schwochau and Herr [63SCH/HER] first described the synthesis of K_2TcF_6(cr) by fusing a mixture of K_2TcBr_6 with KHF_2. Recrystallisation of the product from water gave a 60 to 70% yield of hexagonal plates of K_2TcF_6(cr). They reported the solubility of K_2TcF_6(cr) to be 0.052 mol · kg^{-1} at 298.15 K. No details were given for this solubility determination.

Schwochau later described preparation of Rb_2TcF_6(cr) [64SCH]. A simpler method of synthesis has since been given by Alberto and Anderegg [85ALB/AND]. They reacted aqueous $TcBr_6^{2-}$ with 40% HF and then removed Br^- by precipitation with Ag(I). After 24 hours of reaction at 353 K, precipitation with ethanol gave an 89 to 98% yield of $K_2TcF_6 \cdot H_2O$(s) as a white powder.

Crystal structure data have been reported for M_2TcF_6(cr) (M = K, Rb) at room temperature [63SCH/HER, 64SCH] and also magnetic susceptibilities have been reported for K_2TcF_6(cr) [64SCH/KNA]. A summary of the crystal structure parameters was given by Melnik and van Lier [87MEL/LIE]. Table V.21 in Section V.4.2.2.2 gives a complete listing of the unit cell parameters and space groups for these compounds. No thermodynamic data are available.

V.4.1.2.2.b $MTcF_6$(cr) (M = Na, K, Rb, Cs)

Edwards, Hugill and Peacock [63EDW/HUG] and Hugill and Peacock [66HUG/PEA] described the preparation of the double fluorides of Tc(V): $NaTcF_6$(cr), $KTcF_6$(cr), $RbTcF_6$(cr), and $CsTcF_6$(cr). They were prepared by reduction of TcF_6 by alkali metal chlorides in IF_5 solutions, and refluxing for several minutes was required to complete the reaction. Cooling the solutions then gave crystalline powders of $MTcF_6$(cr). The use of alkali metal iodides rather than chlorides as the reducing agents caused reduction of TcF_6 to a Tc(IV) complex. Dissolution of $MTcF_6$(cr) in water gave decomposition to approximately 2:1 mole ratios of Tc(IV) ($TcO_2 \cdot xH_2O$(s) + TcF_6^{2-}) and TcO_4^-.

The unit cell parameters for these $MTcF_6$(cr) are listed in Table V.21 in Section V.4.2.2.2, along with those for the more numerous Tc(IV) double halides. No thermodynamic data are available.

V.4.1.2.3 Oxyfluorides

Two reviews are available for technetium halides and oxyhalides that cover the pertinent literature up to the early to mid 1960s [65COL, 68CAN/COL]. They contain discussions of methods of preparation, chemical properties, and thermodynamics and phase behaviour.

There is a lack of thermodynamic data for most of the technetium oxyhalides, but, since they hydrolyse in water, they should decompose under normal environmental conditions.

V.4.1.2.3.a TcO_3F(s)

Selig and Malm [63SEL/MAL] prepared this compound by reaction of TcO_2(cr) with flowing F_2 gas at 423 K. The volatile product was isolated as a solid by cooling the vapour, and it was purified by sublimation. TcO_3F melted at 291.4 K and boiled around 373 K at 1 atm. Vapour pressure measurements were reported for the solid from 264.37

to 291.43 K, and for the liquid from 291.43 to 324.97 K. They found that TcO_3F(s) hydrolysed in aqueous alkali to form aqueous TcO_4^-.

The results of vapour pressure measurements for TcO_3F(s) using a quartz differential Bourdon gauge were reported as least-squares equations [63SEL/MAL] which are equivalent to

$$\ln(p/\text{bar}) = (22.042 \pm 0.266) - (7459.0 \pm 73.6)/T$$

for the solid, and

$$\ln(p/\text{bar}) = (12.761 \pm 0.099) - (4753.9 \pm 29.3)/T$$

for the liquid. Reported uncertainty limits are presumed to have been one standard deviation and were converted to 1.96 σ values. These equations yield an enthalpy of sublimation of (62.0±0.6) kJ·mol^{-1}, an enthalpy of vaporisation of (39.5±0.2) kJ·mol^{-1}, and an enthalpy of fusion of (22.5 ± 0.7) kJ·mol^{-1}.

Reaction of NH_4TcO_4 [74BIN/EL-] or $KTcO_4$ [82FRA/LOC] with anhydrous HF also produced TcO_3F(s), and addition of AsF_5 to such a solution yielded $Tc^VO_3AsF_6$(s) [82FRA/LOC].

V.4.1.2.3.b $TcOF_4$(cr)

Edwards, Hugill and Peacock [63EDW/HUG] found that $TcOF_4$(cr) was produced as a byproduct of the direct fluorination of Tc metal. It was similar to $ReOF_4$(cr) in behaviour, and they are isostructural [68EDW/JON]. $TcOF_4$(cr) melted at 407 K and had an effective magnetic moment of 1.76 B.M. at 298.15 K [63EDW/HUG]. A trimeric polymorph of $TcOF_4$(cr) was also formed during fluorination [68EDW/JON]. Structural information for these solids is given in Table V.16.

Peacock [73PEA] reported some additional information for $TcOF_4$(cr) based on unpublished measurements by A.J. Edwards. Technetium oxytetrafluoride underwent a solid-solid phase transition at 357.7 K and melted at 406 to 407 K. The vapour pressures of the two solid forms and liquid were given as least-squares equations, but no raw data or experimental details were given. These vapour pressure equations are equivalent to

$$\begin{aligned} \ln p/\text{bar (solid I, 298.15 to 357.7 K)} &= 31.718 - 12793/T \\ \ln p/\text{bar (solid II, 357.7 to 406 K)} &= 21.702 - 9210/T \\ \ln p/\text{bar (l, 406 to 423 K)} &= 16.682 - 5844/T \end{aligned}$$

These equations yield an enthalpy of sublimation for the low-temperature solid of 106.4 kJ·mol^{-1}, an enthalpy of sublimation of the higher-temperature solid of 76.6 kJ·mol^{-1}, an enthalpy of transition of 29.8 kJ·mol^{-1}, an enthalpy of vaporisation of 48.6 kJ·mol^{-1}for the liquid, and an enthalpy of fusion of 28.0 kJ·mol^{-1}. The uncertainties in these $\Delta_r H_m$ values cannot be rigorously determined since the precision of the vapour pressures was not given, but ±1.0 kJ·mol^{-1} should be a reasonable estimate for enthalpies of sublimation and vaporisation and ±1.4 kJ·mol^{-1} for transition and fusion. $TcOF_4$(cr) was hydrolysed completely by water to HF, $HTcO_4$, and $TcO_2 \cdot xH_2O$(s).

Table V.16: Crystal structure parameters for Tc oxyfluorides.

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}/m$)	Reference
$TcOF_4$(cr)	monoclininic	C2/c	16	$a = 18.93$ $b = 5.49$ $c = 14.43$	[67EDW/JON]
$(TcOF_4)_3$(cr)	hexagonal	$P6_3/m$		$a = b = 9.00 \pm 0.02$ $c = 7.92 \pm 0.02$	[68EDW/JON]
TcO_2F_3(cr)	triclinic[(a)]	$P\bar{1}$	8	$a = 7.774 \pm 0.006$ $b = 7.797 \pm 0.002$ $c = 11.602 \pm 0.006$	[93MER/SCH]

[(a)] $\alpha = (89.41 \pm 0.04)°$, $\beta = (88.63 \pm 0.06)°$, and $\gamma = (84.32 \pm 0.04)°$.

V.4.1.2.3.c TcO_2F_3(cr) and $Tc_2O_5F_4$(s)

Reaction of TcO_3F(s) in anhydrous HF with either XeF_6 or KrF_2 yielded a new oxyfluoride, and an additional compound was produced after further reaction with KrF_2 [82FRA/LOC]. Measurement of the ^{99}Tc, ^{17}O, and ^{19}F NMR spectra led to the tentative identification of these compounds as $Tc_2O_5F_4$(s) and TcO_2F_3(cr). They were only partially characterised since they were dissolved in HF, but XeF_6 and KrF_2 are such strong oxidising agents that these two new compounds were undoubtedly Tc(VII) compounds.

The compound TcO_2F_3(cr) prepared by Franklin *et al.* [82FRA/LOC] in an HF solution has since been synthesised, isolated, and characterised in pure form by Mercier and Schrobilgen [93MER/SCH], (Appendix A). Pure TcO_2F_3(cr) melted at (473 ± 1) K, and was sparingly soluble in anhydrous HF, but it dissolved in such solutions when excess XeF_6 was present. The dissolved species was probably $(XeF_5^+)(TcO_2F_4^-)$. Structural information for TcO_2F_3(cr) is given in Table V.16.

V.4.1.3 Gaseous technetium fluorides and oxyfluorides

V.4.1.3.1 TcF_6(g)

V.4.1.3.1.a General properties

Vapour density measurements performed by Selig, Chernick and Malm [61SEL/CHE], indicated that TcF_6(g) was monomeric.

Claassen, Selig and Malm [62CLA/SEL] reported IR spectra of gaseous TcF_6(g) at several pressures, and a partial Raman spectrum for the liquid. From these spectra they evaluated five of the six vibration fundamentals: $\nu_1 = 705$, $\nu_2 = 551$, $\nu_3 = 748$, $\nu_4 = 265$, and $\nu_5 = 255$ cm^{-1}. They later reported additional Raman spectra measurements for gaseous TcF_6(g) [70CLA/GOO] and revised the frequencies to $\nu_1 = 712.9$, $\nu_2 = 639$, $\nu_3 = 748$, $\nu_4 = 265$, $\nu_5 = 297$, and $\nu_6 = 145$ cm^{-1}. However, ν_2 and ν_5 are "estimated best values", and ν_6 was obtained from the tentative assignment of the 289 cm^{-1} frequency as the first overtone of ν_6. Unfortunately, gas phase entropies from statistical thermodynamic calculations are very sensitive to the frequency of low lying levels like ν_6, and a reinvestigation would be most helpful. Force constants have been derived from these frequencies [87GEL/MCD].

V.4.1.3.1.b Thermodynamic data

Osborne *et al*. [78OSB/SCH] calculated the entropy of TcF_6(g) from the entropy of the liquid at 320 K, together with the entropy of vaporisation of the liquid from the earlier vapour pressure study [62SEL/MAL]. This review now repeats their type of calculation, but at 298.15 K rather than 320 K, using TcF_6(cr, cubic) as the reference condensed phase, (see discussion in Appendix A under Ref. [78OSB/SCH]). The calculated value is 363.03 J·K^{-1}·mol^{-1} which is within about 0.1% of Osborne *et al*. 's [78OSB/SCH] derived "experimental" value, after adjustment for the temperature differences. This review calculates the uncertainty for this value to be 2.44 J·K^{-1}·mol^{-1}. The value resulting is thus

$$S^\circ_m(TcF_6, g, 298.15\ K) \quad = \quad (363.0 \pm 2.4)\ J{\cdot}K^{-1}{\cdot}mol^{-1} \qquad (V.33)$$

Osborne *et al*. [78OSB/SCH] also calculated the statistical thermodynamic entropy of TcF_6(g) using the vibration frequencies of Claassen *et al*. [70CLA/GOO]. Their calculated statistical entropy at 320 K was about 1% below their "experimental" entropy (which agrees with the experimental value derived in this review). Osborne *et al*. [78OSB/SCH] assumed the 1% discrepancy between their "experimental" and statistical thermodynamic entropies was due to inaccuracy in ν_6, and adjusted it to give better agreement.

This review has also recalculated the ideal gas thermodynamic properties of TcF_6(g), see Table V.17. The entropy value at 298.15 K is

$$S^\circ_m(TcF_6, g, 298.15\ K) \quad = \quad 359.136\ J{\cdot}K^{-1}{\cdot}mol^{-1} \qquad (V.34)$$

A rigorous estimation of the uncertainties in the statistical thermodynamic values for TcF_6(g) is not really possible, (*cf.* Appendix A). Based on very conservative estimates, this review calculates that this value of S°_m is uncertain by about 5.5 J·K^{-1}·mol^{-1} at 298.15 K and 6.3 at 1000 K. However, the calculated experimental value, Eq.(V.33), and the derived statistical thermodynamic value, Eq.(V.34), agree to 3.86 J·K^{-1}·mol^{-1} at 298.15 K, so the estimated uncertainty limits may be slightly too large.

The calculation of the experimentally-based value of $S^\circ_m(TcF_6, g, 298.15\ K) = (363.0 \pm 2.4)$ J·K^{-1}·mol^{-1} given in this section, was performed by the same basic

Table V.17: Ideal gas thermodynamic properties of TcF_6(g) from statistical thermodynamic calculations. [(a)]

T (K)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$[H^\circ_m(T) - H^\circ_m(0\ K)]$ ($kJ \cdot mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(0\ K)]/T$ ($J \cdot K^{-1} \cdot mol^{-1}$)
0	0.000	0.000	0.000	–
10	33.258	165.785	0.332	132.527
25	33.673	196.314	0.832	163.007
50	41.226	221.480	1.751	186.458
100	65.968	257.636	4.431	213.323
200	100.210	314.977	12.900	250.475
298.15	120.703	359.136	23.822	279.235
300	121.001	359.883	24.046	279.730
400	133.421	396.550	36.821	304.497
500	140.847	427.188	50.565	326.057
600	145.475	453.308	64.898	345.144
700	148.503	475.976	79.607	362.251
800	150.573	495.949	94.567	377.740
900	152.042	513.774	109.702	391.882
1000	153.120	529.851	124.963	404.888

[(a)] Calculated with a symmetry number of 24; vibrational frequencies of 712.9 (multiplicity = 1), 639 (multiplicity = 2), and of 748, 265, 297, and 145 cm^{-1} (multiplicity = 3); a molar mass of 212.897 $g \cdot mol^{-1}$; and a Tc-F bond distance of 1.85×10^{-10} m.

method used by Osborne *et al*. [78OSB/SCH] and which, in essence, is a second-law evaluation.

However, since experimental heat capacities are available for TcF_6(cr, cubic), (see Table V.15 in Section V.4.1.2.1), and statistical thermodynamic calculations are available for TcF_6(g), (see Table V.17), a third-law evaluation of the standard enthalpy of sublimation for TcF_6(cr, cubic) can be done, the results of which are presented in Table B.12. Third-law-based evaluations are generally more accurate than second-law-based evaluations of enthalpy changes. Details of the calculation are given in Appendix A under Ref. [78OSB/SCH].

The more reliable value of $\Delta_{sub}H^\circ_m(TcF_6, \text{cr cubic}, 298.15\ K) = (34.536 \pm 0.094)\ kJ \cdot mol^{-1}$ was obtained from a third-law analysis of the experimental vapour pressures of TcF_6(cr, cubic) along with statistical-thermodynamic calculations of thermodynamic properties for TcF_6(g). This very small uncertainty is based on the precision of the input data. However, the uncertainty limit does not yet include uncertainties and errors arising from inaccuracies in the statistical-thermodynamic functions. As noted in the previous section, the frequencies of two of the six vibrational fundamentals for TcF_6(g) used in the statistical thermodynamic calculations were estimated and another was a tentative assignment [70CLA/GOO] (see also [78OSB/SCH] in Appendix A). Thus the calculated values of $\Delta_{sub}H^\circ_m(TcF_6, \text{cr cubic}, 298.15\ K)$ could slightly differ systematically from the correct values.

The one case that we can make a direct comparison between experimental and

calculated values is for the molar entropy of the ideal gas $S^\circ_m(TcF_6, g, 298.15\ K)$. As noted above, the experimental and statistical-thermodynamic values disagree by 3.86 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, but a sensitivity analysis, using estimated uncertaintites for the vibration frequencies of TcF_6(g) gave a larger uncertainty of about 10 $J{\cdot}K^{-1}{\cdot}mol^{-1}$. We will assume that the entropy of TcF_6(g) is uncertain by an intermediate amount but closer to the observed difference, and thus our recommended value is

$$\begin{aligned} S^\circ_m(TcF_6, g, 298.15\ K) &= (359.14 \pm 4.50)\ J{\cdot}K^{-1}{\cdot}mol^{-1} \\ C^\circ_{p,m}(TcF_6, g, 298.15\ K) &= (120.70 \pm 2.63)\ J{\cdot}K^{-1}{\cdot}mol^{-1} \end{aligned}$$

This then yields a standard entropy of sublimation of $\Delta_{sub}S^\circ_m(TcF_6,$ cr cubic, 298.15 K) = (105.6 ± 4.5) $kJ{\cdot}mol^{-1}$. Although this value is smaller than the derived "experimental" entropy of sublimation (109.5 $kJ{\cdot}mol^{-1}$), it is recommended here since it maintains consistency with the third-law calculation of $\Delta_{sub}H^\circ_m(TcF_6,$ cr cubic, 298.15 K). Based on the precision of the experimental vapour pressures, the uncertainty in $\Delta_{sub}G^\circ_m(TcF_6,$ cr cubic, 298.15 K) is about ±0.012 $kJ{\cdot}mol^{-1}$. However, the larger uncertainty assigned to $\Delta_{sub}S^\circ_m(TcF_6,$ cr cubic, 298.15 K) implies that a more realistic uncertainty limit for the standard enthalpy of sublimation is ±1.3 $J{\cdot}K^{-1}{\cdot}mol^{-1}$.

The recommended values are thus

$$\begin{aligned} \Delta_{sub}H^\circ_m(TcF_6, \text{cr cubic}, 298.15\ K) &= (34.54 \pm 1.30)\ kJ{\cdot}mol^{-1} \\ \Delta_{sub}S^\circ_m(TcF_6, \text{cr cubic}, 298.15\ K) &= (105.6 \pm 4.5)\ J{\cdot}K^{-1}{\cdot}mol^{-1} \\ \Delta_{sub}G^\circ_m(TcF_6, \text{cr cubic}, 298.15\ K) &= (3.055 \pm 0.012)\ kJ{\cdot}mol^{-1} \end{aligned}$$

A more detailed spectroscopic characterisation of TcF_6(g) is needed in order to refine the statistical thermodynamic calculations. The resulting improved free energy functions will then allow more accurate enthalpies and entropies of sublimation of TcF_6(cr, cubic) to be derived. Also needed is a determination of the enthalpy of formation of TcF_6(cr, cubic) or of TcF_6(g).

V.4.1.3.2 Gaseous technetium oxyfluorides

Two gaseous oxyhalides, TcO_3F(g) and $TcOF_4$(g) have been identified. Binenboym, El-Gad and Selig [74BIN/EL-] reported vibrational frequencies for TcO_3F(g). They are, ν_1(Tc-O symmetric stretch) = 962, ν_2(Tc-F stretch) = 696, ν_3(O-Tc-O symmetric bend) = 317, ν_4(Tc-O asymmetric stretch) = 951, ν_5(O-Tc-O asymmetric bend) = 347, and ν_6(F-Tc-O rocking motion) = 231 cm^{-1}. Force constants were derived from that study by Baran [75BAR].

Rakov *et al.* [72RAK/KOS] calculated the heat capacities, entropies, relative enthalpies, and $[G^\circ_m(T) - H^\circ_m(298.15\ K)]/T$ values for $TcOF_4$(g) from 298 to 2000 K. Since the vibrational fundamentals have not been measured, they used estimated molecular parameters (their estimated vibrational frequencies were not given) and bond distances. Because the uncertainty of these calculated values is reasonably large, this review does not recommend their reported values.

Zavalishin and Mal'tsev did similar statistical thermodynamic calculations for TcO_3F, [76ZAV/MAL2], and for $TcOF_4$ [76ZAV/MAL], from 100 to 4000 K, as well as for some oxychlorides (Section V.4.2.3). However, the English language translation of this journal, Moscow University Chemical Bulletin, which claims to be a cover-to-cover translation, did not contain these articles. These articles appear in the Russian language edition, but they are one paragraph each and contain no details of the calculations. In addition, only the values at 298.15 K were tabulated. Since their accuracy cannot be assessed, these results are not recommended.

This review performs ideal gas statistical thermodynamic calculations for TcO_3F(g) and TcO_3Cl(g) (Section V.4.2.3) using the harmonic oscillator approximation and published vibrational frequencies [72GUE/HOW, 74BIN/EL-, 78GUE/HOW]. For TcO_3F(g) 1.85×10^{-10} m is used for the Tc-F bond length, which is the same value used for TcF_6(g) (see Section V.4.1.3.1). Table V.18 contains these thermodynamic values for TcO_3F(g). The uncertainty limits are obtained by assuming the uncertainties in all of the ν_i values is 5 cm^{-1}.

$$S^\circ_m(TcO_3F, g, 298.15\ K) = (306.879 \pm 0.677)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$
$$C^\circ_{p,m}(TcO_3F, g, 298.15\ K) = (77.261 \pm 0.308)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

Table V.18: Ideal gas thermodynamic properties of TcO_3F(g) from statistical thermodynamic calculations[(a)]

T (K)	$C^\circ_{p,m}$ ($J \cdot K^{-1} \cdot mol^{-1}$)	S°_m ($J \cdot K^{-1} \cdot mol^{-1}$)	$[H^\circ_m(T) - H^\circ_m(0\ K)]$ ($kJ \cdot mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(0\ K)]/T$ ($J \cdot K^{-1} \cdot mol^{-1}$)
0	0.000±0.000	0.000±0.000	0.000±0.000	—
10	33.258±0.000	160.181±0.000	0.332±0.000	126.923±0.000
25	33.263±0.001	190.655±0.001	0.831±0.000	157.397±0.000
50	34.366±0.114	213.891±0.023	1.670±0.001	180.473±0.004
100	45.120±0.448	240.609±0.225	3.629±0.017	204.314±0.060
200	64.801±0.397	278.541±0.537	9.215±0.062	232.463±0.231
298.15	77.261±0.308	306.879±0.677	16.222±0.096	252.470±0.358
300	77.457±0.307	307.357±0.680	16.365±0.096	252.807±0.360
400	86.249±0.240	330.926±0.758	24.578±0.123	269.479±0.450
500	92.157±0.187	350.850±0.806	33.518±0.144	283.813±0.517
600	96.120±0.146	368.027±0.836	42.945±0.161	296.450±0.568
700	98.851±0.116	383.062±0.856	52.702±0.174	307.772±0.607
800	100.78±0.09	396.394±0.869	62.689±0.185	318.032±0.640
900	102.17±0.08	408.349±0.880	72.840±0.193	327.415±0.666
1000	103.21±0.06	419.170±0.888	83.112±0.200	336.058±0.687

(a) Calculated with a symmetry number of 3; vibrational frequencies of 962, 317 and 696 (multiplicity = 1), and of 951, 347, and 231 cm^{-1} (multiplicity = 2); a molar mass of 165.903 $g{\cdot}mol^{-1}$; a Tc-O bond distance of 1.69×10^{-10} m and Tc-F bond distance of 1.85×10^{-10} m.

Gibson [91GIB] investigated the formation of gas phase technetium oxyfluorides and oxychlorides (Section V.4.2.3) by mass spectrometry. He used a sample of ^{99}Tc

metal powder with an oxide coating, and studied its oxidation by F_2(g) from 573 to 848 K and by ClF_3(g) from 573 to 923 K. A large number of ions were detected whose probable "parent" molecules ions were TcF_5(g), TcO_3F(g), $TcOF_4$(g), TcO_2F_3(g), $TcOF_2Cl$(g), and $TcOFCl_2$(g).

V.4.2 Chlorine, bromine and iodine compounds and complexes

V.4.2.1 Aqueous technetium chlorides, bromides and iodides

V.4.2.1.1 Aqueous Tc(IV) halides

Several reported UV-optical spectra of M_2TcX_6(s) dissolved in aqueous HX are in good agreement [59BOY, 65JØR/SCH, 69KAN, 74VIN/ZAI]. These measurements leave no doubt that the TcX_6^{2-} species can exist over quite wide ranges of HX concentrations.

Solutions of TcX_6^{2-} (X = Cl, Br, I) are generally prepared by direct reduction of aqueous TcO_4^- with concentrated HCl, with moderately concentrated HBr, or with approximately 4 to 5 M HI. Solubility studies of various solids containing TcX_6^{2-} ions have also been reported [63SCH/HER, 74VIN/ZAI] (see Sections V.4.1.2.2 and V.4.2.2.2).

Dissolution of $TcCl_4$(s) in concentrated aqueous HCl also yielded $TcCl_6^{2-}$ solutions [62COL/PEA]. Reduction of TcO_4^- with $SnCl_2$ in aqueous HCl gave more rapid formation of $TcCl_6^{2-}$ than reduction by HCl alone, for HCl concentrations of 0.4 M and higher [87FAR/GAR].

Solutions of TcF_6^{2-} are quite stable at most pH values, and hot concentrated alkali metal hydroxide was required to hydrolyse TcF_6^{2-} [63SCH/HER]. However, concentrated solutions of HX were required to prevent TcX_6^{2-} ($X^- = Cl^-$, Br^-) from hydrolysing. Solutions of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ showed little tendency to hydrolyse in aqueous solutions at lower HX concentrations provided they were stored in the dark, but photochemical aquation occurred under irradiation with UV light. (See Ref. [69KAN] in Appendix A).

It has been conclusively demonstrated [63SCH/HER, 64OSS/SAR, 65JØR/SCH, 76KAW/KOY, 85ARO/HWA] that the tendency for aquation and the subsequent hydrolysis of TcX_6^{2-} follows the order $TcI_6^{2-} \gg TcBr_6^{2-} > TcCl_6^{2-} \gg TcF_6^{2-}$ in their respective HX solutions, and that TcF_6^{2-} is stable even in water and dilute solutions of alkali metal hydroxide. In addition, $TcCl_6^{2-}$ could be stabilised in concentrated Cl^- solutions even in the absence of H^+, whereas to stabilise $TcBr_6^{2-}$ in concentrated Br^- solutions appeared to require pH < 1. (see Refs. [64OSS/SAR, 65JØR/SCH, 85ARO/HWA] in Appendix A).

Results have been published for the characterisation of several of the chloro complexes of Tc(IV). These studies were mentioned very briefly in a preliminary note by Fujinaga, Koyama and Kanchiku [67FUJ/KOY], and described in detail by Koyama, Kanchiku and Fujinaga [68KOY/KAN] and Kanchiku [69KAN]. Similar results were reported later for bromo complexes [76KAW/KOY], (see comments under [69KAN] in Appendix A). Knowledge of the absorption spectra of chloro

[59BOY, 65JØR/SCH, 68KOY/KAN, 69KAN, 74VIN/ZAI, 81IAN/KOS] and bromo [65JØR/SCH, 76KAW/KOY] complexes of Tc(IV) allows chemical speciation to be determined for the products of chemical, photochemical, or radiolytic experiments. For example, Ianovici *et al*. [81IAN/KOS] (Appendix A) were able to determine the relative amounts of the products of photochemical decomposition of $TcCl_6^{2-}$ in 1 M solutions of HCl, $HClO_4$, or H_2SO_4 as a function of irradiation time, and similar experiments were done by Colin, Ianovici and Lerch [88COL/IAN] for $TcBr_6^{2-}$ in 2 M HBr, 1 M $HClO_4$, and 1 M H_2SO_4. All these studies claimed the existence of species such as $TcCl_5^-$, $TcCl_5(OH)^{2-}$, $TcCl_4$(aq), $TcCl_3^+$, $TcBr_5^-$ and $TcBr_4$(aq), but no thermodynamic data are available. Evidence for these chemical species is described in the discussions of [64OSS/SAR, 69KAN, 81IAN/KOS, 81RAJ/MAC, 87HUB/HEI] in Appendix A.

Crystal structure studies are available for many of the ternary chlorides, bromides, hydroxy chlorides, and hydroxybromides of Tc(IV) obtained by precipitation from aqueous solutions; see Tables V.21 and V.26. In all examples studied, the Tc(IV) is hexacoordinated, with six halide ligands or five halides and one hydroxide ligand. In addition, most complexes of Tc(IV) with simple inorganic ligands contain hexacoordinated technetium [82BAN/MAZ, 87MEL/LIE, 94BAL]. Thus the chemical formulae of the pentahalo and tetrahalo complexes of Tc(IV) might, more properly, be written as $TcCl_5(OH_2)^-$, $TcBr_5(OH_2)^-$, $TcCl_4(OH_2)_2$(aq), and $TcBr_4(OH_2)_2$(aq), to show the complete inner coordination sphere. However, for thermodynamic calculations involving aqueous solution species, it is irrelevant whether the coordinated waters are included explicitly in the chemical formulae, or whether they are implied by the phase designation "aqueous". Following the usual convention of solution thermodynamics, in this book these waters are omitted from the formulae of species present in aqueous solution.

Münze and Großmann [75MÜN/GRO] studied the kinetics of the hydrolysis of $TcBr_6^{2-}$ in aqueous 0.001 to 3.0 M HBr (Appendix A). Kinetic rate information is also available for isotopic exchange reactions involving Cl^- in $TcCl_6^{2-}$ and Br^- in $TcBr_6^{2-}$ [65SCH2]. These experiments indicate that isotopic ligand exchange occurred over a several day period. Rate constants have been published [76KAW/KOY, 81RAJ/MAC] for the two following reactions at various temperatures:

$$TcCl_6^{2-} \rightleftharpoons TcCl_5^- + Cl^- \qquad \text{(V.35)}$$

$$TcBr_6^{2-} \rightleftharpoons TcBr_5^- + Br^- \qquad \text{(V.36)}$$

Both studies were done at $I = 4.0$ M solutions of Cl^- or Br^-. In both cases concentrations of technetium species were determined by spectrophotometry. The rate constants are listed in Table A.7 (see Appendix A under Ref. [81RAJ/MAC]).

The three kinetic studies [65SCH2, 65SCH, 76KAW/KOY, 81RAJ/MAC] gave also values of the equilibrium constants for these two reactions. Ref. [65SCH] is a short English language summary of Ref. [65SCH2].

In this system, equilibrium is only reached after several weeks for the aquation of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ (unless Tc(III) is used as catalyst, (see Appendix A, under Ref. [81RAJ/MAC]). The measurements of Schwochau [65SCH2, 65SCH] were done be-

fore it was known that slow reaction kinetics are involved, and he did not mention changes in the spectra of their solutions with time. Thus, his reported values actually represent non-equilibrium conditions with much more $TcCl_5^-$ (or $TcBr_5^-$) complex present than should be present at equilibrium. Therefore, we consider those values to be inaccurate and they are not considered in this review. Preference is given to the results of Kawashima, Koyama and Fujinaga [76KAW/KOY] and of Rajac and Macášek [81RAJ/MAC] since they allowed sufficient time to reach equilibrium or at least steady state conditions (see Ref. [81RAJ/MAC] in Appendix A).

Table V.19 contains a summary of the reported equilibrium constants. Extrapolation of the values of [76KAW/KOY] to 298.15 K using the equation

$$\ln K_c(\text{V.35 or V.36}) \quad = \quad A + BT^{-1}$$

where A formally denotes $\Delta_r S_m^\circ /R$ and B denotes $-\Delta_r H_m^\circ /R$, yields

$$K(\text{V.35},\ 4\ \text{M HCl},\ 298.15\ \text{K}) \quad = \quad 0.81 \pm 0.42$$
$$K(\text{V.36},\ 4\ \text{M HBr},\ 298.15\ \text{K}) \quad = \quad 0.52 \pm 0.08$$

It is hardly possible to extrapolate these values to infinite dilution with the SIT equation (Appendix C) as no values of $\Delta\varepsilon$ can be calculated because only one ionic strength was studied at each temperature. In addition, no specific ion interaction results are available for chemically similar systems so it is not straightforward to estimate $\Delta\varepsilon$ by analogy. The available equilibrium constant values are at fairly high ionic strengths; thus the $\Delta\varepsilon I_m$ term is probably significant for these systems. Neglecting this term could make extrapolated values of K° uncertain by as much as factors of 10 to 100. Therefore we do not further analyse these values. No thermodynamic data can be recommended.

V.4.2.1.2 Aqueous Tc(V) halides

In aqueous media, the Tc(V) oxychloride $TcOCl_5^{2-}$, has been spectroscopically identified [67JEŻ/NAT, 67JEŻ/WAJ, 72BAL/HAN]. Early studies on the reduction of TcO_4^- by aqueous HCl [59BUS, 64OSS/SAR] indicated that the initial reduction of TcO_4^- by HCl was to Tc(V) and this was strongly dependent on HCl concentration, (see Ref. [59BUS] in Appendix A). Various claims have been made for the fate of Tc(V) oxychlorides in aqueous HCl when the HCl was diluted below certain critical concentrations [59BUS, 66SHU, 71SPI/GLI, 79RAJ/MIK]. For instance, Spitsyn, Glinkina and Kuzina [71SPI/GLI] found that the Tc(V) species $TcOCl_5^{2-}$ underwent a slow and progressive hydrolysis to Tc(V)-hydroxyoxychlorides for HCl concentrations of 3.7 M and lower, but for 5.5 M and higher concentrations of HCl, Tc(V) was reduced to Tc(IV) by this HCl. No conclusive results are available.

Spitsyn, Glinkina and Kuzina [71SPI/GLI] isolated a brownish-green crystalline material which they formulated as $K_2TcO(OH)Cl_4$(cr), based on elemental analysis for technetium and chlorine, along with a determination of the average valence of the technetium present using oxidation with Ce(IV). However, an attempt to repeat this synthesis at the Australian Radiation Laboratory yielded negative results [99BAL]. Thus

Table V.19: Equilibrium constant data for the Tc(IV) chloride and bromide system.

Method	Ionic media	T (K)	K_c [(a)]	Reference
$TcCl_6^{2-} \rightleftharpoons TcCl_5^- + Cl^-$				
pot	3 M $HClO_4$	288.2	4.6×10^4	[65SCH2, 65SCH]
sp	4 M HCl	348.2	1.25±0.05 [(b)]	[76KAW/KOY]
sp	4 M HCl	353.7	1.29±0.05 [(b)]	
sp	4 M HCl	357.7	1.33±0.05 [(b)]	
sp	4 M HCl	363.2	1.39±0.05 [(b)]	
sp	4 M HCl	298	1.25±0.12	[81RAJ/MAC]
rev	4 M HCl	298.15	0.81±0.42 [(c)]	from [76KAW/KOY]
.....				
$TcBr_6^{2-} \rightleftharpoons TcBr_5^- + Br^-$				
pot	3 M $HClO_4$	288.2	3.8×10^3	[65SCH2, 65SCH]
sp	4 M HBr	313.2	0.756±0.030 [(b)]	[76KAW/KOY]
sp	4 M HBr	318.2	0.901±0.035 [(b)]	
sp	4 M HBr	323.2	1.02±0.040 [(b)]	
sp	4 M HBr	327.7	1.14±0.045 [(b)]	
rev	4 M HBr	298.15	0.52±0.08 [(d)]	from [76KAW/KOY]

(a) Refers to the reactions indicated in the ionic medium and at the temperature given in the table.

(b) The uncertainty limits are calculated from $1.96 \times 0.02 \times K_c$ based on the reported estimated 2% errors for K_c in [76KAW/KOY].

(c) A least-squares fit of experimental K_c values gave $\ln K_c = (2.7998 \pm 0.3364) - (898.54 \pm 119.62)\, T^{-1}$ with a correlation coefficient of 0.99542. This equation yields $K_c = (0.807 \pm 0.423)$ M at 298.15 K.

(d) A least-squares fit of experimental K_c values gave $\ln K_c = (8.0095 \pm 0.1097) - (2581.92 \pm 35.43)\, T^{-1}$ with a correlation coefficient of 0.99997. This equation yields $K_c = (0.522 \pm 0.084)$ M at 298.15 K. The experimental value of K_c at 313.2 K is not very consistent with the higher temperature values and is given zero weight.

the identification of this substance as being $K_2TcO(OH)Cl_4(cr)$ is questionable. See the discussion of [71SPI/GLI] in Appendix A.

Thomas *et al*. [85THO/HEE] using Raman spectroscopy measured the equilibrium constant for the reaction

$$\textit{trans}\text{-}TcOCl_4^- + Cl^- \quad \rightleftharpoons \quad TcOCl_5^{2-} \tag{V.37}$$

At room temperature and 12 M HCl, the equilibrium constant was K(V.37) $= (0.0015 \pm 0.0010)\ \text{mol}^{-1} \cdot \text{dm}^3$. This established that $TcOCl_4^-$ was by far the dominant Tc(V) species in concentrated HCl.

The kinetics of the hydrolysis of $TcOCl_5^{2-}$ have been studied in aqueous HCl using spectrophotometry [84KOL/GOM], as have the oxidation of this species by HNO_3 [84KOL/GOM2] and HNO_2 [84KOL/GOM3]. As discussed in Appendix A (under [84KOL/GOM]) the experimental data were interpreted by Koltunov and Gomonova using the following equilibrium

$$TcOCl_5^{2-} + H_2O(l) \quad \rightleftharpoons \quad TcO_2Cl_4^{3-} + 2H^+ + Cl^- \tag{V.38}$$

The available equilibrium constants derived from reaction kinetics measurements are compiled in Table V.20. The reported $\log_{10} K$ values are converted to molal units (*cf.* Section II and Table II.5) and corrected to $I = 0$ using the specific ion interaction model, SIT (Appendix C). The resulting values show that $\Delta\varepsilon \approx 0$, hence $\log_{10} K^\circ = \log_{10} K - 8D$. From the corrected data listed in Table V.20, this review selects the simple average

$$\log_{10} K^\circ(\text{V.38}, 298.15\ \text{K}) \quad = \quad -2.95 \pm 0.15$$

Table V.20: Experimental equilibrium constant data for the Tc(V) oxychloride system.

Ionic Medium	T(K)	$\log_{10} K$ [a]	$\log_{10} K^\circ$ [a]	Reference
$TcOCl_5^{2-} + H_2O(l) \rightleftharpoons TcO_2Cl_4^{3-} + 2H^+ + Cl^-$				
1 M HCl	298.15	−1.30	−2.91	[84KOL/GOM]
2 M HCl	298.15	−1.22	−3.03	[84KOL/GOM3]
3 M HCl	298.15	−1.00	−2.90	[84KOL/GOM3]

[a] Refers to the reaction indicated, $\log_{10} K$ in the ionic medium at the temperature given in the table, $\log_{10} K^\circ = -295 \pm 0.15$ at $I = 0$ and 298.15 K.

The validity of this value of $\log_{10} K^\circ$(V.38, 298.15 K) obviously depends on whether Reaction (V.38) is correct. This reaction was inferred by Koltunov and Gomonova [84KOL/GOM, 84KOL/GOM3] from kinetic data, rather than being based on a more direct measurement of the equilibrium constant. However, Reaction (V.38) requires a double deprotonation of the water ligand, which seems unlikely given that

no solid complexes containing the $TcO_2X_4^{3-}$ complex have been identified, where X is a halide. In Appendix A, under the discussion of [84KOL/GOM], we noted that the more hydrolysed form of Tc(V) could be $TcOCl_4(OH)_2^{3-}$, rather than $TcO_2Cl_4^{3-}$, or possibly some other species. Among these possible other species are dimeric complexes of Tc(V). Several dimeric complexes of technetium have been identified that contain $[Tc(IV)(\mu - O)_2Tc(IV)]^{4+}$ and $[Tc(V)_2O_3]^{4+}$ cores [94BAL, 98KRY]. Further clarification of the equilibrium reaction is necessary before the value of $\log_{10} K°$ (V.38, 298.15 K) can be recommended.

Rajec and Macášek [81RAJ/MAC] also studied the kinetics of electrolytic reduction of $TcOCl_5^{2-}$ in 4.0 M HCl at 298.15 K by using simultaneous coulometry and UV-visible spectrophotometry. A detailed study of the reproportionation of TcO_4^- and $TcCl_6^{2-}$ was done by Koltunov and Gomonova [85KOL/GOM]. A preliminary experiment indicated that no detectible reaction occurred between TcO_4^- and $TcCl_6^{2-}$ below room temperature, but at 353 K the reaction occurred at a significant rate producing the complex $TcOCl_5^{2-}$ (Appendix A).

Several studies have been published in which paper chromatography was used to separate TcO_4^- from the products of its reduction by HCl or HBr, and the relative amounts of various reduced forms of technetium were determined [64OSS/SAR, 66SHU, 71SHU, 71SHU2, 71WIL/DEE, 78SHU, 82LIV/WOL]. In general, in these studies it was assumed that TcO_4^- was first reduced to one (or sometimes more than one) Tc(V) oxyhalide, with subsequent reduction to Tc(IV) halides generally also being "observed". Chromatographically separated peaks were then assigned to TcO_4^- and to one or more Tc(V) and Tc(IV) species. However, as noted by de Liverant and Wolf [82LIV/WOL], there were no direct measurements that allow an unambiguous assignment of the technetium valence to the reduction products. The spectrophotometric study by Truffer-Caron, Ianoz and Lerch [88TRU/IAN] reported that the initial stage of the reduction of TcO_4^- by concentrated HBr was found to occur too rapidly to be quantitatively studied, but it was possible to do kinetic studies in 6 M HBr.

Information obtained from all these studies indicates that:

1) The rates of reduction of TcO_4^- to Tc(V) or Tc(IV) species by halides in acidic solution followed the order $I^- > Br^- > Cl^-$. The rates of the subsequent reduction of Tc(V) to Tc(IV) followed the order $Br^- > Cl^-$.

2) Reduction rates for TcO_4^- by HCl or HBr increased as the acid concentration was increased.

3) Increasing the reaction temperature increased the rate at which TcO_4^- was reduced to Tc(V) by HCl or HBr, and it also increased the rate at which Tc(V) was subsequently reduced to Tc(IV).

V.4.2.1.3 Other aqueous Tc halides

V.4.2.1.3.a Tc(III)

Münze [68MÜN, 75MÜN] studied the electrochemical reduction of TcX_6^{2-} as a function of HX concentration, (X = Cl, Br). The reduction at a gold microelectrode was

nearly reversible in terms of the change of emf with pH [75MÜN]. Their claimed reactions are

$$TcCl_6^{2-} + H_2O(l) + e^- \rightleftharpoons TcCl_5(OH)^{3-} + Cl^- + H^+$$
$$TcBr_6^{2-} + H_2O(l) + e^- \rightleftharpoons TcBr_5(OH)^{3-} + Br^- + H^+$$

These Tc(III) complexes could be reoxidised to the parent species either electrolytically or by atmospheric $O_2(g)$.

Redox potential measurements by Hurst [80HUR] gave $E^\circ = 0.23$ V for the reduction of $TcCl_6^{2-}$ in a 1.2 M HCl/2.65 M NaCl mixture, and 0.18 V for the reduction of $TcBr_6^{2-}$ in 6 M HBr. Huber, Heineman and Deutsch [87HUB/HEI] reported redox potentials of (0.082±0.008) V for the chloride complex in 2.0 M HCl/3.0 M NaCl, and (0.240±0.034) V for the bromide complex in 2.0 M HBr/3.0 M NaBr, relative to the saturated sodium chloride calomel electrode. These electrochemical results indicated that $TcCl_3OH^-$ and $TcCl_3(OH)_2^{2-}$ are the predominant species in the chloride system. No bromide complexes were identified (see Appendix A). The redox reactions were reported to involve one electron and to be reversible or nearly reversible in all three studies [75MÜN, 80HUR, 87HUB/HEI].

Rajec and Macášek [82RAJ/MAC] studied the electrochemical behaviour of the reduction of TcO_4^- in HCl concentrations by simultaneous coulometry and spectrophotometry. These spectrophotometric results showed that the Tc(IV) species $TcCl_6^{2-}$ and the Tc(III) species $TcCl_5^{2-}$ were formed in approximately equal amounts. Busey [60BUS] postulated the equilibirum

$$TcCl_4^- + H_2O(l) \rightleftharpoons TcCl_3(OH)^- + H^+ + Cl^-$$

from spectroscopic measurements. As discussed in Appendix A, the existence of the Tc(III) species $TcCl_3(OH)^-$ must be regarded with some scepticism.

There is a total absence of thermodynamic data for the Tc(III) species. However, they are sensitive to aerial oxidation.

V.4.2.1.3.b Tc(VI)

Busey [59BUS] found no evidence for the formation of intermediate species between Tc(VII) and Tc(V) during the reduction of TcO_4^- by HCl. However, the spectroscopic measurements of Ryabchikov and Pozdnyakov [64RYA/POZ] were interpreted as indicating that TcO_4^- reduction by moderate to concentrated HCl occurred by way of a Tc(VI) species, and this Tc(VI) then disproportionated to TcO_4^- and Tc(IV). This disproportionation was found to be slow at room temperature, but it was rapid at the boiling point of the solution. Little reduction of TcO_4^- was observed for HCl concentrations below 7 M, but for 10 M and higher HCl the reduction of TcO_4^- went directly to Tc(IV).

When TcO_4^- was reduced by HCl in concentrated sulphuric acid, a deep blue solution was obtained and it remained that colour for about one hour [85KIR/STA]. Measurements of the EPR spectra indicated that a Tc(VI) complex was present, most probably $TcOCl_5^-$. No Tc(VI) oxybromide was detected when HBr in concentrated H_2SO_4 was used instead of HCl.

V.4.2.2 Solid technetium chlorides, bromides and iodides

V.4.2.2.1 Binary halides

No binary iodides have been reported for technetium. Thakur and Sandwar [80THA/SAN] estimated the crystal field stabilisation energies and lattice energies for $TcCl_2$, $TcBr_2$, and TcI_2. However, none of these compounds has actually been prepared.

V.4.2.2.1.a $TcCl_4$(cr) and $TcCl_6$(s)

Knox *et al*. [57KNO/TYR] found that technetium tetrachloride, $TcCl_4$(cr), was formed by the reaction of Tc_2O_7(cr) and CCl_4 at 673 K. The formation of this compound was also indicated by Colton [62COL] and Guest and Lock [72GUE/LOC]. Colton also reported obtaining small amounts of the very unstable dark green compound $TcCl_6$(s), but Guest and Lock were unable to systhesise it and its existence is problematical.

The unit cell of $TcCl_4$(cr) is orthorhombic with space group Pbca. It contains distorted octahedral "$TcCl_6$" units linked in linear polymeric chains [65ELD/PEN, 66ELD/PEN]. Unit cell parameters were given as $a = 11.58 \times 10^{-10}$ m, $b = 13.97 \times 10^{-10}$ m, $c = 5.98 \times 10^{-10}$ m, and $Z = 8$ in the preliminary report [65ELD/PEN], but they were later refined to $a = (11.65 \pm 0.02) \times 10^{-10}$ m, $b = (14.06 \pm 0.02) \times 10^{-10}$ m, $c = (6.03 \pm 0.02) \times 10^{-10}$ m, and $Z = 8$ [66ELD/PEN].

$TcCl_4$(cr) is unstable with regard to hydrolysis in the presence of water vapour [66ELD/PEN], and it has an effective magnetic moment of 3.14 B.M. [59KNO/COF].

More recent studies have given further information on the properties of $TcCl_4$(cr), [91MIR/BOR, 93ABR/WOL2]. However, no thermodynamic data are available.

V.4.2.2.1.b $TcBr_4$(s)

Fergusson and Hickford [70FER/HIC] prepared a technetium bromide by oxidising technetium metal with H_2O_2(aq), followed by evaporation of this solution with concentrated HBr four times under vacuum.

The compound formed was chemically analysed as being $TcBr_4$(s). It slowly and spontaneously lost bromine, and it was rapidly hydrolysed by moist air.

Abram, Wollert, and Hiller [93ABR/WOL2] also prepared $TcBr_4$(s) by reaction of $TcCl_4$(cr) with $(CH_3)_3SiBr$ in CH_2Cl_2. Their elemental analyses for Tc and Br were in approximate agreement with a composition of $TcBr_4$. They reported that $TcBr_4$(s) was insoluble in most common solvents, but it did dissolve in acetonitrile and *tert*-butylisonitrile.

V.4.2.2.1.c $TcBr_3$(cr)

Miroslavov *et al*. [91MIR/BOR] studied the sublimation of $(Tc(CO)_3Br)_4$(s) under reduced pressure in the presence of flowing Br_2(g). One of the reaction products was purified by sublimation at 673 to 723 K and yielded a material whose elemental analyses for Tc and Br were in good agreement with the formula $TcBr_3$. The IR spectrum of a suspension of this material in mineral oil showed no bands between 400 and 4000 cm^{-1}. Powder pattern X-ray diffraction positions and intensities were reported, but the structure was not solved.

V.4.2.2.2 Ternary halides

A number of double metal halides have been reported for technetium. Early data for them have been summarised by Colton [65COL] and Peacock [66PEA].

V.4.2.2.2.a M_2TcX_6(cr)

The most commonly used method for preparing alkali metal or ammonium hexahalotechnetates, M_2TcX_6(cr), involved the direct reduction of $MTcO_4$(cr) with aqueous HX followed by addition of stoichiometric amounts of MX [69KAN, 72ZAI/KON, 73KUZ/KOZ, 73ZAI/KON, 74ZAI/KON5, 79IAN/LER].

Some authors recommended the addition of H_3PO_2 or KI to solutions of HCl and TcO_4^- to enhance the rate of formation of M_2TcCl_6(cr) [54NEL/BOY, 58DAL/GIL, 59BOY], where M denotes a monovalent cation. However, reduction of TcO_4^- by H_3PO_2 in the presence of HCl has been reported to form $MTcOCl_4$(s) [81COT/DAN] or $M_2Tc_2Cl_8$(s) [77SCH/HED] initially (see Section V.4.2.2.3). Although M_2TcCl_6(cr) will ultimately form from reaction of $TcOCl_4^-$ with HCl in time, the use of H_3PO_2 seems to offer little advantage. The use of I^- caused problems since $M_2TcCl_5(OH)$(cr) generally formed instead, and it was reduced only very slowly to M_2TcCl_6(cr) by HCl [67ELD/FER]. The likelihood of misidentification is great in this case since both solids have the identical crystallographic cubic space group (Fm3m) and nearly identical unit cell parameters for any particular M^+.

Fergusson and Hickford [70FER/HIC] prepared Ag_2TcCl_6(s) by precipitation of K_2TcCl_6 solutions with $AgNO_3$ in cold concentrated HNO_3. Reaction of 11.6 M HCl with TcO_2(cr) took several months at room temperature and (in the absence of MX) yielded shiny plates of $H_2TcCl_6 \cdot 9H_2O$(cr) [72KOZ/NOV2]. Hydrothermal reduction of $HTcO_4$ at 453 K and 51 bar H_2(g) pressure in concentrated aqueous HBr gave about a 2% yield of $(H_3O)_2TcBr_6$(cr) [87KRY/GRI2] after evaporation of the solution in a vacuum desiccator for two weeks.

Several other M_2TcX_6(s) of monovalent cations have been prepared but not structurally characterised [72KUZ/OBL]. Mixed anion and cation complexes of these compounds have also been reported [86FLI/LAN, 91PRE/WEN, 92WEN/PRE]; see discussion under Ref. [86FLI/LAN] in Appendix A. The preparation of other M_2TcX_6(cr) compounds with various organic ligands has been reported [79TRO/DAV, 84BAL/BON2, 89BAL/COL].

Table V.21: Crystal structure parameters for ternary halides of technetium.[(a)]

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$ /m)	Reference
		Tc(IV)			
K_2TcF_6(cr)	trigonal	$P\bar{3}m$	1	$a = 5.807 \pm 0.004$	[63SCH/HER]
				$c = 4.645 \pm 0.004$	[64SCH]
Rb_2TcF_6(cr)	trigonal	$P\bar{3}m$		$a = 5.986 \pm 0.004$	[64SCH]
				$c = 4.798 \pm 0.004$	
K_2TcCl_6(cr)	cubic			$a = 9.805 \pm 0.004$	[51ZAC]
	cubic			$a = 9.89$	[52ELL]
	cubic			$a = 9.82 \pm 0.02$	[58DAL/GIL]
	cubic			$a = 9.90 \pm 0.02$	[59SHE]
	cubic	Fm3m		$a = 9.825 \pm 0.004$	[64SCH]
	cubic	Fm3m	4	$a = 9.83 \pm 0.03$	[67ELD/FER]
	cubic	Fm3m		$a = 9.811 \pm 0.002$	[72ZAI/KON]
Rb_2TcCl_6(cr)	cubic	Fm3m		$a = 9.965 \pm 0.004$	[64SCH]
	cubic	Fm3m		$a = 9.949 \pm 0.002$	[72ZAI/KON]
Cs_2TcCl_6(cr)	cubic	Fm3m		$a = 10.237 \pm 0.008$	[72ZAI/KON]
$(NH_4)_2TcCl_6$(cr)	cubic	Fm3m		$a = 9.936 \pm 0.002$	[72ZAI/KON]
	cubic	Fm3m	4	$a = 9.917 \pm 0.004$	[72NOV]
	cubic			$a = 9.92 \pm 0.02$	[73KUZ/KOZ]
	cubic	Fm3m	4	$a = 9.9072 \pm 0.0016$	[79ELD/EST]
$((CH_3)_4N)_2TcCl_6$(cr)	cubic			$a = 12.74 \pm 0.04$	[90KRY/GRI]

(Continued on next page)

Table V.21: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$ /m)	Reference
$((C_4H_9)_4N)_2TcCl_6$(cr)	triclinic[b]	$P\bar{1}$	4	$a = 11.099 \pm 0.006$	[89KRY/GRI]
				$b = 18.628 \pm 0.008$	
				$c = 22.361 \pm 0.008$	
$(AsPh_4)_2TcCl_6$(cr)	triclinic[c]	$P\bar{1}$	1	$a = 10.111 \pm 0.008$	[84BAL/BON2]
				$b = 12.165 \pm 0.006$	
				$c = 10.263 \pm 0.010$	
$[Fe(C_5H_5)_2]_4 \cdot [H_3O(H_2O)_4]_2 \cdot (TcCl_6)_3$(cr)	monoclinic[d]	$P2_1/c$	2	$a = 14.918 \pm 0.010$	[94GRI/KRY]
				$b = 11.448 \pm 0.004$	
				$c = 19.914 \pm 0.008$	
$H_2TcCl_6 \cdot 9H_2O$(cr)	triclinic[e]	P1(or $P\bar{1}$)	1	$a = 8.30 \pm 0.08$	[72KOZ/NOV2]
				$b = 7.35 \pm 0.08$	
				$c = 8.04 \pm 0.08$	
K_2TcBr_6(cr)	cubic	Fm3m	4	$a = 10.37 \pm 0.04$	[58DAL/GIL]
	cubic	Fm3m		$a = 10.371 \pm 0.004$	[64SCH]
	cubic	Fm3m		$a = 10.354 \pm 0.002$	[72ZAI/KON]
Rb_2TcBr_6(cr)	cubic	Fm3m		$a = 10.460 \pm 0.004$	[64SCH]
	cubic	Fm3m		$a = 10.461 \pm 0.004$	[73ZAI/KON]
Cs_2TcBr_6(cr)	cubic	Fm3m		$a = 10.650 \pm 0.006$	[73ZAI/KON]
$(NH_4)_2TcBr_6$(cr)	cubic	Fm3m	4	$a = 10.417 \pm 0.002$	[75SHE/KON]
	cubic	Fm3m		$a = 10.417 \pm 0.002$	[72ZAI/KON]
$((CH_3)_4N)_2TcBr_6$(cr)	cubic			$a = 13.34 \pm 0.04$	[90KRY/GRI]
$(H_3O)_2TcBr_6$(cr)	cubic	Fm3m	4	$a = 10.410 \pm 0.008$	[87KRY/GRI2]

(Continued on next page)

Table V.21: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$ /m)	Reference
K_2TcI_6(cr)	orthorhombic		4	$a = 11.22 \pm 0.06$	[58DAL/GIL]
				$b = 8.00 \pm 0.06$	
				$c = 7.84 \pm 0.06$	
	orthorhombic			$a = 11.24 \pm 0.04$	[74ZAI/KON5]
				$b = 7.96 \pm 0.04$	
				$c = 7.85 \pm 0.04$	
	monoclinic[(f)]	$P2_1/c$	2	$a = 11.352 \pm 0.004$	[87KRY/GRI]
				$b = 7.846 \pm 0.004$	(probably best)
				$c = 13.817 \pm 0.006$	
Rb_2TcI_6(cr)	cubic	Fm3m		$a = 11.301 \pm 0.004$	[64SCH]
	cubic			$a = 11.286 \pm 0.010$	[74ZAI/KON5]
Cs_2TcI_6(cr)	cubic			$a = 11.410 \pm 0.004$	[74ZAI/KON5]
$(NH_4)_2TcI_6$(cr)	orthorhombic			$a = 11.24 \pm 0.04$	[74ZAI/KON5]
				$b = 8.02 \pm 0.04$	
				$c = 7.92 \pm 0.04$	
$((CH_3)_4N)_2TcI_6$(cr)	cubic			$a = 14.20 \pm 0.04$	[90KRY/GRI]
$MgTcCl_6$(cr)	orthorhombic		2	$a = 9.85 \pm 0.04$	[87ZAI/KRU5]
				$b = 6.95 \pm 0.04$	
				$c = 6.98 \pm 0.04$	
$CaTcCl_6$(cr)	orthorhombic		2	$a = 9.93 \pm 0.04$	[87ZAI/KRU2]
				$b = 6.99 \pm 0.04$	
				$c = 7.03 \pm 0.04$	

(Continued on next page)

Table V.21: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$ /m)	Reference
$SrTcCl_6$(cr)	orthorhombic		2	$a = 9.96 \pm 0.04$	[87ZAI/KRU3]
				$b = 7.01 \pm 0.04$	
				$c = 7.04 \pm 0.04$	
$BaTcCl_6$(cr)	orthorhombic		2	$a = 10.07 \pm 0.04$	[86ZAI/KRU2]
				$b = 7.03 \pm 0.04$	
				$c = 7.06 \pm 0.04$	
$CdTcCl_6$(cr)	orthorhombic		2	$a = 9.91 \pm 0.04$	[87ZAI/KRU7]
				$b = 6.97 \pm 0.04$	
				$c = 7.02 \pm 0.04$	
$PbTcCl_6$(cr)	orthorhombic		2	$a = 9.97 \pm 0.04$	[87ZAI/KRU6]
				$b = 7.00 \pm 0.04$	
				$c = 7.03 \pm 0.04$	
$MgTcBr_6$(cr)	orthorhombic		2	$a = 10.32 \pm 0.04$	[87ZAI/KRU]
				$b = 7.30 \pm 0.04$	
				$c = 7.40 \pm 0.04$	
$CaTcBr_6$(cr)	orthorhombic		2	$a = 10.39 \pm 0.02$	[83ZAI/VIN]
				$b = 7.34 \pm 0.02$	
				$c = 7.45 \pm 0.02$	
$SrTcBr_6$(cr)	orthorhombic		2	$a = 10.41 \pm 0.04$	[87ZAI/KRU]
				$b = 7.37 \pm 0.04$	
				$c = 7.46 \pm 0.04$	

(Continued on next page)

Table V.21: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$ /m)	Reference
$BaTcBr_6$(cr)	orthorhombic		2	$a = 10.42 \pm 0.04$	[86ZAI/KRU]
				$b = 7.41 \pm 0.04$	
				$c = 7.48 \pm 0.04$	
$PbTcBr_6$(cr)	orthorhombic		2	$a = 10.41 \pm 0.04$	[86ZAI/KRU3]
				$b = 7.35 \pm 0.04$	
				$c = 7.45 \pm 0.04$	
		Tc(V)			
$NaTcF_6$(cr)	rhombohedral[g]			$a = 5.77$	[63EDW/HUG]
$KTcF_6$(cr)	rhombohedral [h]			$a = 4.97$	[66HUG/PEA]
$RbTcF_6$(cr)	rhombohedral[i]			$a = 5.09$	
$CsTcF_6$(cr)	rhombodedral[j]			$a = 5.25$	

[a] The reported uncertainties are assumed to be 1σ values, and are converted to 1.96σ. Some of the variation in unit cell parameters reported in the 1950's may be due to misidentification of $M_2TcX_5(OH)$(cr) as being M_2TcX_6(cr), (see text).

[b] $\alpha = (105.86 \pm 0.06)°$, $\beta = (90.84 \pm 0.06)°$, $\gamma = (105.17 \pm 0.06)°$

[c] $\alpha = (93.86 \pm 0.06)°$, $\beta = (114.51 \pm 0.08)°$, and $\gamma = (99.08 \pm 0.06)°$

[d] $\beta = (91.96 \pm 0.04)°$.

[e] $\alpha = (95 \pm 1.0)°$, $\beta = (98 \pm 1.0)°$, and $\gamma = (117.5 \pm 1.0)°$

[f] $\beta = (145.63 \pm 0.10)°$

[g] $\alpha = 55.8°$

[h] $\alpha = 97.0°$

[i] $\alpha = 95.5°$

[j] $\alpha = 96.2°$

Crystal structure data have been obtained for many M_2TcX_6(cr) at room temperature. A summary of some of these crystal structure parameters was given by Melnik and van Lier [87MEL/LIE]. Table V.21 gives a complete listing of the unit cell parameters and space groups for these solids.

It has been reported that K_2TcCl_6(cr) underwent a phase transition from cubic to lower symmetry when it is cooled below 34 K, and similarly for K_2TcBr_6(cr) below 236 K, but K_2TcI_6(cr) remained orthorhombic below 480 K [77RÖS/WIN].

Thermal decomposition of K_2TcCl_6(cr) at 1370 K produced technetium metal, Cl_2(g), and (presumably) KCl [54NEL/BOY]. M_2TcBr_6(cr) (M = K, Rb, Cs) similarly decomposed in a single step in argon producing technetium metal, Br_2(g), and MBr(l), at 1003 K, 1183 K, and 1268 K, respectively [78VIN/KON]. Thermal decomposition of K_2TcI_6(cr) (presumably in argon) occurred in two stages, the first with a mass decrease corresponding to a loss of three I atoms per Tc at 793 K, and the second corresponding to formation of KI and hcp Tc above 863 K. Thermal decompostition of $((CH_3)_4N)_2TcCl_6$(cr), $((CH_3)_4N)_2TcBr_6$(cr), $((CH_3)_4N)_2TcI_6$(cr), and $((C_4H_9)_4N)_2TcCl_6$(cr) in an atmosphere of argon began in the temperature range of 553 to 663 K and resulted in the formation of technetium metal and TcC_x(s) [89KRY/GRI, 99GUE].

Magnetic susceptibilities have been reported for the following solids:

- K_2TcCl_6(cr) [54NEL/BOY, 58DAL/GIL, 64SCH/KNA, 67ELD/FER];
- K_2TcX_6(cr) (X = Br, I) [58DAL/GIL, 64SCH/KNA, 90KRY/GRI];
- Rb_2TcI_6(cr) [64SCH/KNA];
- $((C_4H_9)_4N)_2TcCl_6$(cr) [89KRY/GRI];
- $((CH_4)_4N)_2TcI_6$(cr) [90KRY/GRI].

The magnetic moments ranged from 3.6 to 4.3 B.M. at room temperature, which roughly corresponds to spin-only values for 3 unpaired electrons.

Electronic spectra have been reported for K_2TcCl_6(cr) [67ELD/FER, 90DI /BET] as well as the IR and Raman spectra for several M_2TcX_6(cr) [69SCH/KRA, 72BAL/HAN, 73ZAI/KON, 89KRY/GRI, 90DI /BET]. These solids are insoluble in benzene, CCl_4, diethyl ether, and ethanol [72ZAI/KON, 73ZAI/KON].

As noted in Section V.4.2.2.2 a), the known compounds of the type M_2TcCl_6(cr) and $M_2TcCl_5(OH)$(cr), where M is a particular monovalent cation, have identical crystal structures and nearly identical unit cell parameters. This situation also occurs for Cs_2TcBr_6(cr) and $Cs_2TcBr_5(OH)$(cr). This can be seen by comparing the unit cell dimensions listed in Tables V.21 and V.26. Presumably, this is also true for $(NH_4)_2TcBr_6$(cr) and $(NH_4)_2TcBr_5(OH)$(cr). Furthermore, the reported unit cell parameters for $(H_3O)_2TcBr_6$(cr) and $(NH_4)_2TcBr_6$(cr) are identical within their experimental uncertainties. Since the X-ray scattering factors of oxygen and nitrogen atoms differ very little, the possibility exists that these compounds could be misidentified unless additional physicochemical characterisation methods are used.

Kryuchkov *et al.* [87KRY/GRI2] prepared their presumed $(H_3O)_2TcBr_6$(cr) by dissolving Tc_2O_7 in concentrated aqueous HBr, followed by reaction of the solution with H_2(g) in an autoclave at 453 K and at an initial H_2(g) pressure of 50 bar. If some N_2(g) was initially present in the sample container, then some NH_3 could conceivably have formed. No elemental analysis was performed on the presumed $(H_3O)_2TcBr_6$(cr), which was a minor impurity phase obtained in low yield. They reported the precence of IR bands corresponding to O–H and H–O–H bonds in this compound, which seems to exclude the possibility that the isolated phase was $(NH_4)_2TcBr_6$(cr). More direct evidence for $(H_3O)_2TcBr_6$(cr) is certainly desirable.

In his review, Boyd [59BOY] cited a value of S°_m (K_2TcCl_6, cr, 298.15 K) = (332.6 ± 8.2) J·K^{-1}·mol^{-1}. No details or references were given, and it was not stated whether this is an experimental or an estimated value. We ultimately found this value given in Appendix V.E of Cobble's thesis [52COB]. It was calculated by him by using estimated ionic contributions to the total entropy for solids of this type.

Vinogradov *et al.* [74VIN/ZAI] reported the solubilities of M_2TcCl_6(cr) (M = NH_4, K, Rb, Cs) in 3, 5, and 10 M HCl, and of the corresponding bromide solids in 3.5, 7.0, and 9.52 M HBr at 298 K. As discussed in Appendix A, the data are reanalysed by this review according to the reaction

$$M_2TcX_6(cr) \quad \rightleftharpoons \quad 2M^+ + TcX_6^{2-}$$

Table V.22: Selected solubility constants for M_2TcX_6(cr) at 298.15 K and $I = 0$.

	M = NH_4	M = K	M = Rb	M = Cs
$M_2TcCl_6(cr) \rightleftharpoons 2M^+ + TcCl_6^{2-}$				
$\log_{10} K^\circ_s$	-7.98 ± 1.00	-9.61 ± 1.00	-11.12 ± 1.00	-11.43 ± 1.00
.....				
$M_2TcBr_6(cr) \rightleftharpoons 2M^+ + TcBr_6^{2-}$				
$\log_{10} K^\circ_s$	-6.68 ± 1.00	-6.92 ± 1.00	-9.47 ± 1.00	-11.24 ± 1.00

The selected solubility constants are given in Table V.22. No Gibbs energy of formation can be recommended because there is no selected value for the TcX_6^{2-} ions.

V.4.2.2.2.b $MTcX_6$(cr)

Zaitseva and co-workers reported the synthesis and characterisation of the following Tc(IV) solids:

- $MgTcCl_6$(cr), $CaTcCl_6$(cr), $SrTcCl_6$(cr) and $BaTcCl_6$(cr) [86ZAI/KRU2, 87ZAI/KRU2, 87ZAI/KRU3, 87ZAI/KRU5];
- $MgTcBr_6$(cr), $CaTcBr_6$(cr), $SrTcBr_6$(cr) and $BaTcBr_6$(cr) [83ZAI/VIN, 86ZAI/KRU, 87ZAI/KRU]; and
- $PbTcCl_6$(cr), $CdTcCl_6$(cr) and $PbTcBr_6$(cr) [86ZAI/KRU3, 87ZAI/KRU6, 87ZAI/KRU7].

The corresponding unit cell parameters are given in Table V.21. Grigor'ev *et al.* [94GRI/KRY] have prepared and characterised a mixed ferricinium tetraaquaoxonium hexachlorotechnetate $[Fe(C_5H_5)_2)]_4[H_3O(H_2O)_4]_2(TcCl_6)_3$(cr). Structural parameters are also given in Table V.21.

All of these $MTcX_6$(cr) were generally prepared by dissolution of MCO_3(s) or MX_2(s) in a concentrated solution of $HTcO_4$ in HX. Thermal analysis of these solids in argon indicated that they generally decomposed producing technetium metal, X_2(g), and MX_2(s), which is equivalent to the mode of decomposition of alkali metal M_2TcX_6(cr).

The $MTcX_6$(cr) solids are insoluble in CCl_4, $CHCl_3$, and benzene; they dissolve in water with hydrolytic decomposition to form hydrated $TcO_2 \cdot xH_2O$(s); and they show individual variations for their solubilities in ethanol and acetone.

V.4.2.2.3 Binuclear halides

Crystal structure data have been reported for some binuclear technetium chlorides [65COT/BRA, 70BRA/COT, 72KOZ/NOV, 75COT/SHI, 75KOZ/NOV, 77COT/GAG, 77SCH/HED, 81COT/DAN, 81KOZ/LAR, 82COT/DAV, 82KOZ/LAR, 83KOZ/LAR, 85SPI/KUZ, 86KRY/GRI, 90GRI/KRY, 91COT/DAN]. Structural information is summarised in Table V.23.

Although there are no experimental thermodynamic data for any of the binuclear technetium halides reviewed here, these compounds are unstable under typical environmental conditions since they hydrolyse and are readily oxidised by O_2(g).

V.4.2.2.3.a $M_3Tc_2Cl_8 \cdot x\ H_2O$(s)

In 1963, Eakins, Humphreys and Mellish [63EAK/HUM] described the preparation of some solids by reduction of solutions of $TcCl_6^{2-}$ compounds at 373 K using zinc metal in O_2-free concentrated HCl. They thus prepared:

- $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$(s),
- $YTc_2Cl_8 \cdot 9H_2O$(s), and
- $K_3Tc_2Cl_8 \cdot xH_2O$(s),

all of which should contain mixed valence Tc(II, III). Oxidation studies confirmed that the average technetium valence in these compounds was 2.5.

Further reports of the reduction reaction by H_2(g) in an autoclave at 443 K claimed that the products were actually $K_8(Tc_2Cl_8)_3 \cdot 4H_2O$(s) and $M_8(Tc_2Cl_8)_3 \cdot 2H_2O$(s), (M = NH_4, Cs) [73GLI/KUZ, 75KOZ/NOV] or $K_8(Tc_2Cl_8)_3 \cdot H_3O \cdot 3H_2O$(s) [75KOZ/NOV].

Table V.23: Crystal structural parameters for binuclear technetium chlorides and bromides.

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Tc valence	Reference
$K_3Tc_2Cl_8 \cdot 2H_2O(cr)$ [a]	trigonal	$P3_121$ (or $P3_221$)	3	12.80 ± 0.10 $c = 8.30 \pm 0.08$	2,3	[72KOZ/NOV]
$K_3Tc_2Cl_8 \cdot xH_2O(cr)$ [a]	trigonal	$P3_121$ (or $P3_221$)	3	$a = 12.838 \pm 0.006$ $c = 8.187 \pm 0.004$	2,3	[75COT/SHI]
$K'_{3-x}K''_6(H_3O)_x(Tc_2Cl_8)_3$- $\cdot nH_2O(cr)$ [a]	trigonal	$P3_121$	3	$a = 12.817 \pm 0.006$ $c = 8.185 \pm 0.004$	2,3	[85SPI/KUZ]
$K_8(Tc_2Cl_8)_3 \cdot H_3O \cdot$ $3H_2O(cr)$ [a]	trigonal	$P3_121$ (or $P3_221$)	3	$a = 12.80 \pm 0.12$ $c = 8.30 \pm 0.08$	2,3 ($2\frac{1}{2}$ ave.)	[75KOZ/NOV]
$Cs_3Tc_2Cl_8 \cdot 2H_2O(cr)$ [a]	trigonal	$P3_121$ (or $P3_221$)	3	$a = 12.90 \pm 0.10$ $c = 8.70 \pm 0.08$	2,3	[72KOZ/NOV]
$Cs_8(Tc_2Cl_8)_3 \cdot 2H_2O(cr)$ [a]	trigonal	$P3_121$ (or $P3_221$)	3	$a = 12.90 \pm 0.12$ $c = 8.70 \pm 0.08$	2,3 ($2\frac{2}{3}$ ave.)	[75KOZ/NOV]
$(NH_4)_3Tc_2Cl_8 \cdot 2H_2O(cr)$	trigonal	$P3_121$ (or $P3_221$)	3	$a = 13.03 \pm 0.04$ $c = 8.40 \pm 0.02$	2,3	[65COT/BRA]
	trigonal	$P3_121$ (or $P3_221$)	3	$a = 13.04 \pm 0.04$ $c = 8.40 \pm 0.02$	2,3	[70BRA/COT]
$YTc_2Cl_8 \cdot 9H_2O(cr)$	tetra-gonal	$P42_12$ (or $P42_1m$)	4	$a = 11.712 \pm 0.004$ $c = 7.661 \pm 0.004$	2,3	[82COT/DAV]

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Table V.23: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Tc valence	Reference
$((n\text{-}C_4H_9)_4N)_2Tc_2Cl_8$(cr)	mono-clinic[(b)]	$P2_1/c$	(2)	$a = 10.922$ $b = 15.384$ $c = 16.439$	3,3	[77SCH/HED]
	mono-clinic [(c)]	$P2_1/c$	4	$a = 10.915 \pm 0.002$ $b = 15.382 \pm 0.006$ $c = 16.409 \pm 0.004$	3,3	[81COT/DAN]
$(C_5H_5NH)_3[Tc_2Cl_8]$(cr)	triclinic[(d)]	$P\bar{1}$	1	$a = 8.323 \pm 0.004$ $b = 8.780 \pm 0.002$ $c = 8.830 \pm 0.004$	2,3	[90GRI/KRY]
$K_2Tc_2Cl_6 \cdot 2H_2O$(cr)	mono-clinic[(e)]	Cc	4	$a = 8.287 \pm 0.004$ $b = 13.956 \pm 0.006$ $c = 8.664 \pm 0.004$	2,2	[86KRY/GRI]
	mono-clinic[(f)]	C	1	$a = 8.268 \pm 0.004$ $b = 13.943 \pm 0.004$ $c = 8.669 \pm 0.004$	2,2	[91COT/DAN]
	mono-clinic [(g)]	C	1	$a = 8.224 \pm 0.004$ $b = 13.924 \pm 0.002$ $c = 8.654 \pm 0.004$	2,2	[91COT/DAN]
$K[Tc_2(CH_3COO)_4Cl_2]$(cr)	tetra-gonal	$P4_2/n$	4	$a = 11.9885 \pm 0.0006$ $c = 11.2243 \pm 0.0004$	2,3	[82KOZ/LAR]
$Tc_2(CH_3COO)_4Cl$(cr)	mono-clinic[(h)]	C2/c	1	$a = 15.035 \pm 0.006$ $b = 7.801 \pm 0.002$ $c = 12.894 \pm 0.008$	2,3	[81KOZ/LAR]

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Table V.23: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Tc valence	Reference
$Tc_2(CH_3COO)_4Br$(cr)	mono-clinic[(i)]	C2/m	1	$a = 7.102 \pm 0.006$ $b = 14.772 \pm 0.008$ $c = 7.095 \pm 0.004$	2,3	[83KOZ/LAR]
$Tc_2\{(CH_3)_3CCOO\}_4Cl_2$(cr)	tetra-gonal	I4/m	2	$a = 11.515 \pm 0.004$ $c = 10.625 \pm 0.006$	3,3	[77COT/GAG]

[(a)] These four potassium compounds probably represent the same basic class of compounds, as do the two caesium compounds. According to Spitzyn *et al.* [85SPI/KUZ], the formulae should be written as $M'_{3-x}M''_6(H_3O)_x(Tc_2Cl_8)_3 \cdot nH_2O$(cr), where x and n vary from 1 to 3. The degree of substitution of H_3O^+ ions for K^+ and Cs^+ ions depends on the concentration of hydrochloric acid used when these compounds are synthesised, along with other reaction conditions. The small variations between the reported unit cell parameters presumably result mainly from different crystals having slightly different values of x.

[(b)] $\beta = 122.37°$.

[(c)] $\beta = (122.37 \pm 0.02)°$. The Tc-Tc bond length is about 2.15×10^{-10} m.

[(d)] $\alpha = (78.60 \pm 0.02)°$, $\beta = (70.02 \pm 0.04)°$, and $\gamma = (85.78 \pm 0.04)°$.

[(e)] $\beta = (93.99 \pm 0.05)°$.

[(f)] At 288 K; $\beta = (94.17 \pm 0.02)°$.

[(g)] At 220 K; $\beta = 94.05°$.

[(h)] $\beta = (109.65 \pm 0.04)°$.

[(i)] $\beta = (113.36 \pm 0.06)°$.

In a later review paper on the cluster compounds of technetium [85SPI/KUZ], the same group indicated that they now preferred a formulation with variable coefficients: $M'_{3-x}M''_6(H_3O)_x(Tc_2Cl_8)_3 \cdot nH_2O$(cr), where x and n vary from 1 to 3 and depend on the concentration of HCl used in the reaction. It seems unlikely that reduction by H_2(g) gave a less reduced product with a lower monovalent cation-to-technetium ratio than reduction by zinc metal. Unit cell parameters reported for $M_3Tc_2Cl_8 \cdot xH_2O$(s) and $M_8(Tc_2Cl_8)_3 \cdot xH_2O$(s) are identical within experimental error, and the space groups are the same for both crystals [65COT/BRA, 75COT/SHI, 72KOZ/NOV, 75KOZ/NOV]. It is thus reasonable to assume identical compounds were prepared in both studies, and the simpler formulation $M_3Tc_2Cl_8 \cdot xH_2O$(s) is accepted. We also note that the evidence for salts of the type $M_8(Tc_2Cl_8)_3 \cdot xH_2O$(cr) has been disputed by Cotton and Shive [75COT/SHI] and by Guerman and co-workers [99GUE].

Another method for the preparation of these mixed valency halides has been described by Peters, Skowronek and Preetz, (*cf.* Ref. [92PET/SKO] in Appendix A).

The thermal stability of $K_3Tc_2Cl_8 \cdot 2H_2O$(s) in argon was studied by differential thermal analysis, IR spectroscopy, and X-ray diffraction [82OBL/KUZ]. This compound underwent dehydration to $K_3Tc_2Cl_8$(s) by 433 K, followed by disproportionation to $K_2Tc_2Cl_6$(s), KCl, and Tc metal at 699 K. Crystallisation of technetium metal began around 873 K.

A similar thermal decomposition study was done for $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$(s) in argon and argon-helium mixtures [87SPI/KUZ]. Water was lost between 413 and 443 K, anhydrous $(NH_4)_3Tc_2Cl_8$(s) decomposed to technetium metal, $(NH_4)_2TcCl_6$, NH_4Cl, and Cl_2(g) around 553 to 613 K, and the $(NH_4)_2TcCl_6$ subsequently decomposed to TcN via a claimed TcNCl intermediate.

Magnetic susceptibilities have been reported for the following solids:

- $K_3Tc_2Cl_8 \cdot xH_2O$(s) [73ZEL/SUB],
- $Cs_3Tc_2Cl_8 \cdot 2H_2O$(s) [73ZEL/SUB],
- $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$(s) [70BRA/COT, 75COT/PED],
- $YTc_2Cl_8 \cdot 9H_2O$(s) [75COT/PED], and
- the alleged mixed-valence compounds $K_8(Tc_2Cl_8)_3 \cdot 4H_2O$(s) and $Cs_8(Tc_2Cl_8)_3 \cdot 2H_2O$(s) [73GLI/KUZ], which would require the technetium to have an average valence of 8/3. Subsequently, some of the same authors [85SPI/KUZ] reformulated these compounds as having a general formula of the type $M'_{3-x}M''_6(H_3O)_x(Tc_2Cl_8)_3 \cdot nH_2O$(s), where x and n range from 0 to 3, and the average valence of the technetium is 2.5.

In each case the magnetic susceptibilities yielded magnetic moments of about 2 B.M. which indicated the presence of one unpaired electron per $Tc_2Cl_8^{3-}$ formula unit.

The stability of $M_3Tc_2Cl_8 \cdot xH_2O$(s) in aqueous solutions has been investigated both in the absence and presence of oxygen [70BRA/COT, 77SPI/KUZ2, 77SPI/KUZ, 80SPI/KUZ, 81KRY, 83KRY/KUZ]. Different aqueous species were suggested but no thermodynamic data were reported (see discussion under [77SPI/KUZ] in Appendix A).

V.4.2.2.3.b $M_2Tc_2Cl_8(s)$

Based on the experimental results given by Cotton and Pedersen [75COT/PED], it could be possible to prepare compounds of the type $M_2Tc_2Cl_8(s)$. Several authors have reported the synthesis and characterisation of $((n\text{-}C_4H_9)_4N)_2Tc_2Cl_8(cr)$ [77SCH/HED, 80PRE/PET2, 81COT/DAN] (see Ref. [75COT/PED] in Appendix A). Preetz and Peters [80PRE/PET2] also prepared the corresponding bromide compound.

V.4.2.2.3.c $M_2Tc_2Cl_6 \cdot xH_2O(s)$ and $M_2Tc_2Br_6 \cdot 2H_2O(s)$

Other types of binuclear halides were also reported by Kryuchkov and co-workers [82KRY/KUZ]: $M_2Tc_2Cl_6 \cdot xH_2O(s)$ and $M_2Tc_2Br_6 \cdot 2H_2O(s)$ (where M = NH_4 or an alkali metal cation). They were prepared from $MTcO_4$ compounds in HCl or HBr by reduction with $H_2(g)$ at 30.4 bar in an autoclave at 413 to 423 K.

$K_2Tc_2Cl_6 \cdot 2H_2O(cr)$ was described in detail and structurally characterised [86KRY/GRI, 91COT/DAN]. The thermal stability of these binuclear clusters has been reviewed and studied by Kryuchkov, German and Simonov [91KRY/GER], who found that the hydrated compounds lose water over a broad temperature range (333 - 673 K) and that the dehydrated cluster compounds with stable ligands decompose with disproportionation by cleavage of the Tc-Tc bonds, *e.g.*, $Tc_2Cl_6^{2-} \rightarrow TcCl_6^{2-} + Tc$.

V.4.2.2.3.d $MTc_2Br_9(s)$, $M_2Tc_2Cl_{10}(s)$ and $M_2Tc_2Br_{10}(s)$

More recently, Wendt and Preetz prepared Tc(IV) halides containing $Tc_2Br_9^-$, $Tc_2Br_{10}^{2-}$ and $Tc_2Cl_{10}^{2-}$ ions with various organic cations [93WEN/PRE, 94WEN/PRE]. IR and Raman measurements were reported (see Ref. [94WEN/PRE] in Appendix A).

V.4.2.2.3.e $K[Tc_2X_4Cl_2](s)$, $Tc_2X_4Y(s)$ and $Tc_2X_4Cl_2(s)$, where X denotes a carboxylate anion and Y a chloride or bromide ion

Several binuclear technetium compounds have been reported which contain one or more halide ligands (chloride or bromide) and four carboxylate ligands. These compounds are obtained [85SPI/KUZ] either by ligand exchange at evelated temperatures and pressures using the corresponding carboxylic acid and $M_3Tc_2Cl_8 \cdot 2H_2O(cr)$ or $M_2Tc_2Br_6 \cdot 2H_2O(cr)$ in argon or nitrogen atmosphere, where M denotes a monovalent cation, or by reduction of TcO_4^- with $H_2(g)$ in the presence of HCl and a carboxylic acid. The following compounds have been prepared and partially characterised by physicochemical methods:

- $K[Tc_2(CH_3COO)_4Cl_2](s)$ [81SPI/BAI, 82KOZ/LAR]
- $Tc_2(CH_3COO)_4Cl(s)$ [81KOZ/LAR, 81SPI/BAI]
- $Tc_2(CH_3COO)_4Br(s)$ [82KRY/KUZ, 83KOZ/LAR]
- $Tc_2\{(CH_3)_3CCOO\}_4Cl_2(s)$ [77COT/GAG]

V.4.2.2.4 Polynuclear technetium cluster halides

Several polynuclear technetium cluster halides containing mainly organic cations have been synthesised and characterised [82KRY/KUZ, 83KOZ/LAR2, 85KOZ/SUR, 86GER/KRY, 86KRY/KUZ, 87KRY/GRI3, 88KRY/GRI, 88KRY/KUZ, 93GRI/KRY]. These are mainly chloride or bromide complexes, although one iodine complex [93GRI/KRY] and one mixed bromide-iodide complex [88KRY/GRI] were also reported. However, no thermodynamic data are available for any of these technetium cluster halides. Their solutions are stable only in concentrated acid under reducing conditions, and they would decompose under normal environmental conditions. The thermal stability of the polyuclear clusters has been reviewed and studied by Kryuchkov, German and Simonov [91KRY/GER], who found that the hydrated compounds lose water over a broad temperature range (333 - 673 K) and that the dehydrated polynuclear cluster compounds, which do not contain any other metallic cations, decompose to give Tc, TcC or TcN and gaseous species which do not contain technetium.

Rinke, Klein and Schäfer [67RIN/KLE] prepared mixed solid phases of technecium and rhenium chlorides, and used mass spectrometry to study the vapor phase above them at 623 K and higher tempertaures. Parent gas phase molecules observed were Tc_3Cl_9, Tc_3Cl_{12}, $TcCl_4$, Re_2TcCl_9, $ReTc_2Cl_9$, $ReTc_2Cl_{12}$, are incude many trinuclear clusters containing Tc(III) or Tc(IV).

Table V.24 contains a summary of the X-ray structural information for the polynuclear cluster halides of technetium.

V.4.2.2.5 Oxyhalides

Two reviews are available for technetium halides and oxyhalides that cover the pertinent literature up to the early to mid 1960s [65COL, 68CAN/COL]. They contain discussions of methods of preparation and chemical properties.

The following compounds are known:

- $TcOX_3$(s) (X = Cl, Br) [68CAN/COL2, 68COL/TOM, 72GUE/LOC],
- $TcOCl_4$(s) [72GUE/LOC],
- TcO_3Cl(s) [72GUE/LOC],
- $K_3Tc_2O_2Cl_8$(s) [85SPI/KUZ],
- M_2TcOCl_5(s) (M = NH_4, K, Cs) [67JEŻ/NAT, 67JEŻ/WAJ, 72BAL/HAN]
- Cs_2TcOX_5(s) (X = Cl, Br) [85THO/HEE].

$TcOCl_3$(s) was prepared by reaction of TcO_2(cr) with Cl_2(g) at 573 to 623 K [68COL/TOM] as well as by chlorination of technetium metal at 573 to 823 K [72GUE/LOC]. The corresponding oxybromide, $TcOBr_3$(s), was produced by reaction of TcO_2(cr) with Br_2(g) at 573 to 623 K in the absence of O_2(g) [68CAN/COL2, 68COL/TOM].

Table V.24: Crystal structural parameters of polynuclear cluster halides.

Phase	Crystal symmetry	Space group Z	Lattice parameters ($\times 10^{10}$/m)	Reference
Hexameric Clusters				
$((CH_3)_4N)_3Tc_6Cl_6(\mu\text{-}Cl)_6Cl_2$(cr)	orthorhombic	Pcmn 4	$a = 11.583\pm0.004$ $b = 13.527\pm0.006$ $c = 24.387\pm0.006$	[83KOZ/LAR2] [86GER/KRY]
$((CH_3)_4N)_2Tc_6Cl_6(\mu\text{-}Cl)_6$(cr)	triclinic[(a)]	P1 2	$a = 11.614\pm0.008$ $b = 11.633\pm0.008$ $c = 14.017\pm0.012$	[86GER/KRY]
$((CH_3)_4N)_3Tc_6Br_6(\mu\text{-}Br)_6Br_2$(cr)	hexagonal	$P6_3/mmc$ 3	$a = 13.781\pm0.006$ $c = 12.801\pm0.008$	[87KRY/GRI3]
$((CH_3CH_2)_4N)_2Tc_6Br_6(\mu\text{-}Br)_6Br_2$(cr)	triclinic[(b)]	$P\bar{1}$ 2	$a = 12.877\pm0.006$ $b = 13.684\pm0.006$ $c = 14.613\pm0.008$	[87KRY/GRI3]
$((n\text{-}C_4H_9)_4N)_2Tc_6Br_6(\mu\text{-}Br)_5$(cr)	monoclinic [(c)]	$P2_1/c$	$a = 9.999\pm0.006$ $b = 14.072\pm0.004$ $c = 21.127\pm0.008$	[88SPI/KRY]
$[(H_2O)_3H_3O]_2Tc_6Br_6(\mu\text{-}Br)_5$(cr)	monoclinic[(d)]	$P2_1/c$ 2	$a = 9.258\pm0.008$ $b = 9.211\pm0.006$ $c = 17.437\pm0.014$	[83KOZ/LAR2] [86KRY/KUZ]
$[Fe(C_5H_5)_2]_3Tc_6I_6(\mu\text{-}I)_6I_2$(cr)	tetragonal	P6/m 2	$a = 13.34\pm0.04$ $b = 12.70\pm0.02$	[93GRI/KRY]

(Continued on next page)

Table V.24: (continued)

Phase	Crystal symmetry	Space group Z	Lattice parameters ($\times 10^{10}$/m)	Reference
Octameric Clusters				
$Tc_8Br_4(\mu\text{-}Br)_8Br \cdot 2H_2O$(cr)	monoclinic[e]	$P2_1/n$	$a = 7.573 \pm 0.004$	[86KRY/GRI2]
		2	$b = 13.428 \pm 0.006$	[88SPI/KRY]
			$c = 12.661 \pm 0.004$	
$[H(H_2O)_2]Tc_8Br_4(\mu\text{-}Br)_8Br$(cr)	monoclinic[f]	$P2_1/n$	$a = 7.561 \pm 0.002$	[82KOZ/SUR]
		2	$b = 13.553 \pm 0.010$	[86KRY/KUZ]
			$c = 12.620 \pm 0.006$	
$[H(H_2O)_2)_2]Tc_8Br_4(\mu\text{-}Br)_8Br_2$(cr)	monoclinic[g]	$P2_1/a$	$a = 22.151 \pm 0.018$	[86KRY/KUZ]
		2	$b = 9.026 \pm 0.006$	
			$c = 9.396 \pm 0.008$	
$((n\text{-}C_4H_9)_4N)_2Tc_8(Br_{0.5}I_{0.5})_4$-$(\mu\text{-}Br_{0.5}\mu\text{-}I_{0.5})_8I_2$(cr)	monoclinic[h]	$P2_1/c$	$a = 16.875 \pm 0.012$	[88KRY/GRI]
		4	$b = 23.842 \pm 0.010$	
			$c = 17.539 \pm 0.006$	

[a] $\alpha = 69.66°$, $\beta = 65.89°$, and $\gamma = 60.13°$.
[b] $\alpha = (81.24 \pm 0.04)°$, $\beta = (67.45 \pm 0.04)°$, and $\gamma = (63.91 \pm 0.04)°$.
[c] $\beta = 107.76°$.
[d] Originally formulated by them as being $[(H_2O)_3H_3O]_2Tc_6(Br, OH)_6Br_6$ [83KOZ/LAR2]; $\beta = (101.09 \pm 0.06)°$.
[e] $\beta = (103.05 \pm 0.04)°$.
[f] Also given as $Tc_8Br_{13} \cdot 2H_2O$ [82KOZ/SUR]; $\beta = (102.62 \pm 0.04)°$.
[g] $\beta = 105.95°$.
[h] $\beta = (111.11 \pm 0.04)°$.

Both $TcOX_3(s)$ compounds were readily hydrolysed with disproportionation to form solid hydrated $TcO_2 \cdot xH_2O(s)$ and aqueous TcO_4^- in a 2:1 mole ratio [68COL/TOM]. The mixed-valence Tc(IV, V) compound, $K_3Tc_2O_2Cl_8(s)$, was described by Spitsyn *et al.* [85SPI/KUZ] (Appendix A). The authors reported that this substance disproportionated in concentrated aqueous HCl to form equimolar amounts of $TcCl_6^{2-}$ and $TcOCl_5^{2-}$, which is consistent with the mixed-valence formulation. No structural results are available for this solid, but results from IR spectroscopy indicated that two types of non-equivalent oxygens were present, and electronic spectra indicated the absence of a bridging chlorine atom [85SPI/KUZ]. Given the lack of direct structural information, however, the formulation of this substance as $K_3Tc_2O_2Cl_8$ is unproven.

The synthesis of some Tc(V) oxyhalides was achieved by reduction of TcO_4^- with HCl or HBr, *e.g.*, $M_2TcOCl_5(s)$, (M = NH_4, K, Cs) [67JEŻ/WAJ, 67JEŻ/NAT, 72BAL/HAN]; $Cs_2TcOX_5(s)$, (X = Cl, Br) [85THO/HEE]. Lower temperatures of around 265 to 273 K are advantageous for preparation of Tc(V) oxybromides in order to reduce the amount of Tc(IV) formed by further reduction of Tc(V) by HBr. Jeżowska-Trzebiatowska and coworkers [67JEŻ/WAJ, 67JEŻ/NAT, 72BAL/HAN] reported IR and UV-visible spectra for the $M_2TcOCl_5(s)$ solids, and made magnetic susceptibility measurements for $(NH_4)_2TcOCl_5(s)$ which was diamagnetic, at least from 82.5 to 293 K.

In addition to the preparation of these oxyhalides, the synthesis and characterisation of several Tc(V) oxyhalides containing organic cations has been described [79COT/DAV, 80PRE/PET, 80THO/DAV, 81DAV/JON, 81PET/PRE, 82DAV/TRO, 89BAL/COL, 90KIR/KÖH, 90MAN/IAN, 92HÜB/ABR]. A summary of the available crystal structure information is given in Table V.25.

From the above information on Tc(V) oxyhalides, it appears that precipitation with bulkier cations generally yields $TcOX_4^-$ salts, whereas smaller and intermediate sized cations yield $TcOX_5^{2-}$ salts.

There are no published thermodynamic data for any of the oxyhalides described in this section. They disproportionate, hydrolyse, or are oxidised by atmospheric $O_2(g)$ under normal environmental conditions.

V.4.2.2.6 Hydroxyhalides

In 1965, Colton [65COL] reported the synthesis of a Tc(IV) hydroxychloride by addition of $KTcO_4$ to concentrated HCl in the presence of KI; this was originally assumed to be $K_4Tc_2OCl_{10} \cdot H_2O(s)$. However, the results of a powder pattern X-ray diffraction study [65COL] raised the possibility that this compound might actually be $K_2TcCl_5(OH)(cr)$, which has the same empirical formula as one half unit of $K_4Tc_2OCl_{10} \cdot H_2O(s)$ [65COL].

Elder *et al.* [67ELD/FER] prepared crystals of $K_2TcCl_5(OH)(cr)$ by addition of KI to a solution of $KTcO_4$ in 11.3 M HCl. It was characterised by a single crystal X-ray structural determination. Electronic spectra were also reported by them for $K_2TcCl_5(OH)(cr)$ at room temperature and at liquid air temperature.

Fergusson, Greenaway and Penfold [83FER/GRE] prepared additional compounds

Table V.25: Crystal structure parameters for Tc(V) oxyhalide compounds.

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
$(Ph_3P)_2N[TcOCl_4](cr)$ [(a)]	orthorhombic	$Pna2_1$	4	$a = 21.618 \pm 0.010$ $b = 16.870 \pm 0.010$ $c = 9.658 \pm 0.006$	[79COT/DAV]
$AsPh_4[TcOCl_4](cr)$ [(b)]	tetragonal	P4/n	2 or 4	$a = 12.664 \pm 0.002$ $c = 7.822 \pm 0.002$	[89BAL/COL]
	tetragonal	P4/n	2	$a = 12.670 \pm 0.002$ $c = 7.824 \pm 0.002$	[90KIR/KÖH]
$AsPh_4[TcOBr_4](cr)$ [(b)]	tetragonal	P4/n	2	$a = 12.766 \pm 0.002$ $c = 8.032 \pm 0.002$	[92HÜB/ABR]
$(CH_3CH_2)_4N[TcOBr_4$-$(OH_2)](cr)$ [(c)]	orthorhombic	Pmma	4	$a = 11.155 \pm 0.008$ $b = 12.929 \pm 0.004$ $c = 11.531 \pm 0.002$	[90MAN/IAN]

(a) The $TcOCl_4^-$ ion had a distorted square pyramidal structure with C_{2v} symmetry.

(b) The $TcOX_4^-$ ions are square pyramidal in shape, with C_{4v} symmetry, with the O-Tc-X angle slightly smaller than the tetrahedral value.

(c) The oxygen atom and water oxygen were trans to each other, with Tc=O and Tc-O bond lengths of 1.62×10^{-10} and 2.32×10^{-10} m, respectively.

of this type. They added various alkali metal chlorides or bromides to solutions of $NaTcO_4$, subsequently added HI to these solutions, and concentrated the solutions by evaporation.

They obtained and characterised the following hydroxychlorides and hydroxybromides of Tc(IV):

- $M_2TcCl_5(OH)$(cr) (M = K, Rb, Cs) and
- $Cs_2TcBr_5(OH)$(cr).

$K_2TcCl_5(OH)$(cr) and $Cs_2TcCl_5(OH)$(cr) were paramagnetic with magnetic moments of 3.6 and 3.5 B.M., respectively [67ELD/FER, 83FER/GRE]. When these solids were treated with hot aqueous HCl or HBr, they slowly dissolved to form solutions of $TcCl_6^{2-}$ or $TcBr_6^{2-}$.

Zaitseva *et al*. [87ZAI/KRU4] prepared crystals of $ZnTcCl_5(OH)$(cr) by reducing $Zn(TcO_4)_2$ with concentrated HCl in the presence of $ZnCl_2$. Its identification was based on IR, EPR, and ^{1}H-NMR, and on elemental analyses for Zn, Tc, and Cl. It was hydrolysed by water, and it decomposed when heated in an argon atmosphere above 670 K. The same authors also prepared $La_2[TcCl_5(OH)]_3$(cr) by heating an aqueous HCl solution of $La(TcO_4)_3$ and $LaCl_3$ [88ZAI/KRU]. This material was paramagnetic, and it was characterised by IR, ESR, ^{1}H-NMR, and thermal analysis. It was hydrolysed by water, and it was insoluble in CCl_4 and benzene. Thermal decomposition of $La_2[TcCl_5(OH)]_3$(cr) occurred between 678 and 753 K in an argon atmosphere.

The experiments performed by Spitsyn, Glinkina and Kuzina [71SPI/GLI] gave some evidence for the formation of Tc(V) hydroxychlorides, but no reliable identification was obtained (Appendix A).

There is a total absence of thermodynamic data for these technetium hydroxyhalides. However, these compounds probably would undergo extensive or complete hydrolysis (and, possibly disproportionation for Tc(V)) at normal environmental pH values. Crystallographic information for the Tc(IV) compounds is given in Table V.26.

V.4.2.3 Gaseous technetium chlorides, bromides and iodides

Rudolph and Bächmann [80RUD/BÄC] reported the formation of two volatile technetium chlorides at high temperatures (650 to 1100 K) in a CCl_4(g) atmosphere at 0.33 to 1.2 bar pressure, and assumed they were $TcCl_4$(g) and $TcCl_5$(g). No direct evidence is available for $TcCl_5$(g). They also studied the high-temperature chromatography of gaseous Tc species obtained by reacting Tc metal with CCl_4, and "observed" the presence of $TcOCl_3$(g) and $TcOCl_4$(g). Actually, the presence of these compounds was deduced indirectly.

Vibrational spectra have been reported for solid, liquid, and gaseous TcO_3Cl [72GUE/HOW, 78GUE/HOW]. These vibrational frequencies are [78GUE/HOW] ν_1(Tc-O symmetric stretch) = 948, ν_2(Tc-Cl stretch) = 451, ν_3(O-Tc-O symmetric bend) = 299, ν_4(Tc-O asymmetric stretch) = 932, ν_5(O-Tc-O asymmetric bend) = 342, and ν_6(rocking motion) = 197 cm^{-1}. Electronic transitions occurred around 4170,

Table V.26: Crystal structure parameters for hydroxyhalide compounds of Tc(IV)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
$K_2TcCl_5(OH)(cr)$[(a)]	cubic	Fm3m	4	$a = 9.829 \pm 0.014$	[67ELD/FER]
	cubic			$a = 9.851 \pm 0.004$	[83FER/GRE]
$Rb_2TcCl_5(OH)(cr)$	cubic			$a = 9.964 \pm 0.002$	[83FER/GRE]
$Cs_2TcCl_5(OH)(cr)$	cubic			$a = 10.315 \pm 0.004$	[83FER/GRE]
$Cs_2TcBr_5(OH)(cr)$	cubic			$a = 10.715 \pm 0.006$	[83FER/GRE]
$ZnTcCl_5(OH)(cr)$[(b)]	orthorhombic		2	$a = 9.87 \pm 0.04$ $b = 6.96 \pm 0.04$ $c = 7.01 \pm 0.04$	[87ZAI/KRU4]
$La_2[TcCl_5(OH)]_3(cr)$	orthorhombic		2	$a = 10.11 \pm 0.04$ $b = 7.08 \pm 0.04$ $c = 7.09 \pm 0.04$	[88ZAI/KRU]

(a) Isostructural with $K_2TcCl_6(cr)$. As noted by Elder *et al.* [67ELD/FER] the m3m point symmetry indicated that technetium was in a regular octahedral environment.
(b) Isostructural with $MTc^{(IV)}Cl_6(cr)$

16000, 32000, and 43000 cm^{-1} [78GUE/HOW]. These gas phase vibrational frequencies were used by Baran [76BAR] to calculate ideal gas thermodynamic properties of $TcO_3Cl(g)$ by using statistical methods. Baran's calculated values at 298.15 K and 1 atm pressure are $C^\circ_{p,m} = 80.5$ J·K^{-1}·mol^{-1}, $S^\circ_m = 317.6$ J·K^{-1}·mol^{-1}, $H^\circ_m(T) - H^\circ_m(0\ K) = 17.0$ kJ·mol^{-1}, and $G^\circ_m(T) - H^\circ_m(0\ K) = -77.7$ kJ·mol^{-1}.

Zavalishin and Mal'tsev did statistical thermodynamic calculations for TcO_3Cl, and TcO_3Br [76ZAV/MAL2], and for $TcOCl_4$ [76ZAV/MAL], all from 100 to 4000 K, as well as for some oxyfluoride compounds (Section V.4.1.3.2). Since the accuracy of their calculations cannot be assessed, their results are not recommended.

This review performs ideal gas statistical thermodynamic calculations for $TcO_3Cl(g)$ and $TcO_3F(g)$ (Section V.4.1.3.2, Table V.18) using the harmonic oscillator approximation and published vibrational frequencies [72GUE/HOW, 74BIN/EL-, 78GUE/HOW]. We adopt the assertion of Guest, Howard-Lock and Lock [78GUE/HOW] that the Tc-Cl and Tc-O bond lengths in TcO_3Cl should be essentially equal to those corresponding ones in ReO_3Cl,2.23×10^{-10} and 1.70×10^{-10} m, respectively. The reversal of assigned values for ν_1 and ν_2 for TcO_3Cl [74BIN/EL-] (which does not matter for statistical thermodynamic calculations since they have the same degeneracies) is also accepted. Table V.27 contains these thermodynamic values for $TcO_3Cl(g)$. The recommended thermodynamic data at 298.15 K are

$$S^\circ_m(TcO_3Cl, g, 298.15\ K) = (317.636 \pm 0.797)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$C^\circ_{p,\mathrm{m}}(\mathrm{TcO_3Cl,\ g,\ 298.15\ K}) \quad = \quad (80.365 \pm 0.308)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

Table V.27: Ideal gas thermodynamic properties of TcO_3Cl(g) from statistical thermodynamic calculations. [(a)]

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	S°_m ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)	$[H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(0\ \mathrm{K})]$ ($\mathrm{kJ \cdot mol^{-1}}$)	$-[G^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(0\ \mathrm{K})]/T$ ($\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$)
0	0.000±0.000	0.000±0.000	0.000±0.000	—
10	33.258±0.000	165.796±0.000	0.332±0.000	132.538±0.000
25	33.284±0.006	196.273±0.001	0.831±0.000	163.013±0.000
50	35.317±0.198	219.732±0.051	1.680±0.002	186.125±0.009
100	47.780±0.511	247.748±0.311	3.737±0.022	210.373±0.093
200	68.410±0.419	287.927±0.653	9.653±0.071	239.660±0.300
298.15	80.365±0.308	317.636±0.797	16.995±0.106	260.633±0.443
300	80.547±0.306	318.133±0.799	17.144±0.106	260.986±0.445
400	88.597±0.231	342.486±0.876	25.628±0.133	278.415±0.544
500	93.919±0.177	362.869±0.922	34.772±0.153	293.323±0.615
600	97.469±0.138	380.327±0.950	44.353±0.169	306.404±0.669
700	99.898±0.109	395.546±0.969	54.229±0.181	318.075±0.710
800	101.61±0.09	409.003±0.982	64.309±0.191	328.616±0.744
900	102.85±0.07	421.047±0.991	74.535±0.199	338.229±0.771
1000	103.77±0.06	431.933±0.998	84.869±0.205	347.064±0.793

[(a)] Calculated with a symmetry number of 3; vibrational frequencies of 948, 451 and 299 (multiplicity = 1), and of 932, 342, and 197 $\mathrm{cm^{-1}}$ (multiplicity = 2); a molar mass of 182.357 $\mathrm{g{\cdot}mol^{-1}}$; a Tc-O bond distance of 1.70×10^{-10} m and Tc-Cl bond distance of 2.23×10^{-10} m.

The uncertainty limits are obtained by assuming $\Delta\nu_i = 5\ \mathrm{cm^{-1}}$ for 1.96 times their standard errors for all of the ν_i. The calculations for TcO_3Cl(g) agree well with those reported previously by Baran [76BAR]. We neglect the contributions of higher electronic levels reported for TcO_3Cl [78GUE/HOW] since their degeneracies are unknown. However, S°_m is affected by them by only $0.3\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ at 1000 K, and to a much lesser extent at lower temperatures. The effect of this approximation on S°_m is less than the variation due to uncertainties in ν_i values.

Gibson [91GIB] investigated the formation of gas phase technetium oxychlorides and oxyfluorides (Section V.4.1.3.2) by mass spectrometry. He used a sample of ^{99}Tc metal powder with a oxide coating, and studied its oxidation by ClF_3(g) from 573 to 923 K. A large number of ions were detected whose probable "parent" molecules were TcO_3Cl(g), $TcOCl_3$(g), TcO_2Cl_x(g) (with x = 2 or 3), $TcOF_2Cl$(g), and $TcOFCl_2$(g).

Some evidence of the formation of $TcOBr_3$(g) was given by Colton and Tomkins [68COL/TOM], but no thermodynamic data are available.

The vaporisation of an ill-defined solid technetium oxide was studied in the presence of Br_2(g) at partial pressures of about 10 Pa from ~373 to 1073 K [94GIB]. Gibson stated that their oxide was probably TcO_2(s) but it may also have contained some higher oxide. Various technetium ions were detected whose probable parent molecules were TcO_3Br(g), and either TcO_2Br_2(g) or TcO_2Br_3(g).

Gibson [94GIB] also investigated the formation of technetium oxyiodides. Direct reaction of the solid technetium oxide with I_2(g) produced only a small amount of volatilisation, but addition of O_2(g) to the vapour phase caused a substantial enhancement of the reaction. Obviously, I_2(g) alone was not a strong enough oxidising agent. The maximum yield of technetium oxyiodide ions occurred at ~1023 K, but the intensities of the mass spectrometric peaks were much lower that for the oxybromide system under comparable conditions, and most of the technetium was present instead as technetium oxide ions. The observed oxyiodide ions can all be accounted for by assuming that TcO_3I(g) was the parent molecule.

V.5 Group 16 (chalcogen) compounds and complexes

V.5.1 Sulphur compounds and complexes

V.5.1.1 Technetium sulphides

V.5.1.1.1 Binary sulphides

Addition of H_2S to 0.5 to 5.0 M HCl solutions of TcO_4^- yielded "complete precipitation" of a technetium sulphide. In 10 M HCl only a small fraction of technetium precipitated, in contrast to rhenium which had more complete precipitation under that condition [39PER/SEG]. The solid compound was dark black and had the chemical formula Tc_2S_7(s) [52COB/NEL, 52RUL/MEI]. The initial precipitate contained up to 20% excess sulphur, which was removed by extraction with CS_2 [52RUL/MEI]. Spitsyn and Kuzina [59SPI/KUZ] confirmed that this procedure yielded stoichiometric Tc_2S_7(s).

Tc_2S_7(s) was also prepared by treatment of acidic TcO_4^- solutions with sodium thiosulphate [77ECK/LEV] or thioacetamide [60AND]. Trace amounts of technetium can be co-precipitated as sulphides with certain second and third row transition metals [60AND]. Dissolution of Tc_2S_7(s) with ammoniacal H_2O_2(aq) solutions yielded NH_4TcO_4 solutions [52RUL/MEI].

Lee and Bondietti [83LEE/BON] studied the precipitation of technetium sulphide. Chemical analysis of the black precipitate by neutron activation yielded a composition of $TcS_{3.23}$(s) (or $Tc_2S_{6.5}$(s)), which is close to the expected composition of Tc_2S_7(s), (*cf.* Appendix A).

The retention of technetium by sulphide minerals, *eg*. stibnite (Sb_2S_3), pyrrhotite (FeS), pyrite (FeS_2), galena (PbS), and the sorption onto several minerals and synthetic compounds, *eg*. CdS(s), has been investigated by various authors [89BOC/BRÜ, 92EL-/GER, 95ZHU/ZHE]. A brief summary of each reference is given in Appendix A.

Amorphous TcS_2(am) has been obtained by heating Tc_2S_7(s) in the absence of O_2(g) [59BOY2]. Crystalline TcS_2(cr) was prepared by chemical transport along a temperature gradient in a sealed tube, with temperatures of 1423 and 1353 K at the two ends of the tube. An excess of sulphur, along with Cl_2(g), Br_2(g), or I_2(g) as a carrier gas, improved transport [71WIL/JEL]. TcS_2(cr) formed triclinic crystals.

Its structure is probably a distorted $Cd(OH)_2$-type cell. Differential thermal analysis experiments give no evidence for a structural change between 93 and 1423 K. Lamfers *et al*. [96LAM/MEE] performed a more detailed study of the crystal structure of TcS_2(cr). Their single-crystal X-ray structural determination was done using the same crystals prepared by Wildervanck and Jellinck [71WIL/JEL]. Lamfers *et al*. confimed Wildervanck and Jellinck's conclusion that its structure was a distorted $Cd(OH)_2$-type cell, but showed that the value of the angle γ in the earlier study was too small by about a factor of two. The lattice parameters and structural information of this compound are given in Table V.42 (see Section V.9). The unit cell parameters of the more recent study are to be preferred.

Tc_2S_7(s) that was heated to as low as 373 K in a Cl_2(g) stream reportedly was completely volatilised, and solids were collected in the cooler parts of the reaction tube [39PER/SEG]. The Cl_2(g) apparently functioned as a carrier gas for vapour phase transport.

McDonald and Cobble [62MCD/COB] measured combustion enthalpies for several rhenium sulphides, and they used these results to estimate $\Delta_f G^\circ_m$, $\Delta_f H^\circ_m$ and S°_m for TcS_2(cr), TcS_3(s), and Tc_2S_7(s). No direct thermodynamic data are available for these technetium sulphides. In addition, there are no reports of the preparation of TcS_3(s), so we shall not consider it further.

McDonald and Cobble [62MCD/COB] estimated the following values at 298.15 K: $\Delta_f H^\circ_m = -(223.8 \pm 41.0)$ kJ·mol^{-1}, $\Delta_f G^\circ_m = -(216.1 \pm 42.1)$ kJ·mol^{-1}, and $S^\circ_m = (71.1 \pm 31.6)$ J·K^{-1}·mol^{-1} for TcS_2(cr); and $\Delta_f H^\circ_m = -(615.0 \pm 57.4)$ kJ·mol^{-1}, $\Delta_f G^\circ_m = -(580.9 \pm 60.4)$ kJ·mol^{-1}, and $S^\circ_m = (175.7 \pm 63.2)$ J·K^{-1}·mol^{-1} for Tc_2S_7(s). These very conservative error estimates were made by this review. Experimental values are certainly needed for these quantities.

El-Wear, German, and Peretrukhin [92EL-/GER] studied the solubility of Tc_2S_7(s) in water. However, the experiments and the corresponding data analysis have serious limitations, (see Appendix A). Therefore, no attempt has been made to extract thermodynamic data from this study.

More recently Kunze *et al*. [96KUN/NEC] studied the precipitates formed in the reaction of 10^{-5} M NH_4TcO_4 with 3.2×10^{-4} to 5.1×10^{-3} M solutions of Na_2S. No precipitation was observed in water, apparently because of hydrolysis of the Na_2S; however, precipitation did occur when the pH was reduced below 3 by addition of HCl. Kunze *et al*. were not able to calculate a solubility product since much of the technetium in solution was present as a fine colloid that could not be removed by filtration.

Kunze *et al*. [96KUN/NEC] also studied the solubility of Tc_2S_7(s) in various concentrated brines at pH = 8 to 10. Solubilities of technetium after 150 days were typically 2×10^{-7} to 2×10^{-6} M in the presence of simulated waste glass, stainless steel, and UO_2; they were much lower at about 5×10^{-9} M in the presence of iron, zircaloy and UO_2. They also found that the UO_2 had no effect on the solubilities. As noted in that study, the low solubility is consistent with reduction of TcO_4^- to $TcO_2 \cdot xH_2O$(s), which becomes the solubility-limiting phase under these experimental conditions.

We note that calculation of solubility products for metal sulphides from the measured concentration of dissolved metal ion and the solution pH is fraught with difficulties. First, the sulphide ion resulting from this dissolution process is hydrolysed

almost completely to form the HS^- ion, and the second acid dissociation constant of H_2S(aq) is not accurately known. Furthermore, depending on the pH of the solution, additional hydrolysis may occur to form H_2S. Secondly, if the solution is made alkaline to increase the solubility of the metal sulphide, then a mixture of polysulphides of the general formula S_xS^{2-} can also form, which adds to the difficulties of calculating the equilibrium concentrations of S^{2-} or HS^-. See the discussion in reference [86MYE] for more information. The situation for dissolution of technetium sulphides is even more complicated because of formation of colloidal material [96KUN/NEC] and uncertainty about the exact chemical state or states of the dissolved technetium [92EL-/GER].

We note that calculation of solubility products for metal sulphides from the measured concentration of dissolved metal ion and the solution pH is fraught with difficulties. First, the sulphide ion resulting from this dissolution process is hydrolysed almost completely to form the HS-ion, and the second acid dissociation constant of H_2S(aq) is not accurately known. Furthermore, depending on the pH of the solution, additional hydrolysis may occur to form H_2S. Secondly, if the solution is made alkaline to increase the solubility of the metal sulphide, the difficulties of calculating the equilibrium concentrations of S_2^- or HS^-. See the discussion in reference [86MYE] for more information. The situation for dissolution of technetium sulphides is even more complicated because of formation of colloidal material [96KUN/NEC] and uncertainty about the exact chemical state or states of the dissolved technetium [92EL-/GER].

There are no reliable solubilities for Tc_2S_7(s) and the estimated thermodynamic values [62MCD/COB] are very uncertain. Additional experimental measurements are definitely needed.

V.5.1.1.2 Ternary sulphides

V.5.1.1.2.1 $M_10Tc_6S_14$(cr) (M = Rb, Cs)

Bronger *et al.* [93BRO/KAN] synthesised two ternary alkali metal technetium sulphides by reaction, at 1073 K for 10 to 16 hours, of Rb_2CO_3 or Cs_2CO_3 and metallic technetium with sulphur vapour in a flowing H_2(g) stream. The resulting black coloured rubidium and caesium compounds formed were $Rb_{10}Tc_6S_{14}$(cr) and $Cs_{10}Tc_6S_{14}$(cr); they are isostructural and contain isolated $Tc_6S_6S_8 = Tc_6S_{14}$ anion clusters. These compounds were found to be diamagnetic from 10 to 295 K, which is consistent with a 24-electron Tc_6 configuration and with Tc being in the +3 oxidation state.

These compounds crystallised in the fcc space group $Fm\bar{3}m$ with $a = (15.006 \pm 0.004) \times 10^{-10}$ m for $Rb_{10}Tc_6S_{14}$(cr) and $a = (15.619 \pm 0.004) \times 10^{-10}$ m for $Cs_{10}Tc_6S_{14}$(cr). The rhenium analogues of these compounds were also prepared.

No thermodynamic data are available for $Rb_{10}Tc_6S_{14}$(cr) or $Cs_{10}Tc_6S_{14}$(cr).

V.5.1.1.2.2 $K_4Tc_6S_12$(cr), $M_4Tc_6S_13$(cr) (M = Rb, Cs)

$K_4Tc_6S_{12}$(cr), $Rb_4Tc_6S_{13}$(cr), and $Cs_4Tc_6S_{13}$(cr) were synthesised by the reaction of technetium metal, K_2CO_3, Rb_2CO_3, or Cs_2CO_3, and sulphur in an Ar(g) atmosphere for 8 hours at 1073 K, [93BRO/KAN2]. The cooled melts were extracted with water

and ethanol, and well-formed shiny crystals of these solids were isolated.

The structure and lattice parameters of these solid phases are:

- $K_4Tc_6S_{12}$(cr), monoclinic, space group C2/c $a = (16.463 \pm 0.008) \times 10^{-10}$ m, $b = (9.667 \pm 0.006) \times 10^{-10}$ m, $c = (11.841 \pm 0.004) \times 10^{-10}$ m, and $\beta = (91.40 \pm 0.04)°$.
- $Rb_4Tc_6S_{13}$(cr) monoclinic, space group C2/c, $a = (9.745 \pm 0.004) \times 10^{-10}$ m, $b = (16.595 \pm 0.008) \times 10^{-10}$ m, $c = (13.913 \pm 0.006) \times 10^{-10}$ m, and $\beta = (99.83 \pm 0.04)°$.
- $Cs_4Tc_6S_{13}$(cr), monoclinic, space group C2/c, $a = (9.983 \pm 0.002) \times 10^{-10}$ m, $b = (17.120 \pm 0.008) \times 10^{-10}$ m, $c = (13.643 \pm 0.006) \times 10^{-10}$ m, and $\beta = (100.68 \pm 0.02)°$.

These compounds contain Tc_6S_8 clusters which are linked to the neighboring clusters by S or S_2 groups, the alkali metal cations being located in the interstices. Magnetic measurements indicated the presence of a weak temperature-independent paramagnetism. Bronger *et al.* [93BRO/KAN2] concluded that the Tc in these clusters was in the +3 oxidation state.

No thermodynamic data are available for these compounds.

V.5.1.1.3 Gaseous sulphides

Little is known of the existence, behaviour or stability of gaseous technetium sulphides. However, Langhoff *et al.* [89LAN/BAU] have performed theoretical calculations using two different approximation methods, giving calculated spectroscopic constants, the dissociation energy and dipole moment; there are no experimental results for comparison. The molecular parameters calculated by Langhoff *et al.* [89LAN/BAU], which are summarised in Table B.13 (*cf.* Appendix B), have been used to compute the ideal gas thermal functions of TcS(g), (see Table B.14 in Appendix B).

The values at 298.15 K, with estimated uncertainties, are:

$$S^\circ_m(\text{TcS, g, 298.15 K}) = (255.990 \pm 1.000)\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$C^\circ_{p,m}(\text{TcS, g, 298.15 K}) = (34.474 \pm 1.000)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

An approximate value for D_0(TcS, g) can be derived from the (adjusted) calculated value of 2.91 eV, given by Langhoff *et al.* [89LAN/BAU]. If this is multiplied by the same factor as is applicable to MoO(g) (see discussion in Section V.3.3.2) this becomes D_0(TcS, g) = (400 ± 60) kJ·mol^{-1}. After correction to 298.15 K, with our selected value for $\Delta_f H^\circ_m$ (Tc, g, 298.15 K) and the well-defined value of (277.17 ± 0.15) kJ·mol^{-1} for $\Delta_f H^\circ_m$ (S, g, 298.15 K) [89COX/WAG], this finally gives the selected value

$$\Delta_f H^\circ_m(\text{TcS, g, 298.15 K}) = (549^{+61}_{-72})\ \text{kJ·mol}^{-1}$$

The Gibbs energy of formation is calculated from the selected enthalpy of formation and entropy.

$$\Delta_f G^\circ_m(\text{TcS, g, 298.15 K}) = (491^{+61}_{-72})\ \text{kJ·mol}^{-1}$$

V.5.1.2 Technetium sulphates

Constant current electrolysis and potentiostatic reductions were performed for dilute aqueous TcO_4^- in the presence of SO_4^{2-}, but no details were provided [82PAQ/LIS]. Both Tc(III) and Tc(IV) were obtained, and spectroscopic evidence was found for complexes with sulphate in both valence states.

Spitsyn *et al.* [76SPI/KUZ] prepared a non-colloidal brown complex of technetium by electrolysis of TcO_4^- in aqueous H_2SO_4, followed by separation using electrophoresis. Oxidation of this complex to TcO_4^- in solution by use of Ce(IV) sulphate indicated a 3 e^- change per technetium, so Tc(IV) was present in the brown complex. Based on absorption spectrum measurements as a function of pH, they suggested the brown complex was $Tc(OH)_2(SO_4)_2^{2-}$ [76SPI/KUZ].

Ianovici *et al.* [81IAN/KOS] studied photolysis of 0.005 M $TcCl_6^{2-}$ in 1 M H_2SO_4, and they isolated both a pink cationic complex in several percent yield and a neutral species, both of unknown composition, using low-voltage electrophoresis.

Photolysis of 10^{-3} M $TcBr_6^{2-}$ in 1 M H_2SO_4 gave small amounts of pink and orange cationic species, larger amounts of a brown-orange neutral species, and a yellow anionic species [88COL/IAN].

Electrolysis of 0.006 M NH_4TcO_4 in 1 M $(NH_4)_2SO_4$ with added H_2SO_4 also gave either pink or brown solutions, with pink solutions usually (but not always) obtained at $0.5 \leq pH \leq 1.5$ [67VOL/HOL].

When TcO_4^- was reduced by $SnCl_2$ in the presence of potassium ferrocyanide and H_2SO_4, a transient blue species formed which then turned reddish-violet. After some time a dark violet compound, of uncertain composition, was precipitated [62AL-/MAG].

Several polarographic studies have been made for TcO_4^- reduction in H_2SO_4 and in alkaline SO_4^{2-} solutions. Reduction potentials for TcO_4^- in 0.25 M K_2SO_4, with H_2SO_4 or KOH added to obtain pH = 4 to 13, are essentially identical to the potentials for the first two reduction waves of TcO_4^- in KCl with added HCl or KOH at any specific pH value, although there are some differences at lower pH [63SAL/RUL]. This implies that SO_4^{2-} complexes of Tc(IV) and Tc(III) are weak or non-existent at $pH \geq 4$ owing to competition from hydrolysis.

Polarographic reduction of TcO_4^- in $NaHSO_4$-Na_2SO_4 mixtures at $pH \approx 1$ to 3.5 gave three reduction waves, with the first two being irreversible [63SAL/RUL, 79GRA/DEV, 78RUS/CAS].

The first reduction wave was 4 e^- to Tc(III), the second was apparently 7 e^- for TcO_4^- to metallic Tc [78RUS/CAS] or 3 e^- to Tc(III) [63SAL/RUL, 79GRA/DEV], and the third was a catalytic hydrogen discharge wave. The first two waves were diffusion controlled, and the second had a maximum.

Grassi, Devynck and Tremillon [79GRA/DEV] also performed similar measurements from pH = 1.5 to 13.0.

Broadly similar results were obtained by [90ZAK/BAG] in H_2SO_4 solutions at pH= 1 for TcO_4^- concentrations from 0.003 to 0.125 M, although they inferred that all three reductions were diffusion-controlled and that the first step involved a three-electron reduction to Tc(IV) species, which could not be further reduced to Tc.

Horányi and Bakos [93HOR/BAK, 94HOR/BAK] have also studied the reduction of TcO_4^- at gold and platinised gold electrodes in 1 molar H_2SO_4 solutions, and found, contrary to previous assumptions, that deposition of solid Tc species can occur at a constant rate without the formation of gaseous hydrogen, and that the average number of electrons involved in the intermediate reduction was 3.3.

The polarographic behaviour of TcO_4^- in aqueous Na_2SO_4 and Na_2SO_4-H_2SO_4 mixtures was very similar to its behaviour in ClO_4^- and $HClO_4$ solutions [70ZHD/KUZ]. This implies that reduced forms of technetium complexed little with sulphate.

Cyclic voltammetry of TcO_4^- in 0.5 to 1.5 M H_2SO_4 gave anodic and cathodic peaks that involved Tc(III) and Tc(IV) hydrous oxides. These potentials were concordant with results in HCl, $HClO_4$, NaOH, and other ionic media [74MAZ/MAG]. No well defined polarographic reduction waves were observed for the reduction of TcO_4^- in 2 to 10 M H_2SO_4 [59MAG/SCO, 60MIL/KEL].

Since none of the reduction waves for TcO_4^- in H_2SO_4 or $NaHSO_4 - Na_2SO_4$ solutions were reversible, and the nature of sulphate complexes of technetium not completely certain, no useful thermodynamic data can be derived from these reduction potentials.

The $K_2[Tc_2(SO_4)_4] \cdot 2H_2O$(cr) crystallised in the triclinic space P1 with $a = (7.522 \pm 0.004) \times 10^{-10}$ m, $b = (7.666 \pm 0.004) \times 10^{-10}$ m, $c = (7.684 \pm 0.004) \times 10^{-10}$ m, $\alpha = 101.63°$, $\beta = 100.25°$ and $\gamma = 112.32°$ [90KRY/GRI]. The following two solid dimeric Tc(III) complexes have been described and partially characterised using IR spectroscopy [98KRY], $K_2[Tc_2(SO_4)_4] \cdot 2H_2O$(cr) and $K_4(H_3O)_2[Tc_2(SO_4)_6]$(cr). No thermodynamic data are available for them.

V.5.2 Selenium and tellurium compounds

V.5.2.1 Binary selenides and tellurides

V.5.2.1.1 $TcSe_2$(cr), $TcTe_2$(cr)

Very little information is available for the selenides and tellurides of technetium. Reaction of technetium with these chalcogens in excess in a sealed reaction tube with a temperature gradient, and with Br_2(g) or I_2(g) as carriers, gave chemical transport of $TcSe_2$ or $TcTe_2$ to form crystals at the cool end of the tube. Temperatures at the two ends of the tube were 1353 and 1273 K for the selenide, and 1253 and 1113 K for the telluride [71WIL/JEL].

Single crystal X-ray determination for $TcTe_2$(cr) showed this compound had monoclinic symmetry with space group Cc or C2/c and $a = 12.522 \times 10^{-10}$ m, $b = 7.023 \times 10^{-10}$ m, $c = 13.828 \times 10^{-10}$ m, $\alpha = 90°$, $\beta = 101.26°$, and $\gamma = 90°$ [71WIL/JEL]. The unit cell was said to be similar to that of high-temperature $MoTe_2$, but with a doubling of the *a* and *b* axes.

$TcSe_2$(cr) seemed to be isostructural with TcS_2(cr), but the diffraction spots were too diffuse to allow determination of unit cell parameters [71WIL/JEL]. No thermodynamic data are available for $TcSe_2$(cr) or $TcTe_2$(cr).

V.5.2.1.2 Tc_2Se_7(s)

Müller and Diemann [69MÜL/DIE] reacted aqueous $KTcO_4$ with H_2Se(g) at pH = 7. The black amorphous precipitate, after having been washed with CS_2 and diethylether, was chemically analysed and found to be Tc_2Se_7(s). No further characterisation of this material was reported.

No thermodynamic data are available for Tc_2Se_7(s).

V.5.2.2 Ternary selenides

V.5.2.2.1 $M_4Tc_6Se_12$(s)(M= K, Rb), $Cs_4Tc_6Se_13$(cr)

Bronger *et al.* [93BRO/KAN2] reported the synthesis of several ternary technetium selenides. These were prepared by reacting K_2CO_3, Rb_2CO_3, or Cs_2CO_3, technetium metal, and selenium in a H_2(g) atmosphere for 8 hours at 1073 K. The cooled melts were extracted with water and ethanol, and well-formed shiny crystals of $K_4Tc_6Se_{12}$(cr), $Rb_4Tc_6Se_{12}$(cr), and $Cs_4Tc_6Se_{13}$(cr) were isolated. All three of these compounds crystallised in the monoclinic space group C2/c and the unit cell parameters are:

- $K_4Tc_6Se_{12}$(cr), $a = (17.165 \pm 0.004) \times 10^{-10}$ m, $b = (10.019 \pm 0.004) \times 10^{-10}$ m, $c = (12.301 \pm 0.004) \times 10^{-10}$ m, and $\beta = (91.42 \pm 0.02)°$.
- $Rb_4Tc_6Se_{12}$(cr), $a = (17.640 \pm 0.008) \times 10^{-10}$ m, $b = (10.092 \pm 0.002) \times 10^{-10}$ m, $c = (12.464 \pm 0.002) \times 10^{-10}$ m, and $\beta = (91.30 \pm 0.02)°$.
- $Cs_4Tc_6Se_{13}$(cr), $a = (10.275 \pm 0.004) \times 10^{-10}$ m, $b = (17.826 \pm 0.006) \times 10^{-10}$ m, $c = (14.161 \pm 0.008) \times 10^{-10}$ m, and $\beta = (100.89 \pm 0.04)°$.

The structural features of these compounds are essentially identical to those of the sulphur analogs, which are described in Section V.5.1.1.2.

No thermodynamic data are available for these compounds.

V.5.2.3 Organoselenium compounds

There are a number of studies on the synthesis and characterisation of organoselenium compounds of the type $(CH_3CH_2)_4NTcOL_2$, where L^{2-} represents $(CN)_2C{=}CSSe^{2-}$ [81SPI/JOH, 84ABR/SPI], $(CN)_2C{=}CSe_2^{2-}$, and $(CN)_2C{=}CS_2^{2-}$, [84ABR/SPI] as well as nitrido complexes of the type $TcNL_2$(aq) where $L^- = (CH_3CH_2)_2NCSe_2^-$ or $(CH_3CH_2)_2NCSSe^-$, [85ABR/SPI]. A compound with the formula $[Tc(CO)_3(SePh_2)Cl]_2$ has also been reported [68HIE/OPA2].

However, these studies are outside the scope of this review and will not be considered further.

V.6 Group 15 compounds and complexes

V.6.1 Nitrogen compounds and complexes

There are no experimental studies involving the thermodynamic properties for technetium nitrogen compounds, so this review summarised the preparative and corresponding structural data.

V.6.1.1 Technetium nitrides

V.6.1.1.1 TcN_m(cr) ($m \leq 0.76$)

When powdered technetium, prepared by reduction of NH_4TcO_4 with H_2(g), was heated to 670 to 1170 K in a nitrogen atmosphere, no reaction occurred [64TRZ/RUD]. However, powdered technetium reacted with ammonia at 970 to 1370 K to produce a face centred cubic phase TcN_m(cr) where $m \leq 0.76$ with a lattice constant $a =$ (3.980 to 3.985) $\times 10^{-10}$ m. They suggested that the "ideal" phase could actually be TcN(cr) with a NaCl-type structure [64TRZ/RUD].

Thermal decomposition of NH_4TcO_4 in argon yielded TcO_2(cr), but when NH_4TcO_4 was heated to 570 K in a NH_3-Ar mixture, a nitride was produced in both cases with $a = 3.970 \times 10^{-10}$ m [78VIN/KON3].

Thermal decomposition of $(NH_4)_2TcCl_6$ in argon began at 633 K and was complete by 728 K. For $(NH_4)_2TcBr_6$ decomposition began at 643 K and was complete by 758 K. A nitride phase was produced in both cases by their thermal decomposition. It had the composition $TcN_{0.75}$(cr) with $a = 3.980 \times 10^{-10}$ m, but when this $TcN_{0.75}$(cr) was heated to 770 K almost no nitrogen remained and the unit cell parameter was $a = 3.954 \times 10^{-10}$ m [78VIN/KON2, 83VIN/ZAI]. Heating the residue to even higher temperatures yielded technetium metal.

The corresponding thermal decomposition of $(NH_4)_2TcI_6$ yielded only metallic technetium [81VIN/KON]. Similarly, the thermal decomposition of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ in argon or argon-helium mixtures produced "TcN(cr)" around 673 to 733 K, with a unit cell parameter of $a = (3.945 \pm 0.006) \times 10^{-10}$ m and it was isostructural with TcC(cr) [87SPI/KUZ].

TcN_m(cr) is black, brittle, and insoluble in 30% H_2O_2(aq)-concentrated alkali. It dissolved in warm concentrated nitric acid [78VIN/KON2]. No thermodynamic data are available.

V.6.1.1.2 TcNX(cr) (X = F, Cl)

There are claims about the existence of "TcNF(cr)" produced by thermal decomposition of $(NH_4)_2TcF_6$ in argon, (see [66LAV/STE] in Appendix A). However, other authors [70COW/LOC] pointed out that this evidence was ambiguous, (*cf.* Appendix A). In addition, Spitsyn *et al.* [87SPI/KUZ] suggested that thermal decomposition of $(NH_4)_3Tc_2Cl_8 \cdot 2H_2O$ in argon or argon-helium mixtures yielded thermally unstable TcNCl around 633 to 723 K. It readily decomposed to "TcN(cr)" at higher temperatures.

It must be acknowledged that more direct evidence for TcNF(cr) and possibly TcNCl(cr) is desirable.

V.6.1.2 Technetium nitrates

Spitsyn, Kryuchkov and Kuzina [83SPI/KRY] reported the isolation and identification of the solid $TcO(NO_3)_3 \cdot H_2O(s)$. They described the aqueous acidic solutions of this substance as having neutral, anionic or cationic forms, depending on the concentration of added acid, which suggests that the solid substance could have a structure with ionic nitrate anions. However, they did not describe how the empirical formula of this proposed technetium oxynitrate compound was determined, and thus its actual stoichiometry and chemical nature are uncertain.

The TcO_4^- ion has been proposed as a co-ligand, along with nitrate, in various systems involved in the liquid-liquid extraction of TcO_4^- from aqueous solutions [75MAC, 79MAC/KAD, 81LIE/KRÜ, 81PRU, 87ROZ/ZAK, 89KAN/NEC, 90AKO/KRI]. These complexes were formulated generally as tributylphosphate solvates.

The polarographic reduction of NH_4TcO_4 was studied in various ionic media [65SPI/KUZ]. In HNO_3 solutions, this polarographic study provided no evidence for technetium nitrate complexes.

Nitrate salts of technetium complexes with various organic ligands have also been reported [64BEC/DYR, 86LIN/DAV] and also a nitrate salt of the $[Tc(dppe)_2Cl_2]^+$ cation which is solvated with a molecule of HNO_3 (see [88LIB/NOO] in Appendix A).

V.6.1.3 Other technetium nitrogen compounds and complexes

V.6.1.3.1 Technetium nitrido compounds

The preparation and properties of various technetium nitrido compounds have been the subject of extensive study. They are usually prepared by the reduction of TcO_4^- with sodium azide, NaN_3, in acidic solutions.

Almost no thermodynamic data are available for these nitrido compounds, but they are unlikely to form under normal environmental conditions. However, if they are formed, they are likely to persist since the Tc≡N group is very stable against chemical attack, even when it undergoes oxidation-reduction ($TcN^{2+} \rightarrow TcN^{3+}$) or ligand substitution reactions. In addition, the technetium nitrido group is preserved during most reduction reactions, as when the $[TcNCl_4]^-$ or $[TcNBr_4]^-$ ions, which contain the TcN^{3+} group, undergo ligand exchange/reduction with certain "soft" ligands, such as thiols or phosphines, to produce TcN^{2+} complexes [86BAL/BON, 94BAL].

The great stability of Tc≡N during chemical reactions and oxidation-reduction holds for ^{99}Tc, but not for ^{99m}Tc. Alagui *et al*. [89ALA/APP] found that $^{99m}TcNCl_4^-$ spontaneously converted to $^{99m}TcO_4^-$ at pH = 4 and higher pHs, by way of an unknown intermediate, due to radiolytic effects. This reaction reached completion within 30 minutes for pH ≥ 5.

Descriptions of halonitridotechnetium species such as

- $TcNF_4^-$ [89BAL/BOA],

Table V.28: Experimental equilibrium constants reported by [90KIR/ABR, 91KÖH/KIR] for the replacement of Cl^- by Br^- in $TcNBr_nCl_{4-n}^-$ at 295 K. The constants refer to the following ligand exchange reaction:

$$TcNBr_nCl_{4-n}^- + Br^- \rightleftharpoons TcNBr_{n+1}Cl_{3-n}^- + Cl^-$$

Ionic Strength	K_{n+1}	K_{n+1} [(a)]	K_{n+1} [(b)]
8 M	K_1	0.78	0.88
8 M	K_2	0.47	0.69
8 M	K_3	0.30	0.53
8 M	K_4	0.12	0.22

[(a)] Based on reaction of Br^- with $TcNCl_4^-$

[(b)] Based on reaction of Cl^- with $TcNBr_4^-$

- $TcNCl_4^-$ [84BAL/BOA, 86BAL/BON, 87BAL/BOA, 88BAL/BOA, 89BAL/BOA],
- $TcNCl_5^{2-}$ [85ABR/SPI, 86BAL/BON, 88BAL/BOA],
- $TcNBr_4^-$ [84BAL/BOA, 85BAL/BON, 87BAL/BOA],
- $TcNCl_3F^-$, $TcNFCl_2F^-$ and $TcNClF_3^-$ [89BAL/BOA]

are available, but no stability constants can be derived from the reported information.

The halide ligands are somewhat labile in these nitrido compounds, [86BAL/BON, 86KIR/STA]. Kirmse and coworkers [90KIR/ABR, 91KÖH/KIR] reported equilibrium constants at 295 K for formation of mixed halide ligand complexes of the type $TcNBr_nCl_{4-n}^-$, based on the ligand exchange of Br^- with $TcNCl_4^-$ and of Cl^- with $TcNBr_4^-$. These equilibrium constants were determined by use of EPR spectra for solutions of TcN^{3+} in HCl-HBr mixtures, which required use of the assumption that EPR peak areas are proportional to the concentrations of the individual complexes. Table V.28 summarises these equilibrium constants. The ionic strengths in these studies [90KIR/ABR, 91KÖH/KIR] are too high for a valid SIT extrapolation (*cf.* Appendix C), and no thermodynamic data can be derived.

Baldas and coworkers have extensively investigated the properties of a nitridotechnetic(VI) acid compound along with the formation of salts and the de-dimerisation reactions of this compound, *cf.* Appendix A [89BAL/BOA, 90BAL/BOA, 91BAL/BOA, 93BAL/BOA2, 93BAL/BOA]. No thermodynamic data can be extracted.

Mixed halide-azido complexes containing the Tc(VI) nitrido group, *e.g.*, $TcNCl_{4-n}(N_3)_n^-$ and $TcNBr_{4-n}(N_3)_n^-$ with $n = 0, 1, ..., 4$, have been reported [90ABR/KÖH].

Two salts of the Tc(VII) chloronitridodiperoxo complex $TcNCl(O_2)_2^-$ and several additional Tc(VII) nitridodiperoxo complexes have been investigated by Baldas and Colmanet [89BAL/COL2, 90BAL/COL]. Technetium nitrido salts containing cyanide have also been reported by Baldas *et al.* [90BAL/BOA2], *cf.* Section V.7.1.3.

In addition, there are several studies on the synthesis and characterization of technetium nitrido compounds containing various organic ligands [81KAD/LOR, 88ABR/LOR, 88BAL/COL, 90KIR/KÖH, 90KÖH/KIR, 91BAL/BOA2, 91KÖH/KIR, 91KÖH/KIR2, 93ABR/WOL].

The application of EPR spectroscopy in elucidating the properties of nitrido, nitrosyl and thionitrosyl complexes of Tc(II) and Tc(VI), the two valency states for which well-resolved EPR spectra can be obtained at convenient temperatures, has been recently reviewed by Abram and Kirmse [93ABR/KIR]. They summarise studies concerning structural characterisation and bonding parameters and discuss the use of EPR spectra for monitoring chemical reactions.

Structural parameters for some nitrido compounds are summarised in Table V.29.

V.6.1.3.2 Nitrite and ammonia salts and complexes

Koltunov and Gomonova [88KOL/GOM] studied the oxidation of Tc(IV) to TcO_4^- by HNO_2 in $HClO_4$ solutions at 298 K. According to the authors, the rate-limiting step may have been transfer of a hydroxyl group from the HNO_2 to the TcO^{2+} ion to form the intermediate species $HTcO_2^{2+}$. No complex between Tc and NO_2^- was suggested.

Solutions of $NaNO_2$ in H_2SO_4, HCl, or H_2SO_4-H_3PO_4 mixtures did not reduce TcO_4^- even with heating [70RUL/BOY]. In fact, dilute solutions of HNO_2 in 1 to 4 M HCl oxidised Tc(V) oxychlorides to TcO_4^- [84KOL/GOM3].

Heitzmann *et al*. [81HEI/YAN] studied the reduction of 3×10^{-3} M NH_4TcO_4 in 6 M HCl in the presence of excess $NaNO_2$. They obtained greenish-yellow solutions upon addition of a reducing agent (ascorbic acid, KI, $SnCl_2$, or $FeSO_4$). The authors reported that ESR spectra for solutions prepared by reduction with ascorbic acid or KI were identical to ESR spectra for solutions prepared with hydroxylamine hydrochloride (instead of the $NaNO_2$) plus reducing agent. Since reduction of TcO_4^- by hydroxylamine hydrochloride is known to produce nitrosyl complexes [87LAT/THO], this implies that reduction of TcO_4^- by a reducing agent in acidic NO_2^- solutions yielded nitrosyl complexes also.

Polarographic studies on the reduction of TcO_4^- in various ionic media in the presence of NH_4^+ ions have been reported [60MIL/KEL, 65SPI/KUZ, 70SPI/KUZ, 79DAV], but no evidence for the formation of ammonia complexes of technetium was observed.

Complexes of technetium that contain ammonia ligands along with a nitrosyl ligand are described in Section V.6.1.3.5.

V.6.1.3.3 Hydrazine complexes and salts

Several studies have been reported for the reduction of TcO_4^- by hydrazine in solutions of aqueous alkali [56GER, 67RUL/PAC2, 69MAJ/PAC, 77GĂL/BRA]. In three of these studies it was reported that the initial reduction of TcO_4^- is to TcO_4^{2-}, which then reacted with water and disproportionated into TcO_4^- and hydrated TcO_2 [56GER, 67RUL/PAC2, 69MAJ/PAC]. Attempts to isolate this TcO_4^{2-} as a

Table V.29: Crystal structure parameters of nitrido compounds [a].

Compound	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
		Tc(V)			
$(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$	mono. [b]	$P2_1/n$	4	$a = 17.107 \pm 0.010$ $b = 19.965 \pm 0.014$ $c = 15.473 \pm 0.010$	[90BAL/BOA2]
$TcN(AsPh_3)_2Cl_2$	mono. [c]	I2/a	4	$a = 15.823 \pm 0.008$ $b = 9.638 \pm 0.004$ $c = 22.490 \pm 0.014$	[91BAL/BOA2]
cis-$[TcNBr(bipy)_2]_2[TcBr_4]\cdot 0.5CH_3OH$	mono. [d]	$P2_1/c$	4	$a = 9.143 \pm 0.004$ $b = 35.014 \pm 0.014$ $c = 15.581 \pm 0.006$	[89ARC/DIL] [92ARC/DIL]
		Tc(VI)			
$AsPh_4TcNCl_4$	tetrag.	P4/n	2	$a = 12.707 \pm 0.004$ $c = 7.793 \pm 0.002$	[84BAL/BOA]
$AsPh_4TcNBr_4$	tetrag.	P4/n	2	$a = 12.875 \pm 0.004$ $c = 7.992 \pm 0.002$	[85BAL/BON]
$[\{TcN(S_2CNEt_2\}_2(\mu\text{-}O)_2]$	triclin. [e]	$P\bar{1}$	2	$a = 8.069 \pm 0.004$ $b = 9.224 \pm 0.004$ $c = 14.017 \pm 0.006$	[90BAL/BOA]
$(AsPh_4)_4[Tc_4N_4O_2(ox)_6]$	mono. [f]	$P2_1/n$	4	$a = 14.433 \pm 0.002$ $b = 13.229 \pm 0.002$ $c = 27.020 \pm 0.002$	[88BAL/COL]
		Tc(VII)			
$Cs[TcNCl(O_2)_2]$	ortho.	$P2_12_12_1$	4	$a = 6.376 \pm 0.004$ $b = 8.552 \pm 0.004$ $c = 11.406 \pm 0.006$	[89BAL/COL2]
$(AsPh_4)_2[\{TcN(O_2)_2\}_2(ox)]\cdot 2(CH_3)_2CO$	mono. [g]	C2/c	8	$a = 34.49 \pm 0.02$ $b = 14.684 \pm 0.006$ $c = 22.776 \pm 0.012$	[91BAL/COL]

[a] No attempts were made to give a comprehensive coverage of complexes with organic ligands.
[b] $\beta = (101.70 \pm 0.04)°$
[c] $\beta = (101.91 \pm 0.04)°$
[d] $\beta = (105.96 \pm 0.04)°$
[e] $\alpha = (107.77 \pm 0.04)°$, $\beta = (102.05 \pm 0.04)°$ and $\gamma = (93.80 \pm 0.04)°$
[f] $\beta = (92.90 \pm 0.02)°$
[g] Poorly crystalline sample, with $\beta = (107.18 \pm 0.06)°$

barium salt did not give reproducible results [67RUL/PAC2, 69MAJ/PAC], but a salt of TcO_4^{2-} has since been prepared electrochemically under anhydrous conditions [74SCH/AST, 76AST/SCH].

In another study [77GĂL/BRA], however, it was claimed that the initial reduction of TcO_4^- by hydrazine involved 2 e^- per technetium rather than 1 e^-. Guedes de Carvalho [58CAR] similarly found that aqueous hydrazine sulfate at pH > 8 rapidly reduced TcO_4^- to an insoluble black compound, which presumably was $TcO_2 \cdot x H_2O$(s). In $HClO_4$ solutions, hydrazine ultimately reduced TcO_4^- completely to hydrolysed forms of Tc(IV) [69GOR/KOC]. Reduction of TcO_4^- by hydrazine in aqueous H_2SO_4 yielded dissolved Tc(IV) [56GER]. No complexes between technetium and hydrazine were suggested in those studies.

There is no direct evidence for TcO_4^{2-} being formed as an intermediate in the reduction of TcO_4^-, as proposed in several of the cited studies [56GER, 67RUL/PAC2, 77GĂL/BRA]. However, TcO_4^{2-} has clearly been identified in electrochemical reduction of TcO_4^- using fast-scan cyclic voltammetry [78DEU/HEI, 80HUR] and pulse polarography [87FOU/AIK]. In these two studies it was demonstrated that TcO_4^{2-} is highly unstable with regard to disproportionation, with a lifetime of only tens of milliseconds. In the presence of a reducing agent such as hydrazine, the reduction of TcO_4^- to Tc(V) and Tc(IV) is probably too rapid to allow TcO_4^{2-} to be observed as an intermediate species.

Kinetic studies of the reduction of technetium (Tc(VII) and Tc(IV)) with hydrazine in HCl medium have been perfomed by Koltunov and coworkers, [86KOL/GOM, 88KOL/GOM2]. The authors found the formation of chloride complexes of technetium and they only invoked the formation of $N_2H_5TcO_4$ ion pairs as intermediate products.

The oxidation of hydrazine by aqueous HNO_3 [82AKO/KRI, 84GAR/WIL, 88ZEL, 88ZIL/LEL, 93KEM/THY] and by ClO_4^- ions [93KEM/THY2] using technetium as a catalyst has been studied. Various complex reaction schemes were proposed but the formation of technetium hydrazine species was not observed.

Frlec, Selig and Hyman [67FRL/SEL] reacted $N_2H_4 \cdot 2HF$ with TcF_6 in anhydrous HF. They thus prepared a yellowish-orange hydrazinium salt with the empirical composition $N_2H_6(TcF_6)_2$, and brown coloured $N_2H_6TcF_6$. This $N_2H_6(TcF_6)_2$ decomposed to $N_2H_6TcF_6$ at about room temperature in the presence of excess fluoride. The magnetic moment of $N_2H_6TcF_6$ was 3.79 B.M. at 300 K, its crystals had a cubic unit cell with $a = 10.48 \times 10^{-10}$ m, and it was slightly soluble in an excess of HF. IR spectra were also reported. $N_2H_6(TcF_6)_2$ would be expected to react readily with water, with the TcF_6^- ion being converted to TcF_6^{2-} and TcO_4^-.

V.6.1.3.4 Molecular dinitrogen complex

There are several studies on the synthesis, characterisation and general properties of technetium complexes containing molecular dinitrogen in their structures. These complexes are of the type $TcCl(N_2)(dppe)_2$ [94BUR/BRY], TcN_2L_2 [79KAD/LOR], $HTc(N_2)L_2$ [82STR/BAZ], $HTc(N_2)(dppe)_2$ [92KAD/FIN], and $[\{HB(3,5\text{-}(CH_3)_2C_3N_2)_3\}Tc(CO)_2]_2(\mu\text{-}N_2)$, [93JOA/APO]. A brief summary of

each reference is given in Appendix A.

V.6.1.3.5 Nitrosyl complexes

In 1963, Eakins, Humphreys and Mellish [63EAK/HUM] reported the preparation of a crystalline complex which they formulated as "$[Tc(NH_2OH)_2(NH_3)_3(H_2O)]Cl_2$". A later detailed study by Armstrong and Taube [76ARM/TAU] leaves no doubt that the complex previously prepared by Eakins, Humphreys and Mellish was actually *trans*-$[Tc(NH_3)_4(NO)(OH_2)]Cl_2$, (see discussion on Ref. [76ARM/TAU] in Appendix A). In most nitrosyl complexes the nitrosyl group is assigned a +1 charge, so Armstrong and Taube assumed their complex contained Tc(I). Their results from potentiometric pH titration indicate that the H_2O in *trans*-$Tc(NH_3)_4(NO)(OH_2)^{2+}$ behaved as an acid with $pK_a = 7.3$ at I = 0.01 M and 298 K.

Armstrong and Taube [76ARM/TAU] also investigated the oxidation of this complex by electrochemical or chemical methods (Ce^{4+} or MnO_4^-) in acidic solutions. This yielded the complex of Tc(II), *trans*-$[Tc(NH_3)_4(NO)(OH_2)]Cl_3$. Results from cyclic voltammetry in 3.0 M trifluoromethanesulphonate indicated that water in the aqueous complex $[Tc(NH_3)_4(OH_2)]^{3+}$ behaved as an acid with $pK_a \approx 2.0$. With regard to the thermodynamic data, there is insuficient information to calculate reliable values, (*cf.* Appendix A).

ESR spectra for these nitrosyl chloride salts have been reported by Yang *et al.* [82YAN/HEI].

Radonovich and Hoard [84RAD/HOA] published the results of their crystal structural determination for *trans*-$[Tc(NH_3)_4(NO)(OH_2)]Cl_2$, (see Table V.30). The Tc-NO linkage was nearly linear with a bond distance of $(1.716 \pm 0.004) \times 10^{-10}$ m. They found that the charge on the nitrosyl group was about -0.5 e$^-$, so this complex contained Tc with a valence of about +2.5.

Holloway and Selig [68HOL/SEL] investigated reactions of nitric oxide, nitrosyl fluoride, and nitryl fluoride with solid TcF_6. The reactions produced $(NO)TcF_6$, $(NO)_2TcF_8$, and $(NO_2)TcF_7$, as indicated by elemental analyses, IR spectra, and magnetic susceptibilities. They were ionic compounds, and they were hydrolysed by water to form aqueous TcF_6^{2-}. Hugill and Peacock [66HUG/PEA] reported a nearly identical preparation for $(NO)TcF_6$ by reaction of TcF_6 with NO at 228 K, but found that more than one solid compound was produced. Structural parameters of $(NO)TcF_6$ are given in Table V.30.

The original preparation of $TcBr_4(NO)^-$ was attributed to Kuzina, Oblova and Spitsyn [72KUZ/OBL] in several review articles [83DEU/LIB, 82CLA/FAC], but that report was concerned with organic amine chloride complexes of technetium, rather than nitrosyl bromide complexes.

ESR spectra have been reported for frozen solutions of $Tc(NCS)_5(NO)^{2-}$, $TcCl_5(NO)^{2-}$, $TcBr_4(NO)^-$, and $TcI_4(NO)^-$ [88ABR/KIR]. Kirmse and Abram [89KIR/ABR] dissolved mixtures of the *n*-$(C_4H_9)_4N^+$ salts of $TcCl_5(NO)^{2-}$ and $TcBr_4(NO)^-$, $TcCl_5(NO)^{2-}$ and $TcI_4(NO)^-$, and $TcBr_4(NO)^-$ and $TcI_4(NO)^-$ in 10:1, 3:1, 1:1, 1:3 and 1:10 mole ratios in acetone. After allowing ligand exchange to occur, they measured ESR spectra for their solutions at 295 K and of

their frozen solutions at 130 K. They were able to assign the spectra to the various $TcBr_{4-x}Cl_x(NO)^-$, $TcCl_xI_{4-x}(NO)^-$, and $TcBr_xI_{4-x}(NO)^-$ complexes with $x = 0$, 1, 2, 3, and 4, and to $TcCl_4I(NO)^{2-}$.

Several organic technetium nitrosyl complexes with various different ligands have been prepared [76ARM/TAU, 81ORV, 82JON/DAV, 86LIN/DAV, 87BRO/NEW, 88BRO/NEW2, 88BRO/NEW, 90VRI/COO, 96BLA/NIC]. Four of these complexes have been structurally characterised, see Table V.30, [86LIN/DAV, 87BRO/NEW, 88BRO/NEW2, 88BRO/NEW, 90VRI/COO].

A fairly general method has been described for the synthesis of complexes of technetium containing both tertiary phosphine and nitrosyl ligands [76FER/HEV, 83KIR/LOR, 87ABR/KIR, 89PEA/DAV]. This method involves displacing a tertiary phosphine group from a technetium complex, and replacing it with a nitrosyl group.

Several nitrosyl complexes of technetium containing hydrido and deuterido ligands with organic ligands have also been reported [90ROS/DAV].

V.6.1.3.6 Thionitrosyl complexes

The preparation of several thionitrosyl complexes has been described in the literature [84BAL/BON, 85KAD/LOR, 87ABR/HAR, 87ABR/KIR, 88ABR/KIR, 90KAD/LOR, 90LU/CLA, 91HIL/HÜB]. These complexes are chemical analogues of the nitrosyl complexes. Structural determination for four of these complexes [84BAL/BON, 90KAD/LOR, 90LU/CLA, 91HIL/HÜB] indicates that the thionitrosyl ligand bonds to the technetium by way of the nitrogen atom, as in nitrosyl complexes.

Table V.30 contains a summary of the crystal structure information for nitrosyl and thionitrosyl complexes of technetium. There are no thermodynamic data for the thionitrosyl complexes.

V.6.2 Phosphorus compounds and complexes

V.6.2.1 Phosphorus compounds

Compounds that are formed between technetium and phosphorus were first described in 1982 [82RÜH/JEI2, 82RÜH/JEI]. Six different solid technetium phosphides were prepared by reaction of technetium with red phosphorus at 1220 K either using tin as a flux or iodine as a mineraliser. Samples prepared with a tin flux were subsequently treated for one day with dilute HCl to dissolve away the tin matrix. Three of these phosphides were characterised by X-ray diffraction: Tc_3P(cr), TcP_3(cr) and TcP_4(cr). TcP_3(cr) was black with a metallic lustre and was not attacked by boiling HCl [82RÜH/JEI].

The oxidation state of Tc was +2 in TcP_4(cr) and +3 in TcP_3(cr). Three other phases were found but not identified [82RÜH/JEI2]. They have the composition TcP_q(s), with q approximately 0.7, 1.2, and 2.0. Thermodynamic data have not been reported for any of these phosphides.

Dietrich and Jeitschko [86DIE/JEI] later determined the structure of one of the three previously uncharacterised phases, Tc_2P_3(cr). It was prepared by the tin-flux method.

Table V.30: Crystal structure parameters of nitrosyl and thionitrosyl complexes.

Complex	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
$(NO)TcF_6$	cubic			$a = 10.09$	[66HUG/PEA]
trans-$[Tc(NH_3)_4(NO)(OH_2)]Cl_2$	mono.[a]	$P2_1/m$	2	$a = 6.858 \pm 0.004$ $b = 10.579 \pm 0.006$ $c = 6.646 \pm 0.004$	[84RAD/HOA]
$[TcBr_2(NO)\{CNC(CH_3)_3\}_3]$	ortho.	$P2_1cn$	4	$a = 10.985 \pm 0.004$ $b = 14.250 \pm 0.004$ $c = 14.677 \pm 0.004$	[86LIN/DAV]
$TcCl(NO)(tmbt)_3$	mono. [b]	C2/c	8	$a = 24.420 \pm 0.010$ $b = 14.701 \pm 0.008$ $c = 17.500 \pm 0.008$	[90VRI/COO]
$(n\text{-}C_4H_9)_4N[TcCl_4(NO)(CH_3OH)]$	mono. [c]	$P2_1/n$	4	$a = 11.350 \pm 0.020$ $b = 11.450 \pm 0.010$ $c = 22.154 \pm 0.020$	[87BRO/NEW]
$AsPh_4[TcCl_3(NO)(acac)]$	triclin. [d]	P1	2	$a = 10.261 \pm 08$ $b = 11.261 \pm 0.020$ $c = 13.686 \pm 0.020$	[88BRO/NEW2] [88BRO/NEW]
$[TcCl_2(NS)\{S_2CN(CH_2CH_3)_2\}_2]$	ortho.	Pcmm	8	$a = 8.936 \pm 0.002$ $b = 15.681 \pm 0.002$ $c = 28.445 \pm 0.014$	[84BAL/BON]
$[TcCl_3(NS)\{PPh(CH_3)_2\}\{POPh(CH_3)_2\}]$	ortho.	$P2_12_12_1$	4	$a = 10.513 \pm 002$ $b = 14.274 \pm 0.004$ $c = 15.187 \pm 0.004$	[90KAD/LOR]
mer-$[TcCl_2(NS)(picoline)_3]\cdot CHCl_3$	ortho.	$Pna2_1$	4	$a = 19.628 \pm 0.002$ $b = 11.848 \pm 0.006$ $c = 11.332 \pm 0.008$	[90LU/CLA]
mer-$[TcCl_2(NS)\{PPh(CH_3)_2\}_3]$	mono.[e]	$P2_1/c$	4	$a = 9.4630 \pm 0.0012$ $b = 18.6904 \pm 0.0018$ $c = 16.1676 \pm 0.0012$	[91HIL/HÜB]

[a] $\beta = (94.01 \pm 0.04)^\circ$

[b] Here "tmbt" denotes the 2,3,5,6-tetramethylbenzenethiol ligand: $\beta = (93.50 \pm 0.04)^\circ$

[c] $\beta = (91.5 \pm 0.4)^\circ$

[d] Here "acac" denotes the acetylacetonato ligand $C_5H_7O_2$; a pentane-2,4-dionato is also known: $\alpha = (101.7 \pm 1.0)^\circ$, $\beta = (91.9 \pm 1.0)^\circ$ and $\gamma = (97.3 \pm 1.0)^\circ$

[e] $\beta = (93.467 \pm 0.008)^\circ$

Determination of the structure was rather difficult because all of their crystals were twinned, and because of the presence of a superstructure.

Structural parameters of Tc_3P(cr), TcP_4(cr), TcP_3(cr), and Tc_2P_3(cr) are given in Table V.31.

Table V.31: Structural information for technetium phosphorus and arsenic compounds.

Compound	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
Tc_3P	tetragonal[(a)]		8	$a = 9.568 \pm 0.010$ $c = 4.736 \pm 0.006$	[82RÜH/JEI2]
TcP_4	orthorhombic[(b)]		8	$a = 6.238 \pm 0.002$ $b = 9.215 \pm 0.006$ $c = 10.837 \pm 0.006$	[82RÜH/JEI2]
TcP_3	orthorhombic	Pnma	4	$a = 15.359 \pm 0.010$ $b = 3.092 \pm 0.002$ $c = 5.142 \pm 0.004$	[82RÜH/JEI2]
Tc_2P_3	triclinic[(c)]	$P\bar{1}$	4	$a = 6.266 \pm 0.002$ $b = 6.325 \pm 0.002$ $c = 7.683 \pm 0.004$	[86DIE/JEI]
Tc_2As_3	triclinic[(d)]	$P\bar{1}$	4	$a = 6.574 \pm 0.002$ $b = 6.632 \pm 0.002$ $c = 8.023 \pm 0.004$	[85JEI/DIE]
$[Tc(diars)_2Cl_4]PF_6$	orthorhombic	Fddd	8	$a = 13.821 \pm 0.008$ $b = 21.159 \pm 0.016$ $c = 21.227 \pm 0.036$	[80GLA/WHI]
$[Tc(diars)_2Cl_2]Cl$	monoclinic[(e)]	$P2_1/c$	2	$a = 9.354 \pm 0.010$ $b = 9.662 \pm 0.004$ $c = 15.341 \pm 0.008$	[80ELD/WHI]
$[Tc(diars)_2Cl_2]ClO_4$	monoclinic[(f)]	C2	2	$a = 13.001 \pm 0.020$ $b = 10.409 \pm 0.006$ $c = 11.796 \pm 0.016$	[80ELD/WHI]

[(a)] Fe_3P-type structure.
[(b)] ReP_4-type structure.
[(c)] $\alpha = (96.79 \pm 0.02)°$, $\beta = (101.76 \pm 0.02)°$ and $\gamma = (104.34 \pm 0.02)°$.
[(d)] $\alpha = (95.69 \pm 0.02)°$, $\beta = (102.03 \pm 0.02)°$ and $\gamma = (104.31 \pm 0.04)°$.
[(e)] $\beta = (98.75 \pm 0.12)°$.
[(f)] $\beta = (114.50 \pm 0.30)°$.

V.6.2.2 Phosphorus complexes

A number of studies have been reported in which redox potentials or related data were given for inorganic oxyphosphorus(V) complexes of technetium. These include phosphate, pyrophosphate, and tripolyphosphate complexes. Some of these complexes contained hydroxide or halide ligands, and some may have been dimers or higher order polymers. Unfortunately, almost no structural data are available for any of these com-

plexes, and the stoichiometry is not completely known for any of the aqueous complexes. Oxyphosphorus(V) complexes that also contain $SnCl_q^{2-q}$, Sn^{2+}, or Sn^{4+} are described in Section V.7.3. A number of solid organotechnetium phosphine, phosphonate, phosphonite, and phosphonium complexes have been prepared and structurally characterised. Three recent reviews tabulated structural data for them [82BAN/MAZ, 83DEU/LIB, 87MEL/LIE], and one of them, Deutsch *et al*. [83DEU/LIB] tabulated the methods of synthesis.

In several aqueous media a reversible or nearly reversible redox potential was observed. Although the valences of the oxidised and reduced forms of technetium are known, the stoichiometries of these complexes are not. Thus, no thermodynamic data can be derived.

V.6.2.2.1 Phosphate complexes

There are several studies available in the literature on technetium complexation by phosphate anions. Most of these studies were performed by electrochemical reduction of TcO_4^- in phosphate solutions [58THO, 60MIL/KEL, 67RUL/PAC2, 78STE/MEI, 82PAQ/LIS]. There are some indications on the formation of Tc(III) and Tc(IV) phosphate complexes but no single species has been identified.

Mazzochin *et al*. [74MAZ/MAG] reduced TcO_4^- to solid hydrous oxides on platinum by means of cyclic voltammetry. They identified the solid precipitate as $TcO_2 \cdot xH_2O$(s) for pH $>$ 3 and a Tc(III)/Tc(IV) hydrous oxide mixture at pH $<$ 3. Solutions of TcO_4^- in NaH_2PO_4 and Na_2HPO_4 mixtures at various pH values gave anodic and cathodic peak potentials that were consistent with those for solutions containing no complex forming ions. Thus phosphate complexes cannot be very significant under these conditions.

Polarographic measurements have been reported for TcO_4^- in aqueous phosphate solutions at several pH values [60MIL/KEL, 63SAL/RUL, 78RUS/CAS]. The first reduction wave was diffusion-controlled and irreversible for acidic to neutral pH values, so no thermodynamic data are obtained. Maxima were generally found during polarographic reduction of TcO_4^- solutions and mixtures of TcO_4^- and Tc(IV) with phosphate in HCl or in H_3PO_4(aq), which made the determination of limiting currents unreliable [72HOD/SIL].

V.6.2.2.2 Pyrophosphate complexes

The chemistry of technetium in the presence of pyrophosphate and simple organic diphosphonate ligands is of interest mainly because these complexes are used in nuclear medicine. They are generally prepared by reduction of aqueous TcO_4^- (^{99m}Tc) with Sn^{2+} in the presence of the appropriate ligand [63SAL/RUL, 79RUS/CAS2, 79RUS/CAS, 83MIL, 78STE/MEI]. No solid pyrophosphate complex has been characterised (see Ref. [78STE/MEI] in Appendix A).

Polarographic experiments by Miller, Kelley and Thomason [60MIL/KEL], and Russell and coworkers [78RUS/CAS, 79RUS/CAS] have also been reported (*cf.* Appendix A).

Russell and Bischoff [84RUS/BIS] investigated the ionic charge on technetium

pyrophosphate complexes at various pH values, *cf.* Appendix A. Two principal technetium pyrophosphate complexes were separated by ion-exchange chromatography. The authors reported the following conclusions:

- Increasing the electrolyte concentration decreased the retention times of the two technetium pyrophosphate complexes, and also of a reference ion species with a charge of -3. This similar behaviour implies that the technetium pyrophosphate complexes also have negative charges.

- At any specific pH value the charges on the two technetium pyrophosphate complexes were not very different, but the size of these charges increased with an increase in pH.

Their derived values of the charges on these two complexes are -4.5 ± 0.5 and -4.9 ± 0.5 at pH $= 4.3$, and -11.2 ± 1.3 and -10.1 ± 1.0 at pH $= 7.0$. Because of the difficulties of such measurements, and because of the presence of other solutes in these solutions, we believe these uncertainty limits should be doubled. The stoichiometries of these complexes are unknown, but the magnitude of the charges at pH $= 7.0$ suggests that they are polymeric. It is not known whether tin is incorporated into these complexes under the experimental conditions.

V.6.2.2.3 Tripolyphosphate complexes

Terry and Zittel [63TER/ZIT] studied the coulometric reduction of TcO_4^- in sodium tripolyphosphate ($Na_5P_3O_{10}$) solutions at various pH values and also reported polarographic measurements, (see Appendix A). Their experiments indicate the formation of some complexes. Since their stoichiometries are unknown, no thermodynamic data can be derived.

Miller [83MIL] did a fairly extensive investigation of the electrochemical behaviour of TcO_4^- in tripolyphosphate solutions. A variety of different technetium tripolyphosphate (TPP) complexes were produced depending on differences in experimental conditions: bulk (coulometric) electrolysis of TcO_4^-, polarographic reduction of TcO_4^-, or ligand exchange with $TcBr_6^{2-}$, (*cf.* Appendix A), but unfortunately no thermodynamic data can be extracted.

A few results have been reported for higher-order polyphosphates of technetium. Steigman, Meinken and Richards [78STE/MEI] reduced TcO_4^- with Sn^{2+} at pH $= 7.0$ and then reacted the solution with a sodium polyphosphate of molecular weight of approximately 5100 g $\cdot$ mol^{-1}. The result was a yellowish solution containing mainly Tc(III). Addition of sodium pyrophosphate to the Tc(III) polyphosphate solution produced the blue colour of the Tc(III) pyrophosphate complex, which indicated that the pyrophosphate complex was stronger than the polyphosphate complex. A somewhat lower molecular weight (approximately 1800 g $\cdot$ mol^{-1}) polyphosphate complex of technetium was separated by gel chromatography [74PER/DAR].

V.6.2.2.4 Diphosphonate complexes

Several organic diphosphonate complexes of technetium have been used with ^{99m}Tc as a γ-ray emitting isotope. They are particularly useful in nuclear medicine. Further information can be found in [78MÜN, 79RUS/CAS2, 79RUS/CAS, 79RUS/CAS3, 80DEU/LIB, 80LIB/DEU, 80PIN/HEI, 81MUL/OLD, 83PIN/HEI, 83TAN/ZOD, 85WIL/PIN, 86MIK/PIN, 87MIK/PIN, 90TJI/VIN, 91HUI/DIE].

It should be noted that technetium forms a considerable number of diphosphonate complexes. At the concentrations typical of "chemical" experiments, dimeric and possibly higher order complexes are of major importance, but for tracer experiments, monomeric complexes should predominate [78MÜN].

V.6.2.2.5 Other phosphorus complexes

Klimov, Mamchenko, and Babichev [91KLI/MAM] synthesised a ternary complex of technetium by the following approach. Their reaction vessel consisted of a closed glass vessel containing a technetium metal cathode and a nickel metal anode. The vessel was degassed and PF_3 was added, condensed, and frozen on to the walls; subsequently the technetium was "sputtered" for about an hour, a new layer of frozen PF_3 was added, and the process was repeated several times. Excess PF_3 was distilled off and the black-coloured residue was purified by sublimation under reduced pressure at 400 to 430 K. The resulting white complex was obtained in about 2 to 3% yield. Elemental analysis indicated that it contained only Tc, P, and F, with a F-to-P mole ratio of (3.0 ± 0.1) to 1. However, they did not synthesise sufficient material to quantitatively determine the mole ratio of technetium to the other elements. They performed IR spectroscopic and mass spectrometric measurements on this and the known complex $Re_2(PF_3)_{10}$; for both types of measurements the technetium and rhenium complexes exhibited considerable similarities.

Various ion fragments detected by mass spectrometry suggested that this technetium complex was dinuclear. From this information Klimov, Mamchenko, and Babichev deduced that the technetium complex was $Tc_2(PF_3)_{10}$, which contains technetium in the zerovalent state.

This $Tc_2(PF_3)_{10}$ slowly hydrolysed in moist air, rapidly decomposed in aqueous alkaline solutions, and was soluble in 1-to-1 mixtures (by volume) of HNO_3+H_2O_2(aq) and $HNO_3 + H_2SO_4$. Its vapour pressure at 343 K was determined to be (0.07 ± 0.03) Pa. No other thermodynamic information is available.

V.6.3 Arsenic compounds

Hulliger [66HUL] reported preparation of the non-metallic arsenide Tc_3As_7(cr), along with a number of other compounds of this structure type not containing technetium. Hulliger stated that these phases "...were prepared either by sintering the components in the form of pressed powder pellets or by melting, quenching and subsequent annealing at temperatures between 450 and 900°C". The phase of interest formed peritectically. Unfortunately, no specific details were given for the preparation or characterisation of Tc_3As_7(cr). It formed a cubic unit cell with $a = (8.702 \pm 0.004) \times 10^{-10}$ m.

Jeitschko and Dietrich [85JEI/DIE] investigated the reaction of technetium with arsenic in a sealed silica tube with a small amount of I_2 added to promote crystal growth. Samples with initial Tc:As atomic ratios of 1:3 and 1:9 that were annealed at 1223 K for two weeks and then quenched produced Tc_2As_3 along with excess arsenic. Another sample with a Tc:As starting ratio of 1:2 gave a different and unidentified phase. A single crystal X-ray structural determination [85JEI/DIE] indicated that Tc_2As_3(cr) crystallised in the triclinic system with $Z = 4$. Each of the four nonequivalent Tc atoms had six neighboring As atoms that formed very distorted octahedra. Structural parameters for this compound are given in Table V.31.

Several organometallic complexes have been reported in which technetium is directly coordinated with an arsenic atom, [59FER/NYH, 60FER/NYH, 65HIE/LUX, 65LEW/NYH, 66FER/HIC, 68HIE/OPA, 80ELD/WHI, 80GLA/WHI, 80HUR, 81HUR/HEI, 87NEV/LIB]. All of these complexes contain organoarsenic ligands: diarsine (diars denotes *o*-phenylenebis(dimethylarsine)), thiphenylarsine Ph_3As, or diphenylarsine Ph_2As. Crystal structure parameters for $[Tc(diars)_2Cl_4]PF_6$(cr), $[Tc(diars)_2Cl_2]Cl$(cr) and $[Tc(diars)_2Cl_2]ClO_4$(cr) are given in Table V.31. Crystal structural parameters for the triphenylarsine complex $TcN(AsPh_3)_2Cl_2$ [91BAL/BOA2] are given in Table V.29, along with those for other technetium nitrido compounds.

The three structurally characterised complexes contain the diarsine ligand. Two of them, $[Tc(diars)_2Cl_2]Cl$(cr) and $[Tc(diars)_2Cl_2]ClO_4$(cr), have Tc(III) coordinated with two chloride ions in a *trans* configuration and with four arsenic atoms from the diarsine ligands [80ELD/WHI, 80GLA/WHI]. The other structurally characterised complex, $[Tc(diars)_2Cl_4]PF_6$(cr), has Tc(V) coordinated with four chloride ions and four arsenic atoms [80GLA/WHI]. The single reported triphenylarsine complex was only characterised by elemental analysis [65HIE/LUX], and the only reported diphenylarsine complex by elemental analysis and IR spectrocopy [68HIE/OPA]. The latter complex was formulated by the authors [68HIE/OPA] as being the dimeric complex $[Tc(AsPh_2)(CO)_3Cl]_2$(s), which presumably would require the arsenic atoms of these ligands to serve as bridges between the two technetium atoms. However, since their characterisation of this complex is incomplete, its structure is unknown.

No thermodynamic data are available for these compounds and complexes.

V.7 Group 14 compounds and complexes

V.7.1 Carbon compounds and complexes

V.7.1.1 Technetium carbides

The gaseous monocarbide TcC(g) has been identified by Rinehart and Behrens [79RIN/BEH] over a technetium carbide of unknown composition. The authors measured the intensities of Tc^+(g) and TcC^+(g) over the (carbon-saturated) sample from 2229 to 2650 K for Tc^+(g) and 2293 to 2595 K for TcC^+(g) by using Knudsen effusion mass spectrometry. With the assumption of equal ionisation cross-sections for Tc and TcC and reasonable thermal functions for TcC(g), calculated from estimated

molecular parameters, the enthalpy change for the reaction

$$\mathrm{Tc(g) + C(cr,\ graphite)} \quad \rightleftharpoons \quad \mathrm{TcC(g)} \tag{V.39}$$

was calculated by them to be $\Delta_r H^\circ_m$(V.39, 0 K) = (151 ± 30) kJ·mol^{-1}.

Conversion to 298.15 K using H°_m(298.15 K) − H°_m(0 K): estimated by Rinehart and Behrens [79RIN/BEH] for TcC(g); from Table B.2 for Tc(g) (see Appendix B) and from Chase *et al.* [85CHA/DAV] for C(cr, graphite), gives a correction of +1.5 kJ·mol^{-1} and thus the standard enthalpy of formation.

$$\Delta_f H^\circ_m(\mathrm{TcC,\ g,\ 298.15\ K}) \quad = \quad (826.5 \pm 40.0)\ \mathrm{kJ{\cdot}mol^{-1}}$$

The standard entropy calculated from the molecular parameters estimated by Rinehart and Behrens [79RIN/BEH] is

$$S^\circ_m(\mathrm{TcC,\ g,\ 298.15\ K}) \quad = \quad (242.5 \pm 15.0)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

with an appreciable uncertainty. The selected enthalpy of formation and entropy are used to calculate the Gibbs energy of formation.

$$\Delta_f G^\circ_m(\mathrm{TcC,\ g,\ 298.15\ K}) \quad = \quad (765.6 \pm 40.2)\ \mathrm{kJ{\cdot}mol^{-1}}$$

These thermodynamic data are recommended values.

The intercalation of TcF_6 and other metal hexafluorides into graphite was studied by Vankin, Davidov and Selig [86VAN/DAV]. Parameters were reported for the temperature dependence of the electrical conductivities of the two identified compounds, stage-I (C_9TcF_6) and stage-II ($C_{20}TcF_6$), based on measurements from about 10 to 280 K, *cf.* Appendix A.

The solid technetium carbide system is discussed in Section V.9.2.4.

V.7.1.2 Technetium carbonates

The reduction of TcO_4^- in carbonate media has been investigated by Salaria, Rulfs and Elving [63SAL/RUL] and Russell and Cash [78RUS/CAS]. These studies gave no evidence for complex formation between carbonate and technetium(IV) (Appendix A).

Solubility measurements of $TcO_2 \cdot x H_2O$(s) in carbonate media at pH values higher than 9.27 were performed by Meyer and coworkers [87MEY/ARN, 89MEY/ARN], but no evidence for carbonate complexes was observed under those conditions, *cf.* Appendix A.

Paquette, Lister and Lawrence [82PAQ/LIS] reported some spectroscopic evidence for complex formation between carbonate ions and both Tc(III) and Tc(IV). In a later study [85PAQ/LAW], they provided further experimental details and also information on the redox behaviour of the Tc(IV)/Tc(III) couple in carbonate solutions at pH = 8. Although species such as $Tc(CO_3)_q(OH)_n^{4-n-2q}$ and $Tc(CO_3)_q(OH)_{n+1}^{3-(n+1)-2q}$ were suggested with $n+q > 4$, no thermodynamic data can be derived (see comments under [82PAQ/LIS] in Appendix A).

More recently, Eriksen *et al*. [92ERI/NDA, 93ERI/NDA] have reported the results of a solubility study for $TcO_2 \cdot xH_2O$(s) as a function of pH in the absence and presence of carbonate. They found an increase of the solubility of $TcO_2 \cdot xH_2O$(s) in the presence of CO_2(g) at a partial pressure up to 1 bar in the pH range 6.26 to 8.56 and interpreted this effect in terms of the formation of two hydroxide-carbonate complexes, a neutral and an anionic one, see Table V.9 in Section V.3.

$$TcO(OH)_2(aq) + CO_2(g) \rightleftharpoons TcCO_3(OH)_2(aq) \quad \text{(V.40)}$$

$$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \rightleftharpoons TcCO_3(OH)_3^- + H^+ \quad \text{(V.41)}$$

The experiments seem to be reliable, *cf*. Appendix A, and their constants are selected here with increased uncertainties due to the fact that only few experimental points and no independent measurements are available. Since the measurements were carried out at very low ionic strength ($I < 0.01$ M) the correction factor to $I = 0$ is negligible.

$$\log_{10}{}^{*}K^\circ(\text{V.40}, 298.15\ \text{K}) = 1.1 \pm 0.3$$

$$\log_{10}{}^{*}K^\circ(\text{V.41}, 298.15\ \text{K}) = -7.2 \pm 0.6$$

From these equilibrium constants we can derive the selected Gibbs energies of formation of the two Tc(IV) carbonate complexes :

$$\Delta_f G_m^\circ(TcCO_3(OH)_2, aq, 298.15\ \text{K}) = -(968.9 \pm 9.0)\ \text{kJ·mol}^{-1}$$

$$\Delta_f G_m^\circ(TcCO_3(OH)_3^-, aq, 298.15\ \text{K}) = -(1158.7 \pm 9.5)\ \text{kJ·mol}^{-1}$$

The formulation by these authors [92ERI/NDA, 93ERI/NDA] of the carbonate complexes of Tc(IV), as being $Tc(CO_3)(OH)_2$(aq) and $Tc(CO_3)(OH)_3^-$, is consistent with the formulations used for the various hydrolysed Tc(IV) species in Section V.3.1.1 and elsewhere in this book. Alternate formulations for the primary coordination spheres of the Tc(IV) hydrolysed species are given in Section V.3.1.3.

V.7.1.3 Technetium cyanides and oxycyanides

The preparation of a hydroxo tetracyanide salt of Tc(IV) (formulated as "$Tl_3Tc(OH)_3(CN)_4$" or "$Tl_3TcO(OH)(CN)_4$") was reported by Herr and Schwochau [61HER/SCH, 62SCH/HER]. However, later studies [80TRO/JON, 82FRA/LOC] suggest that Schwochau and co-workers actually had studied the Tc(V) complex $TcO(CN)_5^{2-}$ rather than the Tc(IV) complex "$Tc(OH)_3(CN)_4^{3-}$", (see Appendix A).

Trop, Jones and Davison [80TRO/JON] identified the following compounds:

- $K_2TcO(CN)_5 \cdot 4H_2O$
- $K_4Tc(CN)_7 \cdot 2H_2O$
- $K_3TcO_2(CN)_4$

The $TcO_2(CN)_4^{3-}$ complex has since been studied by ^{99}Tc-NMR [82FRA/LOC].

Roodt *et al.* [92ROO/LEI] have described the preparation and characterisation by chemical analysis, infra-red, visible and ultra-violet spectroscopy, of a number of oxo and hydroxo tetracyanides of Tc(V) derived from the $TcO_2(CN)_4^{3-}$ ion. These included:

- $K_3TcO_2(CN)_4$, also described by [80TRO/JON] and [82FRA/LOC];
- $(CH_3)_4N[TcO(OH_2)(CN)_4]\cdot 2H_2O$(cr), which crystallises in the orthorhombic system, space group Pmmn, with $a = 12.11\times10^{-10}$ m, $b = 9.04\times10^{-10}$ m, $c = 7.10\times10^{-10}$ m, and $Z = 2$;
- $Cd_2[Tc_2O_3(CN)_8]\cdot 10H_2O$(cr)
- $K_4[Tc_2O_3(CN)_8]\cdot 6H_2O$, and
- the 2,2'-bipyridinium salt $(2,2'\text{-bpyH})_2[TcO(NCS)(CN)_4]$(cr), which crystallises in the monoclinic system, space group C2/c, with $a = (18.210 \pm 0.008)\times10^{-10}$ m, $b = (19.473 \pm 0.002)\times10^{-10}$ m, $c = (15.501 \pm 0.006)\times10^{-10}$ m, and $\beta = (107.501 \pm 0.028)°$.

Roodt and his colleagues also studied spectrophotometrically the kinetics of the displacement of the H_2O ligand in the $TcO(OH_2)(CN)_4^-$ ion by the NCS^- ligand as well as the kinetics of proton transfer reactions of these tetracyanotechnetates, [92ROO/LEI, 94ROO/LEI, 95ROO/LEI] (see Appendix A).

Preparation of a reduced valence Tc(I) complex was also reported by Schwochau and Herr [62SCH/HER2], by reaction of TcO_4^- or "$Tc(OH)_3(CN)_4^{3-}$" with potassium amalgam in the presence of KCN. The product was $K_5Tc(CN)_6$(cr) and it formed cubic crystals with $a = (12.106 \pm 0.002) \times 10^{-10}$ m (isostructural with $K_5Mn(CN)_6$(cr) and $K_5Re(CN)_6$(cr)). Its aqueous solutions were very air-sensitive. Both the potassium and thallium salts of $Tc(CN)_6^{5-}$ had low solubilities in water.

Krasser, Bohres and Schwochau [72KRA/BOH] reported Raman spectrum of $K_5Tc(CN)_6$(cr) and its IR spectrum in CsCl. From these results they derived the vibrational fundamentals and force constants.

Polarographic measurements of the reduction of TcO_4^- in various aqueous cyanide media have been reported [60COL/DAL, 64MÜN, 78RUS/CAS]. No useful thermodynamic data can be derived.

Results from microcoulometry [68MÜN2] indicated 3 to 4 e^- reductions of TcO_4^- occurred in 0.1 mol·kg^{-1} KOH-0.5 mol·kg^{-1} KCN, depending on the applied potential. Al-Kayssi, Magee and Wilson [62AL-/MAG] found that reduction of TcO_4^- in aqueous HCl by bismuth amalgam or mercury in the presence of potassium ferrocyanide yielded an anionic blue complex. In contrast, for the corresponding reduction with $SnCl_2$, a yellowish-brown complex was obtained. The stoichiometries of these complexes are unknown.

Baldas *et al.* [90BAL/BOA2] synthesised and characterised a complex of Tc(V), $(AsPh_4)_2[TcN(CN)_4(OH_2)]\cdot 5H_2O$(cr) (Appendix A). It crystallised in the monoclinic space group $P2_1/n$ with $a = (17.107 \pm 0.010) \times 10^{-10}$ m, $b = (19.965 \pm 0.014) \times$

10^{-10} m, $c = (15.473 \pm 0.010) \times 10^{-10}$ m, $\beta = (101.70 \pm 0.04)°$, and $Z = 4$. In the same study, the possible formation of the following Tc(VI) species was also suggested: $TcNCl_3(CN)^-$, $TcNCl_2(CN)_2^-$, or $TcNCl(CN)_3^-$.

No thermodynamic data are available for these compounds.

V.7.1.4 Isothiocyanates and oxyisothiocyanates

The chemical and redox behaviour of technetium in the presence of thiocyanate ions has been investigated [57CRO, 64MÜN, 68MÜN2, 78RUS/CAS, 79TRO/DAV, 87GRA/FAR]. These studies gave some evidence for the formation of Tc(V), Tc(IV) and Tc(III) complexes, but no single species was identified.

Various studies have been reported in which solid complexes of technetium with SCN^- have been prepared, and they indicate that bonding in these complexes is through nitrogen, so these complexes are actually isothiocyanates. Schwochau and coworkers [68SCH/PIE, 73SCH/AST] reported preparation of different salts of Tc(V) and Tc(IV) containing the $Tc(NCS)_6^-$ and $Tc(NCS)_6^{2-}$ ions, respectively. Reinvestigation of technetium isothiocyanato solutions and salts by Trop *et al.* [80TRO/DAV] indicated that Schwochau and coworkers were probably in error in assigning the technetium valences in these salts. Their investigations indicated the formation of Tc(IV) and Tc(III) salts, i.e., $Tc(NCS)_6^{3-}$ and $Tc(NCS)_6^{2-}$ ions. (See comments under [68SCH/PIE] in Appendix A). The existence of these two species $Tc(NCS)_6^{3-}$ and $Tc(NCS)_6^{2-}$, has been confirmed by other studies [88MAR/GRA, 90YAM/KUB].

An oxopentakis(isothiocyanato)technetate(V) complex containing $TcO(NCS)_5^{2-}$ was prepared and characterised by Davison *et al.* [81DAV/JON2], *cf.* Appendix A. Previous studies by Spitsyn, Glinkina and Kuzina [71SPI/GLI] indicated the formation of $TcO(OH)(NCS)_4^{2-}$, but it may well have been identical to the $TcO(NCS)_5^{2-}$ of Davison *et al.* [81DAV/JON2].

Abram, Abram, and Dilworth [96ABR/ABR] have recently synthesised and characterised a crystalline solid of Tc(III) as *mer*, *trans* $-[TcCl_2(NCS)\{(CH_3)_2PhP\}_3](cr)$. This compound crytallises in the monoclinic space gropup $P2_1/n$ with $a = (14.997 \pm 0.014) \times 10^{-10}$ m, $b = (10.840 \pm 0.004) \times 10^{-10}$ m, $c = (19.160 \pm 0.016) \times 10^{-10}$ m, $\beta = (113.04 \pm 0.04)°$, and Z = 4. It was found to be readily soluble in CH_2Cl_2 and $CHCl_3$, moderately soluble in methanol, and was stable in air both as a solid compound and in solutions of these organic solvents.

Orvig [81ORV] reported the synthesis of $[(n-C_4H_9)_4N]_2[Tc(NO)(NCS)_5](cr)$ and $[(n-C_4H_9)_4N]_3[Tc(NO)(NCS)_5] \cdot H_2O(cr)$, but they were not structurally characterised.

No thermodynamic data are available for these complexes.

V.7.2 Silicon compounds

Numerous studies have been published on the sorption of technetium on quartz, crystalline silica, and silicate minerals, *e.g.*, [80BIR/LOP, 81PAL/MEY, 88ITO/KAN], but these sorption studies give no indication for significant interaction between TcO_4^- or Tc(IV) and silica or silicate minerals.

Other compounds, *e.g.*, Ba-Tc and Sr-Tc silicates, have been reported by Muller *et al*. [64MUL/WHI, 68MUL], but these products were highly heterogeneous and were not characterised.

There is no published study of the Tc-Si-O phase system. However, borosilicate glass is frequently used to immobilise reactor wastes, and these studies should have some relevance to the Tc-Si-O system. Although the incorporation of technetium into borolicate glass has been reported (see Refs. [79BRA/HAR, 85ANT/MER, 89FRE/LUT] in Appendix A), there is disagreement whether technetium occurred as Tc(VII) [79BRA/HAR, 89FRE/LUT] or Tc(IV) [85ANT/MER] in borosilicate glass prepared under oxidising conditions. However, there is agreement that TcO_2 and metallic technetium precipitated from such glass prepared under reducing conditions.

These results suggest that the solubility of TcO_2 in borosilicate glass is quite low, and this is likely to be true for TcO_2 in SiO_2 (glassy). It is possible, however, that amorphous ternary oxides or hydrous oxides of the type $(Si,Tc)O_2 \cdot xH_2O$ could be prepared by the simultaneous hydrolytic precipitation of a solution of Si(IV) and Tc(IV).

A literature search was done of Chemical Abstracts, of the Gmelin Handbuch der Anorganischen Chemie, of Structure and Bonding, and of several review articles. No information about silicon complexes of technetium was located. Technetium alloys with silicon are discussed in Section V.9.2.20.

V.7.3 Tin compounds and complexes

Several studies on the reduction of TcO_4^- to Tc(IV) species by $SnCl_2$ and $Sn(ClO_4)_2$ in aqueous acidic solutions are reported in the literature [75BRA/BRA, 75STE/MEI, 77OWU/MAR, 87FAR/GAR], but these investigations gave no evidence for technetium-tin complexes.

However, there is indirect evidence of the formation of technetium complexes with Sn^{2+} or its chloride complex. For example, reduction of TcO_4^- in aqueous HCl containing potassium ferrocyanide gave a blue product when reduced with Bi(Hg) or Hg, but a yellowish-brown complex formed instead when $SnCl_2$ was used [62AL-/MAG]. These observations suggest interaction between technetium and tin(II) may be occuring in certain cases.

Evidence of a somewhat more direct nature exists for the presence of technetium complexes with $SnCl_q^{2-q}$. Steigman, Meinken and Richards [78STE/MEI] reduced technetium electrolytically to Tc(III) in a phosphate buffer. Addition of $SnCl_2$ caused no further reduction of technetium, but it did cause large changes in the absorption spectrum. They found similar evidence for association of $SnCl_q^{2-q}$ with a mixed valence Tc(III, IV) phosphate complex. Kroesbergen *et al*. [86KRO/STE] studied $^{99m}TcO_4^-$ that was reduced by $SnCl_2$ in aqueous HCl in the presence of pyrophosphate ions. Absorption of these reduction products on solid $Ca_3(PO_4)_2$ at various pH values indicated that a negatively charged Tc-Sn-pyrophosphate complex was initially present. Either that complex or its dissociation products were absorbed on the $Ca_3(PO_4)_2$.

The preparation and characterisation of several organic complexes of technetium with tin has also been reported, [76DEU/ELD, 80DEU/LIB, 81BRA/DAS, 82BRA/DAS, 86MIK/PIN, 89HUI/TJI, 90LIN/MAL, 91KAN/RAP]. Several of these

complexes contain the "$SnCl_3$" ligand, where it is not certain whether it occurs as $SnCl_3^-$ or $SnCl_3^+$. There is no consensus among these studies whether this tin present as $Sn(II)Cl_3^-$ or as $Sn(IV)Cl_3^+$ and it is possible that different complexes may contain tin in different valence states.

No thermodynamic data are available for these complexes of tin with technetium. However, they do not seem to be strong enough to form under normal environmental conditions.

V.7.4 Boron compounds and complexes

A literature search uncovered no reports containing information about inorganic compounds or complexes of boron other than those found in the Tc-B system, see Table V.42 in Section V.9.

However, there are several reports of the synthesis of complexes of technetium that contain the hydrotris(1-pyrazolyl)borate [84ABR/DAV, 91THO/DAV, 93JOA/APO2], hydrotris(3,5-dimethyl-1-pyrazolyl)borate [93JOA/APO, 93JOA/APO2], or the boronic acid (BATO) [89TRE/FRA, 93LI/WAN] ligands. In none of these complexes is the boron atom directly coordinated to a technetium atom. There is also an absence of thermodynamic data for these complexes, and they are not considered further.

V.8 Pertechnetates and mixed oxides

Aqueous pertechnetic acid, $HTcO_4$, is a very strong acid in aqueous solution; see Section V.3.1.2.1 for details. The pertechnetate anion TcO_4^- has little tendency to form complexes with cations in aqueous solution. In this regard it resembles other MO_4^- anions such as perchlorate ClO_4^-, perrhenate ReO_4^-, and permanganate MnO_4^-. These anions can form crystalline salts with virtually every known cation. A large number of pertechnetate salts have been prepared, the largest number of these by Zaitseva and her colleagues in the USSR. In this section we discuss known pertechnetate salts, their structural data, thermodynamic data and other physicochemical properties.

The synthesis of pertechnetate salts generally involves precipitation from aqueous solutions. An aqueous solution of $HTcO_4$ is reacted with a hydroxide, oxide, or, sometimes, the carbonate of the desired cation to form a solution of about pH = 7, followed by evaporation of the solution until crystals precipitate. However, it is also possible to prepare metal pertechnetates by evaporation of NH_4TcO_4-MOH solutions, because NH_3(g) is expelled by heating alkaline solutions.

Most of our information about dehydration temperatures comes from thermogravimetric analysis or differential thermal analysis. The temperatures at which dehydrations occur during such measurements depend on whether the system is open or closed and on how fast the temperature is changed relative to how fast the phase transitions occur, and the phase changes are generally slower than the heating rate. Transition temperatures determined by quasi-static measurements (*e.g.*, isothermal dehydration in a closed system) should be much more meaningful. The lowest temperatures observed

in thermogravimetric or differential thermal analysis experiments with pertechnetate salts are normally 0 to 55 K higher.

Structural data have been reported for a number of hydrated and anhydrous pertechnetates. The structural information is summarised in Table V.32.

Table V.32: Crystal structure parameters of pertechnetate salts.

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
		Anhydrous salts			
$NaTcO_4$(cr)	tetragonal	$I4_1/a$	4	$a = 5.339 \pm 0.002$	[62SCH]
				$c = 11.869 \pm 0.010$	
				$a = 5.337 \pm 0.004$	[63KEL/KAN]
				$c = 11.88 \pm 0.04$	
$KTcO_4$(cr)	tetragonal	$I4_1/a$		$a = 5.654$	[62MCD/TYS][a]
				$c = 13.030$	
				$a = 5.630 \pm 0.004$	[63KEL/KAN]
				$c = 12.87 \pm 0.04$	
			4	$a = 5.630 \pm 0.004$	[76KRE/HAS]
				$c = 12.867 \pm 0.008$	
$RbTcO_4$(cr)	tetragonal			$a = 5.758 \pm 0.004$	[63KEL/KAN]
				$c = 13.54 \pm 0.04$	
$CsTcO_4$(cr)	orthorhombic	Pnma	4	$a = 5.718$	[62MCD/TYS]
				$b = 5.918$	
				$c = 14.304$	
				$a = 5.726 \pm 0.004$	[63KEL/KAN]
				$b = 5.922 \pm 0.004$	[66KAN]
				$c = 14.36 \pm 0.04$	
		Pnma	4	$a = 5.727$	[76MEY/HOP]
				$b = 5.921$	
				$c = 14.34$	
	tetragonal[b]			$a = 5.898$	[66KAN]
				$c = 14.38$	
$AgTcO_4$(cr)	tetragonal	$I4_1/a$	4	$a = 5.319 \pm 0.002$	[62SCH]
				$c = 11.875 \pm 0.010$	
				$a = 5.317 \pm 0.004$	[63KEL/KAN]
				$c = 11.87 \pm 0.04$	
$TlTcO_4$(cr)	orthorhombic			$a = 5.501 \pm 0.004$	[63KEL/KAN]
				$b = 5.747 \pm 0.004$	[66KAN]
				$c = 13.45 \pm 0.02$	
	tetragonal[c]			$a = 5.665$	[66KAN]
				$c = 13.47$	

(Continued on next page)

[a] Somewhat discrepant from the other two studies, which appear to be more reliable.

[b] High-temperature form; parameters determined at 463 K.

[c] High temperature form; parameters determined at 493 K.

Table V.32: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
NH_4TcO_4(cr)	tetragonal	$I4_1/a$		$a = 5.790$	[62MCD/TYS]
				$c = 13.310$	
				$a = 5.794 \pm 0.004$	[63KEL/KAN]
				$c = 13.29 \pm 0.04$	
		$I4_1/a$	4	$a = 5.775 \pm 0.004$	[80FAG/LOC][(d)]
				$c = 13.252 \pm 0.010$	
		$I4_1/a$	4	$a = 5.769 \pm 0.004$	[80FAG/LOC][(e)]
				$c = 13.090 \pm 0.010$	
		$I4_1/a$	4	$a = 5.741 \pm 0.004$	[80FAG/LOC][(f)]
				$c = 13.121 \pm 0.014$	
$(CH_3)_4NTcO_4$(cr)	orthorhombic	$P2_12_12$	4	$a = 12.142 \pm 0.008$	[86GER/GRI]
				$b = 12.223 \pm 0.008$	[87GER/GRI]
				$c = 5.928 \pm 0.004$	
			4	$a = 12.14 \pm 0.04$	[87KUZ/GER]
				$b = 12.22 \pm 0.04$	
				$c = 5.93 \pm 0.02$	
$(C_2H_5)_4NTcO_4$(cr)	orthorhombic		4	$a = 7.14 \pm 0.02$	[87KUZ/GER]
				$b = 7.16 \pm 0.02$	
				$c = 26.3 \pm 0.04$	
$(n\text{-}C_4H_9)_4NTcO_4$(cr)	orthorhombic	$Pna2_1$	4	$a = 15.403 \pm 0.004$	[87GER/GRI]
				$b = 13.785 \pm 0.006$	
				$c = 9.864 \pm 0.012$	
			4	$a = 15.4 \pm 0.2$	[87KUZ/GER]
				$b = 13.8 \pm 0.2$	
				$c = 9.87 \pm 0.02$	
$Pt(NH_3)_4(TcO_4)_2$(cr)	orthorhombic[(g)]			$a = 7.86$	[80SHA/VAR]
				$b = 7.63$	
				$c = 10.79$	
	triclinic[(h)]	$P\bar{1}$	1	$a = 5.178 \pm 0.004$	[90ROC/KON]
				$b = 7.725 \pm 0.006$	
				$c = 7.935 \pm 0.006$	
$Mg(TcO_4)_2$(cr)	hexagonal		6	$a = 9.93$	[83KRU/ZAI]
				$c = 12.54$	
$Tc(pda)_3TcO_4$(cr)[(i)]	orthorhombic	$Pna2_1$	4	$a = 13.869 \pm 0.008$	[92GER/KEM]
				$b = 12.799 \pm 0.010$	
				$c = 10.815 \pm 0.006$	

(Continued on next page)

[(d)] Parameters determined at 295 K.

[(e)] Parameters determined at 208 K.

[(f)] Parameters determined at 141 K.

[(g)] Incorrectly indexed.

[(h)] $\alpha = (69.33 \pm 0.06)°$, $\beta = (79.74 \pm 0.06)°$, and $\gamma = (77.41 \pm 0.06)°$.

[(i)] pda = ortho-$(HNC_6H_4NH)^{2-}$.

Table V.32: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
		Hydrated salts			
$Mg(TcO_4)_2$·$4H_2O$(cr)	triclinic[j]		1	$a = 7.44$ $b = 7.03$ $c = 6.46$	[83KRU/ZAI]
$Ho(TcO_4)_3$·$4H_2O$(cr)	triclinic[k]	$P\bar{1}$	2	$a = 7.157$ $b = 8.787$ $c = 12.278$	[74ZAI/KON] [83VAR/ZAI][l]
$Er(TcO_4)_3$·$4H_2O$(cr)	triclinic[m]	$P\bar{1}$	2	$a = 7.251$ $b = 8.759$ $c = 12.083$	[74ZAI/KON] [83VAR/ZAI][l]
$Tm(TcO_4)_3$·$4H_2O$(cr)	triclinic[n]	$P\bar{1}$	2	$a = 7.249$ $b = 8.777$ $c = 12.038$	[74ZAI/KON2] [83VAR/ZAI][l]
$Lu(TcO_4)_3$·$4H_2O$(cr)	triclinic[o]	$P\bar{1}$	2	$a = 7.193$ $b = 8.686$ $c = 11.943$	[75ZAI/BEL] [83VAR/ZAI][l]
$Y(TcO_4)_3$·$4H_2O$(cr)	triclinic[p]	$P\bar{1}$	2	$a = 7.393$ $b = 8.615$ $c = 11.819$	[75ZAI/BEL] [83VAR/ZAI][l]
$(NpO_2)_2(TcO_4)_4$·$3H_2O$(cr)	triclinic[q]	$P\bar{1}$	2	$a = 5.332 \pm 0.010$ $b = 13.034 \pm 0.014$ $c = 15.460 \pm 0.018$	[98GUE/FED]

[j] $\alpha = 108.01°$, $\beta = 92.32°$, and $\gamma = 120.45°$.

[k] $\alpha = 73.62°$, $\beta = 95.32°$, and $\gamma = 102.55°$.

[l] In the first of these pairs of references, powder-pattern results were reported but the structures were not analysed. The other reference [83VAR/ZAI] gave the unit cell parameters, and the space group was reported by [83TET/ZAI].

[m] $\alpha = 73.13°$, $\beta = 96.07°$, and $\gamma = 102.81°$.

[n] $\alpha = 73.94°$, $\beta = 96.38°$, and $\gamma = 103.71°$.

[o] $\alpha = 73.99°$, $\beta = 96.43°$, and $\gamma = 102.62°$.

[p] $\alpha = 75.65°$, $\beta = 96.43°$,and $\gamma = 104.56°$.

[q] $\alpha = (107.08 \pm 0.10)°$, $\beta = (98.05 \pm 0.14)°$,and $\gamma = (93.86 \pm 0.12)°$.

V.8.1 Pertechnetate salts of monovalent cations

V.8.1.1 $KTcO_4$(cr)

V.8.1.1.1 General properties

Evaporation of a solution of $KTcO_4$ at room temperature yielded unhydrated $KTcO_4$(cr) [57BUS/LAR, 76KRE/HAS], although heating of the residue to about 773 K was required to completely drive off occluded water [72BUS/BEV].

Three structural studies at room temperature are available [62MCD/TYS, 63KEL/KAN, 76KRE/HAS], *cf*. Table V.32, and IR and Raman spectra have also been reported [64BUS/KEL, 72BAL/HAN, 73JEŻ/HAN].

Busey and Larson [57BUS/LAR] reported that impure $KTcO_4$(cr) decomposed upon heating, but that pure $KTcO_4$(cr) can be melted and even sublimed without decomposition. Busey, Bevan and Gilbert [72BUS/BEV] prepared high-purity anhydrous $KTcO_4$(cr) from NH_4TcO_4(cr) by reaction with aqueous KOH containing H_2O_2(aq) (H_2O_2(aq) oxidises any Tc(IV) formed by self-radiolysis of NH_4TcO_4), followed by evaporation of the solution to dryness to expel NH_3(g), and this $KTcO_4$(cr) was subsequently purified by recrystallisation from water. Heating air-dried $KTcO_4$(cr) to about 773 K was sufficient to produce an anhydrous product, and fusing the sample caused no further mass decrease. They reported that $KTcO_4$(cr) was solid at 793 K but was liquid at 848 K, and earlier they reported a melting temperature of about 813 K [58BUS/LAR]. Vaporisation of this compound occurred around 1270 K. Gilbert and Busey [65GIL/BUS] determined the fraction of $KTcO_4$(cr) that had melted as a function of temperature, and extrapolated these temperatures to complete melting to give a melting temperature of (803.4 ± 1.0) K. This value should be more reliable than their earlier result [58BUS/LAR]. They also reported that the enthalpy of fusion of $KTcO_4$(cr) was (27.03 ± 0.16) kJ·mol^{-1}.

German *et al*. [93GER/GRU] have reported a similar fusion temperature of 815 K. These authors also found that $KTcO_4$(cr) undergoes a reversible phase transition at around 753 K, with an observable colour change [93GER/GRU]. The enthalpy change for this transition was reported to be $\Delta_{trs}H = (5.4 \pm 0.6)$ kJ·mol^{-1} and the enthalpy of fusion as being $\Delta_{fus}H = (28.4 \pm 3.9)$ kJ·mol^{-1}, based on DTA measurements.

Miller, Kelley and Thomason [60MIL/KEL] reported values for the conductance $\Lambda^\circ(TcO_4^-, \text{aq}, 298.15\,\text{K}) = 58.1\ \text{S·cm}^2\text{·equiv}^{-1}$ and for the tracer diffusion coefficient $D^\circ(TcO_4^-, \text{aq}, 298.15\,\text{K}) = 1.56 \times 10^{-5}\ \text{cm}^2 \cdot \text{s}^{-1}$. However, no experimental results were presented, so the accuracy of these derived quantities cannot be assessed.

Schwochau and Astheimer [62SCH/AST] also reported electrical conductances of aqueous $KTcO_4$ solutions at (298.15 ± 0.10) K for eight concentrations from 5.83×10^{-5} to 9.716×10^{-3} M. Their electrical conductance values, Λ, have been reanalysed by this review (Appendix A). The resulting recommended values are $\Lambda^\circ(TcO_4^-, \text{aq}, 298.15\ \text{K}) = (55.4 \pm 0.5)\ \text{S} \cdot \text{cm}^2 \cdot \text{eq}^{-1}$ and $D^\circ(TcO_4^-, \text{aq}, 298.15\,\text{K}) = (1.48 \pm 0.01) \times 10^{-5}\ \text{cm}^2 \cdot \text{s}^{-1}$.

Shvedov and Kotegov [63SHV/KOT] performed electromigration experiments for aqueous $NaTcO_4$ and $KTcO_4$ solutions at 291 K. As discussed in Appendix A, this review has not considered their experimental values.

V.8.1.1.2 Thermodynamic data

In 1957 Busey and Larson [57BUS/LAR] reported experimental heat capacities of $KTcO_4$(cr) at 66 temperatures from 16.31 to 310.51 K. Their data, after correcting their assumed atomic mass of 99 g·(mol)$^{-1}$ for ^{99}Tc to the current value of 98.9063, yielded S°_m ($KTcO_4$, cr, 298.15 K) = 166.20 J·K^{-1}·mol^{-1}. Unfortunately, the sample used for calorimetric measurements was not completely anhydrous. They estimated the water content as being ~0.83 mass-% (8.5 mol-%) based on the excess heat absorbed in the vicinity of the fusion temperature of water. However, according to them, this estimate of the water content was uncertain by ±3 mol-%, which makes it impossible to reliably correct for the water present. Busey and Larson were unable to determine the water content by thermal dehydration because their $KTcO_4$(cr) was slightly impure and decomposed upon heating.

Busey, Bevan and Gilbert [72BUS/BEV] repeated these low-temperature calorimetric measurements with high-purity anhydrous $KTcO_4$(cr). They reported heat capacities for anhydrous $KTcO_4$(cr) at 76 temperatures from 9.00 to 308.56 K. Their derived thermodynamic results are listed in Table V.33. They gave an extrapolated Debye temperature of Θ_D(0 K) = 132 K. Inasmuch as their results were done carefully with high-purity $KTcO_4$(cr), they are our recommended values.

$$S^\circ_m(KTcO_4, \text{cr}, 298.15\ \text{K}) = (164.78 \pm 0.33)\ \text{J·K}^{-1}\text{·mol}^{-1}$$
$$C^\circ_{p,m}(KTcO_4, \text{cr}, 298.15\ \text{K}) = (123.30 \pm 0.25)\ \text{J·K}^{-1}\text{·mol}^{-1}$$

This value of S°_m indicates that their earlier result [57BUS/LAR] was too high by 1.4 J·K^{-1}·mol^{-1} due to occluded solution.

Busey and Bevan [60BUS/BEV] reported integral enthalpies of solution of solid $KTcO_4$(cr) into water at 298.15 K. Final molalities of $KTcO_4$ after dissolution ranged from 0.00476 to 0.02592 mol · kg^{-1}. They reported that they extrapolated these results to infinite dilution by the Debye-Hückel limiting law to obtain $\Delta_{sol}H^\circ_m$($KTcO_4$, cr, 298.15 K) = (53.41 ± 0.13) kJ·mol^{-1}. However, the simple average of their five experimental values is (53.41 ± 0.27) kJ·mol^{-1}, which suggests that they actually neglected to do the extrapolations. Their integral enthalpies of solution are tabulated in Table V.34, and they are illustrated in Figure V.5. As indicated by the dashed line in this figure, their value for the final dilution molality of 0.00476 m seems to be about 0.3 kJ·mol^{-1} less endothermic than expected from the trend observed for the other four points. They reported that the sensitivity for their isothermal solution calorimeter was 0.05 cal. However, since they did not report their sample sizes, it is not clear how much this will affect $\Delta_{sol}H_m$. In addition, they did not report any information about the purity of their $KTcO_4$(cr), and it may well have contained occluded solution. Based on these considerations, we assign an uncertainty of 0.4 kJ·mol^{-1} to their $\Delta_{sol}H_m$ values, with an experimental precision of 0.1 kJ·mol^{-1} in most cases.

The integral enthalpy of solution values in Table V.34 still need to be extrapolated to infinite dilution to obtain $\Delta_{sol}H^\circ_m$ of $KTcO_4$(cr). The enthalpy change for dilution of a solution is given by the difference of the relative apparent molar enthalpy values L_ϕ of the final and initial solutions. However, our final solutions are to be infinite dilution where L_ϕ(at $m = 0$) =0. Thus, $\Delta_{sol}H^\circ_m = \Delta_{sol}H_m - L_\phi$.

Table V.33: Thermodynamic properties of solid $KTcO_4$(cr) [72BUS/BEV][(a)].

T (K)	$C^\circ_{p,m}(T)$ ($J\cdot K^{-1}\cdot mol^{-1}$)	$S^\circ_m(T)$ ($J\cdot K^{-1}\cdot mol^{-1}$)	$H^\circ_m(T)-H^\circ_m(0\ K)$ ($kJ\cdot mol^{-1}$)	$-[G^\circ_m(T)-H^\circ_m(0\ K)]/T$ ($J\cdot K^{-1}\cdot mol^{-1}$)
0	0.0000	0.000	0.00000	—
20	7.2549	2.494	0.03766	0.6109
40	28.543	13.924	0.39245	4.1128
50	38.082	21.338	0.72654	6.8072
60	46.358	29.028	1.1495	9.8699
80	59.830	44.287	2.2168	16.577
100	70.499	58.830	3.5241	23.589
120	79.411	72.491	5.0252	30.614
140	87.109	85.331	6.6934	37.526
160	93.552	97.393	8.5011	44.262
180	99.075	108.74	10.428	50.805
200	103.97	119.43	12.459	57.136
220	108.49	129.56	14.584	63.265
240	112.63	139.18	16.796	69.198
260	116.52	148.35	19.088	74.938
280	120.25	157.13	21.456	80.499
298.15	123.30	164.78	23.666	85.398
300	123.63	165.54	23.895	85.888
310	125.22	169.62	25.139	88.523

(a) Reported thermodynamic values were multiplied by (202.0022/202.006) = 0.999981 to convert to current molar masses. Heat capacities are uncertain by about 9.8% at 15 K, by about 2.0% at 25 K, and about 0.2% over most of the remaining temperature range for 95% confidence limits. However, near room temperature the uncertainties increase from 0.2% to 2-3 times as large due to increasing heat leaks from the calorimeter. Changes in thermodynamic values due to conversion of 1 atm to 1 bar standard pressure are much less than the experimental precision and were neglected. The temperature scale used for these heat capacity measurements was not identified, but we presume that it was the International Practical Temperature Scale of 1968 (IPTS-68). Thermodynamic values were not corrected to the most recent temperature scale (ITS-90) because any resulting changes for the various thermodynamic properties would be significantly less than their corresponding experimental uncertainties. Most of these thermodynamic values are given to one more significant figure than reported in the original publication, in order to prevent a loss of information when converting results from calories to joules.

Figure V.5: Integral enthalpy of solution of solid $KTcO_4$(cr) into water at 298.15 K [60BUS/BEV]. Reported $\Delta_{sol}H_m$ to various final molalities (•); the dashed line represents the least-squares fit to these values. Values of $\Delta_{sol}H_m - L_\phi$ (△), where L_ϕ was estimated from values for $KClO_4$(cr) [65PAR]; the full line represents the least-squares fit to those values. In each case the discrepant value at the lowest molality was given zero weight. Note that if the corrections to infinite dilution were completely accurate, then $\Delta_{sol}H_m - L_\phi$ would equal $\Delta_{sol}H_m^\circ$.

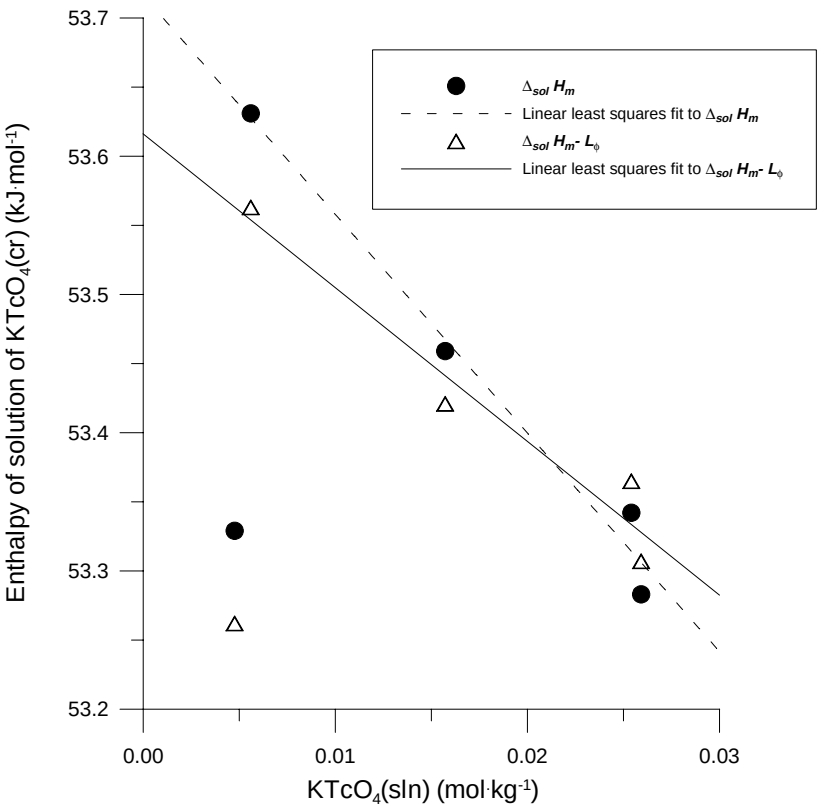


Table V.34: Integral enthalpies of solution of solid $KTcO_4$(cr) in water at 298.15 K [60BUS/BEV].

Molality[(a)] ($mol \cdot kg^{-1}$)	$\Delta_{sol}H_m^{(b)}$ ($kJ \cdot mol^{-1}$)	L_ϕ[(c)] ($kJ \cdot mol^{-1}$)	$\Delta_{sol}H_m - L_\phi$ ($kJ \cdot mol^{-1}$)
0.02592	53.283 ± 0.4	-0.024 ± 0.03	53.307 ± 0.40
0.02541	53.342 ± 0.4	-0.023 ± 0.03	53.365 ± 0.40
0.01572	53.459 ± 0.4	0.038 ± 0.02	53.421 ± 0.40
0.00560	53.631 ± 0.4	0.068 ± 0.01	53.563 ± 0.40
0.00476	53.329 ± 0.4	0.067 ± 0.01	53.262 ± 0.40

(a) Final molality of solution formed by dissolution of solid $KTcO_4$(cr) into water. All five molalities in this column are uncertain by 0.05% due to a lack of information about the atomic mass of ^{99}Tc assumed for calculating molalities. It was common around that time to use 99 $g \cdot mol^{-1}$, which differs from the current value of 98.9063$g \cdot mol^{-1}$.

(b) Integral enthalpy of solution from dissolution of solid $KTcO_4$(cr) to form a solution of the given molality.

(c) Relative apparent molar enthalpy of dilution as estimated by this review from the values for $KClO_4$(cr); $-L_\phi$ is equal to the enthalpy change from diluting the solution from the given molality to infinite dilution.

There are no experimental dilution enthalpies for $KTcO_4$ solutions. Calculations were performed by this review in which L_ϕ was obtained from the Debye-Hückel limiting law and was used to correct $\Delta_{sol}H_m$ to infinite dilution. When this was done, the "corrected" data showed more variation with molality than the uncorrected data. Obviously, this estimated correction is not reliable.

Although enthalpies of dilution are not available for $KTcO_4$ solutions, they are available for the chemically similar systems $KClO_4$, $KClO_3$, $KBrO_3$, and KIO_3 [65PAR, 80VAN/WAU]. The chemical system that should be most similar to $KTcO_4$(cr) is $KClO_4$(cr); consequently, L_ϕ for $KClO_4$ [65PAR] were analysed graphically and then used as estimates for the corresponding $KTcO_4$(cr) values. These L_ϕ and $(\Delta_{sol}H_m - L_\phi)$ are tabulated in Table V.34, and Figure V.5 is a plot of these values. We estimate that the uncertainty in the estimated L_ϕ increases from 0.01 to 0.03 $kJ \cdot mol^{-1}$ as the molality increases. We expect that L_ϕ of $KClO_4$ and $KTcO_4$ should exhibit some minor differences at the higher molalities due to salt-specific ionic interactions, and indeed the corrected $(\Delta_{sol}H_m - L_\phi)$ do have a slight trend with molality. However, any error in the estimated L_ϕ should vanish as the molality goes to zero, so an extrapolation of $(\Delta_{sol}H_m - L_\phi)$ to $m = 0$ should yield the correct value of $\Delta_{sol}H_m^\circ$ for $KTcO_4$(cr). A least-squares fit of the values in Table V.34 gives $\Delta_{sol}H_m^\circ - L_\phi = 53.616 - 11.12m$, with a correlation coefficient of 0.973. Finally, our selected value is

$$\Delta_{sol}H_m^\circ(KTcO_4, cr, 298.15\ K) \quad = \quad (53.62 \pm 0.42)\ kJ \cdot mol^{-1}$$

Parker and Martin [52PAR/MAR] determined the solubilities of $KTcO_4$(cr) at

280.15 and 300.15 K; from these two values the solubility at 298.15 K has been interpolated to be 0.63 mol · dm^{-3} [53COB/SMI, 57BUS/LAR] or 0.63 mol · kg^{-1} [60BUS/BEV]. Colton *et al.* [60COL/DAL] reported that the solubility of $KTcO_4$(cr), presumably at "room temperature", was "ca. 12 g/100 mL". This corresponds to a molality of ∼ 0.60 mol · kg^{-1}, provided they meant mL of H_2O(l) and not of solution. Inasmuch as no details were given, it is not clear if this was a new experimental value or whether they were simply quoting a literature value ultimately derived from Parker and Martin. As discussed in Appendix A the experimental results reported by Parker and Martin [52PAR/MAR] cannot be used to extract reliable thermodynamic data for $KTcO_4$(cr).

A new determination of the solubilities of $KTcO_4$(cr) by Busey and Bevan [60BUS/BEV] gave values which are much lower and more precise than the values reported by Parker and Martin [52PAR/MAR]. Busey and Bevan determined the molal concentrations by weighing aliquots of saturated solutions, followed by drying these samples and weighing the anhydrous salts. Their reported solubilities are 0.1057 mol · kg^{-1} at 298.15 K and 0.0344 mol · kg^{-1} at 273.15 K. Equilibrium was approached both from above and from below saturation. The direct method of determining solubilities that was used by Busey and Bevan appears to be much more accurate than radiometric measurements [52PAR/MAR], and we accept Busey and Bevan's solubilities for thermodynamic calculations. Based on the apparent high quality of this solubility determination, we assign an uncertainty of 0.15% to these saturated molalities.

Neck *et al.* [98NEC/KÖN] recently determined the solubility of $KTcO_4$ (cr) at (298.15 ± 0.2) K, $m_s = (0.1040 \pm 0.0015)$ mol·kg^{-1}, using liquid scintillation counting of ^{99}Tc. This value agrees well with $m_s = 0.1057$ mol·kg^{-1} obtained by Busey and Bevan [60BUS/BEV]. Busey and Bevan's value was used in the subsequent thermodynamic caluclations since their dehydration method for determining the molality at saturation is more precise.

For thermodynamic calculations, we formally treat aqueous $KTcO_4$ as being completely dissociated (see [63SHV/KOT] in Appendix A). We will now derive the standard entropy of the TcO_4^- ion, which requires values of the entropy of a pertechnetate solid salt together with the standard entropy of solution of that same salt in water at 298.15 K.

The only pertechnetate salt with published low temperature calorimetric data is $KTcO_4$(cr), so it is the only one with a directly determined entropy. Entropies of solution are generally obtained from a combination of the standard enthalpies and Gibbs energies of solution of a salt in water. However, standard Gibbs energies of solution are obtained in turn from solubilities and activity coefficients, and only the former quantity is known for $KTcO_4$(cr). Fortunately, the solubility of $KTcO_4$(cr), 0.1057 mol · kg^{-1} at 298.15 K [60BUS/BEV], is low enough that the activity coefficient for that salt at saturation can be estimated with some confidence.

Busey and Bevan [60BUS/BEV] estimated that $\gamma_\pm = 0.74$ for $KTcO_4$ at 0.1057 mol · kg^{-1}, based on available data for $KClO_4$ and $NaClO_4$, but no details were given. A more detailed consideration of estimating activity coefficients was given by Busey, Bevan and Gilbert [72BUS/BEV], who gave three separate estimates. First they

used the enthalpy of solution as a function of temperature (calculated by assuming that $C^\circ_{p,\mathrm{m}}$ of aqueous $KTcO_4$ was approximately equal to that of $NaReO_4$) to compute the ratio of activity coefficients for saturation at 298.15 K to that at saturation at 273.15 K, which equalled 0.84. The activity coefficient ratio was assumed to be independent of temperature and equal to this ratio at 273.15 K. This same ratio was plotted against $\gamma_\pm$ at 0.1057 mol · kg^{-1} for other potassium salts. Interpolation to a ratio of 0.84 then yielded an estimate of the activity coefficient of $KTcO_4$ at 298.15 K. Secondly, the activity coefficient of $KTcO_4$ was estimated to equal that of $KClO_4$, which required an extrapolation of the published $KClO_4$ data to a higher molality. As a third estimate, they equated $\gamma_\pm$ of $KTcO_4$ to $\gamma_\pm(KClO_4) \times \gamma_\pm(NaTcO_4)/\gamma_\pm(NaClO_4)$.

The resulting three estimated activity coefficients given by Busey, Bevan and Gilbert [72BUS/BEV] are 0.685, 0.680, and 0.672. They recommended use of the average of these three values, (0.679 ± 0.010).We will accept this mean value, but we increase the uncertainty limits to ± 0.020, because of the use of an extrapolated activity coefficient for $KClO_4$ for their calculations.

The solubility reaction for $KTcO_4$(cr) is:

$$KTcO_4(\mathrm{cr}) \quad \rightleftharpoons \quad K^+ + TcO_4^- \tag{V.42}$$

for which $\log_{10} K^\circ_{s,0}(\text{V.42}) = -(2.288 \pm 0.026)$ and $\Delta_{\mathrm{sol}} G^\circ_{\mathrm{m}}(\text{V.42}) = -RT \ln(\gamma_\pm^2 m^2) = (13.061 \pm 0.148)$ kJ·mol^{-1}.

Combining this result with the obtained value $\Delta_{\mathrm{sol}} H^\circ_{\mathrm{m}}(\text{V.42}) = (53.62 \pm 0.42)$ kJ · mol^{-1} yields $\Delta_{\mathrm{sol}} S^\circ_{\mathrm{m}}(\text{V.42}) = (136.0 \pm 1.5)$ J·K^{-1}·mol^{-1}. The entropy of the aqueous TcO_4^- ion is then

$$S^\circ_{\mathrm{m}}(TcO_4^-, \mathrm{aq}, 298.15\ \mathrm{K}) \quad = \quad (199.6 \pm 1.5)\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

This value is recommended by this review.

There are several previous calculations of $S^\circ_{\mathrm{m}}(TcO_4^-, \mathrm{aq}, 298.15\ \mathrm{K})$. Two of these were based on the same data as used here, and are in good agreement [72BUS/BEV, 83RAR]. Earlier values of this quantity are slightly discrepant because they were based upon a rejected value for the entropy of $KTcO_4$(cr) [60BUS/BEV] or upon a rejected value for the solubility and an estimated entropy of $KTcO_4$(cr) [53COB/SMI].

In Section V.2.1 we give recommended thermodynamic data for $\Delta_f G^\circ_{\mathrm{m}}$ and $\Delta_f H^\circ_{\mathrm{m}}$ of aqueous TcO_4^-, and here we just report S°_{m}. These values are summarised in Table V.5 in that Section. In addition, we obtain S°_{m} and $\Delta_{\mathrm{sol}} H^\circ_{\mathrm{m}}$ for $KTcO_4$(cr), and $\Delta_{\mathrm{sol}} G^\circ_{\mathrm{m}}$ and $\Delta_{\mathrm{sol}} S^\circ_{\mathrm{m}}$. Thus, all of the necessary information is available for the calculation of $\Delta_f H^\circ_{\mathrm{m}}$, and $\Delta_f G^\circ_{\mathrm{m}}$ of $KTcO_4$(cr).

For the enthalpy of formation,

$$\Delta_f H^\circ_{\mathrm{m}}(KTcO_4, \mathrm{cr}, 298.15\ \mathrm{K}) \quad = \quad -(1035.1 \pm 7.6)\ \mathrm{kJ{\cdot}mol^{-1}}$$

This value allows us to derive the selected Gibbs energy of formation:

$$\Delta_f G^\circ_{\mathrm{m}}(KTcO_4, \mathrm{cr}, 298.15\ \mathrm{K}) \quad = \quad -(932.9 \pm 7.6)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

A summary of the recommended values for $KTcO_4$(cr) is given in Table V.35.

Table V.35: Recommended thermodynamic data of $KTcO_4$(cr) at 298.15 K.

$\Delta_{sol}H^\circ_m$	53.62±0.42	kJ·mol^{-1}
$\Delta_{sol}S^\circ_m$	136.0±1.5	J·K^{-1}·mol^{-1}
$\Delta_{sol}G^\circ_m$	13.061±0.148	kJ·mol^{-1}
$\Delta_f H^\circ_m$	−1035.1±7.6	kJ·mol^{-1}
S°_m	164.78±0.33	J·K^{-1}·mol^{-1}
$\Delta_f G^\circ_m$	−932.9±7.6	kJ·mol^{-1}
$C^\circ_{p,m}$	123.30±0.25	J·K^{-1}·mol^{-1}
$\Delta_{fus}H_m$	27.03±0.16	kJ·mol^{-1}
T_{fus}	803.4±1.0	K

In addition to determining the solubilities in solutions of $KTcO_4$(cr) in water at 298.15 K, Neck *et al.* [98NEC/KÖN] determined its solubility in KCl, $MgCl_2$, $CaCl_2$ and K_2SO_4 solutions with molalities as high as 4.65 mol·kg^{-1}. These systems include both common and non-common ion mixtures. These authors represented their solubilities using Pitzer's equation, rather than with the SIT equation. Grenthe, Plyasunov and Spahiu [97GRE/PLY] describe how to calculate the SIT parameter from the Pitzer parameters.

V.8.1.2 Other group 1 (alkali) pertechnetates

V.8.1.2.1 $NaTcO_4 \cdot xH_2O$(s)

V.8.1.2.1.a General properties

German, Kryuchkov and Belgaeva [87GER/KRY] reported that $NaTcO_4 \cdot 4H_2O$(s) was the precipitating phase from aqueous solution at room temperature. These hydrated crystals were reported to be fairly stable in contact with the saturated solution, but they gradually effloresced in air and became anhydrous when desiccated over P_2O_5(s).

This $NaTcO_4 \cdot 4H_2O$(s) underwent a structural transformation at 313 K and dehydration occurred to $NaTcO_4$(cr) at 383 K. $NaTcO_4$(cr) underwent structural transformations at 610 and 635 K, and it melted at 1063 K. It was significantly volatile above the fusion temperature. Two X-ray structural determinations are available for the low-temperature anhydrous form [62SCH, 63KEL/KAN], *cf.* Table V.32.

V.8.1.2.1.b Thermodynamic data

German, Kryuchkov and Belgaeva [87GER/KRY] studied thermodynamic properties of phase transitions involving $NaTcO_4 \cdot 4H_2O$(s). This solid was reported to undergo:

- an endothermic $\alpha \rightarrow \beta$ phase transition at 313 K with $\Delta_{trs}H^\circ_m = (8.54 \pm 1.6)$ kJ·mol^{-1}, $\Delta_{trs}S^\circ_m = (27.3 \pm 5)$ J·K^{-1}·mol^{-1};
- a single-step dehydration to anhydrous α-$NaTcO_4$(cr) at 383 K with $\Delta_{dehyd}H^\circ_m = (77 \pm 8)$ kJ·mol^{-1}, $\Delta_{dehyd}S^\circ_m = (201 \pm 21)$ J·K^{-1}·mol^{-1};

- a transition to β-$NaTcO_4$(cr) at 610 K with $\Delta_{trs}H^\circ_m = (2.0 \pm 0.3)$ kJ·mol^{-1}, $\Delta_{trs}S^\circ_m = (3.3 \pm 0.5)$ J·K^{-1}·mol^{-1}; and
- a transition to γ-$NaTcO_4$(cr) at 635 K with $\Delta_{trs}H^\circ_m = (11.9 \pm 1.3)$ kJ·mol^{-1}, $\Delta_{trs}S^\circ_m = (18.7 \pm 2)$ J·K^{-1}·mol^{-1};
- fusion of γ-$NaTcO_4$(cr) occurred at 1063 K with $\Delta_{fus}H^\circ_m = (8.3 \pm 3)$ kJ·mol^{-1}, $\Delta_{fus}S^\circ_m = (7.8 \pm 2.8)$ J·K^{-1}·mol^{-1}.

We have changed their notation to reflect our convention that α denotes the lowest-temperature phase, β the next higher temperature phase, *etc*. No details were given by German, Kryuchkov and Belgaeva [87GER/KRY] for their experimental measurements, but they presumably calibrated their apparatus with compounds of known $\Delta_{trs}H^\circ_m$.

Since measurements of this type are sensitive to the kinetics of the phase transitions and to the heating rate, we believe that the uncertainty limits should be increased to 50% of the reported $\Delta_{trs}H^\circ_m$ and $\Delta_{trs}S^\circ_m$ values.

Lemire, Saluja and Campbell [91LEM/SAL] have measured heat capacities of aqueous $NaTcO_4$ solutions at 289.15, 293.15, 298.15, 323.15, 348.15, and 373.15 K, by use of a flow microcalorimeter with aqueous NaCl solutions used as calibration standards. From two to eight compositions were studied at each temperature, with the largest number of experimental points being measured at 298.15 and 348.15 K. At 298.15 K, eight compositions were studied from 0.01016 to 0.25060 mol · kg^{-1}. They reported that the uncertainty in their molalities was ±0.3% over most of the concentration range, and was $\pm 5 \times 10^{-5}$ mol · kg^{-1} at the lowest molalities. Their estimated uncertainties in the derived apparent molar heat capacities $C_{p,\phi}$ are ±(3 to 5) J·K^{-1}·mol^{-1} for $m > 0.03$ mol · kg^{-1}, but this uncertainty increases to as much as ±9 J·K^{-1}·mol^{-1} by 0.01 mol · kg^{-1}. These experiments were performed at a pressure of 6 bar.

These authors represented their apparent molar heat capacities with a Pitzer-type equation using statistical weights. Their derived partial molar heat capacities of $NaTcO_4$ at infinite dilution and 1 bar were represented by them as a function of temperature with:

$$C^\circ_{p,m}(NaTcO_4, aq, T) = -5192.14(T - 261.459)^{-1} + 443.121 - 0.916339\,T$$

At 298.15 K this equation yields $C^\circ_{p,m}(NaTcO_4, aq, 298.15\ K) = (28.4 \pm 8.0)$ J·K^{-1}·mol^{-1}, where the uncertainty limit is our estimate based on their estimated uncertainties of $C_{p,\phi}$ at low molalities.

Desnoyers *et al.* [76DES/VIS] recommended $C^\circ_{p,m}(Na^+, aq, 298.15\ K) = 43$ J·K^{-1}·mol^{-1} based on a critical assessment of literature data, but did not assign uncertainty limits to this value. However, Fortier, Leduc and Desnoyers [74FOR/LED] examined deviations of $C^\circ_{p,m}$ from additivity for the various alkali metal halides, which leads us to an estimate of this uncertainty of ±2.2 J·K^{-1}·mol^{-1}, and they also recommended a value of $C^\circ_{p,m}(Na^+, aq, 298.15\ K) = 41.9$ J·K^{-1}·mol^{-1}. Combining this value with the value for $NaTcO_4$ yields

$$C^\circ_{p,m}(TcO_4^-, aq, 298.15\ K) = -(13.5 \pm 8)\ J{\cdot}K^{-1}{\cdot}mol^{-1}.$$

We will now reanalyse volumetric data for aqueous $NaTcO_4$ solutions. These results yield the partial molar volume of aqueous TcO_4^- at infinite dilution, $\overline{V}_2^\circ$, which is related to the pressure coefficient of $\Delta_f G_m^\circ$ (TcO_4^-, aq, 298.15 K).

Neck and Kanellakopulos [87NEC/KAN] reported densities of aqueous $NaTcO_4$ in $g \cdot mL^{-1}$ at 298.15 K for five concentrations from 0.0982 to 0.3101 $mol \cdot dm^{-3}$. From these data they derived the value $\overline{V}_2^\circ(TcO_4^-, aq, 298.15\,K) = (45.9 \pm 1.0)\ cm^3 \cdot mol^{-1}$. After corrections and recalculations of their data, as discussed in Appendix A under [87NEC/KAN], we extrapolate the value $V_\phi^\circ = \overline{V}_2^\circ(NaTcO_4, aq, 298.15\,K) = (46.3 \pm 1.5)\ cm^3 \cdot mol^{-1}$, where the uncertainty limit is our estimate.

Lemire, Saluja and Campbell [91LEM/SAL] have performed a more extensive series of measurements of densities of aqueous $NaTcO_4$ at 287.43, 291.02, 296.02, 321.10, 346.10, 371.82, and 396.67 K using vibrating densimetry, with some experimental measurements to as low as 0.01 $mol \cdot kg^{-1}$. These molalities are uncertain by about 0.3%, which is slightly better precision than reported by Neck and Kanellakopulos [87NEC/KAN], and the densities of Lemire, Saluja and Campbell are more precise by one to two significant figures. However, their measurements were performed at a pressure of 6 bar, rather than at the standard pressure of 1 bar. Their values also need to be interpolated to 298.15 K, and extrapolated to infinite dilution.

Lemire, Saluja and Campbell [91LEM/SAL] smoothed their experimental results with a Pitzer-type equation. Their derived values of $\overline{V}_2^\circ$ were then represented by the least-squares equation:

$$\overline{V}_2^\circ(NaTcO_4, aq, T) = -25990.1\,T^{-1} + 174.212 - 0.134711\,T$$

in units of $cm^3 \cdot mol^{-1}$. Evaluation of this equation at 298.15 K yields $\overline{V}_2^\circ = 46.88\ cm^3 \cdot mol^{-1}$. Based on the reported uncertainties for molality and density, we assign this value an uncertainty of about 0.80 $cm^3 \cdot mol^{-1}$. The correction of $\overline{V}_2^\circ$ from 6 bar to 1 bar pressure should be less than this uncertainty, and was neglected because of lack of experimental information.

The statistically-weighted average of these two experimental values is $\overline{V}_2^\circ(NaTcO_4, aq, 298.15\,K) = (46.8 \pm 0.7)\ cm^3 \cdot mol^{-1}$. Millero [72MIL] reported that $\overline{V}_2^\circ(Na^+, aq, 298.15\,K) = -1.21\ cm^3 \cdot mol^{-1}$, but did not give an uncertainty. However, using the deviations from additivity for $\overline{V}_2^\circ$ of various alkali metal halides at 298.15 K (his table 2), we estimate an uncertainty of $\pm 0.1\ cm^3 \cdot mol^{-1}$. Thus our recommended value is

$$\overline{V}_2^\circ(TcO_4^-, aq, 298.15\,K) \quad = \quad (48.0 \pm 0.7)\ cm^3 \cdot mol^{-1}.$$

Boyd [78BOY2, 78BOY] reported isopiestic equilibrium molalities for aqueous $NaTcO_4$ from 0.10784 to 9.4640 $mol \cdot kg^{-1}$ and for $HTcO_4$ from 0.10581 to 5.4404 $mol \cdot kg^{-1}$, both at 298.15 K.

More recently, Könnecke *et al.* [97KÖN/NEC] performed additional isopiestic measurements for aqueous $NaTcO_4$ solutions at 298.15 K from 0.5353 to 7.3278 $mol \cdot kg^{-1}$. Their results agreed very well with the results of Boyd [78BOY2] as reanalyzed by Rard and Miller [91RAR/MIL]. Könnecke *et al.* also evaluated the parameters for Pitzer's equation [73PIT] using the combined data sets to 8.0 $mol \cdot kg^{-1}$.

Their Pitzer parameters should be more reliable than the parameters of Rard and Miller, which were based on fewer data points.

Boyd [78BOY2, 78BOY] used an extended form of the specific ion interaction equation to represent his data, and then used this equation to calculate values of the osmotic coefficient and mean molal activity coefficient at various round molalities. However, as noted by Rard and Miller [91RAR/MIL], the tabulated smoothed values of Boyd are not in particularly good agreement with the input values for $HTcO_4$, and are in considerable disagreement for $NaTcO_4$ solutions. Consequently, Rard and Miller reanalysed these results by using a different extended form of the specific ion interaction equation, *cf.* Appendix A. These recalculations gave a water activity, $a_{H_2O} = (0.6442 \pm 0.0079)$, and a mean molal activity coefficient $\gamma_{\pm} = (0.53 \pm 0.02)$ for the saturated solution, *cf.* Table A.8 in Appendix A.

Boyd [78BOY2] also reported the solubility of $NaTcO_4$ as being 11.299 $mol \cdot kg^{-1}$. Based upon the information given by Boyd, as discussed in Appendix A, the good agreement of Boyd's isopiestic molality ratios with those determined independently by Könnecke *et al.* [97KÖN/NEC], along with the familiarity of one of the present authors (Joseph A. Rard) with this method, we estimate that this solubility is uncertain by ±0.3%, and the recommended value is $m_s = (11.299 \pm 0.034)\ mol \cdot kg^{-1}$. Boyd did not report any characterisation of the solid phase used in his solubility determination.

German *et al.* [93GER/GRU] reported that the solubilities of $NaTcO_4 \cdot 4\ H_2O$(s) were 1.48 M at 293.15 K and 1.7 M at 282.15 K, which implies that this salt has retrograde solubility. A linear extrapolation of these solubilities to 298.15 K yields a concentration roughly one order of magnitude smaller than the value reported by Boyd [78BOY2], although the two studies cannot be accurately compared since they reported their solubilities with different concentration units. The densities required to interconvert these concentration scales are not available at such high concentrations. Even if these two studies involved solubility measurements for different hydrates of $NaTcO_4$, it seems unlikely that they would have such large differences.

German *et al.* [93GER/GRU] described their solubilities as having been determined "gravimetrically", from a solution that was saturated initially at 353 K followed by cooling of the solution. They reported that the concentration analyses for their related measurements for perrhenate salts were done by weighing of aliquots dried at 353 K and, presumably, a similar method was used for the $NaTcO_4$ solutions. Since the chemically similar salts $NaClO_4$(s) and $NaReO_4$(s) have much higher solubilities, and because both Boyd [78BOY2] and Könnecke et al. [97KÖN/NEC] were able to prepare solutions having much higher molalities of $NaTcO_4$, it is likely that the solubilities reported by German et al. [93GER/GRU] are too low or pertain to a non-equilibrium solid phase.

German *et al.* [87GER/KRY] reported that evaporation of aqueous solutions of $NaTcO_4$ yields $NaTcO_4 \cdot 4H_2O$(cr), and that this hydrate remains stable in contact with the saturated solution (although it undergoes a structural transition at 313 K) until 383 K, where it loses all four waters to form $NaTcO_4$ (cr).

As described in Appendix A, Guerman [98GUE2] has performed some new solubility experiments. Preliminary results at 298.15 K yield a very large solubility for $NaTcO_4 \cdot xH_2O$(s), in qualitative agreement with the value reported

by Boyd [78BOY2], and indicate that the high solubility values probably refer to $NaTcO_4 \cdot 4H_2O$(cr).

Since Boyd [78BOY2] did not characterise the solid phase in his study, it is not certain whether his reported saturation molality pertains to the reaction

$$NaTcO_4 \cdot 4H_2O(s) \quad \rightleftharpoons \quad Na^+ + TcO_4^- + 4H_2O(l) \qquad \text{(V.43)}$$

or to

$$NaTcO_4(s) \quad \rightleftharpoons \quad Na^+ + TcO_4^- \qquad \text{(V.44)}$$

For the first of these reactions,

$$\log_{10} K^\circ_{s,0}(\text{V.43}, 298.15\ \text{K}) \quad = \quad 0.79 \pm 0.04$$

and for the second reaction

$$\log_{10} K^\circ_{s,0}(\text{V.44}, 298.15\ \text{K}) \quad = \quad 1.56 \pm 0.03$$

where $K^\circ_{s,0}(\text{V.43}, 298.15\ \text{K}) = m_s^2 \cdot \gamma_\pm^2 \cdot a_{H_2O}^4$ and $K^\circ_{s,0}(\text{V.44}, 298.15\ \text{K}) = m_s^2 \cdot \gamma_\pm^2$.

The Gibbs energies of formation can be derived using the auxiliary data selected in this review.

$$\Delta_f G^\circ_m(NaTcO_4 \cdot 4H_2O, s, 298.15\ \text{K}) \quad = \quad -(1843.4 \pm 7.6)\ \text{kJ·mol}^{-1}$$
$$\Delta_f G^\circ_m(NaTcO_4, s, 298.15\ \text{K}) \quad = \quad -(890.5 \pm 7.6)\ \text{kJ·mol}^{-1}$$

Only one of these values can be correct. Based on information provided by Guerman (see the discussion of reference [98GUE2] in Appendix A), the experimental solubility of $m_s = (11.299 \pm 0.034)\ \text{mol} \cdot \text{kg}^{-1}$ most probably refers to reaction V.43. Thus our derived value of $\Delta_f G^\circ_m(TcO_4 \cdot 4H_2O, s, 298.15\ \text{K})$ is accepted by this review and that for $NaTcO_4$(s) is rejected.

V.8.1.2.2 $LiTcO_4 \cdot xH_2O$(s), $RbTcO_4$(cr) and $CsTcO_4$(cr)

V.8.1.2.2.a General properties

Anhydrous $LiTcO_4$(s) is isostructural with $LiReO_4$(s) [63KEL/KAN]. Zaitseva, Konarev and Velichko [77ZAI/KON2] reported that $LiTcO_4 \cdot 2H_2O$(s) was the precipitating phase from aqueous solution at room temperature. Thermogravimetric analysis of this solid indicated:

- structural transitions occurred between 308 and 333 K,
- fusion to form a saturated solution of the anhydrous salt at 338 to 343 K,
- dehydration at 348 to 378 K, and fusion at 638 to 658 K.

IR spectra were reported for $LiTcO_4 \cdot 2H_2O$(s), and X-ray diffraction powder patterns for this solid and $LiTcO_4$(s); however, the structures were not determined.

$RbTcO_4$(cr) was prepared by reaction of Rb_2CO_3 or $RbNO_3$ with aqueous $HTcO_4$. It has been little studied, but unit cell parameters have been reported [63KEL/KAN] (see Table V.32).

$CsTcO_4$(cr) was prepared by reaction of Cs_2CO_3 with aqueous NH_4TcO_4 [76MEY/HOP] or $CsNO_3$ with $HTcO_4$. The low-temperature form is orthorhombic, and it transformed to a tetragonal structure around 390 K [66KAN]. Three structural determinations are available (see Table V.32) at room temperature for the low-temperature form [62MCD/TYS, 63KEL/KAN, 76MEY/HOP], and one structural determination for the high-temperature form was done at 463 K [66KAN]. The $CsTcO_4$(cr) melted at 863 K [66KAN]. German *et al*. [93GER/GRU] reported that the enthalpy change for this structural transition is $\Delta_{trs}H = (0.86 \pm 0.04)$ kJ·mol^{-1}, based on DTA measurements.

A ^{99}Tc and ^{113}Cs NMR study has been performed [92TAR/KIR] for polycrystalline $CsTcO_4$(cr) from 90 to 430 K.

Technetium has been reported to enhance the volatility of caesium and rubidium from borosilicate waste glass under some conditions [86BAU/HEI, 90MIG]. Aerosols collected from the volatilisation of such material at 1173 to 1373 K have been shown by spectroscopy to contain Tc(VII) as $CsTcO_4$ [86BAU/HEI]. If this is the case, then vapour phase transport of $CsTcO_4$ could be of significance for transport of radionuclides in nuclear reactors.

Mass spectrometric experiments [93GIB2] were also performed for mixtures of CsOH(s) with a solid oxide or hydrous oxide of technetium in the presence of O_2(g) at 943 K. Many ions were detected by mass spectrometry whose likely parent species is $CsTcO_4$(g). It was not possible to detect dimeric caesium pertechnetate or its fragmentation products due to an upper detection limit of 400 amu for the mass spectrometer.

Spitsyn *et al*. [86SPI/TAR] and Tarasov *et al*. [86TAR/PET] reported nuclear quadrupole coupling constants for ^{99}Tc in solid $LiTcO_4$(s), $RbTcO_4$(cr), and $CsTcO_4$(cr), and other pertechnetate salts using NMR. The UV absorption spectra were reported at low temperatures for TcO_4^- in K(ClO_4, TcO_4) [72GÜD/BAL] and in Cs(ClO_4,TcO_4) [74DI /ING].

V.8.1.2.2.b Thermodynamic data

Keller and Kanellakopulos [63KEL/KAN] reported experimental values of the solubilities of $RbTcO_4$(cr) at 293.15 K, and of $CsTcO_4$(cr) from 288.15 to 313.15 K. Unfortunately, they did not provide any experimental details, so it is not known how their concentrations were determined, how long the solutions were given to become saturated, how precisely the solubilities were determined, or how well the temperature was controlled. The solubility values are given in Table V.36.

Table V.36: Solubilities of pertechnetate salts in water

Salt	T (K)	c_s (mol · dm^{-3})	m_s (mol · kg^{-1})	Reference
$NaTcO_4 \cdot 4H_2O$(cr)	298.15		11.299 ±0.034[a]	[78BOY2]
	282.15	~1.7		[93GER/GRU]
	293.15	~1.48		
	298.15		~12.6	[98GUE2]
$KTcO_4$	273.15		0.0344	[60BUS/BEV]
	298.15		0.1057 ±0.0002[b]	
	280.15	~0.37		[52PAR/MAR]
	300.15	~0.66		
	298.15		0.1040 ±0.0015	[98NEC/KÖN]
$RbTcO_4$	293.15	0.04699[c]		[63KEL/KAN]
$CsTcO_4$	288.15	0.0115[d]		[63KEL/KAN]
	293.15	0.0139		
	298.15	0.0164[e]	0.0169	
	303.15	0.0205		
	308.15	0.0244		
	313.15	0.0297		
	298.15		0.0184 ±0.0004	[97KÖN/NEC]
$AgTcO_4$	288.15	0.0155[f]		[63KEL/KAN]
	293.15	0.0208		
	298.15	0.0263[g]	0.0270	
	303.15	0.0346		
	308.15	0.0451		
	313.15	0.0602		
$TlTcO_4$	293.15	0.0020[h]		[63KEL/KAN]
	298.15	0.0024[i]	0.00248	
	303.15	0.00319		
	308.15	0.00376		
	313.15	0.00466		
	298.15	0.002116		[81MIK/MIŠ]
NH_4TcO_4	298.15		0.594[j]	[77VOL/KON]
$(CH_3)_4NTcO_4$	293.15	0.13	0.138	[86GER/GRI] [88GER/KRJ]
$(C_2H_5)_4NTcO_4$	293.15	0.012		[88GER/KRJ]
$(n\text{-}C_4H_9)_4NTcO_4$	293.15	0.0042 ±0.0002		[88GER/KRJ]

(Continued on next page)

Table V.36: (continued)

Salt	T (K)	c_s (mol · dm^{-3})	m_s (mol · kg^{-1})	Reference
Ph_4AsTcO_4	298[k]	(2.94±0.14) × 10^{-5}	(2.95±0.14) × 10^{-5}	[80PAC]
$Ba(TcO_4)_2$	293.15	0.165±0.005[l]		[69MAJ/PAC]
	308.15	0.361±0.011[l]		

[a] Error limits were calculated by assuming ±0.3% error for the solubility. Based on information reported by German, Kryuchkov and Belyaeva [87GER/KRY] and Guerman [98GUE2], the thermodynamically solid phase is probably the tetrahydrate.

[b] This is the selected value for $KTcO_4$(cr). The solubilities listed for reference [52PAR/MAR] are discussed in Appendix A.

[c] Calculated from their results in g/100 ml. By assuming that they used ^{99}Tc, the calculated molar mass is 248.372 g · mol^{-1}.

[d] Calculated from their results in g/100 ml. By assuming that they used ^{99}Tc, the calculated molar mass is 295.809 g · mol^{-1}.

[e] Interpolation of the least-squares fit to 298.15 K gave $c_s = 0.0169$ M, which is used in subsequent calculations.

[f] Calculated from their results in g/100 ml. By assuming that they used ^{99}Tc, the calculated molar mass is 270.772 g · mol^{-1}.

[g] Interpolation of the least-squares fit to 298.15 K gave $c_s = 0.0269$ M, which is used in subsequent calculations.

[h] Calculated from their results in g/100 ml. By assuming that they used ^{99}Tc, the calculated molar mass is 367.287 g · mol^{-1}.

[i] Interpolation of the least-squares fit to 298.15 K gave $c_s = 0.00247$ M.

[j] Experimental value. The value used in subsequent calculations was obtained from our reanalysis of solubilities for mixtures of NH_4TcO_4 with NH_4NO_3.

[k] Based on solubility experiments for the temperature range of 297.2 to 298.2 K. Because of its low solubility, Ph_4AsTcO_4(s) is sometimes used as a weighing form for the gravimetric analysis of pertechnetate solutions

[l] We assumed an uncertainty of ±3%, based on their statement that solubilities of NaCl, AgCl, and K_2CrO_4 determined by their method agreed to within 0.8 to 3.1 % of "literature values".

German *et al.* [88GER/KRJ] gave a plot of the solubilities of various pertechnetate salts in water as their Figure V.1. Although the temperature was not given for which those solubilities apply, it is presumably 293 K because their own data at that temperature are given on the same plot. Solubility values were also plotted for $LiTcO_4$(s) and other solids. They referenced these solubility values to two Russian language review articles which, unfortunately, we have been unable to obtain. Thus we cannot analyse the $LiTcO_4$(s) data.

The solubility of $RbTcO_4$(cr) [63KEL/KAN] was determined only at 293.15 K and not at the standard temperature of 298.15 K, so it will not be reanalysed. The solubility of $CsTcO_4$(cr) was studied at six temperatures. We represented this temperature dependence with the equation[4],

$$2 \ln c_s = A + BT^{-1}. \quad \text{(V.45)}$$

[4] The coefficients A and B are given in Table V.37.

This concentration product is equivalent to a solubility product on the molarity scale but without activity coefficient corrections. We intend that this equation be used only for smoothing and interpolation of the experimental solubilities. We do not consider them to be reliable for calculation of enthalpies of solution, because of the fairly large uncertainty in the reported solubilities, and because of the neglect of activity coefficients.

Temperature coefficients for the molar solubilities of various pertechnetate salts, e.g., $CsTcO_4$(cr) [63KEL/KAN], are given in Table V.37, and Figure V.6 is a plot of the solubility as a function of $10^3/T$.

Table V.37: Temperature coefficients for solubilities of aqueous pertechnetate salts as a function of temperature[(a)]

Salt	Temperature Range (K)	A	B (K)	Reference
$CsTcO_4$[(b)]	288.15-313.15	14.8537 ± 1.0652	-6863.32 ± 319.89	[63KEL/KAN]
$AgTcO_4$[(c)]	288.15-313.15	25.2081 ± 1.3729	-9672.04 ± 412.31	[63KEL/KAN]
$TlTcO_4$[(d)]	293.15-313.15	14.3941 ± 2.2130	-7870.51 ± 670.42	[63KEL/KAN]

(a) Coefficients for equation: $2\ln c_s = A + BT^{-1}$
(b) Correlation coefficient = -0.99887 and $1.96\sigma\,(\text{fit}) = 0.0741$
(c) Correlation coefficient = -0.99906 and $1.96\sigma\,(\text{fit}) = 0.0955$
(d) Correlation coefficient = -0.99718 and $1.96\sigma\,(\text{fit}) = 0.1154$

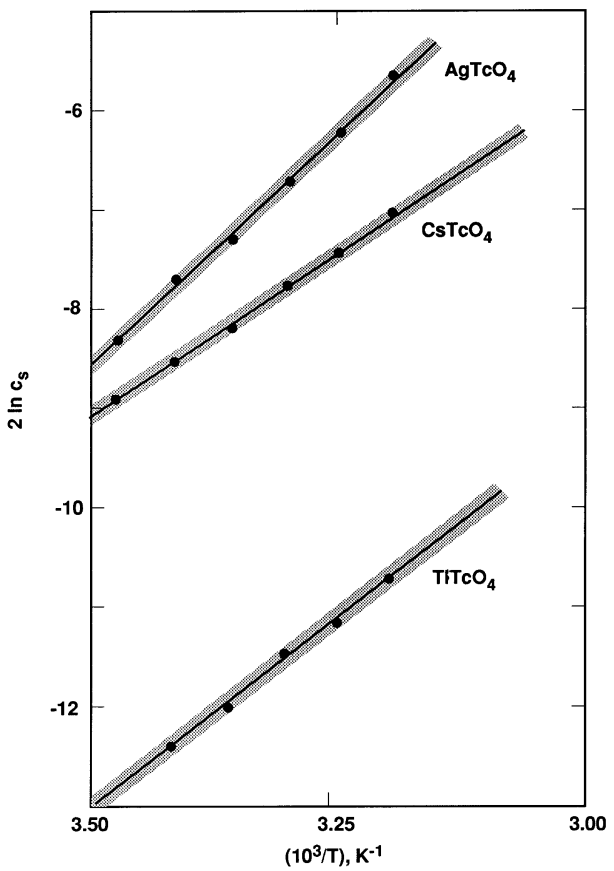
Könnecke *et al.* [97KÖN/NEC] recently determined the solubility of $CsTcO_4$(cr) at (298.15 ± 0.2) K using liquid scintillation counting of ^{99}Tc.

The calculated solubility[5] of $CsTcO_4$(cr) at 298.15 K from Equation (V.45) is $c_s = 0.01686$ M ($m_s = 0.0169$ mol $\cdot$ kg^{-1}) which agrees quite well with the experimental value from that study [63KEL/KAN]. The more recent solubility value of $m_s = (0.0184 \pm 0.0004)$ mol$\cdot$kg^{-1} from Könnecke *et al.* [97KÖN/NEC] is higher by 9 %. Keller and Kannellakopulos [63KEL/KAN] also gave the solubilities of $TlTcO_4$(cr), and an independent determination of its solubility at 298.15 K [81MIK/MIŠ] resulted in a value 13 % lower (see Table V.36). These comparisons suggest that the solubilities reported by Keller and Kannelakopulos may be uncertain by about 10 %.

Because Könnecke *et al.* [97KÖN/NEC] provided experimental details of their solubility measurements, whereas none were provided by Keller and Kannelakopulos [63KEL/KAN], our selected solubility of $m_s = (0.0177 \pm 0.0009)$ mol $\cdot$kg^{-1} for $CsTcO_4$(cr) gives greater weight to the more recent study. The molality of a saturated solution of $CsTcO_4$(cr) at 298.15 K is low enough that the activity coefficient can be estimated from the extended Debye-Hückel part of the SIT, which gives the value $\gamma_\pm = 0.8781$. Assuming that the solid phase is $CsTcO_4$(cr), we calculate the solubility

[5] In Section V.2.1 we give Eq.(V.4) for the conversion of molar concentrations to molal concentrations, $(m/c) \approx 1.00296 + aI_c(\text{dm}^6 \cdot \text{kg}^{-1} \cdot \text{mol}^{-1})$, which is valid at low ionic strengths. We selected a value of $a = (0.027 \pm 0.017)$ M^{-1} as the average for a number of electrolytes. However, the value of a for $NaClO_4$ solutions was 0.0435 M^{-1}, which is at the upper limit of this range. We consider this value for $NaClO_4$ to be a better approximation for 1-1 pertechnetate salts.

Figure V.6: Plot of solubility data of Keller and Kanellakopulos [63KEL/KAN] for aqueous solutions of $CsTcO_4$, $AgTcO_4$ and $TlTcO_4$. Least-square curves are shown for $2 \ln c_s = A + BT^{-1}$, where the values of A and B can be found in Table V.37.



product

$$\log_{10} K^\circ_{s,0}(\text{V.46}, 298.15\text{K}) = -(3.617 \pm 0.047)$$

for the reaction

$$CsTcO_4(cr) \quad \rightleftharpoons \quad TcO_4^- + Cs^+ \qquad \text{(V.46)}$$

where the value of $\gamma_\pm$ was assumed to be uncertain by 2 %. This value of $\log_{10} K^\circ_{s,0}$(V.46, 298.15K) is in nearly perfect agreement with $\log_{10} K^\circ_{s,0}$ (V.46, 298.15K) = $-(3.607 \pm 0.023)$ reported by Könnecke *et al.* [97KÖN/NEC]. Their value was derived from their binary and ternary solution solubility data using Pitzer's equation [73PIT].

The Gibbs energy of formation is derived using the auxiliary data selected in this review.

$$\Delta_f G^\circ_m(CsTcO_4, cr, 298.15\ K) \quad = \quad -(949.5 \pm 7.6)\ \text{kJ·mol}^{-1}$$

V.8.1.3 Other 1:1 pertechnetates

V.8.1.3.1 $AgTcO_4$(cr)

V.8.1.3.1.a General properties

$AgTcO_4$(cr) was prepared by reaction of Ag_2CO_3 with $HTcO_4$ [63KEL/KAN] or by precipitation from an aqueous solution of NH_4TcO_4 by addition of Ag^+ [62SCH]. Two X-ray structural determinations for $AgTcO_4$(cr) are in excellent agreement [62SCH, 63KEL/KAN], *cf.* Table V.32. The IR spectrum of $AgTcO_4$(cr) was also reported [66MÜL/KRE, 72BAL/HAN, 73JEŻ/HAN].

V.8.1.3.1.b Thermodynamic data

Keller and Kanellakopulos [63KEL/KAN] reported solubilites for $AgTcO_4$(cr) from 288.15 to 313.15 K. The experimental data are given in Table V.36 and they are shown in Figure V.6. The temperature coefficients for the solubilities are in Table V.37. Assuming that the solid phase in the solubility study by Keller and Kanellakopulos was anhydrous, the data correspond to the reaction

$$AgTcO_4(cr) \quad \rightleftharpoons \quad Ag^+ + TcO_4^- \qquad \text{(V.47)}$$

The reanalyses of this experimental data are done in exactly the same manner as for $CsTcO_4$(cr) (see Section V.8.1.2.2). The least-squares equation for the temperature dependence of the solubility, Equation (V.45), yields a calculated value of $c_s = 0.02689$ M at 298.15 K for $AgTcO_4$(cr), which is in good agreement with the measured value of 0.0263 M [63KEL/KAN]. Using the least-squares equation value then gives $(m_s/c_s) \approx 1.00413\ \text{dm}^3\text{·kg}^{-1}$ and $m_s = 0.0270\ \text{mol} \cdot \text{kg}^{-1}$. The estimated activity coefficient at this molality is $\gamma_\pm = 0.8568$, which then yields

$$\log_{10} K^\circ_{s,0}(\text{V.47}, 298.15\ \text{K}) \quad = \quad -3.27 \pm 0.13$$

Keller and Kanellakopulos [63KEL/KAN] do not provide sufficient experimental information to allow the accuracy of their reported solubilities to be assessed directly. However, they also reported solubilities of several other pertechnetate salts and for two of them, $TlTcO_4$(cr) and $CsTcO_4$(cr), there are independent determinations of the solubilities at 298.15 K [81MIK/MIŠ, 97KÖN/NEC]. For these two salts the molal solubilities from different laboratories agree to 13 and 9 %, respectively. See the discussion in Section V.8.1.2.2.b. Consequently, as with $CsTcO_4$(cr), we assume that $K^\circ_{s,0}$ is uncertain by 30 %.

The Gibbs energy of formation is derived using the auxiliary data selected in this review.

$$\Delta_f G^\circ_m(AgTcO_4, cr, 298.15\ K) \quad = \quad -(579.0 \pm 7.7)\ kJ{\cdot}mol^{-1}$$

V.8.1.3.2 $TlTcO_4$(cr)

V.8.1.3.2.a General properties

$TlTcO_4$(cr) was prepared by reaction of Tl_2CO_3 with $HTcO_4$ followed by evaporation of the solution [63KEL/KAN]. This $TlTcO_4$(cr) occurred as an orthorhombic crystal at room temperature, it transformed to a tetragonal structure around 368 K, and melted at 803 K [66KAN]. Structural data were published for both of these solid phases [63KEL/KAN, 66KAN], *cf.* Table V.32. The IR spectrum of $TlTcO_4$(cr) was also reported at room temperature [65MÜL/KRE, 66MÜL/KRE].

V.8.1.3.2.b Thermodynamic data

Solubility data were published by Keller and Kanellakopulos [63KEL/KAN] for $TlTcO_4$(cr). The experimental data are given in Table V.36 and they are shown in Figure V.6. Assuming that the solid phase was anhydrous, the data correspond to the reaction,

$$TlTcO_4(cr) \quad \rightleftharpoons \quad Tl^+ + TcO_4^- \qquad \text{(V.48)}$$

The calculated solubility at 298.15 K from the least-squares representation is 0.00247 M, which is in good agreement with the experimental value of 0.0024 M. The molarity-to-molality conversion yields $m_s/c_s \approx 1.00307\ (dm^3 \cdot kg^{-1})$ (see footnote 5) and thus $m_s = 0.00248\ mol \cdot kg^{-1}$. This molality yields an estimated activity coefficient of $\gamma_\pm = 0.9472$, and therefore $\log_{10} K^\circ_{s,0}$(V.48, 298.15 K) $= -5.26$.

Mikulaj, Mišianiková and Macášek [81MIK/MIŠ] reported solubilities of $TlTcO_4$(cr) in water at 298.15 K, along with those of $TlTcO_4$(cr) in solutions of HNO_3, $LiNO_3$, $NaNO_3$, NH_4NO_3, and $Ca(NO_3)_2$ up to quite high ionic strengths, *cf.* Appendix A. This review has reanalysed their experimental data and extrapolated to $I = 0$ using the specific ion interaction model. As discussed in Appendix A, the calculated value is, $\log_{10} K^\circ_{s,0}$(V.48, 298.15 K) $= -(5.39 \pm 0.01)$.

These two values of $K^\circ_{s,0}$ for $TlTcO_4$(cr) are in good agreement. Neither of these experimental studies [63KEL/KAN, 81MIK/MIŠ] provided sufficient experimental detail to allow us to judge which value is more accurate, so we accept the unweighted

average as the best value. We estimate the error in this value as being 1.96 times the average deviation from their mean for the 95 % confidence limits. Our recommended value is

$$\log_{10} K^\circ_{s,0}(\text{V.48}, 298.15\ \text{K}) \quad = \quad -(5.32 \pm 0.12)$$

There are no thermodynamic values for Tl^+ in the CODATA tables, but a value for $\Delta_f G^\circ_m$ is selected in Chapter VI. The Gibbs energy of formation of $TlTcO_4$(cr) is then obtained using our selected value of $K^\circ_{s,0}$(V.48, 298.15 K),

$$\Delta_f G^\circ_m(TlTcO_4, \text{cr}, 298.15\ \text{K}) = -(700.2 \pm 7.6)\ \text{kJ·mol}^{-1}$$

V.8.1.3.3 NH_4TcO_4(cr)

V.8.1.3.3.a General properties

One of the most thoroughly studied pertechnetate salts is NH_4TcO_4(cr). It was prepared by neutralisation of aqueous $HTcO_4$ with NH_3(aq) [63KEL/KAN] or by dissolving metallic technetium in a mixture of aqueous H_2O_2(aq) and NH_3(aq) [78SPI/KUZ]. Fresh samples of NH_4TcO_4 are colourless, but upon storage they gradually darken due to radiolytic self-decomposition (see the discussion of Ref. [59AND] in Appendix A).

The structure of NH_4TcO_4(cr) at room temperature was reported in three publications [62MCD/TYS, 63KEL/KAN, 80FAG/LOC], and results are also available at 208 and 141 K [80FAG/LOC], *cf.* Table V.32.

Various properties of NH_4TcO_4(cr) have been reported. These include magnetic susceptibilities at 78 and 298 K [54NEL/BOY], the IR [65MÜL/KRE, 66MÜL/KRE] and Raman spectra [80FAG/LOC], the nuclear quadrupole coupling constant for ^{99}Tc in NH_4TcO_4(cr) [86SPI/TAR, 86TAR/PET], and the technetium $3d_{5/2}$ binding energy [86THO/NUN].

Thermal decomposition of NH_4TcO_4(cr) in an argon-ammonia atmosphere produced a technetium nitride, see Section V.6.1.1. Decomposition of NH_4TcO_4(cr) in an argon atmosphere was reported to occur at 598 K [78SPI/KUZ] or 513 K [78VIN/KON3], and below 402 K (presumably in air) [54NEL/BOY]. A decomposition temperature of about 823 K was reported for NH_4TcO_4(cr) heated in vacuum[6]. Muller, White and Roy [64MUL/WHI] studied the decomposition of NH_4TcO_4(cr) in a N_2(g) atmosphere with the O_2(g) partial pressure fixed at 4×10^{-6} bar. Decomposition began below 600 K but was not entirely complete until 1023 K.

These major differences in the thermal decomposition behaviour of NH_4TcO_4(cr) are too large to be attributed to experimental differences such as heating rate or the presence or absence of an inert gas. Most likely the decomposition is catalysed by impurities in the NH_4TcO_4(cr), including those arising from radiolytic self decomposition.

Both X-ray diffraction [64MUL/WHI, 78SPI/KUZ, 78VIN/KON3] and thermogravimetric measurements [78SPI/KUZ, 78VIN/KON3] indicated the solid residue was

[6] S. Fried, personal communication to G.E. Boyd, cited in Ref. [59BOY2].

TcO_2(cr). Thus, the thermal decomposition in the absence of oxygen occurred by way of the overall reaction

$$NH_4TcO_4(cr) \rightarrow TcO_2(cr) + \frac{1}{2}N_2(g) + 2H_2O(g)$$

V.8.1.3.3.b Thermodynamic data

Volk, Konarev and Barabash [77VOL/KON] reported values of the solubility of NH_4TcO_4(cr) in water and in aqueous NH_4NO_3 over the whole composition range at 298.15 K (see Table A.4 in Appendix A). Solutions were allowed to equilibrate with a solid phase for four to five hours. They did not report how precisely they controlled their temperature.

Their reported solubilitites have been reanalysed by this review (Appendix A) and the calculated equilibrium constants, $K_{s,0}$, for the reaction

$$NH_4TcO_4(cr) \rightleftharpoons NH_4^+ + TcO_4^- \quad \text{(V.49)}$$

have been extrapolated to $I = 0$ using the specific ion interaction model (SIT, *cf.* Appendix C). As discussed in the Appendix A, the selected value for the solubility equilibrium is

$$\log_{10} K^\circ_{s,0}(\text{V.49}, 298.15\ \text{K}) = -0.91 \pm 0.07$$

The Gibbs energy of formation is derived using the auxiliary data selected in this review.

$$\Delta_f G^\circ_m(NH_4TcO_4, \text{cr}, 298.15\ \text{K}) = -(722.0 \pm 7.6)\ \text{kJ·mol}^{-1}$$

V.8.2 Pertechnetate salts with divalent cations

There are no experimental studies involving the thermodynamic properties for most of these compounds (only for $Mg(TcO_4)_2$ and $Ba(TcO_4)_2$(s)), so this review summarises the preparative and general properties of the known solids, *cf.* Table V.38.

V.8.2.1 Alkaline earth (Group 2) pertechnetates

Zaitseva, Velichko and Kazakov [79ZAI/VEL] reacted magnesium hydroxycarbonate with $HTcO_4$, and evaporated the solution in air to yield crystals. These crystals were readily soluble in water, ethanol, and acetone, but were insoluble in carbon tetrachloride. Chemical analysis indicated the precipitating phase was $Mg(TcO_4)_2{\cdot}4H_2O$(cr). A pycnometric measurement gave a density of 2.30 $\text{g} \cdot \text{cm}^{-3}$. They reported IR spectra and X-ray powder diffraction pattern results for $Mg(TcO_4)_2$(cr) and both of its hydrates, *cf.* Table V.38, but did not determine the crystal structures. However, Kruglov and Zaitseva [83KRU/ZAI] determined the symmetry groups and unit cell parameters for $Mg(TcO_4)_2$(cr) and $Mg(TcO_4)_2{\cdot}4H_2O$(cr). The dehydration temperature of these solids was measured by differential thermal analysis and thermogravimetric analysis.

Table V.38: Pertechnetate salts of divalent cations.

Compound	x	References
$Mg(TcO_4)_2 \cdot xH_2O$	4, 2, 0	[83KRU/ZAI]
$Ca(TcO_4)_2 \cdot xH_2O$	2, 1, 0	[65WAS, 66KEL/WAS, 86TET/ZAI]
$Sr(TcO_4)_2 \cdot xH_2O$	2, 1, 0	[65WAS, 66KEL/WAS]
$Ba(TcO_4)_2$	0	[65WAS, 66KEL/WAS, 69MAJ/PAC]
$Pb(TcO_4)_2 \cdot xH_2O$	2, 0	[77ZAI/KON3]
$Zn(TcO_4)_2 \cdot xH_2O$	4, 2, 0	[82ZAI/VEL2]
$Cd(TcO_4)_2 \cdot xH_2O$	2, 0	[78ZAI/KON]
$Cu(TcO_4)_2 \cdot xH_2O$	4, 2, 0	[77ZAI/KON]
$Co(TcO_4)_2 \cdot xH_2O$	4, 3, 0	[78ZAI/VEL]
$Ni(TcO_4)_2 \cdot xH_2O$	4, 2, 0	[78ZAI/VEL2]

Neck *et al.* [98NEC/KÖN] prepared $Mg(TcO_4)_2 \cdot 2H_2O$ (cr) by reaction of stoichiometric amounts of MgO(s) with aqueous NH_4TcO_4 at 373 K, followed by evaporation of the water at the same temperature.

Wassilopulos [65WAS], Keller and Wassilopulos [66KEL/WAS], and Teterin *et al.* [86TET/ZAI] reacted $CaCO_3$ or CaO with $HTcO_4$, and evaporated the resulting solution to yield crystals of $Ca(TcO_4)_2{\cdot}2H_2O$(s) as the precipitating phase. Differential thermal analysis [66KEL/WAS] indicated the formation of the monohydrate, and the anhydrous $Ca(TcO_4)_2$(s). The IR and the ^{1}H NMR spectra of $Ca(TcO_4)_2{\cdot}2H_2O$(s) were also reported by Teterin *et al.* [86TET/ZAI].

Reaction of $SrCO_3$ with $HTcO_4$, followed by evaporation of the solution, yielded crystals of $Sr(TcO_4)_2{\cdot}2H_2O$(s) [65WAS, 66KEL/WAS]. Differential thermal analysis indicated the formation of the monohydrate and anhydrous $Sr(TcO_4)_2$(s). The structures of these phases are unknown.

The reaction of $BaCO_3$ with $HTcO_4$, followed by evaporation of the solution, gave crystals of anhydrous $Ba(TcO_4)_2$(s). This solid was thermally stable to at least 900 K [65WAS, 66KEL/WAS]. Structural data are not available. Aqueous solubilities of $Ba(TcO_4)_2$(s) were reported at 293 and 308 K [69MAJ/PAC]. As discussed in Appendix A, these experimental values do not provide sufficient information to extract thermodynamic data.

Neck *et al.* [98NEC/KÖN] performed isopiestic vapour-pressure measurements for aqueous $Mg(TcO_4)_2$ solutions from 0.1588 to 3.7929 mol·kg^{-1} at 298.15 K, and analysed these results using Pitzer's equation [73PIT]. Their reported parameters for this equation can be used for the calculation of water activities and mean molal activity coefficients of $Mg(TcO_4)_2$ solutions. The measurements suggest that the solubility of hydrated $Mg(TcO_4)_2$ exceeds 3.8 mol·kg^{-1}.

Neck *et al.* [98NEC/KÖN] also derived Pitzer parameters for aqueous $Ca(TcO_4)_2$ solutions from measurements of the solubility of $KTcO_4$ (cr) in aqueous $CaCl_2$ solutions at 298.15 K. These parameters can be used to estimate the water activity and mean molal activity coefficients of $Ca(TcO_4)_2$ solutions. Similarly, they derived Pitzer parameters for $KTcO_4$ from measurements of the solubilities of $KTcO_4$ in KCl solutions.

V.8.2.2 Other 1:2 pertechnetates

A lead pertechnetate was prepared by reaction of excess lead hydroxycarbonate with $HTcO_4$, followed by evaporation of the solution over P_2O_5 until crystallisation occurred [77ZAI/KON3]. Chemical analyses indicated these crystals were $Pb(TcO_4)_2{\cdot}2H_2O$(s). This solid was soluble in water, ethanol, and acetone, but it was insoluble in diethylether, chloroform, and carbon tetrachloride. The IR spectra and X-ray powder diffraction patterns were reported for $Pb(TcO_4)_2{\cdot}2H_2O$(s) and $Pb(TcO_4)_2$(s), but the structures of these phases were not determined.

A zinc pertechnetate was prepared by reaction of ZnO with $HTcO_4$, followed by evaporation of the solution under vacuum and dehydration over P_2O_5(s) [82ZAI/VEL2]. Chemical analyses indicated the resulting crystals were $Zn(TcO_4)_2{\cdot}4H_2O$(s); they were soluble in polar solvents. The pycnometric density of $Zn(TcO_4)_2{\cdot}4H_2O$(s) was given as 3.06 or 3.45 $g \cdot cm^{-3}$ and that of $Zn(TcO_4)_2$(s) was 3.88 $g \cdot cm^{-3}$. IR spectra and X-ray powder diffraction patterns were given for $Zn(TcO_4)_2$(s) and both of its hydrates, *cf.* Table V.38, but the structures of these phases were not determined.

A cadmium pertechnetate was prepared by reaction of excess $CdCO_3$ with $HTcO_4$, followed by evaporation of the solution to dryness over P_2O_5(s) [78ZAI/KON]. The crystals were highly soluble in water, ethanol, and acetone. Results from chemical analyses indicated their composition was $Cd(TcO_4)_2{\cdot}2H_2O$(s). IR spectra and X-ray powder diffraction patterns were reported for $Cd(TcO_4)_2{\cdot}2H_2O$(s) and $Cd(TcO_4)_2$(s), but the structures were not determined.

Zaitseva *et al*. [77ZAI/KON] prepared a copper(II) pertechnetate by reaction of excess CuO with $HTcO_4$, followed by evaporation of the solution in air. The crystals were found to be $Cu(TcO_4)_2{\cdot}4H_2O$(s) by chemical analysis. They were soluble in water, ethanol, and acetone, and they were stable in air at room temperature. IR spectra and X-ray powder diffraction patterns were reported for anhydrous $Cu(TcO_4)_2$(cr) and its two hydrates, *cf*. Table V.38, but the structures of these phases were not determined.

Reaction of excess cobalt oxycarbonate with $HTcO_4$, followed by evaporation of the solution over P_2O_5(s), produced a crystalline solid which was found to be $Co(TcO_4)_2 \cdot 4H_2O$(s) by chemical analyses [78ZAI/VEL]. The density was determined to be 2.84 $g \cdot cm^{-3}$ by pycnometry. These crystals were hygroscopic and readily soluble in water, ethanol, and acetone, but they were insoluble in diethylether and carbon tetrachloride. IR spectra and X-ray powder diffraction patterns were reported for anhydrous $Co(TcO_4)_2$(s) and the two hydrates, *cf*. Table V.38, but the structures of these phases were not determined.

The reaction of $NiCO_3$ with $HTcO_4$, followed by filtration and evaporation over P_2O_5(s) or anhydrous $CaCl_2$(s), gave a crystalline solid [78ZAI/VEL2]. These crystals were found to be $Ni(TcO_4)_2 \cdot 4H_2O$(s) based upon chemical analyses. This compound as well as its different hydrates, *cf.* Table V.38 were hygroscopic and were soluble in water, ethanol, and acetone, but insoluble in diethylether and carbon tetrachloride. Their IR spectra and X-ray powder diffraction patterns were reported, but the structures of these phases were not determined. They reported that $Ni(TcO_4)_2 \cdot 2H_2O$(s) and $Ni(TcO_4)_2 \cdot 4H_2O$(s) are isostructural with their perrhenate analogues. The density of

Table V.39: Pertechnetate salts of trivalent cations.

Compound	x	References
$Sc(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[82ZAI/VEL]
$Y(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[75ZAI/BEL, 83TET/ZAI, 83VAR/ZAI]
$La(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[74ZAI/KON3]
$Ce(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[74ZAI/KON3]
$Pr(TcO_4)_3 \cdot xH_2O$	4, 3, 1, 0	[72ZAI/VEL2]
$Nd(TcO_4)_3 \cdot xH_2O$	4, 1, 0	[72ZAI/VEL]
$Sm(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[74ZAI/KON4]
$Eu(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[74ZAI/KON4]
$Gd(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[75ZAI/KON]
$Tb(TcO_4)_3 \cdot xH_2O$	4, 2, 1, 0	[76ZAI/KON2, 83TET/ZAI]
$Dy(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[76ZAI/KON, 83TET/ZAI]
$Ho(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[83TET/ZAI, 83VAR/ZAI]
$Er(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[74ZAI/KON, 83TET/ZAI, 83VAR/ZAI]
$Tm(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[74ZAI/KON2, 83TET/ZAI, 83VAR/ZAI]
$Yb(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[74ZAI/KON2, 83TET/ZAI]
$Lu(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[75ZAI/BEL, 83TET/ZAI, 83VAR/ZAI]
$Ga(TcO_4)_3 \cdot xH_2O$	7, 5, 3, 1, 0	[87ZAI/VEL]
$In(TcO_4)_3 \cdot xH_2O$	3, 1, 0	[87ZAI/VEL2]
$Al(TcO_4)_3 \cdot xH_2O$	7, 4, 3, 1, 0	[86ZAI/VEL]
$Fe(TcO_4)_3 \cdot xH_2O$	4, 2, 0	[86ZAI/VEL2]

the tetrahydrate was determined to be 3.04 $g \cdot cm^{-3}$ by using pycnometry.

Differential thermal analysis and thermogravimetric analysis were used to determine the dehydration temperature of all solid pertechnetates listed in Table V.38. See the source papers cited in this section for the detailed information.

V.8.3 Pertechnetate salts of trivalent cations

There are no experimental studies involving the thermodynamic properties for these salts, so this review summarises the preparative and general properties of the known solids, *cf.* Table V.39.

V.8.3.1 Rare earth pertechnetates

Pertechnetate salts have been prepared by Zaitseva and co-workers for all of the rare earths, Ln (lanthanum and the lanthanides, yttrium, and scandium) with the exception of promethium, which has no stable isotopes. Because of considerable similarities of their chemistry, they will be discussed together as a group. Salts of yttrium generally are very similar in properties of those of the heavy lanthanides, whereas scandium salts can show some individualistic behaviour owing to the smaller ionic radius of Sc^{3+}.

The general method of synthesis for rare earth pertechnetates has been to react the sesquioxides Ln_2O_3(s) with $HTcO_4$, followed by evaporation of the solution at room

temperature to yield crystals. Cerium carbonate, terbium oxide, and "Pr_6O_{11}", were used for those rare earths inasmuch as Ln_2O_3(s) were not readily available for them.

Several hydrated pertechnetates that precipitated from aqueous solutions are listed in Table V.39.

The heavier lanthanides (yttrium subgroup) uniformly gave tetrahydrates upon precipitation. However, the lighter rare earths gave either trihydrates or tetrahydrates, which implies these two hydrates differ little in stability for those elements.

X-ray powder diffraction patterns were reported in those studies for the hydrated rare earth pertechnetates that precipitated, the anhydrous and some of the intermediate hydrates obtained by thermal dehydration of the original hydrates. However, the structures of these phases were not determined in those studies. Varofolomeev *et al.* [83VAR/ZAI] determined unit cell parameters for the isostructural triclinic crystals of the yttrium subgroup (Y, Ho, Er, Tm, and Lu) $Ln(TcO_4)_3{\cdot}4H_2O$(cr). Although the space group was not given in that report, it was reported by Teterin and Zaitseva [83TET/ZAI] to be $P\bar{1}$ with $Z = 2$. They also noted that the Yb and, presumably, Tb and Dy analogues are isostructural.

IR spectra were reported for most of the compounds listed in Table V.39 as well as for all of the yttrium subgroup compounds $Ln(TcO_4)_3{\cdot}4H_2O$(cr), (the latter in Ref. [83TET/ZAI]). In addition, electronic absorption spectra were reported for some of the anhydrous and hydrated pertechnetates of praseodymium, holmium, and erbium [72ZAI/VEL2, 74ZAI/KON].

The hydrated $Ln(TcO_4)_3$(cr) were described as being readily soluble in water, ethanol, and in acetone. Given the general similarity of the solubilities of pertechnetate salts to those of the corresponding perchlorate salts (with a few exceptions), we expect their aqueous solubilities to be quite high[7].

In nearly all cases the hydrated and anhydrous rare earth pertechnetates were described as being hygroscopic, with the degree of hygroscopicity increasing as the degree of hydration of the salt decreased.

In all of the experimental investigations listed in Table V.39, dehydration was studied for the hydrated $Ln(TcO_4)_3$(cr). The stoichiometries and temperatures for the stepwise dehydrations were investigated with thermogravimetric analysis and differential thermal analysis. In the majority of cases the authors also determined the dehydration temperatures by isothermal dehydration.

V.8.3.2 Other 1:3 pertechnetates: Ga, In, Al and Fe

A pertechnetate of gallium(III) was prepared by dissolving freshly precipitated gallium hydroxide in $HTcO_4$, followed by evaporation of the solvent over anhydrous $CaCl_2$(s) [87ZAI/VEL]. From the results of chemical analyses, the authors concluded that the precipitating phase was $Ga(TcO_4)_3{\cdot}7H_2O$(s). IR spectra were reported for $Ga(TcO_4)_3{\cdot}7H_2O$(s) and $Ga(TcO_4)_3$(s).

[7] Reported solubilities [74SPE/RAR] for the hydrated $Ln(ClO_4)_3$(cr) range from 4.604 to 4.760 $mol \cdot kg^{-1}$ at 298.15 K.

Indium(III) pertechnetate was prepared by the same method used for gallium(III) [87ZAI/VEL2]. The precipitating phase was found to be $In(TcO_4)_3 \cdot 3H_2O(s)$ by chemical analyses. IR spectra and X-ray powder diffraction patterns were reported for $In(TcO_4)_3 \cdot 3H_2O(s)$, $In(TcO_4)_3 \cdot H_2O(s)$, and $In(TcO_4)_3(s)$, but the structures of these phases were not determined.

Zaitseva, Velichko and Borisov [86ZAI/VEL] prepared a hydrated aluminium(III) pertechnetate by dissolution of $Al(OH)_3(s)$ in $HTcO_4$. Evaporation of this solution over $CaCl_2(cr)$ gave crystals after 3 to 4 days. Chemical analyses indicated that the precipitating phase was $Al(TcO_4)_3 \cdot 7H_2O(s)$. IR spectra and X-ray powder diffraction patterns were reported for $Al(TcO_4)_3(s)$ and all of its hydrates, but the structures of these phases were not determined.

Iron(III) pertechnetate was prepared by dissolving iron(III) hydroxide in $HTcO_4$, followed by evaporating the solution in a vacuum or over $P_2O_5(s)$ [86ZAI/VEL2]. The precipitating phase was $Fe(TcO_4)_3 \cdot 4H_2O(s)$ as determined by chemical analyses. IR spectra and X-ray powder diffraction patterns were reported for anhydrous $Fe(TcO_4)_3(s)$ and both hydrates, but their structures were not determined. Pycnometrically determined densities for $Fe(TcO_4)_3 \cdot 4H_2O(s)$ and $Fe(TcO_4)_3(s)$ were 2.52 and 2.80 $g \cdot cm^{-3}$, respectively.

Differential thermal analysis and thermogravimetric analysis were used to determine the dehydration temperature for all these solids, *cf.* Table V.39.

All these salts were hygroscopic and soluble in water, ethanol, and acetone, but were insoluble in carbon tetrachloride.

V.8.4 Other pertechnetates

V.8.4.1 Tetraalkylammonium and ammine pertechnetates

Tetramethylammonium pertechnetate $(CH_3)_4NTcO_4(cr)$ was prepared by reaction of aqueous $HTcO_4$ with $(CH_3)_4NOH$, followed by slow evaporation. Its IR spectrum was also reported [87GER/GRI]. $(n\text{-}C_4H_9)_4NTcO_4(cr)$ and $(C_2H_5)_4NTcO_4(cr)$ were also prepared by the same method [87GER/GRI, 88GER/KRJ].

Nuclear quadrupole coupling constants have been reported for these three tetraalkylammonium pertechnetates [86SPI/TAR, 86TAR/PET]. German *et al.* [93GER/GRU] determined the enthalpies for phase transitions of $(C_2H_5)_4NTcO_4(cr)$ and $(n\text{-}C_4H_9)_4NTcO_4(cr)$, and the enthalpy of fusion of $(n\text{-}C_4H_9)_4NTcO_4(cr)$, based on DTA measurements.

These same three tetraalkylammonium pertechnetates have been investigated in more detail by Kuzina, German and Spitsyn [87KUZ/GER] and their crystal structures were determined by X-ray diffraction. They studied the thermal decomposition temperatures of these solids in flowing argon by differential thermal analysis.

German *et al.* [88GER/KRJ, 93GER/GRU] reported aqueous solubilities of the three pertechnetates at 293 K. They also reported solubilities of $(n\text{-}C_4H_9)_4NTcO_4(cr)$ in aqueous solutions of 0.25 to 5.00 M $LiNO_3$, in 0.25 to 5.00 M HNO_3, in 0.0042 to 0.210 M $(n\text{-}C_4H_9)_4NOH$, and in mixtures of $LiNO_3$ and HNO_3 at a total ionic strength of 5.00 M. Their reported solubilities for the tetraalkylammonium salts in

water are included in Table V.36. No attempt is made to reanalyse these solubilities [86GER/GRI, 88GER/KRJ] since they were measured at 293.15 K rather than at 298.15 K. A discussion on the solubilities of $(n\text{-}C_4H_9)_4NTcO_4$ in solutions of other electrolytes is given in Ref. [88GER/KRJ] (Appendix A).

The synthesis of $Pt(NH_3)_4(TcO_4)_2$(cr) has been reported by Shakh *et al.* [80SHA/VAR] and by Rochon, Kong and Melanson [90ROC/KON].

V.8.4.2 Other organic pertechnetate salts

Kuzina, Oblova and Spitsyn [78KUZ/OBL] reported the synthesis of a triphenylguanidinium pertechnetate $(PhNH)_3CTcO_4 \cdot H_2O$(s) along with its IR spectrum and differential thermal analysis measurements.

The solubility of Ph_4AsTcO_4(s) has been measured in water at $\approx$ 298 K [80PAC] and in solutions of Ph_4AsCl [52PAR/MAR]; see discussion under Ref. [80PAC] in Appendix A.

Nuclear quadrupole coupling constants were reported for Ph_4AsTcO_4(s) and Ph_4PTcO_4(s) [86SPI/TAR, 86TAR/PET]. The IR spectrum of Ph_4AsTcO_4(s) was also reported [67MÜL/RIT].

The coprecipitation of Ph_4AsTcO_4(s) in Ph_4AsClO_4(s) was studied by Omori *et al.* [84OMO/TAK].

Gerber *et al.* [92GER/KEM] prepared and characterised[8] $Tc(pda)_3TcO_4$(cr) which contains technetium in two different valence states.

The synthesis of a dimeric acetate compound, $Tc_2(\mu\text{-}CH_3COO)_4(TcO_4)_2$(cr). has been reported by Baturin *et al.* [91BAT/GER]. Baturin *et al.* [94BAT/GRI] also prepared a ferricinium pertechnetate $Fe(C_5H_5)_2TcO_4$(cr) by reaction of 1 M $HTcO_4$ with powdered ferrocene. Additional details of the synthesis and characterisation of this material were given by Antipov *et al.* [94ANT/KRY].

V.8.4.3 Oxypertechnetate salts: U(VI), Th(IV) and Np(VI)

A uranyl pertechnetate was prepared by reaction of UO_3(s) with $HTcO_4$, followed by evaporation of the solution in air [76ZAI/SLA]. The resulting hygroscopic precipitate was determined to be $UO_2(TcO_4)_2{\cdot}2H_2O$(s) from chemical analyses. Thermogravimetric analysis and differential thermal analysis were used to determine the dehydration temperature of $UO_2(TcO_4)_2 \cdot xH_2O$(s) ($x = 2, 1.5, 1, 0$). X-ray powder diffraction patterns were reported graphically for the solids with $x = 2, 1.5, 0$ but the structures of these phases were not determined.

Zaitseva and Vakhrushin [84ZAI/VAK] dissolved thorium(IV) hydroxide in $HTcO_4$. The resulting solution was evaporated until crystals formed. IR spectroscopic measurements on these crystals gave no evidence for the presence of a hydroxy ligand. That evidence, together with results from chemical analyses, led them to formulate the solid as being $Th_2O(TcO_4)_6 \cdot 6H_2O$(s). Using thermogravimetric analysis, they observed a mass loss corresponding to the the formation of $Th_2O(TcO_4)_6$(s). IR

[8] H_2pda is 1,2-diaminobenzene.

spectra and X-ray powder diffraction patterns were reported for both solids, but the structures were not determined. The formulation of these salts as dimeric thorium oxypertechnetates is plausible but speculative, and actual structural information is needed to confirm this. Guerman *et al.* [98GUE/FED] prepared the compound $(NpO_2)_2(TcO_4)_4 \cdot 3H_2O$(cr) and determined its structure using single crystal X-ray structural analysis. This compound contains two structurally independent "NpO_2^{2+}" units, one of which is coordinated with pertechnetates and water molecules and the other coordinated solely with pertechnetate ligands. The authors of this study kindly made their results available to this review prior to publication.

V.8.5 Mixed oxides

The most thoroughly studied ternary oxides of technetium contain the pertechnetate ion TcO_4^-. The present section is devoted to all other ternary and quaternary oxides containing Tc(VII), Tc(VI), Tc(V), Tc(IV), or Tc(III). The majority of these mixed metal oxides were prepared by solid state reaction of pertechnetate salts or TcO_2(cr) with oxides of one or more other metals. Technetium metal was also added in some cases to give reduction of Tc(VII) to Tc(VI) or Tc(V), or reduction of Tc(IV) to Tc(III).

Much of the original data can be found in the papers by Muller, White and Roy [64MUL/WHI], Keller and Kanellakopulos [65KEL/KAN], and Keller and Wassilopulos [66KEL/WAS] and also Muller's Ph.D. thesis [68MUL]. Most of these results have been summarised in the Gmelin Handbook [83ALL/BUR, *pp*.55-77]. The basic structural types were reported for many of these oxides in those reports, but the space groups were generally not listed. Space groups for ternary and quaternary oxides of technetium have been summarised by Pies and Weiss [77PIE/WEI]. Crystal structure information for the ternary and quaternary oxides are summarised in Table V.40. Ternary oxides described by Keller and Wassilopulos [66KEL/WAS] as being $M^{II}M^{I}_{0.5}Tc_{0.5}O_3$ were rewritten as $M^{II}_2M^{I}TcO_6$, where M^I denotes Li or Na.

Table V.40: Crystal structure parameters of ternary and quaternary oxides of technetium.

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
Tc(VII)					
Li_5TcO_6(cr)	trigo.	$P3_112$ or $P3_212$	3	$a = 5.04 \pm 0.02$ $c = 14.10 \pm 0.04$	[65KEL/KAN]
Na_5TcO_6(cr)	trigo.	$P3_112$ or $P3_212$	3	$a = 5.65$ $c = 15.69$	[77PIE/WEI]
$Sr_5(TcO_6)_2$(cr)	hexag.	$P6_3mc$	2	$a = 5.74 \pm 0.02$ $c = 18.98 \pm 0.02$	[66KEL/WAS]
Sr_2LiTcO_6(cr)	cubic	Fm3m	4	$a = 7.84 \pm 0.02$	[66KEL/WAS]
Sr_2NaTcO_6(cr)	tetrag.		4	$a = 8.09 \pm 0.02$ $c = 8.14 \pm 0.04$	[66KEL/WAS]
Ba_2LiTcO_6(cr)	cubic	Fm3m	4	$a = 8.092 \pm 0.004$	[66KEL/WAS]
Ba_2NaTcO_6(cr)	cubic	Fm3m	4	$a = 8.292 \pm 0.004$	[66KEL/WAS]

(Continued on next page)

Table V.40: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
Tc(VI)					
β-Li_4TcO_5(cr)	mono.[a]	C2/c	4?	$a = 5.055 \pm 0.004$ $b = 8.755 \pm 0.004$ $c = 9.67 \pm 0.02$	[65KEL/KAN]
α-Li_6TcO_6(cr)[b]	trigo.	$P3_112$ or $P3_212$	3	$a = 5.05 \pm 0.02$ $c = 14.20 \pm 0.04$	[65KEL/KAN]
Na_6TcO_6(cr)	trigo.	$P3_112$ or $P3_212$	3		[77PIE/WEI]
$Ba_3Tc_2O_9$(cr)	trigo.	$R\bar{3}m$	3	$a = 5.800 \pm 0.004$ $c = 21.00 \pm 0.02$	[66KEL/WAS]
$((CH_3)_4N)_2TcO_4$(cr)	cubic(fcc)	$F23$ or $F\bar{4}3m$	4?	$a = 11.20$	[75AST/HAU]
Tc(V)					
α-Li_3TcO_4(cr)	mono. [a]	C2/c	6	$a = 5.038 \pm 0.004$ $b = 8.726 \pm 0.004$ $c = 9.82 \pm 0.02$	[65KEL/KAN]
β-Li_3TcO_4(cr)	cubic	Fm3m	1	$a = 4.17 \pm 0.04$	[65KEL/KAN]
Tc(IV)					
Li_2TcO_3(cr)	mono. [c]	C2/c	8?	$a = 4.988 \pm 0.004$ $b = 8.639 \pm 0.004$ $c = 10.01 \pm 0.02$	[65KEL/KAN]
Na_2TcO_3(cr)	mono.	C2/c	8		[65KEL/KAN]
$CaTcO_3$(cr)	ortho. (perovskite)		1	$a = 3.87 \pm 0.04$ $b = 3.96 \pm 0.04$ $c = 3.76 \pm 0.04$	[66KEL/WAS]
$SrTcO_3$(cr) [d]	cubic	Pm3m	1	$a = 3.949 \pm 0.004$	[66KEL/WAS]
α-$BaTcO_3$(cr) [e]	hexag.	$P6_3/mmc$		$a = 5.763 \pm 0.006$ $c = 14.05 \pm 0.02$	[66KEL/WAS]
	hexag.	$P6_3/mmc$		a = 5.758 c = 10.046	[77PIE/WEI]
β-$BaTcO_3$(cr)	cubic		8	$a = 8.140 \pm 0.004$	[66KEL/WAS]
$PbTcO_3$(cr)	cubic	Fd3m	16	$a = 10.361$	[64MUL/WHI]
Ba_2TcO_4(cr)	tetrag.	I4/mmm	2	$a = 4.011 \pm 0.004$ $c = 13.40 \pm 0.02$	[66KEL/WAS]
Mg_2TcO_4(cr)	cubic	Fd3m	8	$a = 8.498 \pm 0.006$	[64MUL/WHI]
Sr_2TcO_4(cr)	tetrag.	I4/mmm	2	$a = 3.902 \pm 0.004$ $c = 12.72 \pm 0.04$	[66KEL/WAS]
Co_2TcO_4(cr)[f]	cubic	Fd3m	8	$a = 8.450 \pm 0.006$	[64MUL/WHI]
Mn_2TcO_4(cr)	cubic	Fd3m	8	$a = 8.682 \pm 0.006$	[64MUL/WHI]
$Sm_2Tc_2O_7$(cr)	cubic	Fd3m	8	$a = 10.352 \pm 0.008$	[64MUL/WHI]
$Dy_2Tc_2O_7$(cr)[f]	cubic	Fd3m	8	$a = 10.246 \pm 0.008$	[64MUL/WHI]
$Er_2Tc_2O_7$(cr)[f]	cubic	Fd3m	8	$a = 10.194 \pm 0.008$	[64MUL/WHI]

(Continued on next page)

Table V.40: (continued)

Phase	Crystal symmetry	Space group	Z	Lattice parameters ($\times 10^{10}$/m)	Reference
$CoMnTcO_4$(cr)	cubic	Fd3m	8	$a = 8.563 \pm 0.006$	[64MUL/WHI]
$CoNiTcO_4(cr)$[f]	cubic	Fd3m	8	$a = 8.449 \pm 0.006$	[64MUL/WHI]
$NiCdTcO_4(cr)$[f]	cubic	Fd3m	8	$a = 8.768 \pm 0.006$	[64MUL/WHI]
$NiMnTcO_4$	cubic	Fd3m	8	$a = 8.551 \pm 0.006$	[64MUL/WHI]
$NiZnTcO_4$(cr)	cubic	Fd3m	8	$a = 8.462 \pm 0.006$	[64MUL/WHI]
$Ti_{0.6}Tc_{0.4}O_2$(cr)	tetrag.	$P4_2/mnm$	2	$a = 4.636$ $c = 2.974$	[64MUL/WHI]
$Mg_2Ti_{0.95}Tc_{0.05}O_4$(cr)[g]	cubic	Fd3m			[83KHA/WHI]
$Mg_2Ti_{0.93}Tc_{0.07}O_4$(cr)	cubic	Fd3m		$a = 8.448$	[83KHA/WHI]
$Mg_2Ti_{0.83}Tc_{0.17}O_4$(cr)	cubic	Fd3m		$a = 8.451$	[83KHA/WHI]
$Sr_2Ti_{0.90}Tc_{0.10}O_3$(cr)	(perovskite)				[84KHA/WHI]

[a] $\beta = 99.8°$ for both β-Li_4TcO_5(cr) and β-Li_3TcO_4(cr).
[b] β-Li_6TcO_6 is orthorhombic, space goup Immm and $Z = 1$ [65KEL/KAN].
[c] $\beta = 99.4°$.
[d] $SrTcO_3$(cr) was found to be orthorhombic or lower symmetry with a = 3.95×10^{-10}m and $Z = 3$ [64MUL/WHI].
[e] α-$BaTcO_3$(cr) was found to be hexagonal with space group $P6_3/mmc$, $Z = 6$, $a = 5.758$ and $c = 14.046$ [64MUL/WHI].
[f] Slightly non-stoichiometric phase.
[g] Stoichiometry not corrected for technetium loss during sample preparation.

No thermodynamic data are available for these ternary and quaternary oxides of technetium so this review summarises the preparative and structural data for these compounds. Many of the obtained substances are not stable in aqueous solution due to hydrolysis, disproportionation to TcO_4^- and Tc(IV), and precipitation of $TcO_2 \cdot xH_2O$(s).

V.8.5.1 Tc(VII) oxides

Keller and Kanellakopulos [65KEL/KAN] prepared Li_5TcO_6(cr) by reaction of stoichiometric amounts of $LiTcO_4$ with Li_2O at 523 to 723 K, or from $LiTcO_4$ and Li_2CO_3 at 873 to 923 K. It decomposed above 923 K to form α-Li_6TcO_6(cr), Tc_2O_7(g) and (presumably) O_2(g). They also reported preparation of Na_3TcO_5(s) and Na_5TcO_6(cr), and K_3TcO_5(s) by similar methods. All of these double oxides were chemically analysed for technetium and alkali metal, and all were quite hygroscopic with hydrolysis occurring to form $MTcO_4$.

Keller and Wassilopulos [66KEL/WAS] prepared several double oxides of Tc(VII) with alkaline earth metals. $Ca_5(TcO_6)_2$(s) was prepared by reaction of $Ca(TcO_4)_2$ with CaO at 873 K in an O_2(g) atmosphere. Similarly, reaction of $Sr(TcO_4)_2$ with SrO gave $Sr_3(TcO_5)_2$(s) and $Sr_5(TcO_6)_2$(cr), and of $Ba(TcO_4)_2$ with BaO gave $Ba_3(TcO_5)_2$(s). Further reaction with BaO gave $Ba_5(TcO_6)_2$(s). Reaction of $MTcO_4$ (M = Li or Na) with SrO or BaO at 673 to 873 K gave the quaternary oxides $SrLi_{0.5}Tc_{0.5}O_3$(cr),

$BaLi_{0.5}Tc_{0.5}O_3$(cr), $SrNa_{0.5}Tc_{0.5}O_3$(cr), and $BaNa_{0.5}Tc_{0.5}O_3$(cr). Elemental analyses were performed both for technetium and alkaline earth metal in most cases.

V.8.5.2 Tc(VI) oxides

Keller and Kanellakopulos [65KEL/KAN] prepared two crystalline forms, α (the low temperature phase) and β (the higher temperature phase) of both Li_4TcO_5(cr) and Li_6TcO_6(cr). They reacted $LiTcO_4$ with Li_2O and technetium metal in stoichiometric amounts in an evacuated quartz ampoule. α-Li_4TcO_5(cr) was produced at 970 K, and it had transformed to β-Li_4TcO_5(cr) by about 1070 K. The β-form was thermally stable to at least 1173 K. α-Li_6TcO_6(cr) formed below 593 K, and β-Li_6TcO_6(cr) above 623 K. Upon dissolution in water both lithium compounds formed solutions of Tc(VI), which then disproportionated completely to form aqueous TcO_4^- and $TcO_2 \cdot xH_2O$(s) in stoichiometric amounts.

Keller and Wassilopulos [66KEL/WAS] reacted $Ba(TcO_4)_2$ with technetium metal and BaO in stoichiometric amounts in an evacuated quartz ampoule at 973 K to yield $Ba_3Tc_2O_9$(cr). It was isostructural with the rhenium analogue.

Rulfs, Pacer and Hirsch [67RUL/PAC2] attempted to prepare a double oxide of Tc(VI) by reduction of TcO_4^- with hydrazine in aqueous 0.7 M NaOH. Addition of $Ba(OH)_2$ gave precipitates with Tc-to-Ba mole ratios of 1:1.2 and 1:1.1. They concluded that the products were $BaTcO_4$(s) contaminated with TcO_2(cr) and $Ba(TcO_4)_2$(s). However, this was not confirmed by a later study in their laboratory [69MAJ/PAC]. In that study TcO_4^- was reduced by hydrazine in 0.5 and 3 M aqueous NaOH saturated with $Ba(OH)_2$. The products were mixtures of $BaCO_3$(s), $Ba(TcO_4)_2$(s), and (mainly) $TcO_2 \cdot xH_2O$(s). No evidence was found for $BaTcO_4$(s).

The inability to prepare TcO_4^{2-} compounds from aqueous solutions appears to be due to the strong tendency of TcO_4^{2-} to disproportionate. However, since the disproportionation involves hydrogen ions, it should be possible to suppress it by reducing TcO_4^- in a non-aqueous aprotic solvent. Schwochau *et al.* [74SCH/AST] thus prepared K_2TcO_4(s) by reduction of $KTcO_4$ at a mercury cathode in deaerated dimethylsulfoxide using $KClO_4$ as a supporting electrolyte. Chemical analyses and IR and diffuse reflectance spectra indicated that K_2TcO_4(s) was the major component, although the pure phase was not obtained [74SCH/AST, 76AST/SCH].

Schwochau and colleagues [74SCH/AST, 76AST/SCH] also prepared and characterised air-sensitive $((CH_3)_4N)_2TcO_4$(cr) by electrolysis of $(CH_3)_4NTcO_4$ at a platinum sheet electrode in deaerated acetonitrile using $(CH_3)_4NClO_4$ as supporting electrolyte. Decomposition of $((CH_3)_4N)_2TcO_4$(cr) in pH = 7 deaerated water gave a clear brown solution, and DC polarography indicated that the disproportionation products were TcO_4^- and Tc(V) species [76AST/SCH]. This is somewhat surprising, since Tc(VI) compounds generally disproportionate in water to form TcO_4^- and $TcO_2 \cdot xH_2O$(s).

V.8.5.3 Tc(V) oxides

Keller and Kanellakopulos [65KEL/KAN] prepared two crystalline modifications of Li_3TcO_4(cr) by solid state reaction of stoichiometric amounts of $LiTcO_4$, technetium metal, and Li_2O in an evacuated quartz ampoule. The low-temperature phase α-Li_3TcO_4(cr) transformed to β-Li_3TcO_4(cr) around 1223 K, which in turn disproportionated to Li_4TcO_5(cr), technetium metal, and $LiTcO_4$ around 1273 K.

Similarly, they prepared $NaTcO_3$(s) by reaction of $NaTcO_4$, technetium metal, and Na_2O at 773 K; or $NaTcO_4$, TcO_2, and Na_2O in an evacuated quartz ampoule at temperatures from 773 to 1073 K. It was insoluble in water.

V.8.5.4 Tc(IV) oxides

A large number of ternary and quaternary oxides of Tc(IV) have been prepared, generally by reaction of TcO_2(cr) with other oxides in their stoichiometric ratios in sealed ampoules.

Muller, White and Roy [64MUL/WHI, 68MUL] prepared a number of spinel phases by reaction of metal monoxides MO with TcO_2(s) in a platinum crucible for 1.5 to 2 days at 1398 to 1488 K. The following solids were thus prepared:

- Mg_2TcO_4(cr), Co_2TcO_4(cr), Mn_2TcO_4(cr), and
- $CoMnTcO_4$(cr), $CoNiTcO_4$(cr), $NiMnTcO_4$(cr), $NiZnTcO_4$(cr), and $NiCdTcO_4$(cr).

The phases Co_2TcO_4(cr), $CoNiTcO_4$(cr), and $NiCdTcO_4$(cr) were slightly nonstoichiometric. At liquid nitrogen temperature, only Mn_2TcO_4(cr) and $NiMnTcO_4$(cr) became ferrimagnetic.

They [64MUL/WHI] were also able to prepare three phases of the ABO_3-type by the same method. They were:

- a slightly distorted perovskite phase $SrTcO_3$(cr) which was obtained by heating the oxides at 1498 K for 1 to 3 days,
- hexagonal $BaTcO_3$(cr) obtained by heating the oxides at 1303 to 1498 K for 1 to 7 days, and
- a pyrochlore phase $PbTcO_3$(cr) obtained by reaction of the oxides at 1163 K for 3.5 days.

The rutile structure phase $Ti_{0.6}Tc_{0.4}O_2$(cr) was obtained by heating anatase-TiO_2(cr) with TcO_2(cr) at 1483 K for 1 day [64MUL/WHI].

Muller, White and Roy [64MUL/WHI] similarly prepared phases with the pyrochlore structure, $Sm_2Tc_2O_7$(cr), $Dy_2Tc_2O_7$(cr), and $Er_2Tc_2O_7$(cr), by reacting the oxides for 3 days at 1473 to 1503 K. The latter two phases were slightly nonstoichiometric.

Keller and Kanellakopulos [65KEL/KAN] prepared Li_2TcO_3(cr) by reaction of Li_2O and TcO_2(cr) in evacuated quartz ampoules at 673 to 773 K for 10 hours, or

by reaction of $LiTcO_4$, technetium metal, and Li_2O at 723 to 923 K for 30 hours. They similarly prepared Na_2TcO_3(cr) by reaction of $NaTcO_4$, technetium metal, and Na_2O at about 623 K for 2 to 20 hours. It decomposed to form Na_3TcO_5, technetium metal, and Na_2O around 823 K. They also obtained Na_4TcO_4(s) from reaction of Na_2TcO_3 and Na_2O at 723 K; it decomposed to technetium metal and Na_3TcO_5 above about 1273 K. Neither Li_2TcO_3(cr) nor Na_2TcO_3(cr) were dissolved by water, but Na_4TcO_4(s) was very hygroscopic and hydrolysed in water to form $TcO_2 \cdot x H_2O$(s) [65KEL/KAN, 83ALL/BUR].

Keller and Wassilopulos [66KEL/WAS, 83ALL/BUR] reacted TcO_2(cr) and CaO at 823 K in an evacuated quartz ampoule for one day and obtained $CaTcO_3$(cr); it could also be prepared by reacting $Ca(TcO_4)_2$, technetium metal, and CaO at 873 K. Reaction of TcO_2(cr) with SrO at 823 to 873 K gave a mixture of Sr_2TcO_4(cr) and TcO_2(cr), which further reacted at 873 K to yield $SrTcO_3$(cr). Pure Sr_2TcO_4(cr) was prepared by reaction of TcO_2 with SrO in a 1:2 mole ratio at 823 K; it decomposed to $SrTcO_3$ around 903 K. A solid solution formed between Sr_2TcO_4 and SrO, which had better thermal stability than pure Sr_2TcO_4.

The reaction of TcO_2(cr) with BaO at 1073 to 1273 K gave α-$BaTcO_3$(cr) [66KEL/WAS]. At 823 to 873 K a mixture of Ba_2TcO_4 and TcO_2(cr) was obtained, which further reacted to form α-$BaTcO_3$(cr) above 903 K. The reaction of $Ba(TcO_4)_2$, technetium metal, and BaO at 873 K gave β-$BaTcO_3$(cr). β-$BaTcO_3$(cr) was stable to at least 1273 K and did not transform to α-$BaTcO_3$. Reaction of TcO_2(cr) with BaO in a 1:2 mole ratio, or of $BaTcO_3$ with BaO in a 1:1 mole ratio gave Ba_2TcO_4(cr) at 803 K. A solid solution formed between Ba_2TcO_4 and BaO, which had better thermal stability than pure Ba_2TcO_4.

Khalil and White [84KHA/WHI] prepared $SrTi_{0.90}Tc_{0.10}O_3$(cr) by reaction of SrO, TiO_2, and TcO_2 in their correct molar proportions at 1523 K for 1 day. They noted that preparation of technetium containing phases based on titanate ceramics only required reducing or sealed conditions to prevent oxidation of technetium to Tc(VII). They also prepared three compositions of spinel phases $Mg_2Ti_{1-x}Tc_xO_4$(cr) by reaction of TiO_2, MgO, and TcO_2 at 1563 K; a mixture of $MgTiO_3$, MgO, and spinel phase was obtained below 1523 K. The nominal compositions of these phases was $x = 0.05$, 0.10, and 0.20. However, by use of β^-counting of the ^{99}Tc they showed the latter two phases actually had $x = 0.07$ and 0.17 due to some technetium loss during the heat treatments. Also see the discussion in reference [83ALL/BUR].

V.8.5.5 Tc(III) oxides

Keller and Kanellakopulos [65KEL/KAN] prepared $NaTcO_2$(s) by reaction of TcO_2(cr), technetium metal, and Na_2O; or $NaTcO_4$, TcO_2(cr), technetium metal, and Na_2O in an evacuated ampoule at about 873 K.

V.8.5.6 Tc(0) oxide cermets

Zaitseva *et al*. [73ZAI/KON2] prepared various technetium cermets with rare earth oxides. Aqueous solutions containing rare earths and technetium were prepared by dissol-

ution of rare earth oxides or hydroxides in aqueous $HTcO_4$. Evaporation of these solutions gave hydrated rare earth pertechnetates $Ln(TcO_4)_3 \cdot xH_2O(s)$ ($x = 1$ to 4). Either hydrated or anhydrous $Ln(TcO_4)_3(s)$ could be used as starting materials. Samples of $Ln(TcO_4)_3(s)$ were pressed into pellets and reduced with flowing $H_2(g)$ gas for several hours. For samples prepared at 673 K and higher temperatures, particles of metallic technetium were found in rare earth oxide matrices; they were detected by X-ray diffraction. By this procedure they were able to prepare technetium cermets in hexagonal La_2O_3, in cubic CeO_2, in hexagonal Pr_2O_3 (possibly with a second praseodymium oxide phase), in a mixture of hexagonal and cubic Nd_2O_3, in monoclinic Sm_3O_3, in cubic Gd_2O_3, Dy_2O_3, Ho_2O_3, Yb_2O_3, and other cubic yttrium subgroup Ln_2O_3 (Ln was not specified).

Alekseev *et al.* [91ALE/BAR] investigated the superconductivity of various cermets of technetium in rare earth sesquioxide matrices (La, Sm, Eu, Gd, Tb, Ho, Er, Yb, and Lu oxides; Ln_2O_3). Their technetium metal had a superconducting transition temperature of 7.45 K, whereas the transition temperature was always higher for technetium in a Ln_2O_3 matrix. The highest transition temperatures occurred for technetium in a matrix of La_2O_3 and Yb_2O_3, where superconductivity occurred below a temperature of 10.25-10.5 K. In addition, the critical magnetic fields were always higher for technetium in the cermets than for the pure metal.

Several investigations have been made of the behaviour of metallic technetium on an oxide substrate (Al_2O_3 or Y_2O_3), with regard to its utility as a catalyst for specific organic reactions such as the dehydrogenation of cyclohexane to form benzene [84ZAI/VEL, 90PIR/POP].

V.9 Intermetallic compounds

There are very few thermodynamic data for technetium alloys. Indeed, only in the technetium-zinc system [64VEL/JOH] are there any experimental high-temperature thermodynamic data other than solubilities from which alloy stabilities can be derived. The major part of this review therefore summarises the structural and phase diagram information available on binary and higher order systems of technetium alloys. However, a number of groups have made semi-empirical or semi-quantitative predictions of alloy stabilities, and these are noted first.

V.9.1 Theoretical predictions

Three publications [81WAT/BEN, 83NIE/BOE, 85COL/PAS] contain reports of semi-empirical correlation methods to give estimates of the enthalpy of formation of solid and sometimes liquid alloys of technetium, mainly with other transition metals. In Ref. [83NIE/BOE] alloys with non-transition metals are reported as well.

A comparative selection of these values, for alloys of equimolar composition, is given in Table V.41. The differences between $\Delta_f H^\circ_m$ of different structural types of compounds are much less than the likely uncertainties in the estimated values, as can be seen from Table V.41. It should be noted that in the model of Niessen *et al.*

[83NIE/BOE], the enthalpy of formation of the solid equimolar compound is assumed to be 3/8 of the mean enthalpies of solution in the liquids at infinite dilution, see Ref. [80MIE/de , *p*.16]. It is seen that there is often reasonable agreement in the estimates of Watson and Bennet [81WAT/BEN] and Niessen *et al*. [83NIE/BOE], whose values may be taken as an indication of the likely size of the interactions in the relevant systems. The estimates of Colinet, Pasturel and Hicter [85COL/PAS] are often, but not always, much smaller in magnitude than those of the other two studies. Although

Table V.41: Estimated enthalpies of formation of $M_{0.5}Tc_{0.5}$(cr) compounds reported in the literature.

M	Estimated $\Delta_f H^\circ_m$ ($M_{0.5}Tc_{0.5}$, cr, 298.15 K)/ [kJ·mol^{-1}]		
	[81WAT/BEN]	[83NIE/BOE][(a)]	[85COL/PAS]
Co	−4	−0.4	2
Cr	−29	−14	−2
Fe	−12	−5	2
Hf	−72	−70	−20
Ir	−6	−2	−23
Mn	−22	−13	0
Mo	−30.5	−17	−4
Nb	−53	−53	−18
Ni	−5	1	6
Os	0	0.4	−6
Pd	7.4	6	−5
Pt	−0.7	−5	−25
Re	−17	0.4	0
Rh	−5.6	0.4	−11
Ru	−0.3	−0.4	−4
Sc	−48	−56	
Ta	−56	−52	−11
Ti	−63	−58	−8
V	−47	−32	−6
W	−27	−10	−5
Y	−87	−42	
Zr	−74	−80	−19

[(a)] Values in this column are calculated by this review.

the tabulated values are for the formation of solid phases from the solid elements, the related values for $\Delta_f H^\circ_m$ of liquid alloys from liquid metals are generally predicted to be reasonably close [83NIE/BOE, 85COL/PAS].

In addition, Bieber and Gautier [87BIE/GAU] performed purely theoretical elec-

tronic structure calculations in a number of transition metal binary systems, including solid Tc-Ti, which predict semi-quantitatively the stability at 0 K of a number of ordered and disordered structures based on the bcc and fcc lattices. The main purpose of these calculations in their report was to demonstrate the relative importance of the various contributions to the energy, such as the elastic, chemical and relaxation terms. Nevertheless, for Ti-Tc, the calculation correctly predicts the appreciable stability of the partially ordered CsCl-type phase in this system.

V.9.2 Binary systems

The present review collects the available structural and phase diagram information for binary Tc alloys. A short discussion is given for systems for which more than just structural information is available. Otherwise, the structural information is summarised in Table V.42 for intermetallic compounds whose homogeneity range is small, and in Table V.43 for solid phases with a wide range of composition.

Table V.42: Structural information for intermediate phases in technetium alloy systems.

Phase	Symmetry space group	Lattice parameters ($\times 10^{10}$/m)	Prototype structure	Reference
Tc_2Al	tetragonal I4/mmm	$a = 2.977 \pm 0.002$ $c = 9.476 \pm 0.004$	$MoSi_2$	[65DAR/DOW]
$TcAl_2$	unknown			[65DAR/DOW]
$TcAl_3$	unknown			[65DAR/DOW]
$TcAl_{12}$	bcc, $Im\bar{3}$	$a = 7.525 \pm 0.001$ $a = 7.528 \pm 0.002$	WAl_{12}	[64WAL] [65DAR/DOW]
Tc_2Al_3	hexagonal $P\bar{3}m1$	$a = 4.16 \pm 0.02$ $c = 5.13 \pm 0.02$	Ni_2Al_3(?)	[63VEI/WAL]
$TcAl_4$	monoclinic	$a = 5.1 \pm 0.2$ $b = 17.0 \pm 0.2$ $c = 5.1 \pm 0.2$ $\beta = 100°$		[63VEI/WAL]
$TcAl_6$	orthorhombic Cmcm	$a = 6.58 \pm 0.02$ $b = 7.63 \pm 0.02$ $c = 9.00 \pm 0.02$ $a = 6.5944 \pm 0.02$ $b = 7.629 \pm 0.018$ $c = 9.0011 \pm 0.0022$	$MnAl_6$	[62VEI] [67WIL]
Tc_2As_3	triclinic $P\bar{1}$	$a = 6.574 \pm 0.004$ $b = 6.632 \pm 0.004$ $c = 8.023 \pm 0.008$ $\alpha = (102.03 \pm 0.2)°$ $\beta = (95.69 \pm 0.2)°$ $\gamma = (104.371 \pm 0.4)°$	*cf.* Mo_2As_3	[85JEI/DIE]
Tc_3As_7	bcc $Im\bar{3}m$	$a = 8.702 \pm 0.004$	Ir_3Ge_7	[66HUL]

(Continued on next page)

Table V.42: (continued)

Phase	Symmetry space group	Lattice parameters ($\times 10^{10}$/m)	Prototype structure	Reference
Tc_3B	orthorhombic Cmcm	$a = 2.891$ ($Z = 4$) $b = 9.161$ $c = 7.246$	Re_3B	[64TRZ/RUD]
Tc_7B_3	hexagonal $P6_3mc$	$a = 7.417$ ($Z = 2$) $c = 4.777$	Th_7Fe_3	[64TRZ/RUD]
TcB	unknown			[64TRZ/RUD]
Tc_3B_4	unknown			[64TRZ/RUD]
TcB_2	hexagonal $P6_3/mmc$	$a = 2.892$ ($Z = 2$) $c = 7.453$	ReB_2	[64TRZ/RUD]
$TcBe_{22}$	fcc ($Fd\bar{3}m$?)	(Z=8)	unknown	[67BUC/PAL]
Tc_5C-Tc_4C	fcc	$a = 3.7968$ at 16.2 at-% C $a = 3.7984$ at 17.6 at-% C	unknown unknown	[80HAI/POT]
Tc-Cr	tetragonal $P4_2/mnm$	$a = 9.290 \pm 0.006$ $c = 4.846 \pm 0.002$ at 25 at-% Cr $a = 9.217 \pm 0.002$ $c = 4.803 \pm 0.002$ at 40 at-% Cr	σ(Cr-Fe)	[62DAR/LAM]
Tc_2Dy	hcp, $P6_3/mmc$	$a = 5.365$ $c = 8.830$	$MgZn_2$	[64DAR/NOR]
Tc_2Er	hcp, $P6_3/mmc$	$a = 5.340$ $c = 8.792$	$MgZn_2$	[64DAR/NOR]
Tc-Fe	tetragonal, $P4_2/mnm$	$a = 9.130 \pm 0.010$ $c = 4.788 \pm 0.010$ at 40 at-% Fe $a = 9.077 \pm 0.006$ $c = 4.756 \pm 0.006$ at 50 at-% Fe $a = 9.010 \pm 0.002$ $c = 4.713 \pm 0.002$ at 60 at-% Fe	σ(Cr-Fe)	[62DAR/LAM]
Tc_2Gd	hcp, $P6_3/mmc$	$a = 5.397$ $c = 8.883$	$MgZn_2$	[64DAR/NOR]
Tc_7Hf- -Tc_6Hf	cubic, $I\bar{4}3m$	$a = 9.603 \pm 0.002$ at 12.5 at-% Hf	α-Mn	[62DAR/LAM] 61LAM/DAR]
Tc_2Hf	hcp, $P6_3/mmc$	$a = 5.200 \pm 0.002$ $c = 8.616 \pm 0.002$ at 33.3% Hf $a = 5.2001 \pm 0.0008$ $c = 8.6175 \pm 0.0022$ at 33.5% Hf	$MgZn_2$	[62DAR/LAM] [70GIO/SZK]
TcHf	bcc, $Pm\bar{3}m$	$a = 3.270 \pm 0.008$	CsCl	[62DAR/LAM]

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Table V.42: (continued)

Phase	Symmetry space group	Lattice parameters ($\times 10^{10}$/m)	Prototype structure	Reference
Tc_2Ho	hcp, $P6_3/mmc$	$a = 5.353$ $c = 8.813$	$MgZn_2$	[64DAR/NOR]
Tc_2Lu	hcp, $P6_3/mmc$	$a = 5.309$ $c = 8.739$	$MgZn_2$	[64DAR/NOR]
		$a = 5.310 \pm 0.002$ $c = 8.736 \pm 0.004$		[81SZK/GIO]
Tc-Mn	tetragonal, $P4_2/mnm$	$a = 9.15 \pm 0.02$ $c = 4.80 \pm 0.02$ at 40 at-% Mo	σ(Cr-Fe)	[62DAR/LAM]
Tc-Mo	tetragonal, $P4_2/mnm$	$a = 9.5091 \pm 0.0008$ $c = 4.9448 \pm 0.0026$ at 30 at-% Mo	σ(Cr-Fe)	[62DAR/LAM] [62DAR/ZEG]
		$a = 9.552 \pm 0.014$ $c = 4.950 \pm 0.010$ at 36 at-% Mo	σ(Cr-Fe)	[78GIO/MAT]
Tc_9Mo_{11}	cubic, $Pm\bar{3}n$	$a = 4.9408 \pm 0.0004$ at 44 at-% Mo	Cr_3Si	[62DAR/LAM] 62DAR/ZEG]
Tc_6Nb- -Tc_3Nb	cubic, $I\bar{4}3m$	$a = 9.547 \pm 0.002$ at 14.3 at-% Nb	α-Mn	[62DAR/LAM]
	cubic, $I\bar{4}3m$	$a = 9.625 \pm 0.004$ at 25 at-% Nb	α-Mn	[61COM/COR]
		$a = 9.547$ at 15 at-% Nb	α-Mn	[63VAN/LAM]
		$a = 9.592 \pm 0.002$ at 24 at-% Nb	α-Mn	[70GIO/SZK2]
		$a = 9.557 \pm 0.008$ at 42 at-% Nb		
Tc_2Pu	unknown			[76HAI/MAR] [80HAI/POT]
TcS_2	triclinic, P1	$a = 6.465$ $b = 6.375$ $c = 6.659$ $\alpha = (106.61)°$ $\beta = (62.97)°$ $\gamma = (118.96)°$	distorted $Cd(OH)_2$ type	[71WIL/JEL]
TcS_2	triclinic, P1	$a = 6.371$ $b = 6.464$ $c = 6.654$ $\alpha = (62.94)°$ $\beta = (103.61)°$ $\gamma = (213.39)°$	distorted $Cd(OH)_2$ type	[96LAM/MEE]
Tc_7Sc	cubic, $I\bar{4}3m$	$a = 9.509 \pm 0.002$	α-Mn	[61LAM/DAR] [62DAR/LAM]

(Continued on next page)

Table V.42: (continued)

Phase	Symmetry space group	Lattice parameters ($\times 10^{10}$/m)	Prototype structure	Reference
Tc_2Sc	hcp, $P6_3/mmc$	$a = 5.223 \pm 0.002$	$MgZn_2$	[62DAR/LAM]
		$c = 8.571 \pm 0.002$		
		$a = 5.224 \pm 0.002$		[81SZK/GIO]
		$c = 8.570 \pm 0.004$		
Tc_4Si	bcc, $Im\bar{3}m$	$a = 3.009$	W	[65DAR/DOW]
Tc_3Si(?)	bcc, $Im\bar{3}m$ or $I\bar{4}3m$	$a = 9.014 \pm 0.002$	Fe_3Zn_{10} or Cu_5Zn_8	[65DAR/DOW]
Tc_5Si_3	tetragonal, I4/mcm	$a = 9.403 \pm 0.002$	W_5Si_3	[65DAR/DOW]
		$c = 4.849 \pm 0.002$		
TcSi	cubic, $P2_13$	$a = 4.755 \pm 0.002$	FeSi	[65DAR/DOW]
Tc_4Si_7	tetragonal, P4c2	$a = 5.737$	Mn_4Si_7	[65WIT/NOW]
		$c = 18.099$		
TcTa	bcc, $Pm\bar{3}m$	$a = 3.172 \pm 0.006$	CsCl	[62DAR/LAM]
Tc_5Ta- -Tc_4Ta	cubic, $I\bar{4}3m$	$a = 9.565 \pm 0.002$ at 16.6 at-% Ta	α-Mn	[61LAM/DAR] 62DAR/LAM]
Tc_2Tb	hcp, $P6_3/mmc$	$a = 5.375$	$MgZn_2$	[64DAR/NOR]
		$c = 8.843$		
$TcTe_2$	monoclinic, Cc or C2/c	$a = 12.522$	distorted high-T $MoTe_2$ type	[71WIL/JEL]
		$b = 7.023$		
		$c = 13.828$		
		$\beta = (101.26)^\circ$		
Tc_2Th	hcp, $P6_3/mmc$	$a = 5.394 \pm 0.010$	$MgZn_2$	[65DAR/BER]
		$c = 9.222 \pm 0.010$		
		$a = 5.393 \pm 0.002$		[70GIO/SZK]
		$c = 9.223 \pm 0.010$		
		at 44 at-% Th		
Tc_7Ti- -Tc_6Ti	cubic, $I\bar{4}3m$	$a = 9.579 \pm 0.002$	α-Mn	[61LAM/DAR] [62DAR/LAM]
		$a = 9.500$ at 12.5 at-% Ti		[76KOC]
		$a = 9.512$ at 15 at-% Ti		
Tc_2Ti- -TcTi	bcc, $Pm\bar{3}m$	$a = 3.083$ at 33 at-% Ti	CsCl	[76KOC]
		$a = 3.091$ at 50 at-% Ti		
		$a = 3.110 \pm 0.010$ at 50 at-% Ti	CsCl	[62DAR/LAM]
Tc_2Tm	hcp, $P6_3/mmc$	$a = 5.334$	$MgZn_2$	[64DAR/NOR]
		$c = 8.775$		
TcU_2	monoclinic,	$a = 13.407 \pm 0.006$ (Z=4)	U_2Ru	[65BER/DWI]
		$b = 3.271 \pm 0.001$		[65DAR/BER]
		$c = 5.213 \pm 0.001$		
		$\beta = (96.38 \pm 0.4)^\circ$		

(Continued on next page)

Table V.42: (continued)

Phase	Symmetry space group	Lattice parameters ($\times 10^{10}$/m)	Prototype structure	Reference
Tc_2U	unknown		(not $MgZn_2$)	[65DAR/BER]
Tc-V(δ)	unknown			[68KOC/LOV]
Tc-V(γ)	unknown			[68KOC/LOV]
TcV	bcc, $Pm\bar{3}m$	$a = 3.025 \pm 0.010$	CsCl	[62DAR/LAM]
		$a = 3.023$		[62VAN/LAM]
Tc-W	tetragonal, $P4_2/mnm$	$a = 9.479 \pm 0.010$ $c = 5.166 \pm 0.010$ at 25 at-% W	σ(Cr-Fe)	[62DAR/LAM]
		$a = 9.478$ $c = 4.950$ at 25 at-% W	σ(Cr-Fe)	[85GIO]
		$a = 9.504$ $c = 4.971$ at 30 at-% W		
		$a = 9.526$ $c = 5.000$ at 40 at-% W		
		$a = 9.520 \pm 0.002$ $c = 5.003 \pm 0.002$ at 40 at-% W	σ(Cr-Fe)	[65AUT/HUL]
Tc_2Y	hcp, $P6_3/mmc$	$a = 5.373$ $c = 8.847$	$MgZn_2$	[64DAR/NOR]
		$a = 5.371 \pm 0.002$ $c = 8.862 \pm 0.010$		[81SZK/GIO]
$TcZn_6$	fcc	$a = 7.588 \pm 0.002$ (Z=28)	related to $AuCu_3$	[64CHA/JOH]
$TcZn_{15}$--$TcZn_{18}$	unknown			[64CHA/JOH]
Tc_6Zr	cubic, $I\bar{4}3m$	$a = 9.637 \pm 0.002$	α-Mn	[62DAR/LAM]
		$a = 9.636 \pm 0.004$(Z=58?)	α-Mn	[61COM/COR]
Tc_2Zr	hcp, $P6_3/mmc$	$a = 5.219 \pm 0.002$ $c = 8.655 \pm 0.002$ at 33 at-% Zr	$MgZn_2$	[62DAR/LAM]
		$a = 5.2185 \pm 0.0008$ $c = 8.6527 \pm 0.0014$ at 33.2 at-% Zr		[70GIO/SZK]

V.9.2.1 Tc-Al

The number, composition and structure of the intermediate phases in this system is far from clear. D'Alte da Veiga [62VEI, 63VEI/WAL] claimed to have found the four phases Tc_2Al_3, $TcAl_4$, $TcAl_6$ and $TcAl_{12}$ and gave structural details for $TcAl_4$, $TcAl_6$ and $TcAl_{12}$. $TcAl_4$ was indexed on a monoclinic cell, (see Table V.42) with a structure similar to $MoAl_4$, although $MoAl_4$ is in fact orthorhombic. The structures for $TcAl_6$

and $TcAl_{12}$ were subsequently refined by Wilkinson [67WIL] and Walford [64WAL]. However, no details whatsoever of the preparation or analyses of any of these phases were given in any of these four papers. Darby, Downey and Norton [65DAR/DOW] in a more detailed study, found, of these phases, only $TcAl_{12}$, with additionally the phases Tc_2Al, $TcAl_2$ and $TcAl_3$. In view of the complete lack of analytical and preparative detail of the phases Tc_2Al_3, $TcAl_4$, $TcAl_6$ proposed by d'Alte da Veiga, their stability in the Tc-Al binary system must be regarded as unproven.

V.9.2.2 Tc-Au

This system was discussed by Okamoto and Massalski [84OKA/MAS], who quoted the electrical resistivity measurements of Van Rongen, Knook and Van den Berg [65VAN/KNO], which suggest that the solubility of Tc in Au at 1273 K is "very small".

V.9.2.3 Tc-Be

This system was discussed by Okamoto and Tanner [86OKA/TAN], who quoted the measurements by Bucher and Palmy [67BUC/PAL] on the superconducting transition temperature (5.21 K) of an uncharacterised phase $Be_{22}Tc$. Lacking any structural information for this phase, Okamoto and Tanner assumed that it has the same fcc structure ($Al_{18}Cr_2Mg_3$-type), space group $Fd\bar{3}m$, as $Be_{22}Re$, though there is no direct evidence for this.

V.9.2.4 Tc-C

There is not enough information to give more than a schematic of the phase diagram for the Tc-C system. Trzebiatowski and Rudzinski [62TRZ/RUD] showed that there is an fcc carbide co-existing with technetium. They gave the composition as TcC (without any strong evidence). However, Haines and coworkers [76HAI/MAR, 80HAI/POT] showed that this carbide, which also exists in equilibrium with graphite, probably has a range of composition from ~16 to 20 at-% C (see Table V.42) which corresponds to Tc_5C to Tc_4C. It melts, probably peritectically, at a temperature somewhere above 1723 K. On the carbon-rich side there is an eutectic with a liquid composition between 25 and 33 at-% C [76HAI/MAR]. Giorgi and Szklarz [66GIO/SZK] reported that a technetium-carbide phase of unknown composition (fcc, $a = (3.985 \pm 0.004) \times 10^{-10}$ m) , but containing both Tc_5C and graphite, melted at (2108 ± 50) K, which may thus be an approximate value of the eutectic temperature on the carbon-rich side. No carbides other than the fcc phase have been found.

Trzebiatowski and Rudzinski [62TRZ/RUD] suggested that the solubility of carbon in technetium is ~1% at 1183 K, without stating whether this is wt-% or at-%. However, since in similar, contemporaneous, papers (*e.g.*, [64TRZ/RUD] on technetium borides) it is clear that the undefined % means wt-%, it is assumed that this is the case for the carbon system also. This also brings their solubility (~8 at-%) into reasonable agreement with that given by Haines, Potter and Rand [80HAI/POT], up to ~10% at

Table V.43: Solution phases in technetium alloys: maximal solubilities of elements in Tc and vice versa.

Element	Symmetry space group	Prototype structure	Max. solubility (at-%) of Tc in Element	Element in Tc	Reference
C	hexagonal,	graphite		∼8	[62TRZ/RUD]
			∼0	∼10	[80HAI/POT]
Co	fcc, $Fm\bar{3}m$	Cu	< 52	> 75	[63DAR/NOR]
Fe	fcc, $Fm\bar{3}m$	Cu		∼20	[63BUC/HUM]
	bcc, $Im\bar{3}m$	W		∼20	
Ir	hcp, $P6_3/mmc$	Mg	5?	> 67, < 75	[63DAR/NOR]
Mo	bcc, $Im\bar{3}m$	W	∼55	∼20	[62DAR/LAM]
			∼ 50	> 15, < 22	[63NIE3]
Ni	fcc, $Fm\bar{3}m$	Cu	< 25	> 50, < 67	[63DAR/NOR]
			∼28	> 40	[75SPI/GRI]
Nb	bcc, $Im\bar{3}m$	W	> 50, < 60	> 3, < 15	[63VAN/LAM]
			> 31, < 58	> 6, < 24	[70GIO/SZK2]
Os	hcp, $P6_3/mmc$	Mg	100	100	[62DAR/LAM]
			100	100	[65NIE]
Pd	fcc, $Fm\bar{3}m$	Cu	> 25, < 34	> 50, < 67	[63DAR/NOR]
			> 25, < 32	> 47, < 57.5	[63NIE]
Pt	fcc, $Fm\bar{3}m$	Cu	> 14, < 33	> 25, < 34	[63DAR/NOR]
			> 38, < 50	> 24.6, < 34	[63NIE]
Re	hcp, $P6_3/mmc$	Mg	100	100	[63NIE2]
			100	100	[62DAR/LAM]
Rh	fcc, $Fm\bar{3}m$	Cu	< 25	> 50, < 75	[63DAR/NOR]
			> 4.5, < 10	> 66, < 76	[63NIE]
Ru	hcp, $P6_3/mmc$	Mg	100	100	[62DAR/LAM]
Ti	bcc, $Im\bar{3}m$	W	> 35, < 50	4	[76KOC]
	(ordered at low temperatures)				
V	bcc, $Im\bar{3}m$	W	> 30, < 35	> 5, < 10	[68KOC/LOV]
W	bcc, $Im\bar{3}m$	W	> 50, < 68	> 10, < 15	[63NIE2]
			> 40, < 50		[65AUT/HUL]
			> 50, < 60	> 15, < 20	[85GIO]
Zn	hcp, $P6_3/mmc$	Mg	∼0	∼0	[64CHA/JOH]

1073 K. The a parameters of the hcp cell of carbon-saturated Tc given in these two studies are, however, rather different: $a = 2.812 \times 10^{-10}$ m, $c = 4.470 \times 10^{-10}$ m [62TRZ/RUD], $a = 2.9848 \times 10^{-10}$ m, $c = 4.4470 \times 10^{-10}$ m [80HAI/POT] (*cf.* $a = 2.74 \times 10^{-10}$ m, $c = 4.40 \times 10^{-10}$ m for the initial technetium metal), although the compositions may also be a little different.

Burylev [85BUR] gave an estimated Tc-C phase diagram (and component activities), based on the "systematics" of the diagrams of Group V and VI metals with carbon. However, he ignored the formation of the intermediate carbide in the Tc-C system, and based his estimates of the solubility of carbon in Tc on the assessment given by Shunk [69SHU], who interpreted the solubility given by [62TRZ/RUD] to be 1 at-%, rather than 1 wt-%. Burylev suggests a simple eutectic system, similar to the Re-C system, with a eutectic at 1933 K, and mole fractions of carbon of $x(\mathrm{C, hcp}) = 0.0722$ in solid technetium, $x(\mathrm{C, liq}) = 0.292$ in the liquid, but of course with a much lower solubility of carbon in Tc(hcp) at lower temperatures (1 at-% at 1183 K) than that noted above. In view of the lack of any attempt to include the known intermediate phase, and the probable misinterpretation of the solubility data of [62TRZ/RUD], little weight is given to this study.

Teplov and Mikheeva [83TEP/MIK] studied the structural, magnetic and electrical properties of thin films (400 to 500 $\times 10^{-10}$ m) of compositions containing 6.5 to 55 at-% C. The films were prepared by ion-sputtering alternating layers of Tc and C. Electron diffraction and microscopy showed that according to the annealing conditions the thin layers were amorphous or contained an fcc phase with $a = 6.66 \times 10^{-10}$ m or a supersaturated solution of carbon in the technetium hcp lattice. All these structures are presumably metastable.

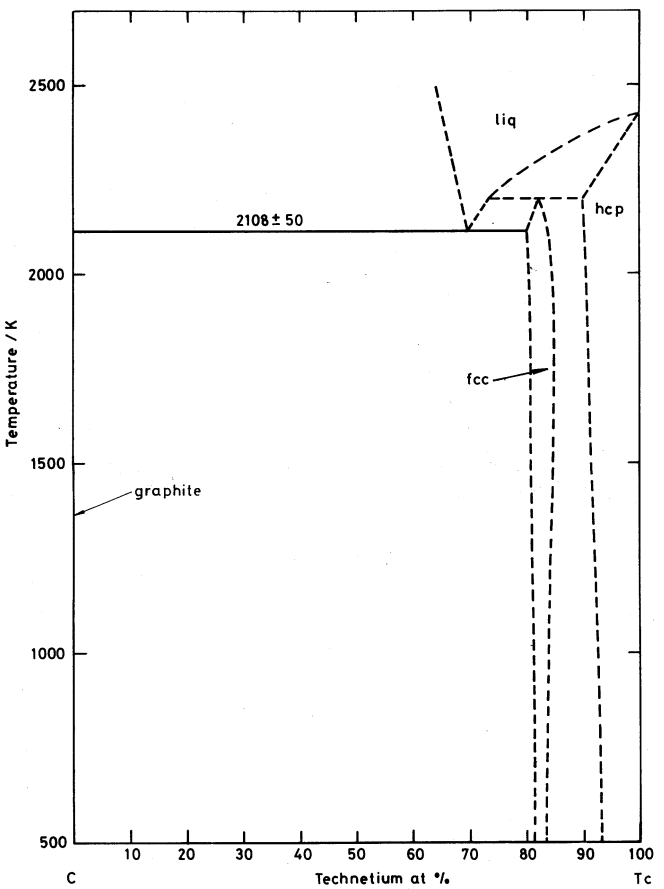
The most probable phase diagram for the Tc-C system is shown schematically in Figure V.7, although the alternative, with the carbide melting congruently and a eutectic on the Tc-rich side also, cannot be excluded. This is similar to that suggested by Eremenko, Velikanova and Bondar [89ERE/VEL]; their assumption that the TcC_{1-x} phase decomposes peritectically is based on a correlation of its (estimated) Gibbs energy of formation with $\Sigma e_M / r_M$ where e and r are (probably) the total valence electrons (sum of s,p and d electrons) and the radius of the metal atom, respectively [83ERE/VEL]. However, since $\Delta_f G^\circ_m$ (TcC_{1-x}) is only an estimate, this merely replaces one assumption by a series of others.

Eremenko, Velikanova and Bondar [89ERE/VEL] do not state explicitly their estimated value for $\Delta_f G^\circ_m$ (TcC_{1-x}), but values given in this paper and the companion paper on scandium carbides [89VEL/ERE] imply that their estimate for $\Delta_f G^\circ_m$ (2000 K) for the metastable NaCl-type phase $TcC_{0.6}$ is approximately zero.

V.9.2.5 Tc-Cu

Bukov *et al.* [90BUK/TIT] have measured the mutual solubilities of Tc and Cu in arc-melted samples annealed at 773, 1173, 1373 and 1573 K for 5-200 hours, by spectrographic, radiometric and metallographic analyses. Further samples were quenched from the melt at 2473 and 2868 K. The maximum solubilities in either the solid or the liquid were 3.4 $\times 10^{-3}$ at% Cu in Tc and 4.3 $\times 10^{-3}$ at% Tc in Cu. These values are

Figure V.7: Schematic of tentative Tc-C phase diagram.



close to the lower limits of measurement, so Tc and Cu are essentially insoluble in both the solid and liquid states, at least at temperatures up to 2873 K. Rhenium and copper also show essentially zero mutual solubility.

Gerasimov *et al*. [85GER/ZEL] studied samples of Tc-Cu alloys weighing 1-10 ng, supported on platinum or copper substrates, by conversion electron spectroscopy. However these samples contained appreciable amounts of oxygen (O/Cu mol ratio ∼0.25) and the observed shifts in spectra from those for the pure elements were attributed to an undefined Cu-Tc-O ternary oxide phase.

V.9.2.6 Tc-Co

Darby, Norton and Downey [63DAR/NOR] found there were no intermediate phases in this system, and studied the solid solubility in the elements at around 1323 K. The solubility of Tc(hcp) in Co(fcc) is $>$ 75 at-%, and that of Co(fcc) in Tc(hcp) is $<$ 25 at-%.

The variation of the unit cell volume with composition shows negative deviations from Végard's law. The hexagonal phase of Co is stable up to about 700 K, and although the solubility of Tc in this phase is not known, it would be expected, on size considerations, to be quite large, with even perhaps a continuous range of hcp solutions.

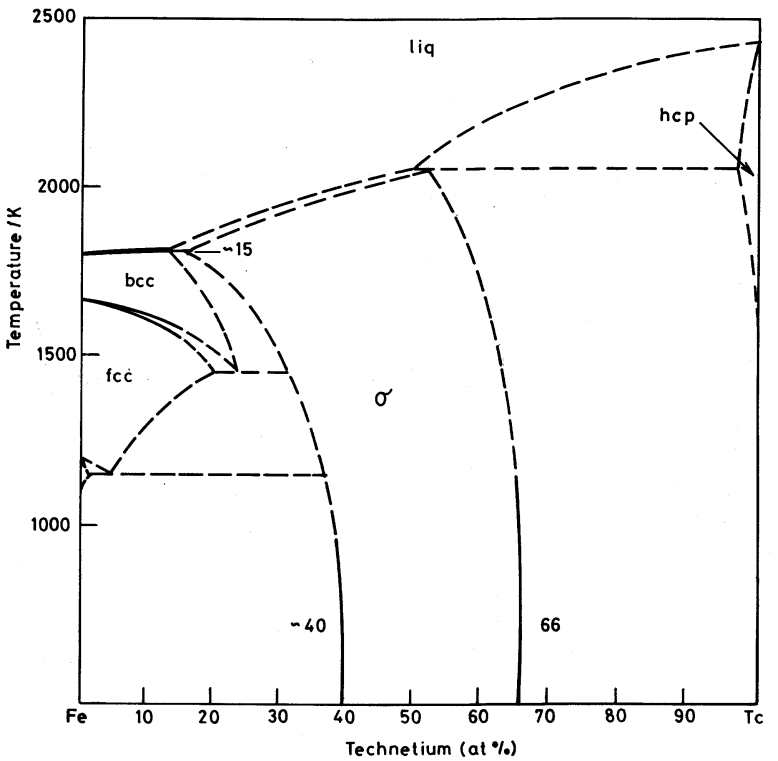
V.9.2.7 Tc-Cr

The only study of the Tc-Cr phase system is that of Darby *et al*. [62DAR/LAM] who established the existence of a σ-phase at compositions of 25 and 40 at-% Cr, see Table V.42. Venkatraman and Neumann [86VEN/NEU] expanded this observation into a "speculative" phase diagram, which has this σ-phase decomposing peritectically at ∼2260 K, and maximal values of the terminal solubilities of ∼50 at-% Tc in Cr at the peritectic melting point of this bcc phase (estimated to be ∼2170 K) and ∼14% Cr in Tc at ∼2260 K. As Venkatraman and Neumann [86VEN/NEU] themselves indicated, this diagram, patterned on the Cr-Re system, should be considered only as a rough guide for future phase diagram studies.

V.9.2.8 Tc-Fe

Kubaschewski [82KUB] presented a tentative phase diagram, shown in Figure V.8, based on two studies. Darby *et al*. [62DAR/LAM] established the existence of a phase with the well-known Fe-Cr σ-phase structure, extending from at least 40 to 60 at-% Tc. Following the suggestion of Raynor [72RAY] concerning the general behaviour of σ-phases, this was assumed to decompose peritectically. Buckley and Hume-Rothery [63BUC/HUM] studied the liquidus-solidus behaviour on the iron-rich side, showing that Tc is appreciably soluble (at least 15 at-%) in both Fe(fcc) and Fe(bcc) from 1569 to 1829 K, and that the liquidus-solidus lines are relatively flat up to ∼15 at-% Tc with a very slight increase with increasing technetium concentration.

Figure V.8: The iron-technetium phase diagram, redrawn from Kubaschewski [82KUB].



V.9.2.9 Tc-Hg

Guminski [93GUM] has recently reviewed the Tc-Hg system, noting that the mutual solubilities are expected to be minute. Three experimentally indistinguishable predictions of the solubility of Tc in liquid mercury at 298.15 K are given by [93GUM]: [64KOZ] 1.1×10^{-9} at-%; [89GUM] 6×10^{-13} at-% and [89GUM] 10^{-10} at-% (different model).

V.9.2.10 Tc-Ir

Darby, Norton and Downey [63DAR/NOR] found there were no intermediate phases in this system, and have determined the approximate limits of solid solubility in the elements at around 1323 K:

$$\text{Tc(hcp)} : \sim 70 \text{ at-\% Ir} \quad ; \quad \text{Ir(fcc)} < 25 \text{ at-\% Tc}$$

The variation of unit cell volume with composition shows negative deviations from Végard's law.

V.9.2.11 Tc-Mo

Alloys in this system have been studied quite extensively, owing to their superconducting properties. Compton *et al*. [61COM/COR] and Matthias [61MAT] first prepared and studied Tc-Mo alloys. They did not characterise the structure of their alloys, assuming they were similar to those present in the Mo-Re system. The subsequent solid-state investigations by Darby and co-workers [62DAR/LAM, 62DAR/ZEG] and by Niemiec [63NIE3] are in good agreement. There are two intermediate phases, a cubic Cr_3Si-type (A-15) phase at 52 to 56 at-% Tc and a tetragonal σ-phase with a composition range of ~66 to 72 at-% Tc. Marples and Koch [72MAR/KOC] found that the cubic A-15 phase formed from the melt at 60 at-% Tc and then decomposed at 970 to 1270 K to give a diphasic A-15 and σ-structure. The solubility of Tc in bcc Mo is between 50 and 60 at-% and that of Mo in hcp Tc is between 15 and 22 at-% Mo.

More recently, Giorgi and coworkers prepared samples of bcc alloys containing 12, 25, 45, 54, and 60 at-% Tc [78GIO/MAT, 78STE/GIO, 79STE/GIO] and hcp alloys containing 70 to 95 at-% Tc [78STE/GIO2] and measured their low temperature heat capacities (1 to 18 K) and superconducting temperatures. Many of these samples were prepared by rapid quenching, and may have contained metastable phases.

No solid-liquid equilibria have been investigated. Calculated phase diagrams were given by Haines, Potter and Rand [80HAI/POT] and by Brewer and Lamoreaux [80BRE/LAM]; they are quite different. That presented by Haines, Potter and Rand was based on regular solutions for the liquid, bcc and hcp in this system, and other phases (σ and A-15) were not included. The Gibbs energies of transformation of the metastable phases, Tc(bcc) and Mo(hcp), and the regular solution parameters were taken from, or estimated using the same procedures as, Kaufman and Bernstein [70KAU/BER]. However, the calculated terminal solubilities are rather different from the experimental values quoted above (the calculated values are 11 to 40 at-%

Table V.44: Parameters of Eq. V.50 for the integral Gibbs energies of mixing of Mo-Tc phases. Derived from the study of Brewer and Lamoreaux [80BRE/LAM].

Reaction/ Mo-Tc-phase	A	B	C	D	x_{Tc} [(a)] (min)	x_{Tc} [(a)] (max)	Temperature-range (K)
			($J \cdot mol^{-1}$)				
(V.51) /liq	0	415.7	-1662.9	831.4	0	0.667	2300-2890
(V.51) /liq	-274.4	274.4	-519.7	-727.5	0.667	1	2350-2500
(V.52) /bcc	0	0	$17577 \pm 0.83T$	1929.0	0	0.500	1200-2890
(V.53) /hcp	0	0	$15197 \pm 0.83T$	1968.5	0.760	1	1200-2500

[(a)] Mole fractions.

Mo in Tc and 25 to 35% Tc in Mo). Moreover, there is a maximum in the predicted solidus-liquidus curve [80HAI/POT], which is perhaps unlikely in comparison with the Mo-Re system [80BRE/LAM].

Brewer and Lamoreaux [80BRE/LAM] included the σ-and A-15-phases in their assessment and gave estimated thermodynamic data consistent with estimated solidus and liquidus curves, probably by assuming some similarity with the Mo-Re system. Their estimated thermodynamic data are cast into an equivalent but preferred equations for the integral excess Gibbs energy of mixing of the form

$$\Delta_{mix}G^{ex} = A + Bx_{Tc} \quad + \quad x_{Mo}x_{Tc}[C + D(x_{Mo} - x_{Tc})] \qquad (V.50)$$

which are, however, valid only over a restricted range of x_{Tc}. In this formalism, the corresponding partial excess Gibbs energies referred to the phase components as given in the Reactions (V.51) to (V.53),

$$Mo(l) + Tc(l) \quad \rightleftharpoons \quad (Mo, Tc)(l) \qquad (V.51)$$

$$Mo(bcc) + Tc(hcp) \quad \rightleftharpoons \quad (Mo, Tc)(bcc) \qquad (V.52)$$

$$Mo(bcc) + Tc(hcp) \quad \rightleftharpoons \quad (Mo, Tc)(hcp) \qquad (V.53)$$

are given by the expressions

$$\overline{G}^{ex}_{Mo} \quad = \quad A + x^2_{Tc}[C + D + 2D(x_{Mo} - x_{Tc})]$$

$$\overline{G}^{ex}_{Tc} \quad = \quad A + B + x^2_{Mo}[C - D + 2D(x_{Mo} - x_{Tc})]$$

for the liquid. Gibbs energies of formation of the Cr_3Si- and σ-type phases are given by

$$Mo(bcc) + \frac{11}{9}\,Tc(hcp) \quad \rightleftharpoons \quad MoTc_{11/9}(bcc, Cr_3Si\text{-type}) \qquad (V.54)$$

$$\Delta_f G^\circ_m \text{ (V.54, 1200 to 1973 K)} \quad = \quad [-(12800 \pm 4200) - 0.831\,T]\ J \cdot mol^{-1}$$

and

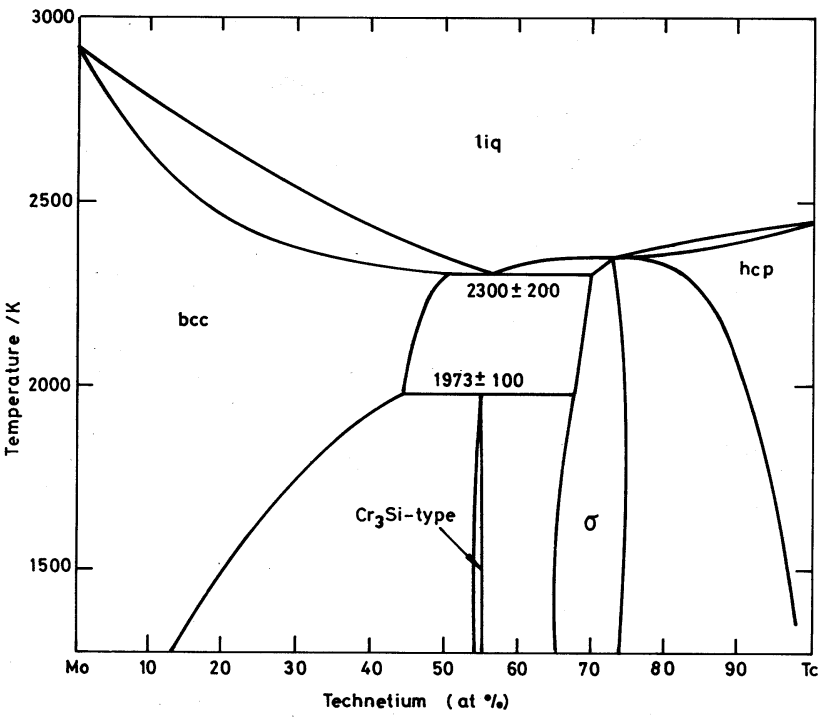
$$\text{Mo(bcc)} + \frac{37}{13}\,\text{Tc(hcp)} \quad \rightleftharpoons \quad \text{MoTc}_{37/13} \qquad (\sigma) \qquad \text{(V.55)}$$

$$\Delta_f G^\circ_m \text{ (V.55, 1200 to 2350 K)} \quad = \quad [-(28244 \pm 8300) - 1.663\,T]\ \text{J} \cdot \text{mol}^{-1}$$

However, it must be emphasised that these expressions are estimates without any experimental confirmation, and are designed to give reasonable solidus and liquidus values (for which, again, there are no experimental data).

The phase diagram proposed by Brewer and Lamoreaux [80BRE/LAM] is shown in Figure V.9, and should be regarded as a guide for future experimental studies. It is qualitatively similar to Mo-Re system [80BRE/LAM], in the regions where this is known reasonably well.

Figure V.9: Tentative phase diagram of the system molybdenum-technetium, redrawn from Brewer and Lamoreaux [80BRE/LAM].



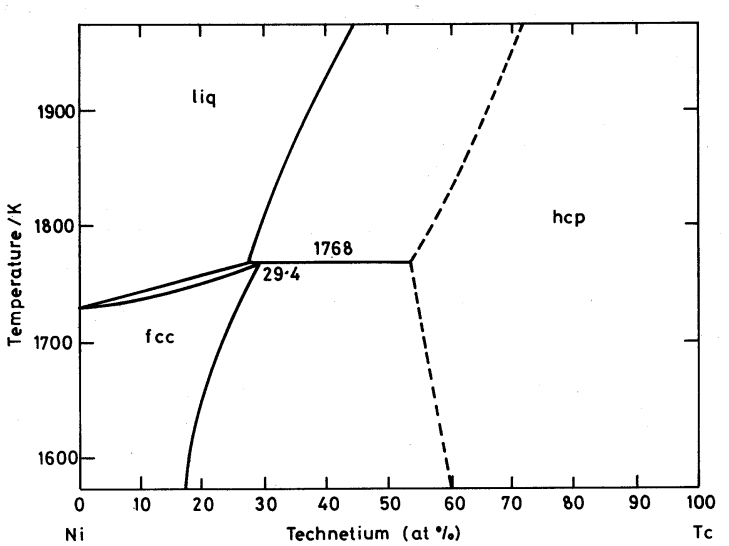
V.9.2.12 Tc-Nb

Alloys in this system have interesting superconducting properties and were studied by Compton *et al.* [61COM/COR], van Ostenburg *et al.* [63VAN/LAM] and Giorgi and Szklarz [70GIO/SZK2], and lattice parameters were reported for 14.3 and 25 at-% Nb [62DAR/LAM] with general agreement. Their solubility of technetium in niobium is about 50 at-%, and that of Nb in Tc about 5 to 10 at-%. Between these two terminal solid solutions, there is a bcc phase with the alpha-manganese structure, extending from at least 75 to 85 at-% Tc [63OST/LAM], and perhaps down to 58 at-% Tc [70GIO/SZK]. Lattice parameters for this phase are given in Table V.42.

V.9.2.13 Tc-Ni

Nash [85NAS] presented an evalution of the Tc-Ni phase diagram, (*cf.* Figure V.10), based on the studies by Darby, Norton and Downey [63DAR/NOR] and Spitsyn *et al.* [75SPI/GRI]. There are no intermediate phases, but substantial mutual solubilities, with a peritectic decomposition of Ni(fcc) containing 29.4 at-% Tc to liquid (∼28 at-% Tc) and to Tc(hcp) containing ∼45 at-% Ni at 1768 K. The lattice parameters of the solid solutions as a function of composition were determined in both studies, with reasonable agreement, see Ref. [85NAS]. The volume of the hcp cell was found to be a linear function of the composition [63DAR/NOR].

Figure V.10: Assessed Ni-Tc phase diagram, redrawn from Nash [85NAS].



V.9.2.14 Tc-Os

Darby *et al*. [62DAR/LAM] and Niemec [65NIE] showed that technetium and osmium form a complete range of solid solutions in the hcp phase. The former gave the variation of lattice parameters as a function of composition. The volume of the hexagonal cell is essentially a linear function of the mole fraction of technetium. Unit cell parameters from Alekseyevskiy, Balakhovskiy and Kirillov [75ALE/BAL] are consistent with those of Darby *et al*.

Savitskii and Gribulya [75SAV/GRI] suggested that there might a σ-phase in the Tc-Os system, based on a computer correlation of the formation of known σ-phases and the distribution of electrons in the isolated component atoms. However, the same analysis forecasts possible σ-phases in the Fe-Mn, Fe-W and Mo-Ni, all systems which have been fairly extensively studied without the detection of σ-phases.

V.9.2.15 Tc-Pd

Darby, Norton and Downey [63DAR/NOR] and Niemec [63NIE] found there were no intermediate phases in this system, and they determined the approximate limits of solid solubility in the elements at around 1323 K, with good agreement:

Tc(hcp) : roughly 50 at-% Pd ; Pd(fcc) : roughly 25 at-% Tc

Haines, Potter and Rand [80HAI/POT] presented an estimated phase diagram for the Tc-Pd system, based on regular solutions for the liquid and hcp phases for the solids in this system. The Gibbs energies of transformation of the metastable phases, Tc(fcc) and Pd(hcp), and the regular solution parameters were taken from, or estimated using the same procedures as, Kaufman and Bernstein [70KAU/BER]. However, the calculated terminal solubilities are rather different from the experimental values quoted above (the calculated values are approximately 11 to 18 at-% Pd in Tc and approximately 15 to 35 at-% Tc in Pd), so it seems likely that more complicated models or better estimates of the Gibbs energies of transformation and interaction parameters are required for this type of calculation.

V.9.2.16 Tc-Pt

Darby, Norton and Downey [63DAR/NOR] and Niemec [63NIE] found that there were no intermediate phases in this system, and have determined the approximate limits of solid solubility in the elements at around 1323 K, with good agreement:

Tc(hcp) : roughly 30 at-% Pt ; Pt(fcc) : roughly 40 at-% Tc

The variation of unit cell volume with composition shows negative deviations from Végard's law.

V.9.2.17 Tc-Rh

Darby, Norton and Downey [63DAR/NOR] and Niemec [63NIE] found there were no intermediate phases in this system, and have determined the approximate limits of solid solubility in the elements at around 1323 K, with good agreement:

Tc(hcp) : roughly 70 at-% Rh ; Rh(fcc) : roughly 8 at-% Tc

The variation of unit cell volume with composition shows negative deviations from Végard's law [63DAR/NOR, 63NIE].

Haines, Potter and Rand [80HAI/POT] have presented an estimated phase diagram for the Tc-Rh system, based on regular solutions for the liquid, fcc and hcp phases in this system. The Gibbs energies of transformation of the metastable phases, Tc(fcc) and Rh(hcp), and the regular solution parameters were taken from, or estimated using the same procedures as, Kaufman and Bernstein [70KAU/BER]. However, the calculated terminal solubilities are rather different from the experimental values quoted above (the calculated values are ~40 at-% Rh in Tc and ~50 at-% Tc in Rh), so it seems likely that more complicated models or better estimates of the Gibbs energies of transformation and interaction parameters are required for this type of calculation.

V.9.2.18 Tc-Ru

Darby *et al*. [62DAR/LAM] and Niemec [65NIE] showed that technetium and ruthenium form a complete range of solid solutions in the hcp phase. The former give the variation of lattice parameters as a function of composition graphically. The volume of the hexagonal cell is essentially a linear function of the mole fraction of technetium. Unit cell parameters from Alekseyevskiy, Balakhovskiy and Kirillov [75ALE/BAL] are reasonably consistent with those of [62DAR/LAM].

V.9.2.19 Tc-Sc

Darby *et al*. [62DAR/LAM] found two phases in the Tc-Sc system, a cubic phase $ScTc_7$ with the α-Mn structure and a Laves-phase ($MgZn_2$-type) at $ScTc_2$, see Table V.42. The latter phase was subsequently found to be superconducting up to 10.9 K by Szklarz and Giorgi [81SZK/GIO], and its heat capacities were measured from about 5 to 18 K by Stewart *et al*. [82STE/COR]. Those results, which were presented graphically, show that above the superconducting transition region, $C^{\circ}_{p,\mathrm{m}}/T$ rises more rapidly than the usual T^2 dependence.

V.9.2.20 Tc-Si

Darby, Downey and Norton [65DAR/DOW] studied ten alloys in this system, finding the five intermediate phases given in Table V.42. Alloys with approximately 25 at-% silicon contained a disordered bcc structure in the as-cast state, which formed an ordered bcc structure (either Fe_3Zn_{10} ($Im\bar{3}m$) or Cu_5Zn_8 ($I\bar{4}3m$) type) when annealed for one week at 1323 K.

Darby, Downey and Norton [65DAR/DOW] suggested that the most silicon-rich phase was isostructural with "$MnSi_2$", but were unable to index their powder patterns consistently. Wittemann and Nowotny [65WIT/NOW] subsequently pointed out that the "$MnSi_2$" phase in fact has an atomic ratio of Si/Mn < 2 and were able to index the d-spacings of "$TcSi_2$" given by [65DAR/DOW] as a tetragonal cell, with a composition close to Tc_4Si_7, based on four $TcSi_2$ subcells, and closely related to the revised "$MnSi_2$", $Mn_{11}Si_{19}$, with eleven subcells. Subsequently, Karpinskii and Evseev [69KAR/EVS] identified the similar phase Mn_4Si_7, with four subcells, and it is assumed that this is the prototype structure for Tc_4Si_7, see Table V.42.

V.9.2.21 Tc-Sn

Alekseyevskiy, Balakhovskiy and Kirillov [75ALE/BAL] measured the superconducting transition temperatures of three incompletely characterised Tc-Sn alloys containing 22, 34 and 37% Sn. The samples with 22 and 37% of Sn were shown to contain an hcp phase, the lattice parameters of which were, in both samples, very close to those of pure technetium. The authors did not, unfortunately, report the lattice parameters of the Tc metal they used. It is thus likely that the solubility of tin in technetium is fairly small (probably < 5 at-%). They did not state whether their per cent compositions were in at-% or mass-%. However, they also gave unit cell parameters for the Tc-Re and Tc-Os systems, and comparison of those values to those of Darby *et al.* [62DAR/LAM] leaves no doubt that the compositions of Alekseyevskiy, Balakhovskiy and Kirillov were given in at-%.

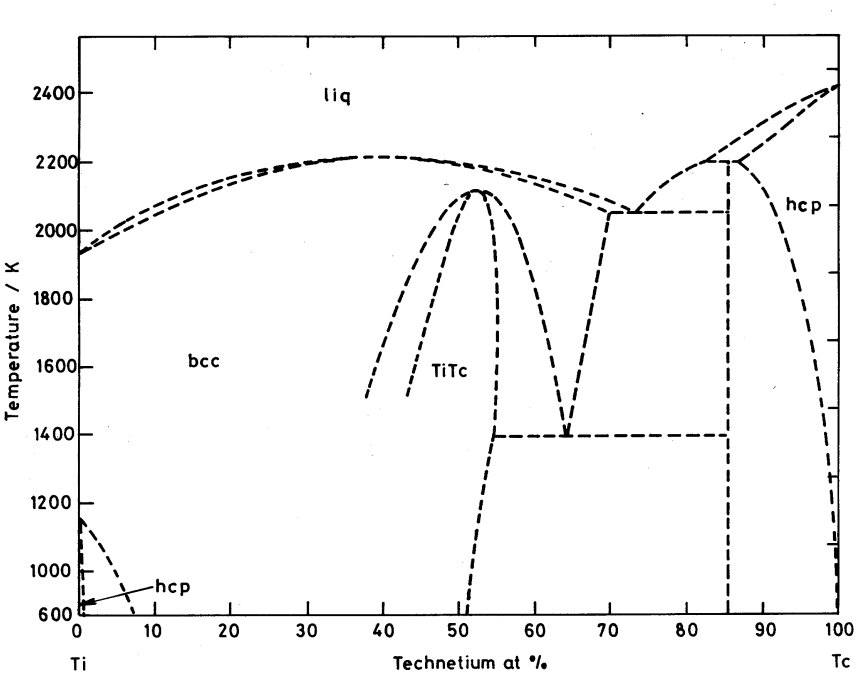
V.9.2.22 Tc-Ti

Darby *et al.* [62DAR/LAM] found two intermediate phases in this system: a phase with the α-Mn stucture in as-cast alloys containing 12.5 and 14.3 at-% Ti, and an ordered bcc phase (CsCl type) in alloys containing 33.3 and 50 at-% Ti annealed at 973 K. Koch [76KOC] studied the structures and superconducting properties of the alloys. He confirmed the presence of the two phases found by Darby *et al.* [62DAR/LAM], showing that an alloy with 15 at-% Ti, annealed at 1773 K was "essentially" single phase cubic α-Mn type, and that the ordered bcc phase at 33 at-% and 50 at-% Ti persists on annealing at 1273 K. However, as-cast alloys did not show any ordering superlattice lines, suggesting that the ordered phase became disordered below the (unknown) liquidus temperature. As-cast alloys containing 25, 33, 50, 65, 75 and 85 at-% Ti showed single phase bcc structures, with strong negative deviations from Végard's law. The solubility of Ti in Tc(hcp) is between 3 and 5 at-% 1773 K [76KOC].

Murray [82MUR] took these observations to estimate a consistent phase diagram for the system. The bcc, hcp and liquid phases were taken to be regular solutions, with interaction parameters about -100 kJ·mol^{-1} (-87 to -109), and the defect CsCl-type phase was modelled with two sublattices: (Ti, va)(Tc, Ti), where "va" represents a vacancy. However, the values for the Gibbs energies of transformation (including fusion) of Ti and Tc used by Murray [82MUR] were those given by Kaufman and Bernstein [70KAU/BER], which differ from more recent values, (see Section V.1.1.3

on elemental Tc and see Dinsdale [89DIN]). In particular, Kaufman's estimate for the enthalpy of fusion of Tc(hcp), 20.7 kJ·mol^{-1}, is appreciably smaller than that suggested in the present assessment (33.3 kJ·mol^{-1}), which will affect the solidus/liquidus lines on the Tc-rich side of the diagram in particular. For this reason Murray's Gibbs energy values are not quoted in detail, since they are not consistent with the present assessment. However, Murray's calculated phase diagram, Figure V.11, can still be regarded as a good indication of the probable form of the diagram, certainly as a good starting point for more detailed experimental investigations.

Figure V.11: Ti-Tc phase diagram, redrawn from Murray [82MUR].

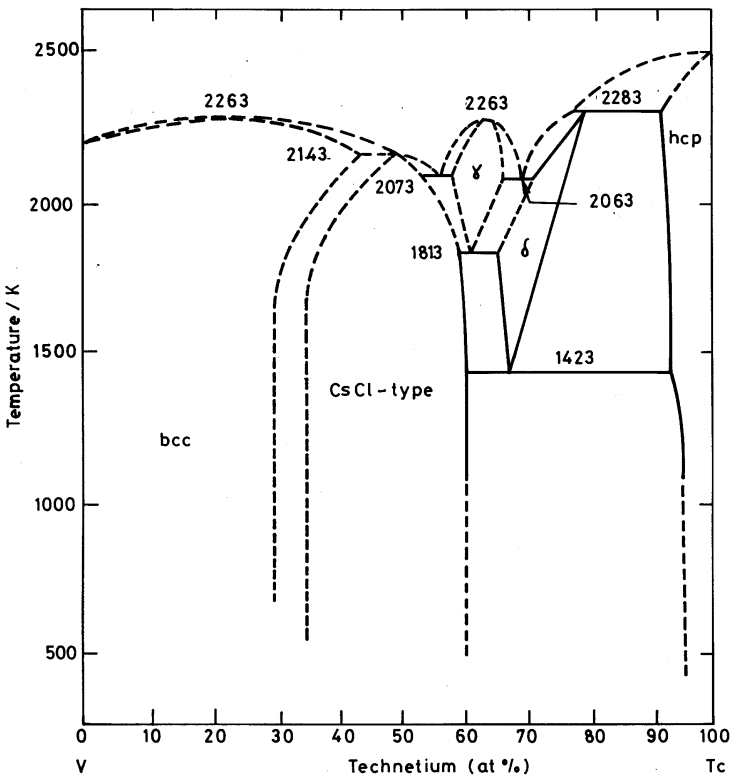


V.9.2.23 Tc-V

Darby *et al*. [62DAR/LAM] and van Ostenburg *et al*. [62VAN/LAM] first studied this system, reporting a CsCl type structure in the middle of the diagram. Koch and Love [68KOC/LOV] made a more extended study and proposed the diagram shown in Figure V.12. In assessing this work, Smith [87SMI, 89SMI] pointed out that the V-rich portion of the diagram is quite uncertain and that the transition between the disordered bcc and the ordered CsCl structures may well be second-order, rather than first-order, with a continuous variation in site occupancy (*cf*. Os-V and Ru-V systems [89SMI]).

The structures of the high-temperature γ-and δ-phases, which could not be quenched to room temperature, are not known. It must also be noted that the starting Tc used in this study may have contained considerable amounts (up to 20 at-%) oxygen [67KOC/LOV] although the analysed amounts in the Tc-V alloys were very much lower (< 0.14 at-%).

Figure V.12: The Tc-V phase diagram, redrawn from that assessed by Smith [87SMI], based on the study of Koch and Love [68KOC/LOV].



V.9.2.24 Tc-W

Technetium-tungsten alloys, which are superconducting at low temperatures, were studied by Niemec [63NIE2], Autler, Hulm and Kemper [65AUT/HUL] and Giorgi [85GIO], with very good agreement. The solubility of tungsten is about 50 at-% at 2000 K, decreasing to ~33 at-% at 1500 K [63NIE3]. There is a σ-phase with a range of homogeneity ~60 to ~77 at-% Tc, while the maximal solubility of W in hcp Tc is 12 to 15 at-% at ~2000 K, decreasing to 7 at-% at ~1500 K. No Cr_3Si-type-phase,

(*cf*. Tc-Mo system), was found in the Tc-W system.

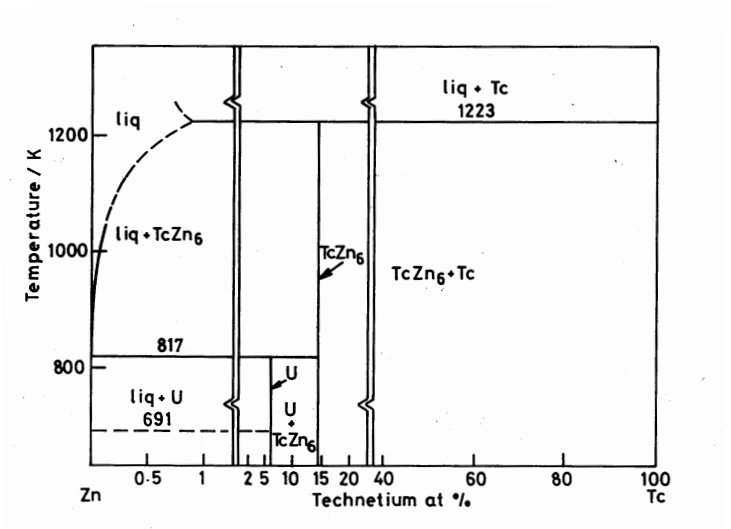
V.9.2.25 Tc-Zn

The technetium-zinc system was studied by Chasanov and Johnson [64CHA/JOH], using thermal, metallographic, X-ray and effusion techniques. Two intermediate phases were identified: an fcc phase with a Zn/Tc atomic ratio between 5 and 7, and probably close to 6, and a more zinc-rich phase with $10 < \text{Zn/Tc} < 18$. Both these phase decomposed peritectically; the zinc-rich phase decomposed at (817 ± 3) K to give $TcZn_6$ and liquid containing 0.0047 at-% Tc, and $TcZn_6$ decomposed to solid Tc and liquid containing ~0.8 at-% Tc at 1223 K. The mutual solubilities in the solid state are negligible, whilst the solubility of Tc in liquid zinc is given by their equations:

$$\log_{10}(x_{\text{Tc}}, \text{743 to 817 K}) = 4.431 - 7159/T$$
$$\log_{10}(x_{\text{Tc}}, \text{817 to 1031 K}) = 7.413 - 15690/T + 4.979 \times 10^6/T^2$$

The phase diagram for this system proposed by Chasanov and Johnson is shown in Figure V.13.

Figure V.13: The zinc-technetium phase diagram, redrawn from Chasanov and Johnson [64CHA/JOH].



To supplement the above study, Veleckis and Johnson [64VEL/JOH] measured the decomposition pressure of $TcZn_6$(cr), by Knudsen effusion from 743 to 843 K. As for pure zinc, monatomic Zn was taken to be the only vapour species present. The pressure of Zn(g) above $TcZn_6$ was represented by them with the equation which on conversion to bar is

$$\log_{10}(p_{Zn}/\text{bar}) \quad = \quad (6.978 - 8242/T)$$

When combined with the vapour pressure of pure zinc given in the CODATA "Key values" [89COX/WAG], which around 800 K can be expressed by the equation

$$\text{Zn(l)} \quad \rightleftharpoons \quad \text{Zn(g)} \qquad \text{(V.56)}$$

where $\Delta_r G^\circ_m$ (V.56) = $(119301 - 101.94\,T)$ J · mol^{-1}. This gives

$$\Delta_r G^\circ_m \text{ (V.57, 743 to 843 K)} \quad = \quad (-38500 + 31.69\,T) \text{ J} \cdot \text{mol}^{-1}$$

$$\frac{1}{x}\text{Tc(hcp)} + \text{Zn(l)} \quad \rightleftharpoons \quad \frac{1}{x}\text{TcZn}_x\text{(fcc)}; \qquad 5 < x < 7 \qquad \text{(V.57)}$$

If this equation is extrapolated upwards in temperature (without any $\Delta_r C^\circ_{p,m}$ correction), the calculated decomposition temperature of "$TcZn_6$" is 1215 K, in satisfactory agreement with the value of 1223 K found from thermal measurements.

In view of the uncertainty in composition of the fcc phase, no further processing of these values to 298.15 K is warranted.

V.9.2.26 Tc-Am, Tc-Cf, Tc-Bk

This review is not aware of any experimental thermodynamic or binary phase equilibrium data for technetium metal with americium, californium, or berkelium. However, Wu and Brewer [96WU/BRE] have provided calculations for the solid-liquid equilibrium regions of their phase diagrams using modified regular solution theory. Values of the entropy of fusion and enthalpy of fusion of technetium metal were required for these calculations, and their selected values are identical or nearly identical, respectively, with those selected by this review. As noted by these authors, the solubility of a refractory (high melting) metal is expected to be quite small in a liquid low melting metal such as Am, Cf, or Bk. Wu and Brewer list the parameters used for the modelling calculations, along with calculated solubilities at several temperatures.

V.9.3 Ternary systems

The little experimental structural information on ternary phases containing technetium there is, is summarised in Table V.45.

V.9.3.1 Tc-C-M (M = 3d, 4d, 5d transition metals)

Eremenko, Velikanova and Bondar [89ERE/VEL] estimated the likely form of the Tc-C-M systems with M = Sc; Ti, Zr, Hf; V, Nb, Ta; Cr, Mo, W; and Re, and they gave sketched isothermal sections of the ternary systems. These estimated sections are based on semiquantitative correlations of the lattice parameters of the hypostoichiometric NaCl-type MC_{1-x} phases and the Gibbs energy differences $\Delta_f G^\circ_m$ (TcC_{1-x}) − $\Delta_f G^\circ_m$

Table V.45: Structural information for intermediate phases in ternary technetium systems.

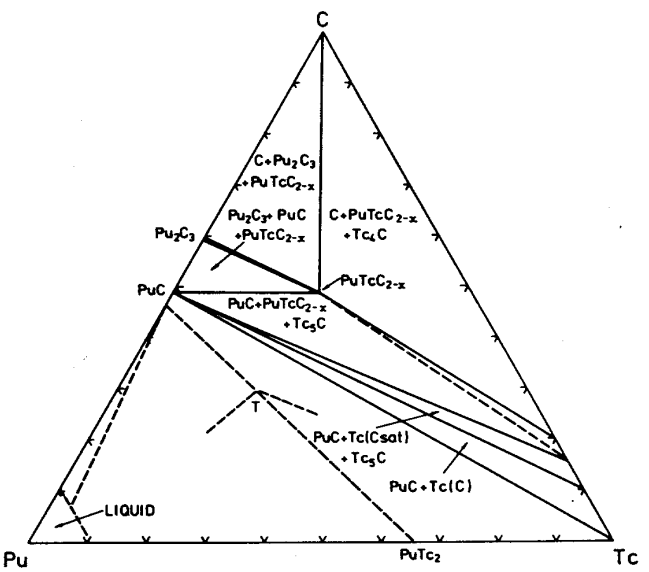
Phase	Symmetry space group	Lattice parameters ($\times 10^{10}$/m)	Prototype structure	Reference
$PuTcB_2$	orthorhombic, Pnma	$a = 5.8415 \pm 0.0016$ $b = 5.3191 \pm 0.0020$ $c = 6.4265 \pm 0.0018$	$LuRuB_2$	[87ROG/POT]
Pu_2TcB_6	orthorhombic, Pbam	$a = 9.2834 \pm 0.0016$ $b = 11.3685 \pm 0.0020$ $c = 3.6264 \pm 0.0012$	Y_2ReB_6	[88ROG/POT]
$PuTcB_4$	orthorhombic, Pbam	$a = 59.595 \pm 0.0010$ $b = 11.5416 \pm 0.0018$ $c = 3.5869 \pm 0.0006$	Y_2CrB_4	[88ROG/POT]
$Pu_2Tc_2C_3$	monoclinic C2/m (Z=2)	$a = 5.401$ to 5.439 $b = 3.206$ to 3.231 $c = 11.159$ to 11.25 $\beta = (109.0)^\circ$	$Ho_2Cr_2C_3$	[76HAI/MAR] [86JEI/BEH]
$Pu_2Tc_3Si_4$	monoclinic, $P2_1/c$ (Z= 2)	$a = 6.843 \pm 0.002$ $b = 8.072 \pm 0.002$ $c = 5.581 \pm 0.002$ $\beta = (103.47 \pm 0.02)^\circ$	$Np_2Tc_3Si_4$	[94WAS/REB]
$Pu_2Tc_3Si_5$	tetragonal P4/mnc (Z= 4)	$a = 10.917 \pm 0.008$ $c = 5.538 \pm 0.004$	$Sc_2Fe_3Si_5$	[96LEI/ROG]
$UTcC_2$	orthorhombic, Pnma	$a = 5.4$ $b = 3.22$ $c = 10.9$	$UMoC_2$ (?)	[64FAR/BOW]
	orthorhombic	$a = 5.550 \pm 0.022$ $b = 3.232 \pm 0.016$ $c = 10.901 \pm 0.056$	$UMoC_2$ (?) some lines not indexed	[76HAI/MAR]
$UTc_3C_{0.55}$ -$UTc_3C_{0.65}$	fcc	$a = 4.1322$ $a = 4.1483$		[80HAI/POT]
~$UTc_3C_{0.65}$	tetragonal	$a = 5.030 \pm 0.010$ $c = 12.493 \pm 0.030$	unknown	[80HAI/POT]
UTc_2Si_2	bcc,Im3m	$a = 8.206$	$U_4Re_7Si_6$	[89DAL/MAP]
$U_4Tc_7Ge_6$	cubic Im3m (Z= 2)	$a = 8.351 \pm 0.004$	$U_4Re_7Si_6$	[94WAS/REB]
$U_2Tc_3Si_5$	tetragonal P4/mnc (Z= 4)	$a = 10.848 \pm 0.004$ $c = 5.533 \pm 0.004$	$U_2Mn_3Si_5$	[94WAS/REB]
$U_4Tc_7Si_6$	cubic Im3m (Z= 2)	$a = 8.194 \pm 0.004$	$U_4Re_7Si_6$	[94WAS/REB]
$Np_2Tc_3Ge_4$	monoclinic, $P2_1/c$ (Z= 2)	$a = 6.778 \pm 0.002$ $b = 8.102 \pm 0.002$ $c = 5.605 \pm 0.002$ $\beta = (104.09 \pm 0.04)^\circ$	$Np_2Tc_3Si_4$	[94WAS/REB]
$Np_2Tc_3Si_4$	monoclinic, $P2_1/c$ (Z= 2)	$a = 6.808 \pm 0.002$ $b = 8.081 \pm 0.002$ $c = 5.567 \pm 0.004$ $\beta = (103.61 \pm 0.04)^\circ$	$Np_2Tc_3Si_4$ (prototype)	[94WAS/REB]

(MC_{1-x}). Since many of the relevant NaCl-type carbides have carbon-poor boundaries around $MC_{0.6}$, this composition is chosen for the correlation. As noted in Section V.9.2.4, their value for $\Delta_f G^\circ_m$ ($TcC_{0.6}$) can be inferred to be close to zero. Clearly there are a great deal of estimated data and assumptions in the derivation of the ternary sections, but they probably form a reasonable basis from which any future experimental work can be planned. The solid solubility between TcC_{1-x} and MC_{1-x} is predicted to be complete for M = Ti, V, Nb, Ta, Mo and W, but quite restricted for M = Sc, Zr and Hf. The elements Cr and Re do not form NaCl-type carbides, leading to even more uncertainty in the predicted sections.

V.9.3.2 Tc-C-Pu

Haines and coworkers [76HAI/MAR, 80HAI/POT] gave a tentative isothermal section at 1273 K, see Figure V.14, for this ternary system. It contains the phase which they described as $PuTcC_{2-x}$, which Jeitshko and Behrens [86JEI/BEH] subsequently suggested had a composition close to $Pu_2Tc_2C_3$, with the $Ho_2Cr_2C_3$-type structure. There is also a phase of unknown structure, with the approximate composition $PuTc_{0.6}C_{0.7}$, close to the "PuC"-$PuTc_2$ join.

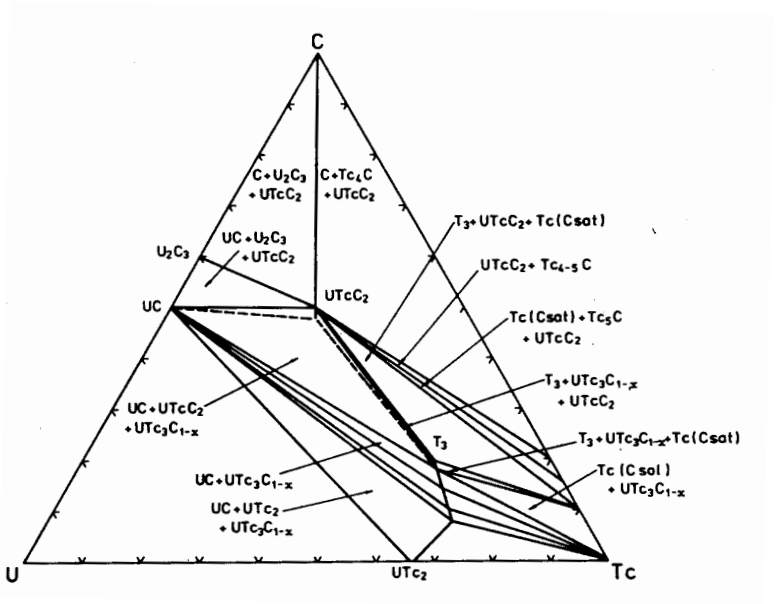
Figure V.14: A tentative phase diagram for the Tc-C-Pu system at 1273 K, reproduced with permission from Haines, Potter and Rand [80HAI/POT].



V.9.3.3 Tc-C-U

Haines and coworkers [76HAI/MAR, 80HAI/POT] gave a tentative isothermal section for temperatures from 1073 to 1273 K, see Figure V.15, for this ternary system. It contains the phase $UTcC_2$ tentatively indexed with an orthorhombic cell, previously described by Farr and Bowman [64FAR/BOW], which melts around 2070 K. It is not clear whether this phase is isomorphous with the similar $PuTcC_{2-x}$ phase (and thus monoclinic in structure), whose true formula is probably $Pu_2Tc_2C_3$, as noted above. There are two other ternary phases, $UTc_3C_{(0.55\ to\ 0.65)}$ with an fcc structure, probably related to the similar phases URu_3C and URh_3C, and a phase close to the carbon-rich end of the $UTc_3C_{0.65}$ phase called T_3 in Figure V.15. This could be partially indexed with a tetragonal cell, see Table V.45.

Figure V.15: A phase diagram for the Tc-C-U system at 1073 to 1273 K, reproduced with permission from Haines, Potter and Rand [80HAI/POT].



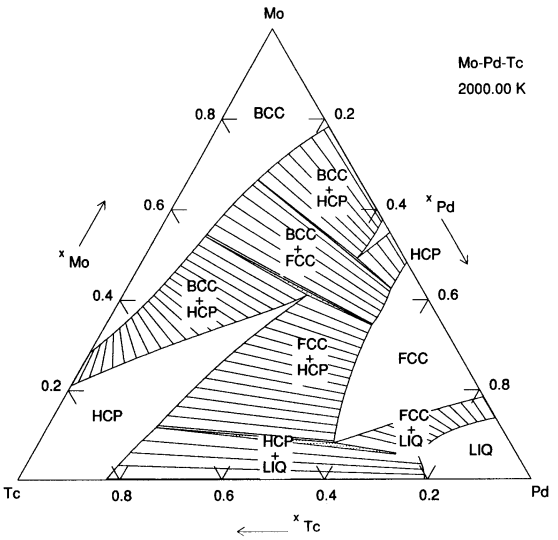
V.9.3.4 Tc-C-W

Giorgi [85GIO] showed that W_2C and Tc form a continuous series of hcp solid solutions all of which become superconducting below 2.5 to 7.5 K, with both *a* and *c* increasing monotonically across the pseudo-binary section.

V.9.3.5 Mo-Tc-Pd, Mo-Tc-Rh

Haines, Potter and Rand [80HAI/POT] calculated ternary sections at 1800, 2000 and 2200 K for the ternary systems Mo-Tc-Pd and Mo-Tc-Rh, using the estimated binary data discussed in Section V.9.2. Although, as noted in that section, the binary data do not give particularly good representations of the limiting solubilities, the general form of these ternary systems is probably correct. The sections for 2000 K are thus given in Figures V.16 and V.17, respectively. These systems are important for the studies of the insoluble intermetallic fission product phases ("white inclusions") found in irradiated nuclear fuels, see below.

Figure V.16: The calculated isothermal section (2000 K) of the Mo-Tc-Pd phase diagram, redrawn from Haines, Potter and Rand [80HAI/POT].

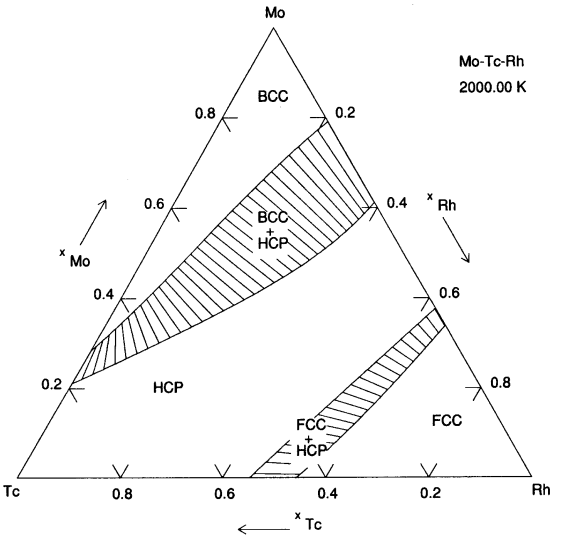


Matsui and Naito [89MAT/NAI] calculated the vaporisation behaviour of Mo-Tc-Pd alloys in the absence and presence of oxygen, using the model and parameters of Haines, Potter and Rand [80HAI/POT] for the solid phases. These calculations indicate that Pd is preferentially lost from the alloys at high temperatures under vacuum, but under oxidising conditions Tc is preferentially lost, especially at "low" temperatures, due to formation of volatile oxides.

V.9.3.6 Tc-An-Ge, Tc-An-Si

Dalichaouch *et al*. [89DAL/MAP] reported preparation of the first ternary technetium-actinide silicide UTc_2Si_2(cr) along with several quaternary structures of URu_2Si_2(cr)

Figure V.17: The calculated isothermal section (2000 K) of the Mo-Tc-Rh phase diagram, redrawn from Haines, Potter and Rand [80HAI/POT].



doped with technetium with the compositions $URu_{2-x}Tc_xSi_2$(cr) where x = 0.44 to 1.43. They were prepared by arc-melting of the constituent elements in stoichiometric amounts under an argon atmosphere, followed by remelting at least six times and then annealing at 1173 K for at least one week. They were partially characterised by X-ray crystallography and by electrical resistivity and dc magnetic susceptibility measurements.

Wastin *et al.* [94WAS/REB] prepared the following four ternary technetium-actinide silicides and two technetium-actinide germanides by the same basic method of synthesis: $Np_2Tc_3Si_4$(cr), $Pu_2Tc_3Si_4$(cr), $U_2Tc_3Si_5$(cr),$U_4Tc_7Si_6$(cr), $Np_2Tc_3Ge_4$(cr), and $U_4Tc_7Ge_6$(cr). These compounds were characterised by powder pattern X-ray crystallography and, in some cases, single-crystal crystallography, by magnetic susceptibility measurements for $U_4Tc_7Si_6$(cr), and (for the compounds containing ^{237}Np) by Mössbauer spectroscopy. The compound $U_4Tc_7Si_6$(cr) becomes antiferromagnetically ordered around 25 K and has a broad maximum in the magnetic susceptibility centered around 150 K. Similarly, Leithe-Jasper, Rogl, and Potter [96LEI/ROG] prepared the ternary compound $Pu_2Tc_3Si_5$(cr) from the pure elements ($>$ 99.9 mass-%). Losses in mass from this melting and remelting were $<$ 2 mass-%. The structure was determined by powder pattern X-ray crystallography to have a tetragonal unit cell and to be isostructural with $Sc_2Fe_3Si_5$(cr), *cf.* Table V.45.

Table V.46: Lattice parameters of hexagonal phases in the Mo-Tc-Ru-Rh-Pd system. All phases are hcp, space group $P6_3/mmc$, Mg type structure.

	Composition (at-%)					Lattice parameters		Reference
	Mo	Tc	Ru	Rh	Pd	*a* ($\times 10^{10}$/m)	*b* ($\times 10^{10}$/m)	
a	43.5	15.3	32.1	7.0	2.1	2.735	4.446	[68BRA/SHA]
a, b	44.7	17.7	34.5	3.1	–	2.761	4.439	
c	43	11	28	8.5	10	2.756	4.42	[84KLE/PEJ]
c	38	14	33	8	7	2.761	4.43	
	37	21	35	4	3	2.746	4.415	[85KLE/PAS]
	25	8	52	7	8	2.752	4.411	
	25	8	44	8	15	2.752	4.415	

(a) Renormalized to 100 at-% total composition; compositions not known to the precision given.
(b) Also contained ~5 volume-% of a phase with approximate composition Mo_5RuTc; this was a synthetic inclusion without Pd.
(c) Average composition of several inclusions.

V.9.4 Higher-order systems

V.9.4.1 Tc-Mo-Pd-Rh-Ru

There is some structural information on the "white inclusions" of metallic fission products, containing the elements Mo, Tc, Ru, Rh and Pd, found in irradiated nuclear fuels, and simulated synthetic materials of similar composition. These inclusions were first identified by Bramman *et al.* [68BRA/SHA], who gave lattice parameters for two multi-component hexagonal phases. More recent work was summarised by Kleykamp [85KLE] and Kleykamp *et al.* [85KLE/PAS] who plotted the compositions found by microprobe analysis of the metallic inclusions found in irradiated fuels as a Mo-(Ru+Tc)-(Pd+Rh) pseudo-ternary diagram. From this they predicted that such inclusions could be single-phase hcp, single-phase bcc (for Mo-rich phases), diphasic mixtures of (hcp + bcc), (hcp + fcc), (hcp + σ), (bcc + σ), triphasic (bcc+hcp+σ) according to the conditions of the fuel irradiation, which will affect the overall composition, particularly the molybdenum content. The lattice parameters of the reported hcp phases are given in Table V.46. A plot of these lattice parameters was given by Kleykamp [88KLE] on a pseudo-ternary diagram. These metallic inclusions of Mo-Tc-Ru-Rh-Pd were formed even when an oxide fuel (UO_2 or $U_xPu_{1-x}O_2$) was used [88KLE], since insufficient oxygen was left in the fuel after the more electropositive fission products had formed oxides.

V.9.4.2 Tc-Ru-Si-U

Dalichaouch *et al.* [89DAL/MAP] studied the structural and physical properties of $URu_{2-x}Tc_xSi_2$ phases. With $x < 1.04$ these have the body-centred tetragonal $BaAl_4$ type structure, space group I4/mmm, similar to the $LnRu_2Si_2$ (Ln = lanthanide element) and $ThCr_2Si_2$ phases, but with $x > 1.43$ have the body-centred cubic $U_4Re_7Si_6$-type

structure, space group $Im\bar{3}m$. The precise boundaries of the bct-bcc diphasic region are not known, nor is the type of defect associated with the change from 1:2:2 to 4:7:6 stoichiometry. The lattice parameters are given in Table V.47, where bct denotes a body-centred tetragonal unit cell. The complex magnetic behaviour of these phases

Table V.47: Lattice parameters of $URu_{2-x}Tc_xSi_2$ phases.

x	Symmetry	a ($\times 10^{10}$/m)	c ($\times 10^{10}$/m)
0.00	bct	4.142	9.559
0.44	bct	4.155	9.552
0.77	bct	4.155	9.601
1.04	bct	4.107	9.606
1.43	bcc	8.150	
2.00	bcc	8.206	

is discussed by [89DAL/MAP]; the solid solutions with $0.4 < x < 1.4$ are, rather unexpectedly, ferromagnetic. The electrical resistivities of these phases below 12 K were also reported by [89DAL/MAP].

V.10 Miscellaneous compounds and complexes

V.10.1 Actinide complexes

Koltunov *et al.* [80KOL/ZAI] studied the oxidation of Pu(III) by HNO_3 at $I = 4$ M at 312 to 347 K, with 3.3×10^{-4} to 1.3×10^{-2} M TcO_4^- present as catalyst. These solutions also contained 10^{-3} M NH_2SO_3H (323 K) or 0.1 M NH_2SO_3H (347 K). This sulfamic acid was added in order to destroy any HNO_2 that might have been produced from the reduction of HNO_3. Separate experiments showed that NH_2SO_3H at these concentrations did not reduce TcO_4^- in 3 M $HClO_4$ at 328 K during the time frame of interest to the kinetic experiments. The kinetic experiments were monitored with spectrophotometry [80KOL/ZAI]. At $I = 4$ M and 323 K they found that

$$-\frac{\mathrm{d[Pu(III)]}}{\mathrm{d}t} = k[\mathrm{Pu(III)}][\mathrm{TcO_4^-}][\mathrm{H^+}]^{2.3}$$

where $k = (3.82 \pm 0.22) \times 10^{-2}$ $\mathrm{mol^{-3.3} \cdot dm^{9.9} \cdot min^{-1}}$. They concluded that this reaction involved formation of an activated-state complex

$$\mathrm{Pu^{3+} + TcO_4^- + 2H^+} \rightleftharpoons [\mathrm{TcO_2Pu(OH)_2^{4+}}]^{\ddagger}$$

as an unstable intermediate.

Kinetic studies have been reported for the reduction of TcO_4^- by U^{4+} in acidic media, both for HCl and HCl-$HClO_4$-$NaClO_4$ mixtures [84KOL/GOM4], and for $HClO_4$-$NaClO_4$ mixtures [90GOM/KOL]. Concentrations of the various chemical forms of

technetium were monitored by spectrophotometry. For both types of ionic media and for different temperatures, the rates of reduction of TcO_4^- by U^{4+} were found to follow the rate equation

$$-d[TcO_4^-]/dt \quad = \quad k_{obs}[TcO_4^-][U^{4+}][H^+]^{-1}.$$

Most of their experiments were done at an ionic strength of 2 M. The most detailed results for the HCl-$HClO_4$ mixtures were presented at 333 K, for which $k_{obs} = (2.53 \pm 0.29)\ s^{-1}$ [84KOL/GOM4]. For HCl-$NaClO_4$ mixtures the emphasis was at 298 K, where $k_{obs} = (0.113 \pm 0.005)\ s^{-1}$ [90GOM/KOL]. In both studies, measurements were also done at other temperatures up to 353 K [84KOL/GOM4] or 314 K [90GOM/KOL]. They found that values of k_{obs} for HCl-$NaClO_4$ solutions were about three times larger than for HCl-$HClO_4$ solutions at any specific temperature. However, kinetic activation energies were nearly identical for these systems, $(98.3 \pm 2.4)\ kJ{\cdot}mol^{-1}$ [84KOL/GOM4] and $(99.3 \pm 10.6)\ kJ{\cdot}mol^{-1}$ [90GOM/KOL].

They [84KOL/GOM4, 90GOM/KOL] suggested that the reduction of TcO_4^- occurred by way of the overall reactions

$$2TcO_4^- + 3U^{4+} + 4H^+ + 10Cl^- \quad \rightleftharpoons \quad 2TcCl_5^- + 3UO_2^{2+} + 2H_2O(sln)$$

in the presence of chloride ions, and by

$$2TcO_4^- + 3U^{4+} \quad \rightleftharpoons \quad 2TcO^{2+} + 3UO_2^{2+}$$

in the absence of chloride. No intermediate chemical species were proposed that involved a Tc-U complex. We note that U(IV) is undoubtably hydrolysed under these reaction conditions, although this was not considered by the authors. As described in Section V.4.2.1.1, the pentachloro Tc(IV) species probable also has a water molecule in its inner coordination sphere, and thus could be written as $TcCl_5(OH_2)^-$.

The catalytic role of technetium in the oxidation of U(IV) by NO_3^- has been studied by a number of authors, with conflicting results. Koltunov and Gomonova [91KOL/GOM] found that using concentrations of 5×10^{-4} M Tc(VII), 0.5 - 5.0 M HNO_3, 0.01 - 0.06 M U(IV) with 0.06 M hydrazine, the rate of this oxidation followed the rate equation

$$-dU(IV)/dt \quad = \quad k_1[Tc] + k_2[Tc][H^+]^2[NO_3^-]$$

and gave values of k_1 and k_2 for 313 K and an ionic strength of 5 M (HNO_3 + $NaNO_3$). The reaction involving U and Tc was assumed to occur via an activated species derived from hydrolysed U(IV) and Tc(VII), $(UOHTcO_4)^{2+}$. By contrast, Zelverte [88ZEL] using concentrations of 1 M HNO_3, < 0.035 M U(IV), 1 - 2.5 M HNO_3 with 0.05 M sulphamic acid in the temperature range 295 to 310 K, found that after a short period attributed to the reduction of Tc(VII) first to Tc(IV) and then to a lower valency (probably Tc(III)), the kinetic law was

$$-dU(IV)/dt \quad = \quad k[Tc]^2[NO_3^-]$$

independent of the H^+ concentration between 1 and 2.5 M. However, this report contains few details of the precise experiments actually carried out. Finally Suslov *et al.*

[86SUS/RAM] found that in the range 1.5 - 3.5 M HNO_3 the reaction order with respect to HNO_3 is about 1 using Tc(IV) rather TcO_4^-, but with HNO_3 concentrations above 4 M, U(IV) oxidation is inhibited as the acid concentration increases. Further work will be required to resolve these discrepancies.

Kulyunov *et al.* [86KOL/MAR]reported some related kinetic experiments for the catalytic effect of TcO_4^- on the oxidation of Pu(III) by HNO_3 in the presence of hydrazine.

Several of liquid-liquid extraction studies cited in SectionV.6.1.2 reported the formation of pertechnetate or mixed nitrate-pertechnetate complexes of UO_2^{2+} [75MAC, 87ROZ/ZAK, 89KAN/NEC] or Pu(IV) [87ROZ/ZAK], which were claimed to be tributylphosphate solvates. No structural information is available to verify the stochiometry of these proposed complexes

V.10.2 Heteropolyoxytungstate complexes

Abrams *et al.* [91ABR/COS] have described the synthesis of three technetium substituted heteropolyoxytungstates, which are presumably of the Keggin structure type. The heteropolyoxytungstate anions (HPT) investigated were $XW_{11}O_{39}^{x-}$, where X = P or Si. These HPT anions readily complex with a metal ion or a cationic metal complex that is of the proper size to fit into the "pocket" in their structures.

Their complexes are formulated as $((n-C_4H_9)_4N)_4PW_{11}(TcO)O_{39}$, $(n-C_4H_9)_4N)_5SiW_{11}(TcO)O_{39}$, and $(n-C_4H_9)_4N)_4(PW_{11}(TcN)O_{39})$. In rewriting the chemical formulas given by Abrams *et al.* [91ABR/COS], we assumed that the TcO^{3+} and TcN^{3+} moieties retain their chemical identity in these complexes. They based their empirical chemical formulations upon chemical analyses for C, H, and N; and upon IR spectra in KBr pellets. In addition, the complex that is formulated as being $(n-C_4H_9)_4N)_4(PW_{11}(TcO)O_{39}$ was further investigated by its UV-visible spectrum in acetonitrile, and by its positive and negative ion fast atom bombardment mass spectra. Unfortunately, they were unable to grow crystals of a quality suitable for an X-ray structural determination.

The IR spectra of these solid Tc-HPT complexes in KBr were essentially indistinguishable from those of the corresponding HPT anions not containing technetium. This implies that the structures of these HPT anions are not perturbed significantly by the TcO^{3+} or TcN^{3+} ions and, thus, presumably the technetium is located in the "pocket" of the ligands. The electronic spectrum of the $PW_{11}(TcO)O_{39}^{4-}$ ion in acetonitrile exhibited two weak bands at 18,900 and 24, 150 cm^{-1}, which were assigned by Abrams *et al.* [91ABR/COS] to Tc-to-W intervalence charge transfer and d-d electronic transitions.

Chapter VI

Discussion of auxiliary data selection

VI.1 Group 13 auxiliary species

VI.1.1 Thallium auxiliary species

VI.1.1.1 Tl^+

Longhi *et al.* [79LON/MUS] have reported emfs for the two cells

$$\mathrm{Pt(cr)}\left|\mathrm{TlHg_q(l)}\right|\mathrm{TlCl(cr)}\left|\mathrm{KCl,\ aq,\ 0.5mol\cdot kg^{-1}}\right|\mathrm{AgCl(cr)}\,|\mathrm{Ag(cr)}|\,\mathrm{Pt(cr)}$$

and

$$\mathrm{Pt(cr)}\left|\mathrm{TlHg_q(l)}\right|\mathrm{TlCl(cr)}\left|\mathrm{KCl,\ aq,\ 0.002mol\cdot kg^{-1}}\right|\mathrm{AgCl(cr)}\,|\mathrm{Ag(cr)}|\,\mathrm{Pt(cr)}$$

from 283.15 to 328.15 K, where q is the mole ratio of mercury to thallium in the liquid amalgam. These emf measurements were performed at various values of q, which allowed the authors to correct for the activity coefficient of thallium in mercury.

Longhi *et al.* [79LON/MUS] combined their emfs with critically assessed literature values for the standard potentials of related cells and auxiliary thermodynamic data to obtain thermodynamic properties for TlCl(cr) and Tl^+. One of these other cells yielded the difference in standard potential between the Tl(cr) and thallium amalgam electrodes. Their evaluation yielded $\Delta_f G^\circ_m$ (Tl^+, aq, 298.15 K) = (31.560 ± 0.025) kJ·mol^{-1}. However, they also reported $\Delta_f G^\circ_m$(TlCl, aq, 298.15 K) = -(162.615 ± 0.029) kJ·mol^{-1}, which indicates that their value of $\Delta_f G^\circ_m$(Tl^+, aq, 298.15 K) should be opposite in sign to the reported value.

Their calculations required, among other quantities, a value for the activity coefficient of 0.002 mol·kg^{-1} aqueous TlCl, which they choose from a much earlier emf study. It is difficult to judge the reliability of the activity coefficient given in that earlier study, and hence the uncertainty in derived quantities such as $\Delta_f G^\circ_m$ (Tl^+, aq, 298.15 K) may be significantly larger than reported. However, a consistency check is possible because Longhi *et al.* reported assessed values of E° for the TlCl/thallium amalgam electrode. According to equation (14) of Longhi *et al.*, the standard potentials of these two electrodes differ by $(RT/F)\ln(10)\log_{10} K^\circ_{s,0}$, where $K^\circ_{s,0}$ is the solubility project for TlCl(cr). They used the difference between their assessed standard potentials for these two electrodes to derive $K^\circ_{s,0} = (1.364 \pm 0.010) \times 10^{-4}$ mol^2·kg^{-2} at 298.15 K.

Khoo *et al.* [94KHO/FER] have determined the solubility of TlCl(cr) in water and in a variety of aqueous uni-uni-valent electrolytes: HCl, LiCl, NaCl, KCl, NH_4Cl, RbCl, and CsCl. They derived seven values of $K^\circ_{s,0}$ for TlCl(cr) from these solubilities, ranging from 1.865×10^{-4} mol^2·kg^{-2} to 1.888×10^{-4} mol^2·kg^{-2}, with an average of $K^\circ_{s,0} = (1.877 \pm 0.018) \times 10^{-4}$ mol^2·kg^{-2}. We consider this value to be more accurate than the value obtained indirectly from emf data [79LON/MUS]. Read and Aldridge [92REA/ALD] obtained a similar value of $K^\circ_{s,0} = (1.84 \pm 0.03) \times 10^{-4}$ mol^2·kg^{-2} from measurements of the solubility of TlCl(cr) in NaCl solutions. The difference in solubility corrections using $K^\circ_{s,0} = (1.364 \pm 0.010) \times 10^{-4}$ mol^2·kg^{-2} and $K^\circ_{s,0} = (1.877 \pm 0.018) \times 10^{-4}$ mol^2·kg^{-2} gives an 8.2 mV difference in standard potentials or 0.79 kJ·mol^{-1} for the Gibbs energy of reaction. The thermodynamic solubility product from the study of Khoo *et al.* yields $\Delta_f G^\circ_m(Tl^+, aq, 298.15\ K) = -(32.35 \pm 0.03)$ kJ·mol^{-1}, which is nearly identical to the value of $\Delta_f G^\circ_m(Tl^+, aq, 298.15\ K) = -32.40$ kJ·mol^{-1} (no uncertainty given) in the NBS tables [82WAG/EVA]. We select the value from the NBS tables but assign the rather conservative uncertainty limits of ± 0.30 kJ·mol^{-1}:

$$\Delta_f G^\circ_m(Tl^+, aq, 298.15\ K) = (32.40 \pm 0.30)\ kJ{\cdot}mol^{-1}$$

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This chapter contains an alphabetical list of the authors of the references cited in this book. The reference codes given with each name corresponds to the publications of which the person is the author or a co-author.

Table VIII.1: Authors list

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Akopov, G. A.	[82AKO/KRI], [90AKO/KRI]
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Al-Kayssi, M.	[62AL-/MAG]
Alagui, A.	[89ALA/APP]
Alberto, R.	[85ALB/AND]
Aldridge, L. P.	[92REA/ALD]
Alekseev, V. A.	[91ALE/BAR]
Alekseyevskiy, N. Y.	[75ALE/BAL]
Allard, B.	[79ALL/KIG]
de Alleluia, I. B.	[82ALL/KEL], [83ALL/BUR]
Almahamid, I.	[95ALM/BRY]
Ananthaswamy, J.	[84ANA/ATK]
Anderegg, G.	[85ALB/AND]
Anders, E.	[59AND], [60AND]
Anderson, A.	[67RUL/PAC]
Anderson, E.	[60AND/BUC]
Anderson, G. M.	[91AND/CAS]
Andersson, G.	[55MAG/AND]
Antel', E.	[80SHA/VAR]
Antipov, B. G.	[94ANT/KRY]
Antonini, M.	[85ANT/MER]
Antonov, V. E.	[79SPI/PON], [81SPI/ANT], [84GLA/IRO], [85SHI/GLA], [91ZAK/BAG]
Antonov, V. Y.	[89ANT/BEL]
Apostolidis, C.	[93JOA/APO], [93JOA/APO2]
Apparu, M.	[89ALA/APP]

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Author	References
Arblaster, J. W.	[95ARB], [96ARB]
Archer, C. M.	[89ARC/DIL], [92ARC/DIL]
Archer, D. G.	[90ARC/WAN]
Armstrong, R. A.	[76ARM/TAU]
Arnold, W. D.	[86MEY/ARN], [87MEY/ARN], [88MEY/ARN], [89MEY/ARN], [91MEY/ARN], [91MEY/ARN2]
Aronson, F. L.	[85ARO/HWA]
Artyukh, L. V.	[89VEL/ERE]
Aschieri, C.	[90DI /BET]
Astheimer, L.	[62SCH/AST], [64AST/SCH], [73SCH/AST], [74SCH/AST], [75AST/HAU], [76AST/SCH]
Atkinson, A.	[89GUP/ATK]
Atkinson, G.	[84ANA/ATK]
Autler, S. H.	[65AUT/HUL]
Avogadro, A.	[86BID/AVO]
Böttcher, R.	[90KIR/KÖH], [90KÖH/KIR], [91KÖH/KIR2]
Bächmann, K.	[78STE/BÄC], [80RUD/BÄC]
Babichev, A. P.	[91KLI/MAM]
Baes, Jr., C. F.	[76BAE/MES]
Bagaev, S. P.	[90ZAK/BAG], [91ZAK/BAG]
Baierl, B.	[81SPI/BAI]
Bailey, S. M.	[82WAG/EVA]
Baker, D. E.	[65BAK]
Bakos, I.	[93HOR/BAK], [94HOR/BAK]
Balakhovskii, O. A. (see also Balakhovskiy, O. A)	[75SPI/ZIN], [79SPI/PON], [81SPI/ANT]
Balakhovskiy, O. A. (see also Balakhovskii, O. A.)	[75ALE/BAL], [75SPI/GRI]
Balasubramanian, K.	[89BAL/WAN], [89WAN/BAL]
Baldas, J.	[84BAL/BOA], [84BAL/BON], [84BAL/BON2], [85BAL/BON], [86BAL/BON], [87BAL/BOA], [88BAL/BOA], [88BAL/COL], [89BAL/BOA], [89BAL/COL], [89BAL/COL2], [90BAL/BOA], [90BAL/BOA2], [90BAL/COL], [91BAL/BOA], [91BAL/BOA2], [91BAL/COL], [92BAL/BOA], [93BAL/BOA], [93BAL/BOA2], [94BAL], [99BAL]
Baldock, R.	[52SIT/BAL]
Ballhausen, C. J.	[72GÜD/BAL]
Balouka, I.	[72HOD/SIL]
Baluka, M.	[65JEŻ/BAL], [67JEŻ/WAJ], [72BAL/HAN]
Bandoli, G.	[82BAN/MAZ], [92GER/KEM]
Barabash, A. I.	[77VOL/KON]
Baran, E. J.	[74BAR], [75BAR], [76BAR]
Baranovsky, V. M.	[91ALE/BAR]
Bardin, V. A.	[67BOL/PLO]
Barnett, B. L.	[80LIB/DEU]
Baron, P.	[91BAR]

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Author	References
Bassett, Jr., J. Y.	[57KNO/TYR]
Bates, J. K.	[79BAT/GRU]
Battles, J. E.	[68BAT/GUN]
Baturin, N. A.	[91BAT/GER], [94BAT/GRI]
Baumgärtner, F.	[86BAU/HEI]
Bauscher, C.	[87LIE/BAU], [87LIE/BAU2]
Bauschlicher, Jr., C. W.	[87LAN/PET], [89LAN/BAU]
Bazanov, A. S.	[82STR/BAZ]
Beasley, T. M.	[86BEA/LOR]
Beattie, I. R.	[96BEA/GIL]
Beck, A.	[64BEC/DYR]
Becker, C. B.	[80DEU/LIB]
Beetham, C. J.	[89BIS/BEE]
Behm, H.	[90KAD/LOR]
Behrens, R. G.	[79RIN/BEH], [80BEH/RIN]
Behrens, R. K.	[86JEI/BEH]
Belash, I. T.	[79SPI/PON], [81SPI/ANT], [89ANT/BEL]
Belikov, A. D.	[74ZAI/KON], [75ZAI/BEL]
Bell, W. A.	[52SMI/LIN]
Belyaeva, L. I.	[77SPI/KUZ], [77SPI/KUZ2], [78SPI/KUZ], [82OBL/KUZ], [87GER/KRY], [88GER/KRJ]
Beneš, P.	[79BEN/GLO]
Bennett, L. H.	[81WAT/BEN]
Benson, W. R.	[81HEI/YAN], [82YAN/HEI]
Berg, R. L.	[74VAN/ROD]
Bergman, G. A.	[82GLU/GUR]
Berndt, A. F.	[65BER/DWI], [65DAR/BER]
Berner, U.	[92PEA/BER]
Berning, D.	[93JUR/BER]
Bernstein, H.	[70KAU/BER]
Besnard, M.	[75BES/COS]
Bettinelli, M.	[90DI /BET]
Beurskens, P. T.	[90KAD/LOR]
Bevan, Jr., R. B.	[60BUS/BEV], [72BUS/BEV]
Bevington, P. R.	[69BEV]
Beyer, H. H.	[69KRE/MÜL]
Beyer, L.	[87ABR/HAR]
Bibler, J. P.	[85BIB/WAL]
Bidoglio, G.	[86BID/AVO], [95SIL/BID]
Bieber, A.	[87BIE/GAU]
Binenboym, J.	[74BIN/EL-], [76BIN/SEL]
Bird, G. W.	[80BIR/LOP]
Bischoff, P. G.	[84RUS/BIS]
Bishop, G. P.	[89BIS/BEE]
Blaise, A.	[94WAS/REB]

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Author	References
Blanchard, S. S.	[96BLA/NIC]
Blau, M.	[77OWU/MAR]
Bleidner, W. E.	[45FLA/BLE]
Blutstein, H.	[85MAG/BLU]
Boas, J. F.	[84BAL/BOA], [87BAL/BOA], [88BAL/BOA], [89BAL/BOA], [90BAL/BOA], [90BAL/BOA2], [91BAL/BOA], [91BAL/BOA2], [92BAL/BOA], [93BAL/BOA], [93BAL/BOA2]
Bobashev, S. V.	[81FEI/COR]
Bock, W. D.	[89BOC/BRÜ]
de Boer, E.	[90KIR/KÖH], [90KÖH/KIR]
de Boer, F. R.	[80MIE/de], [83NIE/BOE]
de Boer, J. L.	[96LAM/MEE]
Bogdanov, D. O.	[86ZAI/KRU], [87ZAI/KRU]
Bohres, E. W.	[72KRA/BOH]
Bol'shakov, K. A.	[67BOL/PLO]
Bondar, A. A.	[89ERE/VEL], [89VEL/ERE]
Bondietti, E. A.	[83LEE/BON]
Bonnyman, J.	[84BAL/BOA], [84BAL/BON], [84BAL/BON2], [85BAL/BON], [86BAL/BON], [87BAL/BOA], [89BAL/BOA], [90BAL/BOA], [91BAL/BOA]
Boom, R.	[83NIE/BOE]
Borisov, S. R.	[86ZAI/VEL]
Borisova, I. V.	[91MIR/BOR]
Borovinskii, V. A.	[86SUS/RAM]
Bouten, P. C. P.	[80BOU/MIE]
Bowman, M. G.	[64FAR/BOW]
Boyd, G. E.	[52BOY/COB], [52COB/NEL], [53COB/SMI], [53SMI/COB], [54NEL/BOY], [59BOY], [59BOY2], [70RUL/BOY], [78BOY], [78BOY2]
Bozman, W. R.	[68BOZ/COR]
Brühl, H.	[89BOC/BRÜ]
Brønsted, J. N.	[22BRØ], [22BRØ2]
Bradley, D. J.	[79BRA/HAR], [79BRA/PIT]
Bramman, J. I.	[68BRA/SHA]
Bratton, W. K.	[65COT/BRA], [70BRA/COT]
Bratu, C.	[75BRA/BRA], [77GĂL/BRA]
Bratu, G.	[75BRA/BRA]
Brewer, L.	[50BRE], [61BRE/ROS], [61LEW/RAN], [80BRE/LAM], [80BRE/WIN], [96WU/BRE]
Brinkley, D. C.	[71NAG/BRI]
Brodsky, M. B.	[75TRA/BRO]
Bronger, W.	[93BRO/KAN], [93BRO/KAN2]
Brookins, D. G.	[86BRO]
Brown, D. S.	[87BRO/NEW], [88BRO/NEW], [88BRO/NEW2]
Bruno, J.	[86BRU], [92ERI/NDA], [93ERI/NDA], [95PUI/BRU]
Bruns, M.	[84KRE/HEN]

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Author	References
Bryan, J. C.	[94BUR/BRY], [95ALM/BRY]
Bucher, E.	[67BUC/PAL]
Bucher, J. J.	[95ALM/BRY]
Buckley, R. A.	[60AND/BUC], [63BUC/HUM]
Bucksch, R.	[73HAU/SCH]
Budantseva, N. A.	[98GUE/FED]
Bukov, K. G.	[88SPI/BUK], [89ANT/BEL], [90BUK/TIT]
Burgess, J.	[82BUR/PEA], [83ALL/BUR]
Burkard, E.	[64SCH/KNA]
Burnett, K. B.	[95BUR/CAM], [97BUR/JOB]
Burrell, A. K.	[94BUR/BRY], [95ALM/BRY]
Bury, R.	[70BUR/JUS]
Burylev, B. P.	[85BUR]
Busch, K. L.	[82SCH/HOL]
Busey, R. H.	[57BUS/LAR], [58BUS/LAR], [59BUS], [60BUS], [60BUS/BEV], [64BUS/KEL], [65GIL/BUS], [72BUS/BEV], [76GAY/HER], [77HER/BUS]
Buslaev, Y. A.	[86TAR/PET]
Caceci, M.	[92ERI/NDA], [93ERI/NDA]
Campbell, A. B.	[91LEM/SAL], [95BUR/CAM]
Canterford, J. H.	[68CAN/COL], [68CAN/COL2]
Capdevila, H.	[93GIF/VIT]
Cardwell, T. J.	[74MAG/CAR]
Carey, G. H.	[79TRO/DAV]
Carpenter, J. H.	[69KRI/CAR]
Cartledge, G. H.	[55CAR/SMI], [71CAR], [71CAR2]
Case, F. I.	[86MEY/ARN], [87MEY/ARN], [88MEY/ARN], [89MEY/ARN], [91MEY/ARN2]
Cash, A. G.	[78RUS/CAS], [79RUS/CAS], [79RUS/CAS2], [79RUS/CAS3]
Castet, S.	[91AND/CAS]
de Châtel, P. F.	[83NIE/BOE]
Chalykh, A. E.	[90PIR/POP]
Chasanov, M. G.	[64CHA/JOH]
Chase, M. W.	[85CHA/DAV]
Chebotarev, N. T.	[72ZAI/VEL], [72ZAI/VEL2], [73ZAI/KON], [73ZAI/KON2], [74ZAI/KON], [74ZAI/KON2], [74ZAI/KON3], [74ZAI/KON4], [74ZAI/KON5], [75SHE/KON], [75ZAI/BEL], [76ZAI/KON], [76ZAI/KON2]
Chekhovskoi, V. Y.	[79KAT/CHE]
Cherniawsky, J. Y.	[77CHE]
Chernick, C. L.	[61SEL/CHE]
Churney, K. L.	[82WAG/EVA]
de Châtel, P. F.	[80MIE/de]
Ciavatta, L.	[80CIA], [87CIA/IUL], [88CIA], [90CIA]
Claassen, H. H.	[62CLA/SEL], [70CLA/GOO]
Clark, H. M.	[87FOU/AIK]

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Author	References
Clarke, M. J.	[82CLA/FAC], [90LU/CLA]
Clegg, S. L.	[94CLE/RAR]
Clyde, D. D.	[80VAN/WAU]
Cobble, J. W.	[52BOY/COB], [52COB], [52COB/NEL], [53COB], [53COB/OLI], [53COB/SMI], [53SMI/COB], [62MCD/COB]
Coffey, C. E.	[59KNO/COF]
Cohen, Y.	[75BES/COS]
Colin, M.	[88COL/IAN]
Colinet, C.	[85COL/PAS]
Colmanet, S. F.	[88BAL/COL], [89BAL/COL], [89BAL/COL2], [90BAL/BOA], [90BAL/BOA2], [90BAL/COL], [91BAL/BOA], [91BAL/BOA2], [91BAL/COL], [92BAL/BOA], [93BAL/BOA]
Colton, R.	[60COL/DAL], [62COL], [62COL/PEA], [65COL], [68CAN/COL], [68CAN/COL2], [68COL/TOM]
Compton, V. B.	[61COM/COR]
Cook, J.	[90VRI/COO]
Cooks, R. G.	[82SCH/HOL]
Corderman, R. R.	[81FEI/COR]
Corenzwit, E.	[61COM/COR]
Corliss, C. H.	[68BOZ/COR]
Cort, B.	[82STE/COR]
Costello, C. E.	[86LIN/DAV], [91ABR/COS]
Costerousse, O.	[75BES/COS]
Cotton, F. A.	[65COT/BRA], [70BRA/COT], [75COT/PED], [75COT/SHI], [77COT/GAG], [79COT/DAV], [81COT/DAN], [82COT/DAV], [84COT/DUR], [88COT/WIL], [91COT/DAN]
Courson, O.	[97COU]
Cowie, M.	[70COW/LOC]
Cox, J. D.	[89COX/WAG]
Creek, G. E.	[52PAR/CRE]
Cross, J. E.	[87CRO/EWA]
Crouthamel, C. E.	[57CRO]
Cuff, Y. S.	[89BIS/BEE]
Cui, D.	[93ERI/NDA]
Cvitaš, T.	[88MIL/CVI]
D'Alte da Veiga, L. M.	[62VEI], [63VEI/WAL]
D'Ans, J.	[77D'A/SUR]
Dalichaouch, Y.	[89DAL/MAP]
Dalziel, J.	[58DAL/GIL], [60COL/DAL]
Daniels, L. (see also Daniels, L. M)	[81COT/DAN]
Daniels, L. M. (see also Daniels, L.)	[91COT/DAN]
Darby, Jr., J. B.	[61LAM/DAR], [62DAR/LAM], [62DAR/ZEG], [63DAR/NOR], [64DAR/NOR], [65DAR/BER], [65DAR/DOW]
Darte, L.	[74PER/DAR]

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Author	References
Dartmann, M.	[84KRE/HEN]
Das, H. A.	[81BRA/DAS], [82BRA/DAS]
Davidov, D.	[86VAN/DAV]
Davies, C. A.	[85CHA/DAV]
Davies, C. W.	[59DAV], [62DAV]
Davis, M. A.	[79TRO/DAV], [80TRO/DAV]
Davis, R. M.	[79DAV]
Davis, W. M.	[89PEA/DAV]
Davison, A.	[79COT/DAV], [79TRO/DAV], [80THO/DAV], [80TRO/DAV], [80TRO/JON], [81COT/DAN], [81DAV/JON], [81DAV/JON2], [82COT/DAV], [82DAV/TRO], [82JON/DAV], [84ABR/DAV], [86LIN/DAV], [88BRO/NEW2], [89PEA/DAV], [90ROS/DAV], [90VRI/COO], [91THO/DAV], [96BLA/NIC]
Day, V. W.	[79COT/DAV], [82COT/DAV]
Decombaz, M.	[79IAN/LER]
Deegan, T.	[71WIL/DEE]
Dekker, B. G.	[81BRA/DAS], [82BRA/DAS]
Demin, A. V.	[82ZAI/VEL], [82ZAI/VEL2]
Desai, P. D.	[73HUL/DES]
Desnoyers, J. E.	[74FOR/LED], [76DES/VIS]
Deutsch, E. (see also Deutsch, E. A.)	[76DEU/ELD], [78DEU/HEI], [79ELD/EST], [80DEU/LIB], [80ELD/WHI], [80GLA/WHI], [80LIB/DEU], [80PIN/HEI], [80THO/DAV], [81HUR/HEI], [82BAN/MAZ], [83DEU/LIB], [83TAN/ZOD], [85THO/HEE], [87HUB/HEI], [87NEV/LIB], [88LIB/NOO]
Deutsch, E. A. (see also Deutsch, E.)	[92ROO/LEI]
Devynck, J.	[78GRA/ROG], [79GRA/DEV]
Dewan, J. C.	[86LIN/DAV]
De Ligny, C. L.	[81BRA/DAS], [82BRA/DAS], [89HUI/TJI], [91HUI/DIE]
De Pamphilis, B. V.	[79TRO/DAV]
Diemann, E.	[69MÜL/DIE]
Diender, M.	[91HUI/DIE]
Dietrich, L. H.	[85JEI/DIE], [86DIE/JEI]
Dilworth, J. R.	[89ARC/DIL], [92ARC/DIL], [96ABR/ABR]
Dinsdale, A. T.	[88SAU/MIO], [89DIN], [91DIN]
Di Sipio, L.	[74DI /ING], [90DI /BET]
Dolmella, A.	[92GER/KEM]
Domanov, V. P.	[75EIC/DOM]
Downey, J. R.	[78DOW], [85CHA/DAV]
Downey, J. W.	[61LAM/DAR], [62DAR/LAM], [63DAR/NOR], [64DAR/NOR], [65DAR/BER], [65DAR/DOW]
Drever, J. I.	[82DRE]
Dronskowski, R.	[88DRO/KRE]
Duraj, S. A.	[84COT/DUR]
Dwight, A. E.	[65BER/DWI]
Dyrssen, D.	[64BEC/DYR]

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Author	References
Eakins, J. D.	[63EAK/HUM]
Eckelman, W. C.	[77ECK/LEV]
Edelstein, N. M.	[95ALM/BRY]
Edwards, A. J.	[63EDW/HUG], [67EDW/JON], [68EDW/JON]
Edwards, R. K.	[68BAT/GUN]
Eichler, B.	[75EIC], [75EIC/DOM]
Ekberg, S.	[64BEC/DYR]
El-Gad, U.	[74BIN/EL-]
El-Wear, S.	[92EL-/GER]
Elder, M.	[65ELD/PEN], [66ELD/PEN], [67ELD/FER]
Elder, R. C.	[76DEU/ELD], [79ELD/EST], [80ELD/WHI], [80GLA/WHI], [85THO/HEE], [88LIB/NOO]
Elison, M.	[92KIP/HER]
Ellison, R. D.	[52ELL]
Elving, P. J.	[63SAL/RUL]
Emel'yanenko, A. M.	[88SPI/BUK]
Eremenko, V. N.	[83ERE/VEL], [89ERE/VEL], [89VEL/ERE]
Eriksen, T. E.	[92ERI/NDA], [93ERI/NDA]
Estes, G. W.	[79ELD/EST]
Evans, W. H.	[82WAG/EVA]
Evseev, B. A.	[69KAR/EVS]
Ewart, F. T.	[87CRO/EWA]
Farga Marti, A.	[87FAR/GAR]
Fackler, P. H.	[82CLA/FAC]
Faggiani, R.	[80FAG/LOC]
Falvello, L. R.	[91COT/DAN]
Fanghänel, T.	[96KUN/NEC], [97KÖN/NEC], [98NEC/KÖN]
Far, G.	[87GRA/FAR]
Farr, J. D.	[64FAR/BOW]
Fedoseev, A. M.	[98GUE/FED]
Fedotov, L. N.	[88SPI/BUK], [90BUK/TIT]
Feigerle, C. S.	[81FEI/COR]
Feklina, L. I.	[91ALE/BAR]
Feldberg, S. W.	[69KIS/FEL]
Ferguson, D. L.	[80DEU/LIB]
Fergusson, J. E.	[59FER/NYH], [60FER/NYH], [66FER/HIC], [67ELD/FER], [70FER/HIC], [76FER/HEV], [83FER/GRE]
Fernández Guillermet, A.	[89FER/GRI]
Fernando, K. R.	[94KHO/FER]
Fernelius, W. C. (chairman)	[77FER]
Ferrante, M. J.	[76STU/FER]
Ferri, D.	[83FER/GRE2], [85FER/GRE]
Findeisen, M.	[91HIL/HÜB], [92KAD/FIN]
Flagg, J. F.	[45FLA/BLE]
Flint, C. D.	[86FLI/LAN]
Floss, J. G.	[60FLO/GRO]

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Author	References
Flowers, G. C.	[81HEL/KIR]
Ford, L. A.	[81HEI/YAN], [82YAN/HEI]
Fortier, J. L.	[74FOR/LED]
Founta, A.	[87FOU/AIK]
Fraga, S.	[76FRA/KAR]
Francesconi, L. C.	[89TRE/FRA]
Francis, M. D.	[80DEU/LIB]
Franco, J. I.	[71FRA/KLE]
Franklin, K. J.	[82FRA/LOC]
Fredrich, M. F.	[82COT/DAV]
Freeman, R. D.	[84FRE]
Freude, E.	[89FRE/LUT]
Fried, S.	[50FRI/HAL], [51FRI/JAF], [71SEL/FRI]
Friedman, H. A.	[81FRI]
Frlec, B.	[67FRL/SEL]
Frolov, K. M.	[80KOL/ZAI]
Frolov, L. V.	[83ZAI/VIN]
Frurip, D. J.	[85CHA/DAV]
Fuger, J.	[92GRE/FUG], [94WAS/REB]
Fujinaga, T.	[67FUJ/KOY], [68KOY/KAN], [76KAW/KOY]
Fukuda, K.	[98MIN/SER]
Görner, W.	[85ABR/SPI]
Galvez Alvarez, J.	[87FAR/GAR]
Garcia Domenech, R.	[87FAR/GAR]
Güdel, H. U.	[72GÜD/BAL]
Gage, L. D.	[77COT/GAG], [79COT/DAV]
Gainsford, G. J.	[67ELD/FER]
Gălăţeanu, I. (see also Galaţeanu, I.)	[77GĂL/BRA]
Galaţeanu, I. (see also Gălăţeanu, I.)	[75BRA/BRA]
Garisto, F.	[88VIK/GAR], [89LEM/GAR]
Garraway, J.	[84GAR/WIL]
Garvin, D.	[87GAR/PAR]
Gautier, F.	[87BIE/GAU]
Gavrish, A. A.	[78SPI/KUZ], [80SHA/VAR]
Gayer, K. H.	[76GAY/HER], [77HER/BUS]
Guedes de Carvalho, R. A.	[58CAR]
Gel'd, P. V.	[75SPI/ZIN]
Geldard, J. F.	[87GEL/MCD]
Gelsema, W. J.	[86KRO/STE], [89HUI/TJI], [90TJI/VIN], [91HUI/DIE]
Gerasimov, V. N.	[82GER/KRY], [85GER/ZEL], [94ANT/KRY]
Gerber, T. I. A.	[92GER/KEM]
Gerlit, J. B.	[56GER]
Germain, M.	[84VIA/GER]

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Author	References
German, K. E. (see also Guerman, K. E.)	[86GER/GRI], [86GER/KRY], [86SPI/TAR], [86TAR/PET], [87GER/GRI], [87GER/KRY], [87KUZ/GER], [88GER/KRJ], [90KRY/GRI], [91BAT/GER], [91KRY/GER], [92EL-/GER], [92TAR/KIR], [93GER/GRU]
Gibson, J. K.	[91GIB], [93GIB], [93GIB2], [94GIB]
Giffaut, E.	[93GIF/VIT], [96NGU/PAL]
Gilbert, R. A.	[65GIL/BUS], [72BUS/BEV]
Gill, N. S.	[58DAL/GIL]
Gillson, J. L.	[69ROG/SHA]
Gilpatrick, L. O.	[52SIT/BAL]
Gilson, T. R.	[96BEA/GIL]
Gingerich, K. A.	[79MIE/GIN]
Ginsberg, A. P.	[64GIN]
Giorgi, A. L.	[66GIO/SZK], [70GIO/SZK], [70GIO/SZK2], [78GIO/MAT], [78STE/GIO], [81SZK/GIO], [82STE/COR], [85GIO], [89DAL/MAP]
Glavan, K. A.	[80ELD/WHI], [80GLA/WHI]
Glazkov, V. P.	[84GLA/IRO], [85SHI/GLA]
Gleiser, M.	[73HUL/DES]
Glendenin, L. E.	[51FRI/JAF]
Glinkina, M. I.	[71SPI/GLI], [73GLI/KUZ], [76SPI/KUZ]
Glos, J.	[79BEN/GLO]
Glushko, V. P.	[82GLU/GUR]
Goffart, J.	[94WAS/REB]
Golič, L.	[90KIR/KÖH]
Golovko, E. I.	[67VOI/GOL]
Golubtsov, I. V.	[84GOL/VEZ]
Gomonova, T. V.	[84KOL/GOM], [84KOL/GOM2], [84KOL/GOM3], [84KOL/GOM4], [85KOL/GOM], [86KOL/GOM], [86KOL/MAR], [88KOL/GOM], [88KOL/GOM2], [90GOM/KOL], [91KOL/GOM]
Gompper, K.	[96KUN/NEC]
Goodman, G. L.	[70CLA/GOO]
Gordiichuk, O. V.	[89VEL/ERE]
Gordon, S.	[78DEU/HEI]
Gorski, B.	[69GOR/KOC]
Gougoutas, J. Z.	[89TRE/FRA], [90LIN/MAL]
Grases, F.	[87GRA/FAR], [88MAR/GRA]
Grassi, J.	[77GRA], [78GRA/ROG], [79GRA/DEV]
Green, J. W.	[60GRE/POL], [62POL/GRE]
Greenaway, A. M.	[83FER/GRE]
Greis, O.	[77SCH/HED]
Grenthe, I.	[83FER/GRE2], [85FER/GRE], [92GRE/FUG], [92GRE/WAN], [97GRE/PLY], [97PUI/RAR]
Gribnau, M. C. M.	[90KÖH/KIR]
Gribulya, V. B.	[75SAV/GRI]
Griffith, W. P.	[60COL/DAL]

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Author	References
Griffiths, D. V.	[92ARC/DIL]
Grigor'ev, M. S. (see also adjacent entries)	[86GER/GRI], [86KRY/GRI], [86KRY/GRI2], [87GER/GRI], [87KRY/GRI], [87KRY/GRI2], [87KRY/GRI3], [88KRY/GRI], [91BAT/GER], [94BAT/GRI], [94GRI/KRY]
Grigoriev, M. (see also adjacent entries)	[98GUE/FED]
Grigoriev, M. S. (see also adjacent entries)	[88SPI/KRY], [91COT/DAN], [93GRI/KRY], [94ANT/KRY]
Grigoryev, M. S. (see also adjacent entries)	[89KRY/GRI], [90GRI/KRY], [90KRY/GRI]
Grimvall, G.	[89FER/GRI]
Grishina, S. P.	[75SPI/GRI]
Großmann, B.	[75MÜN/GRO]
Grosse, A. V.	[60FLO/GRO]
Gruen, D. M.	[79BAT/GRU]
Grushevschkaya, L. N.	[93GER/GRU]
Gschneider, K. A.	[75GSC]
Guénnec, J. Y.	[73GUÉ/GUI]
Guerman, K. E. (see also German, K. E.)	[96GUE], [98GUE], [98GUE2], [98GUE/FED], [99GUE]
Guest, A.	[72GUE/HOW], [72GUE/LOC], [78GUE/HOW]
Guggenheim, E. A.	[35GUG], [66GUG]
Guillaumont, R.	[73GUÉ/GUI]
Gulev, B. F.	[86GER/GRI], [86KRY/GRI], [86KRY/GRI2]
Guminski, C.	[89GUM], [93GUM]
Gundersen, G. E.	[68BAT/GUN]
Gundersen, S.	[92KIP/HER]
Guppy, R. M.	[89GUP/ATK]
Gurvich, L. V.	[82GLU/GUR]
Hübener, R.	[91HIL/HÜB], [92HÜB/ABR]
Haaland, A.	[92KIP/HER]
Haas, N. C.	[80VAN/WAU]
Haines, H. R.	[76HAI/MAR], [80HAI/POT], [87ROG/POT], [88ROG/POT]
Hale, F. V.	[88PHI/HAL]
Hall, N. F.	[50FRI/HAL], [51FRI/JAF]
Halow, I.	[82WAG/EVA]
Hamann, S. D.	[82HAM]
Hanuza, J.	[72BAL/HAN], [73JEŻ/HAN]
den Hartigh, J.	[81MUL/OLD]
Hartung, J.	[87ABR/HAR]
Harvey, C. O.	[79BRA/HAR]
Hasegawa, K.	[93KAW/OMO]
Hasse, K. D.	[76KRE/HAS]
Hauck, J.	[73HAU/SCH], [74SCH/AST], [75AST/HAU]
Hawkins, D. T.	[73HUL/DES]
Hedlund, T.	[88HED]

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Author	References
Hedwig, K.	[77SCH/HED]
Heeg, M. J.	[85THO/HEE]
Heineman, W. R.	[78DEU/HEI], [80PIN/HEI], [81HUR/HEI], [83PIN/HEI], [83TAN/ZOD], [87HUB/HEI]
Heitz, J.	[86BAU/HEI]
Heitzmann, M. W.	[81HEI/YAN], [82YAN/HEI]
Helgeson, H. C.	[74HEL/KIR], [81HEL/KIR], [88SHO/HEL], [88TAN/HEL], [89SHO/HEL], [89SHO/HEL2], [90OEL/HEL], [92SHO/OEL]
Hellawell, A.	[60AND/BUC]
Helm, L.	[94ROO/LEI], [95ROO/LEI]
Henkel, G.	[84KRE/HEN]
Herbert, G.	[52PAR/CRE]
Herget, C.	[65HIE/LUX]
Herr, W.	[61HER/SCH], [62SCH/HER], [62SCH/HER2], [63SCH/HER]
Herrell, A. Y.	[76GAY/HER], [77HER/BUS]
Herrmann, W. A.	[92KIP/HER]
Herzberg, G.	[79HUB/HER]
Hettich, B.	[88DRO/KRE]
Heveldt, P. F.	[76FER/HEV]
Hickford, J. H.	[66FER/HIC], [67ELD/FER], [70FER/HIC]
Hicter, P.	[85COL/PAS]
Hieber, W.	[65HIE/LUX], [68HIE/OPA], [68HIE/OPA2]
Hietanen, S.	[85FER/GRE]
Hillebrecht, H.	[92HOL/PRE]
Hiller, W.	[91HIL/HÜB], [93ABR/WOL2]
Hills, G. J.	[61HIL/IVE]
Hinckley, C. C.	[84COT/DUR]
Hirsch, R. F.	[63RUL/HIR], [67RUL/PAC2]
Hoard, J. L.	[84RAD/HOA]
Hodara, I.	[72HOD/SIL]
Hollar, R. C.	[82SCH/HOL]
Hollman, P.	[92HOL/PRE]
Holloway, J. H.	[57KNO/TYR], [68HOL/SEL], [70CLA/GOO]
Holt, M. L.	[67VOL/HOL]
Homann, K.	[88MIL/CVI]
Hoppe, R.	[76MEY/HOP]
Horányi, G.	[93HOR/BAK], [94HOR/BAK]
Hoshikawa, T.	[94SAS/HOS]
Hostettler, J. D.	[84HOS]
Hotop, H.	[85HOT/LIN]
Howard-Lock, H. E.	[72GUE/HOW], [78GUE/HOW]
Huber, E. W.	[87HUB/HEI]
Huber, K. P.	[79HUB/HER]
Hudson, E. A.	[95ALM/BRY]
Hugill, D.	[63EDW/HUG], [66HUG/PEA]
Huigen, Y. M.	[89HUI/TJI], [91HUI/DIE]

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Author	References
Hulliger, F.	[66HUL]
Hulm, J. K.	[65AUT/HUL]
Hultgren, R.	[73HUL/DES]
Hume-Rothery, W.	[60AND/BUC], [63BUC/HUM]
Hummel, W.	[92PEA/BER]
Humphreys, D. G.	[63EAK/HUM]
Hurst, R.	[78DEU/HEI]
Hurst, R. W.	[80HUR], [81HUR/HEI]
Hwang, L. L. Y.	[85ARO/HWA]
Hyman, H. H.	[67FRL/SEL]
Ianovici, E.	[79IAN/LER], [81IAN/KOS], [88COL/IAN]
Ianoz, E.	[88TRU/IAN], [90MAN/IAN]
Il'yashenko, V. S.	[73ZAI/KON]
Ingletto, G.	[74DI /ING], [90DI /BET]
Irodova, A. V.	[84GLA/IRO], [85SHI/GLA]
Isherwood, D.	[85ISH]
Ito, K.	[88ITO/KAN]
Iuliano, M.	[87CIA/IUL]
Ivanov, Z.	[93BAL/BOA], [93BAL/BOA2]
Ives, D. J. G.	[61HIL/IVE]
Ibañez Zurriaga, A.	[87FAR/GAR]
Jørgensen, C. K.	[65JØR/SCH]
Jaffey, A. H.	[51FRI/JAF]
James, B. D.	[93BAL/BOA2]
Jeżowska-Trzebiatowska, B.	[65JEŻ/BAL], [67JEŻ/NAT], [67JEŻ/WAJ], [72BAL/HAN], [73JEŻ/HAN]
Jeitschko, W.	[82RÜH/JEI], [82RÜH/JEI2], [85JEI/DIE], [86DIE/JEI], [86JEI/BEH]
Jellinek, F.	[71WIL/JEL]
Jensen, B. S.	[82JEN]
Jensen, K. A. (chairman)	[71JEN]
Jia, W.	[93JUR/BER]
Joachim, J. E.	[93JOA/APO], [93JOA/APO2]
Jobe, D. J.	[95BUR/CAM], [96LEM/JOB], [97BUR/JOB], [99JOB/TAY]
Johannsen, B.	[81SPI/JOH]
Johnson, I.	[64CHA/JOH], [64VEL/JOH]
Johnson, J. F.	[80ELD/WHI], [80GLA/WHI]
Johnson, J. W.	[92SHO/OEL]
Johnson, K. S.	[79JOH/PYT]
Jones, A. G.	[79TRO/DAV], [80TRO/DAV], [80TRO/JON], [81DAV/JON], [81DAV/JON2], [82DAV/TRO], [82JON/DAV], [84ABR/DAV], [89PEA/DAV], [90ROS/DAV], [90VRI/COO], [96BLA/NIC]
Jones, G. R.	[67EDW/JON], [68EDW/JON]
Jones, P. J.	[96BEA/GIL]
Jurisson, S.	[83DEU/LIB], [93JUR/BER]
Justice, J. C.	[70BUR/JUS]

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Author	References
Justice, M. C.	[70BUR/JUS]
Köhler, K.	[87ABR/HAR], [87ABR/KIR], [90KÖH/KIR], [91KÖH/KIR], [91KÖH/KIR2], [90ABR/KÖH], [90KIR/KÖH]
Könnecke, T.	[97KÖN/NEC], [98NEC/KÖN]
Kaden, L.	[79KAD/LOR], [81KAD/LOR], [82STR/BAZ], [85KAD/LOR], [87ABR/KIR], [88ABR/LOR], [90KAD/LOR], [91HIL/HÜB], [92KAD/FIN]
Kadrabová, J.	[79MAC/KAD], [79RAJ/MIK]
Kaimin, I. V.	[70SPI/KUZ]
Kalinichenko, N. B.	[90ABR/KÖH]
Kalinina, G. E.	[90PIR/POP]
Kallay, N.	[88MIL/CVI]
Kaltsoyannis, N.	[95ALM/BRY]
Kamoshida, M.	[94SAS/HOS]
Kanchiku, Y.	[67FUJ/KOY], [68KOY/KAN], [69KAN]
Kanellakopulos, B.	[63KEL/KAN], [65KEL/KAN], [66KAN], [87NEC/KAN], [89KAN/NEC], [91KAN/RAP], [93JOA/APO], [93JOA/APO2]
Kanert, M.	[93BRO/KAN], [93BRO/KAN2]
Kanno, T.	[88ITO/KAN]
Karpinskii, O. G.	[69KAR/EVS]
Karwowski, J.	[76FRA/KAR]
Kats, S. A.	[79KAT/CHE]
Katsuki, A.	[63VAN/LAM]
Kaufman, L.	[70KAU/BER]
Kawamura, F.	[94SAS/HOS]
Kawasaki, M.	[93KAW/OMO]
Kawashima, M.	[76KAW/KOY]
Kazakov, V. V.	[79ZAI/VEL]
Kazin, P. E.	[94ANT/KRY]
Keijzers, C. P.	[90KÖH/KIR]
Keller, C.	[63KEL/KAN], [65KEL/KAN], [66KEL/WAS], [82ALL/KEL], [83ALL/BUR]
Keller, Jr., O. L.	[64BUS/KEL]
Kelley, K. K.	[73HUL/DES]
Kelley, M. T.	[60MIL/KEL]
Kelly, J. D.	[89ARC/DIL], [92ARC/DIL]
Kemp, H. J.	[92GER/KEM]
Kemp, T. J.	[93KEM/THY], [93KEM/THY2]
Kemper, R. S.	[65AUT/HUL]
Kenna, B. T.	[62KEN]
Kenna, H. W.	[61KEN/KUR]
Kernohan, R. H.	[67SEK/KER]
Kessler, K. G.	[53KES/TRE]
Khachkuruzov, G. A.	[82GLU/GUR]
Khalil, M. Y.	[83KHA/WHI], [84KHA/WHI]
Kharitonov, V. V.	[94ANT/KRY]

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Author	References
Khoo, K. H.	[94KHO/FER]
Kigatsi, H.	[79ALL/KIG]
Kim, J. I.	[89KAN/NEC], [97KÖN/NEC], [98NEC/KÖN]
Kim, J. J.	[74PIT/KIM]
Kiprof, P.	[92KIP/HER]
Kirakosyan, G. A.	[92TAR/KIR]
Kirby, H. W.	[82KIR]
Kirillov, I. V.	[75ALE/BAL]
Kirkham, D. H.	[74HEL/KIR], [81HEL/KIR]
Kirkpatrick, R. J.	[88KIR]
Kirmse, R.	[83KIR/LOR], [85ABR/SPI], [85KAD/LOR], [85KIR/STA], [86KIR/STA], [87ABR/HAR], [87ABR/KIR], [88ABR/KIR], [89KIR/ABR], [90ABR/KÖH], [90KAD/LOR], [90KIR/ABR], [90KIR/KÖH], [90KÖH/KIR], [91KÖH/KIR], [91KÖH/KIR2], [93ABR/KIR]
Kissel, G.	[69KIS/FEL]
Klein, M.	[67RIN/KLE]
Kleine, M.	[92KIP/HER]
Kleinschmidt, P. D.	[88KLE]
Kleykamp, H.	[71FRA/KLE], [84KLE/PEJ], [85KLE], [85KLE/PAS]
Klimov, V. D.	[91KLI/MAM]
Knappwost, A.	[64SCH/KNA]
Knook, B.	[65VAN/KNO]
Knox, K.	[57KNO/TYR], [59KNO/COF]
Koch, C. C.	[67KOC/LOV], [68KOC/LOV], [72MAR/KOC], [76KOC]
Koch, H.	[69GOR/KOC]
Kolomeitsev, G. Y.	[86ZAI/VEL2]
Kolthoff, I. M.	[52KOL/LIN]
Koltunov, V. S.	[80KOL/ZAI], [84KOL/GOM], [84KOL/GOM2], [84KOL/GOM3], [84KOL/GOM4], [85KOL/GOM], [86KOL/GOM], [86KOL/MAR], [88KOL/GOM], [88KOL/GOM2], [90GOM/KOL], [91KOL/GOM]
Konarev, M. I.	[72ZAI/KON], [73ZAI/KON], [73ZAI/KON2], [74VIN/ZAI], [74ZAI/KON], [74ZAI/KON2], [74ZAI/KON3], [74ZAI/KON4], [74ZAI/KON5], [75SHE/KON], [75ZAI/KON], [76ZAI/KON], [76ZAI/KON2], [77VOL/KON], [77ZAI/KON], [77ZAI/KON2], [77ZAI/KON3], [78VIN/KON], [78VIN/KON2], [78VIN/KON3], [78ZAI/KON], [81VIN/KON], [83VIN/ZAI], [91ALE/BAR]
Kong, P. C.	[90ROC/KON]
Konings, R. J. M.	[92GRE/FUG]
Kontrat'ev, B. A.	[86KOL/MAR]
Korolenko, M. V.	[84GOL/VEZ]
Koshechko, L. G.	[72RAK/KOS]
Kosinski, M.	[81IAN/KOS]
Kostorz, G.	[71KOS/MIH]
Kostyukov, A. S.	[86ZAI/KRU2], [87ZAI/KRU2], [87ZAI/KRU3]
Kotegov, K. V.	[63SHV/KOT], [68KOT/PAV]
Kovalenko, A. S.	[91ALE/BAR]

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Author	References
Koyama, M.	[67FUJ/KOY], [68KOY/KAN], [76KAW/KOY]
Kozhevnikov, P. B.	[72ZAI/KON]
Kozhinov, E. G.	[74ZAI/KON5]
Kozin, L. F.	[64KOZ]
Koz'min, P. A.	[72KOZ/NOV], [72KOZ/NOV2], [73KUZ/KOZ], [75KOZ/NOV], [81KOZ/LAR], [82KOZ/LAR], [82KOZ/SUR], [83KOZ/LAR], [83KOZ/LAR2], [85KOZ/SUR]
Krüger, A.	[81LIE/KRÜ]
Krasovskiy, A. I.	[75SPI/GRI]
Krasser, W.	[69SCH/KRA], [72KRA/BOH]
Krebs, B.	[65MÜL/KRE], [66MÜL/KRE], [69KRE], [69KRE/MÜL], [76KRE/HAS], [84KRE/HEN], [88DRO/KRE]
Krebs, K.	[86BAU/HEI]
Krikorian, O. H.	[69KRI/CAR], [88KRI], [89KRI/LAI]
Krinitsyn, A. P.	[82AKO/KRI], [90AKO/KRI]
Krjuchkov, S. V.	[88GER/KRJ]
Kroesbergen, J.	[86KRO/STE]
Kruglov, A. A.	[72ZAI/KON], [73ZAI/KON], [74ZAI/KON5], [75ZAI/BEL], [78ZAI/VEL], [83KRU/ZAI], [83VAR/ZAI], [83ZAI/VIN], [86ZAI/KRU], [86ZAI/KRU2], [86ZAI/KRU3], [87ZAI/KRU], [87ZAI/KRU2], [87ZAI/KRU3], [87ZAI/KRU4], [87ZAI/KRU5], [87ZAI/KRU6], [87ZAI/KRU7], [88ZAI/KRU]
Kryuchkov, S. V. (see also Kryutchkov, S. V)	[77PIK/KRY], [77SPI/KUZ2], [79KRY/PIK], [80SPI/KUZ], [81KRY], [81SPI/BAI], [82GER/KRY], [82KRY/KUZ], [83KRY/KUZ], [83SPI/KRY], [85SPI/KUZ], [86GER/KRY], [86KRY/GRI], [86KRY/GRI2], [86KRY/KUZ], [86SPI/TAR], [86TAR/PET], [87GER/KRY], [87KRY/GRI], [87KRY/GRI2], [87KRY/GRI3], [87SPI/KUZ], [88KRY/GRI], [88KRY/KUZ], [88SPI/KRY], [91BAT/GER], [91COT/DAN], [91KRY/GER], [94BAT/GRI], [94GRI/KRY]
Kryutchkov, S. V. (see also Kryuchkov, S. V)	[89KRY/GRI], [90GRI/KRY], [90KRY/GRI], [93GER/GRU], [93GRI/KRY], [94ANT/KRY], [98KRY]
Kubas, G. J.	[94BUR/BRY]
Kubaschewski, O.	[82KUB]
Kubota, M.	[90YAM/KUB]
Kuchitsu, K.	[88MIL/CVI]
Kudryavtsev, V. N.	[90ZAK/BAG], [91ZAK/BAG]
Kuhn, F. E.	[92KIP/HER]
Kulakov, V. M.	[82GER/KRY], [85GER/ZEL]
Kunze, S.	[96KUN/NEC]
Kuroda, P. K.	[61KEN/KUR], [82KUR], [93KUR]

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Author	References
Kuzina, A. F.	[59SPI/KUZ], [62KUZ/ZHD], [65SPI/KUZ], [70SPI/KUZ], [70ZHD/KUZ], [71SPI/GLI], [72KOZ/NOV2], [72KUZ/OBL], [73GLI/KUZ], [73KUZ/KOZ], [76SPI/KUZ], [77PIK/KRY], [77SPI/KUZ], [77SPI/KUZ2], [78KUZ/OBL], [78SPI/KUZ], [79KRY/PIK], [80SPI/KUZ], [81SPI/BAI], [82GER/KRY], [82KRY/KUZ], [82OBL/KUZ], [83KRY/KUZ], [83SPI/KRY], [85SPI/KUZ], [86GER/GRI], [86GER/KRY], [86KRY/GRI], [86KRY/GRI2], [86KRY/KUZ], [86SPI/TAR], [87GER/GRI], [87KRY/GRI], [87KRY/GRI2], [87KUZ/GER], [87SPI/KUZ], [88KRY/KUZ], [88SPI/KRY]
LaValle, D. E.	[66LAV/STE]
Laffitte, M. (chairman)	[82LAF]
Lagutina, T. A.	[80SHA/VAR], [90PIR/POP]
Lai, D. Y.	[89KRI/LAI]
Lakosi, L.	[93LAK/SÀF]
Lam, D. J.	[61LAM/DAR], [62DAR/LAM], [62VAN/LAM], [63VAN/LAM]
Lamfers, H. J.	[96LAM/MEE]
Lamoreaux, R. H.	[80BRE/LAM]
Lang, P. F.	[86FLI/LAN]
Lange, B. A.	[76DEU/ELD]
Langhoff, S. R.	[87LAN/PET], [89LAN/BAU]
Lantz, P. M.	[52PAR/CRE]
Larina, T. B.	[81KOZ/LAR], [82KOZ/LAR], [82KOZ/SUR], [83KOZ/LAR], [83KOZ/LAR2], [85KOZ/SUR]
Larson, Q. V.	[57BUS/LAR], [58BUS/LAR]
Latham, I. A.	[87LAT/THO]
Latimer, W. M.	[52LAT]
Lavrukhina, A. K.	[70LAV/POZ]
Lawrence, W. E.	[82PAQ/LIS], [85PAQ/LAW]
Lawson, A.	[88BRO/NEW2]
Lay, D. G.	[76DEU/ELD]
Lederer, M.	[64OSS/SAR]
Leduc, P. A.	[74FOR/LED]
Lee, S. Y.	[83LEE/BON]
Lefort, M.	[63LEF]
Leigh, G. J.	[90LEI]
Leipoldt, J. G.	[92ROO/LEI], [94ROO/LEI], [95ROO/LEI]
Leithe-Jasper, A.	[96LEI/ROG]
Lelyuk, G. A.	[88ZIL/LEL]
Lemire, R. J.	[88VIK/GAR], [89LEM/GAR], [91LEM/SAL], [92GRE/FUG], [95BUR/CAM], [96LEM/JOB], [98LEM]
Lerch, P.	[79IAN/LER], [81IAN/KOS], [88COL/IAN], [88TRU/IAN], [90MAN/IAN]
Leshenko, G. F.	[91ALE/BAR]
Levason, W.	[83LEV/OGD]
Levenson, S. M.	[77ECK/LEV]
Lewis, G. N.	[61LEW/RAN]

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Author	References
Lewis, J.	[65LEW/NYH]
Le Fevre, E. J.	[75LE /NIG]
Li, H.	[93LI/WAN]
Libson, K.	[80DEU/LIB], [80LIB/DEU], [83DEU/LIB], [87NEV/LIB], [88LIB/NOO]
Liebscher, I.	[75LIE/MÜN]
van Lier, J. E.	[87MEL/LIE]
Lieser, K. H.	[81LIE/KRÜ], [83LIE/SIN], [85NAK/LIE], [87LIE/BAU], [87LIE/BAU2], [93LIE]
de Ligny, C. L.	[86KRO/STE], [90TJI/VIN]
Lim, L.-H.	[94KHO/FER]
Linder, K. E.	[86LIN/DAV], [90LIN/MAL]
Lindoy, L. F.	[83DEU/LIB]
Line, Jr., L. E.	[52SMI/LIN]
Lineberger, W. C.	[81FEI/COR], [85HOT/LIN]
Lingane, J. J.	[52KOL/LIN]
Lippard, S. J.	[80TRO/DAV]
Lister, S. J.	[82PAQ/LIS]
Liu, Y.	[93LI/WAN]
de Liverant, J.	[82LIV/WOL]
Lock, C. J. L.	[70COW/LOC], [72GUE/HOW], [72GUE/LOC], [78GUE/HOW], [80FAG/LOC], [82FRA/LOC]
Loevenich, M.	[93BRO/KAN], [93BRO/KAN2]
Longhi, P.	[79LON/MUS]
Lopata, V. J.	[80BIR/LOP]
Lorenz, B.	[79KAD/LOR], [81KAD/LOR], [82STR/BAZ], [83KIR/LOR], [85KAD/LOR], [87ABR/KIR], [88ABR/LOR], [90KAD/LOR], [91HIL/HÜB], [92KAD/FIN]
Lorz, H. V.	[86BEA/LOR]
Love, G. R.	[67KOC/LOV], [67SEK/KER], [68KOC/LOV]
Lu, J.	[90LU/CLA]
Lukens, W. W.	[95ALM/BRY]
Lutze, W.	[89FRE/LUT]
Lux, F.	[65HIE/LUX]
Müller, L.	[81DAV/JON2]
Möbius, S.	[83ALL/BUR]
Müller, A.	[65MÜL/KRE], [66MÜL/KRE], [67MÜL/RIT], [69MÜL/DIE]
Müller, A.	[69KRE/MÜL]
Münze, R.	[64MÜN], [68MÜN], [68MÜN2], [75LIE/MÜN], [75MÜN], [75MÜN/GRO], [78MÜN]
Ma, D.	[93JUR/BER]
Macášek, F.	[75MAC], [79MAC/KAD], [81MIK/MIŠ], [81RAJ/MAC], [82RAJ/MAC]
MacLeod, D. E.	[62VAN/LAM]
Mackay, M. F.	[84BAL/BON], [88BAL/COL], [89BAL/COL2], [90BAL/BOA2]
Maddock, A. G.	[81IAN/KOS]

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Author	References
Magee, R. J.	[59MAG/SCO], [62AL-/MAG], [74MAG/CAR], [85MAG/BLU], [86MAG]
Magnéli, A.	[55MAG/AND]
Magno, F.	[74MAZ/MAG]
Maier, R.	[93JOA/APO], [93JOA/APO2]
Maita, J. P.	[61COM/COR]
Majumdar, S. K.	[69MAJ/PAC]
Maksimov, V. G.	[94ANT/KRY], [94BAT/GRI], [94GRI/KRY]
Maleknia, S.	[86LIN/DAV]
Malley, M. F.	[89TRE/FRA], [90LIN/MAL]
Malm, J. G.	[61SEL/CHE], [62CLA/SEL], [62SEL/MAL], [63SEL/MAL], [78OSB/SCH]
Mal'tsev, A. A.	[76ZAV/MAL], [76ZAV/MAL2]
Mamchenko, A. V.	[91KLI/MAM]
Mann, J. B.	[67MAN]
Mantegazzi, D.	[90MAN/IAN]
Maple, M. B.	[89DAL/MAP]
Maranville, L. F.	[59YOU/MAR]
March, J. G.	[88MAR/GRA]
March, P.	[87GRA/FAR]
Marchenko, V. I.	[84KOL/GOM4], [86KOL/MAR]
Mardon, P. G.	[76HAI/MAR]
Margrave, J. L.	[60GRE/POL], [62POL/GRE]
Marinsky, J.	[77OWU/MAR]
Marov, I. N.	[90ABR/KÖH]
Marples, J. A. C.	[72MAR/KOC]
Marshall, E. M.	[83PED/MAR]
Marshall, W. L.	[84MAR/MES]
Martell, E. A.	[64SIL/MAR], [71SIL/MAR]
Martin, W. J.	[52PAR/CRE], [52PAR/MAR]
Mashkin, A. N.	[88ZIL/LEL]
Massalski, T. B.	[84OKA/MAS]
Mastryukov, V. S.	[72MAS]
Matsui, T.	[89MAT/NAI]
Mattens, W. C. M.	[83NIE/BOE]
Matthias, B. T.	[61COM/COR], [61MAT], [78GIO/MAT]
Matusz, M.	[84COT/DUR]
Matveev, V. V.	[90PIR/POP]
Mayorga, G.	[73PIT/MAY], [74PIT/MAY]
Mazzi, U.	[74MAZ/MAG], [82BAN/MAZ], [90DI /BET]
Mazzocchin, G. A.	[74MAZ/MAG]
McCreary, L. D.	[80DEU/LIB]
McDonald, B. J.	[62MCD/TYS]
McDonald, J. E.	[62MCD/COB]
McDonald, R. A.	[85CHA/DAV]
McDowell, H. K.	[87GEL/MCD]

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Author	References
McPartlin, M.	[89ARC/DIL], [92ARC/DIL]
Medvedev, V. A.	[82GLU/GUR], [89COX/WAG]
Meetsma, A.	[96LAM/MEE]
Meggers, W. F.	[50MEG/SCR], [51MEG]
Meinke, W. W.	[52RUL/MEI]
Meinken, G.	[75STE/MEI], [78STE/MEI]
Melanson, R.	[90ROC/KON]
Mellish, C. E.	[63EAK/HUM]
Melnik, M.	[87MEL/LIE]
Merbach, A. E.	[94ROO/LEI], [95ROO/LEI]
Mercier, H. P. A.	[93MER/SCH]
Merlin, L.	[75BES/COS]
Merlini, A. E.	[85ANT/MER]
Merrill, P. W.	[52MER]
Merte, B.	[86BAU/HEI]
Mesmer, R. E.	[76BAE/MES], [84MAR/MES], [91AND/CAS]
Meyer, D.	[93JOA/APO]
Meyer, G.	[76MEY/HOP]
Meyer, H.	[82STR/BAZ]
Meyer, R. E.	[81PAL/MEY], [86MEY/ARN], [87MEY/ARN], [88MEY/ARN], [89MEY/ARN], [91MEY], [91MEY/ARN], [91MEY/ARN2]
Mišianiková, E.	[81MIK/MIŠ]
Miedema, A. R.	[79MIE/GIN], [80BOU/MIE], [80MIE/de]
Migge, H.	[89MIG], [90MIG]
Mihailovich, S.	[71KOS/MIH]
Mikelsons, M. V.	[86MIK/PIN], [87MIK/PIN]
Mikheeva, M. N.	[83TEP/MIK]
Mikheikin, S. V.	[83VAR/ZAI]
Mikulaj, V.	[79RAJ/MIK], [81MIK/MIŠ]
Mikulenok, V. V.	[72RAK/KOS]
Milazzo, G.	[63MIL]
Miller, D. G.	[81RAR/MIL], [91RAR/MIL]
Miller, G.	[88DRO/KRE]
Miller, G. G.	[83MIL]
Miller, H. H.	[60MIL/KEL]
Millero, F. J.	[72MIL], [79MIL]
Mills, I.	[88MIL/CVI]
Minato, K.	[98MIN/SER]
Miodownik, A. P.	[88SAU/MIO]
Miroslavov, A. E.	[91MIR/BOR]
Moisa, V. S.	[94ANT/KRY]
Monnin, C.	[90MON]
Mooney, R. C. L.	[48MOO]
Moore, C. E.	[51MOO], [58MOO]
Morgan, J. J.	[81STU/MOR]

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Author	References
Morgunova, N. M.	[77ZAI/KON3]
Morgunova, N. V.	[78ZAI/KON], [82ZAI/VEL2]
Morin, F. J.	[61COM/COR]
Morss, L. R.	[76MOR]
du Moulinet d'Hardemare, A.	[89ALA/APP]
Mulac, W. A.	[78DEU/HEI]
Mulder, G.	[81MUL/OLD]
Muller, A. B.	[85MUL], [92GRE/FUG]
Muller, O.	[64MUL/WHI], [68MUL]
Munoz, J. L.	[86NOR/MUN]
Murray, J. L.	[82MUR]
Mussini, T.	[79LON/MUS]
Myers, R. J.	[86MYE]
Mylnikova, T. S.	[91ALE/BAR]
Néher-Neumann, E.	[85FER/GRE]
Noon Doyle, M.	[88LIB/NOO]
Narasa Raju, T. S. B.	[64SCH/KNA]
Nagarajan, G.	[63NAG], [64NAG], [71NAG/BRI]
Naito, K.	[89MAT/NAI]
Nakashima, T.	[85NAK/LIE], [87LIE/BAU2]
Nash, P.	[85NAS]
Natkanei, L.	[67JEŻ/NAT]
Ndalamba, P.	[92ERI/NDA], [93ERI/NDA]
Neck, V.	[87NEC/KAN], [89KAN/NEC], [96KUN/NEC], [97KÖN/NEC], [98NEC/KÖN]
Nelesnik, T.	[88LIB/NOO]
Nelson, C. M.	[52BOY/COB], [52COB/NEL], [54NEL/BOY]
Neumann, J. P.	[86VEN/NEU]
Neves, M.	[87NEV/LIB]
Newbury, R. S.	[69KRI/CAR]
Newman, J. L.	[87BRO/NEW], [88BRO/NEW], [88BRO/NEW2], [87LAT/THO]
Nguyen-Trung, C.	[92GRE/FUG], [96NGU/PAL]
Nicholson, T.	[90VRI/COO], [96BLA/NIC]
Niemiec, J.	[63NIE], [63NIE2], [63NIE3], [65NIE]
Niessen, A. K.	[83NIE/BOE]
Nightingale, M. R.	[75LE /NIG]
Nikiforov, A. S.	[86KOL/MAR]
Nitsche, H.	[95ALM/BRY]
Nordstrom, D. K.	[86NOR/MUN]
Norman, V.	[57KNO/TYR]
Northrop, D. A.	[66SIE/NOR]
Norton, L. J.	[61LAM/DAR], [62DAR/LAM], [63DAR/NOR], [64DAR/NOR], [65DAR/DOW]
Novitskaya, G. N.	[72KOZ/NOV], [72KOZ/NOV2], [72NOV], [73KUZ/KOZ], [75KOZ/NOV]

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Author	References
Novotný, P.	[85SÖH/NOV]
Nowotny, H.	[65WIT/NOW]
Nuber, N.	[91KAN/RAP]
Nunn, A. D.	[86THO/NUN], [89TRE/FRA], [90LIN/MAL]
Nuttall, R. C.	[82WAG/EVA]
Nyholm, R. S.	[58DAL/GIL], [59FER/NYH], [60FER/NYH], [65LEW/NYH]
O'Kelley, G. D.	[88MEY/ARN], [89MEY/ARN], [91MEY/ARN2]
Oblova, A. A.	[65SPI/KUZ], [72KUZ/OBL], [76SPI/KUZ], [77SPI/KUZ], [77SPI/KUZ2], [78KUZ/OBL], [78SPI/KUZ], [82OBL/KUZ], [85SPI/KUZ]
Obruchikov, V. V.	[93GER/GRU]
Oelkers, E. H.	[90OEL/HEL], [92SHO/OEL]
Ogden, J. S.	[83LEV/OGD]
Okamoto, H.	[84OKA/MAS], [86OKA/TAN]
Oldenburg, S. J.	[81MUL/OLD]
Oliver, G. D.	[53COB/OLI]
Omori, T.	[84OMO/TAK], [93KAW/OMO]
van Oort, W. J.	[81MUL/OLD]
Opavsky, W.	[68HIE/OPA], [68HIE/OPA2]
Orvig, C. E. R.	[81COT/DAN], [81ORV], [82COT/DAV]
Osborne, D. W.	[78OSB/SCH]
Ossicini, L.	[64OSS/SAR]
Östhols, E.	[98ÖST/WAN], [98WAN/ÖST], [98WAN/ÖST2]
Otto, K.	[78OSB/SCH]
Owunwanne, A.	[77OWU/MAR]
Ozog, J.	[70COW/LOC]
Pacer, R. (see also Pacer, R. A.)	[67RUL/PAC]
Pacer, R. A. (see also Pacer, R.)	[63RUL/HIR], [67RUL/PAC2], [69MAJ/PAC], [80PAC]
Palmer, D. A.	[81PAL/MEY], [96NGU/PAL]
Palmy, C.	[67BUC/PAL]
Pal'nichenko, A. V.	[89ANT/BEL]
de Pamphilis, B. V.	[82DAV/TRO]
Paquette, J.	[80PAQ/REI], [82PAQ/LIS], [85PAQ/LAW], [88VIK/GAR]
Parker, G. W.	[52COB/NEL], [52PAR/CRE], [52PAR/MAR]
Parker, V. B.	[65PAR], [82WAG/EVA], [87GAR/PAR]
Parshin, A. Y.	[91ALE/BAR]
Partridge, H.	[87LAN/PET]
Paschoal, J. O.	[85KLE/PAS]
Pasturel, A.	[85COL/PAS]
Pavlov, O. N.	[68KOT/PAV]
Peacock, R. D.	[58DAL/GIL], [62COL/PEA], [63EDW/HUG], [66HUG/PEA], [66PEA], [73PEA], [82BUR/PEA], [83ALL/BUR]
Pearlstein, R. M.	[88BRO/NEW2], [89PEA/DAV]
Pearson, F. J.	[92PEA/BER]

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Author	References
Pedan, K. S.	[90ZAK/BAG], [91ZAK/BAG]
Pedersen, E.	[75COT/PED]
Pedley, J. B.	[83PED/MAR]
Pejsa, R.	[84KLE/PEJ], [85KLE/PAS]
Penfold, B. R.	[65ELD/PEN], [66ELD/PEN], [67ELD/FER], [83FER/GRE]
Peretrukhin, V. F.	[92EL-/GER]
Perrier, C.	[37PER/SEG], [39PER/SEG]
Perron, G.	[76DES/VIS]
Persson, B. R. R.	[74PER/DAR]
Peters, G.	[80PRE/PET], [80PRE/PET2], [81PET/PRE], [92PET/SKO]
Peterson, J. R.	[78PIT/PET]
Petride, A.	[77GĂL/BRA]
Petrov, P. N.	[72ZAI/VEL2]
Petrushin, S. A.	[86SPI/TAR], [86TAR/PET]
Pettersson, L. G. M.	[87LAN/PET], [89LAN/BAU]
Phillips, S. L.	[88PHI/HAL]
Picker, P.	[76DES/VIS]
Pieper, H. H.	[68SCH/PIE]
Pies, W.	[77PIE/WEI]
Pihlar, B.	[79PIH]
Pikaev, A. K.	[77PIK/KRY], [79KRY/PIK]
Pilkington, N. J.	[90PIL]
Pinkerton, T. C.	[80PIN/HEI], [83PIN/HEI], [85WIL/PIN], [86MIK/PIN], [87MIK/PIN]
Pirogova, G. N.	[90PIR/POP]
Pirozhkov, S. V.	[82GER/KRY]
Pitzer, K. S.	[61LEW/RAN], [73PIT], [73PIT/MAY], [74PIT/KIM], [74PIT/MAY], [75PIT], [76PIT/SIL], [77PIT/ROY], [78PIT/PET], [79BRA/PIT], [79PIT], [94CLE/RAR]
de Plano, A.	[86BID/AVO]
Plotinskii, G. L.	[67BOL/PLO]
Plyasunov, A. (see also Plyasunov, A. V.)	[97GRE/PLY]
Plyasunov, A. V. (see also Plyasunov, A.)	[97PUI/RAR]
Pocé, J.	[80FAG/LOC]
Poland, D. E.	[60GRE/POL], [62POL/GRE]
Polunin, A. K.	[86KOL/MAR]
Ponyatovskii, E. G.	[79SPI/PON], [81SPI/ANT], [84GLA/IRO], [85SHI/GLA]
Popova, N. N.	[90PIR/POP]
Portanova, R.	[74MAZ/MAG]
Porto, R.	[87CIA/IUL]
Potter, P. E.	[76HAI/MAR], [80HAI/POT], [87ROG/POT], [88ROG/POT], [96LEI/ROG]
Pourbaix, M.	[66ZOU/POU]
Powers, D. A.	[91POW]

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Author	References
Pozdnyakov, A. A.	[64RYA/POZ], [70LAV/POZ]
Preetz, W.	[80PRE/PET], [80PRE/PET2], [81PET/PRE], [84KRE/HEN], [91PRE/WEN], [92HOL/PRE], [92PET/SKO], [92WEN/PRE], [93WEN/PRE], [94WEN/PRE]
du Preez, J. G. H.	[92GER/KEM]
Privalov, V. I.	[86TAR/PET]
Proso, Z.	[79IAN/LER]
Pruett, D. J.	[81PRU]
Puigdomènech, I. (see also Puigdomenech, I.)	[97PUI/RAR]
Puigdomenech, I. (see also Puigdomènech, I.)	[95PUI/BRU], [95SIL/BID]
Pustovalov, V. A.	[93GER/GRU]
Pytkowicz, R. M.	[79JOH/PYT], [79PYT]
Rössler, K.	[77RÖS/WIN]
Rühl, R.	[82RÜH/JEI], [82RÜH/JEI2]
Rüssel, C.	[89FRE/LUT]
Radonovich, L. J.	[84RAD/HOA]
Rajec, P.	[79RAJ/MIK], [81RAJ/MAC], [82RAJ/MAC]
Rakov, E. G.	[72RAK/KOS]
Ramanazov, L. M.	[86SUS/RAM]
Rand, M. H.	[80HAI/POT], [91RAR/RAN], [95SIL/BID], [96RAN]
Randall, M.	[61LEW/RAN]
Raptis, K.	[91KAN/RAP]
Rard, J. A.	[74SPE/RAR], [81RAR/MIL], [83RAR], [91RAR/MIL], [91RAR/RAN], [94CLE/RAR], [97PUI/RAR]
Rashchupkin, V. I.	[81SPI/ANT]
Raynor, G. V.	[72RAY]
Read, A. J.	[92REA/ALD]
Reardon, E. J.	[75REA]
Rebizant, J.	[93JOA/APO], [94WAS/REB]
Reich, T.	[95ALM/BRY]
Reid, J. A. K.	[80PAQ/REI]
Richards, P.	[75STE/MEI], [78STE/MEI]
Riche, F.	[89ALA/APP]
Riglet, C.	[89RIG/ROB]
Rinehart, G. H.	[79RIN/BEH], [80BEH/RIN]
Rinke, K.	[67RIN/KLE]
Rittner, W.	[67MÜL/RIT]
Robinson, R. A.	[59ROB/STO]
Robouch, P. (see also Robouch, P. B.)	[89RIG/ROB]
Robouch, P. B. (see also Robouch, P.)	[95SIL/BID]
Rochon, F. D.	[90ROC/KON]
Rodenburg, M. L. N.	[74VAN/ROD]

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Author	References
Rodley, G. A.	[65LEW/NYH]
Rogelet, P.	[78GRA/ROG]
Rogers, D. B.	[69ROG/SHA]
Rogl, P.	[87ROG/POT], [88ROG/POT], [96LEI/ROG]
Rohm, W.	[68HIE/OPA2]
Roman, M.	[75BRA/BRA]
Romanov, A. V.	[87ZAI/KRU4], [88ZAI/KRU]
Romanov, V. S.	[73ZAI/KON2], [77ZAI/KON]
Ronca, N.	[85ARO/HWA]
Roncari, E.	[82BAN/MAZ]
Rondinini, S.	[79LON/MUS]
Roodt, A.	[92ROO/LEI], [94ROO/LEI], [95ROO/LEI]
Rose, J. W.	[75LE /NIG]
Roseberry, A. M.	[90ROS/DAV]
Rosenblatt, G. M.	[61BRE/ROS]
Rosinger, E. L. J.	[80PAQ/REI]
Roth, W. J.	[84COT/DUR]
Roy, R.	[64MUL/WHI]
Roy, R. N.	[77PIT/ROY]
Rozen, A. M.	[87ROZ/ZAK]
Rudolph, J.	[80RUD/BÄC]
Rudzinski, J.	[62TRZ/RUD], [64TRZ/RUD]
Rulfs, C. L.	[52RUL/MEI], [63RUL/HIR], [63SAL/RUL], [67RUL/PAC], [67RUL/PAC2], [69MAJ/PAC], [70RUL/BOY]
Ruprecht, S.	[83ALL/BUR]
Russel, C. D.	[82RUS]
Russell, C. D.	[78RUS/CAS], [79RUS/CAS], [79RUS/CAS2], [79RUS/CAS3], [84RUS/BIS]
Ryabchikov, D. I.	[64RYA/POZ]
Rypdal, K.	[92KIP/HER]
Ryzkhkov, Y. F.	[91ALE/BAR]
Söhnel, O.	[85SÖH/NOV]
Sàfàr, J.	[93LAK/SÀF]
Sagert, N. H.	[88VIK/GAR]
Sala, B.	[79LON/MUS]
Salaria, G. B. S.	[63SAL/RUL]
Saluja, P. P. S.	[88VIK/GAR], [91LEM/SAL]
Salvatore, F.	[83FER/GRE2], [85FER/GRE]
Samsonov, V. E.	[86TET/ZAI], [87ZAI/KRU4], [88ZAI/KRU]
Samuels, D. L.	[84BAL/BON2]
Sanchez, J. P.	[94WAS/REB]
Sandwar, B. B.	[80THA/SAN]
Saracino, F.	[64OSS/SAR]
Sasahira, A.	[94SAS/HOS]
Sasaki, T. A.	[81SAS/SOG]
Saunders, N.	[88SAU/MIO]

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Author	References
Savitskii, E. M.	[75SAV/GRI]
Saxena, K. M. S.	[76FRA/KAR]
Sayer, B. G.	[82FRA/LOC]
Scatchard, G.	[36SCA], [76SCA]
Schäfer, H.	[67RIN/KLE]
Schablaske, R. V.	[64CHA/JOH]
Schaeffer, H. A.	[89FRE/LUT]
Scheifers, S. M.	[82SCH/HOL]
Scheller, D.	[88ABR/LOR]
Schenk, H. J.	[73SCH/AST], [74SCH/AST], [75AST/HAU], [77SCH/HED]
Scherer, W.	[92KIP/HER]
Schick, H. L.	[66SCH]
Schmidt, K.	[79KAD/LOR], [81KAD/LOR], [83KIR/LOR], [92KAD/FIN]
Schmitz, D.	[93BRO/KAN], [93BRO/KAN2]
Schott, J.	[91AND/CAS]
Schreiner, F.	[78OSB/SCH]
Schrobilgen, G. J.	[82FRA/LOC], [93MER/SCH]
Schumm, R. H.	[82WAG/EVA]
Schwochau, K.	[61HER/SCH], [62SCH], [62SCH/AST], [62SCH/HER], [62SCH/HER2], [63SCH/HER], [64AST/SCH], [64SCH], [64SCH/KNA], [65JØR/SCH], [65SCH], [65SCH2], [68SCH/PIE], [69SCH/KRA], [72KRA/BOH], [73HAU/SCH], [73SCH/AST], [74SCH/AST], [75AST/HAU], [76AST/SCH], [77SCH/HED], [82RÜH/JEI2], [93BRO/KAN2]
Scott, I. A. P.	[59MAG/SCO]
Scribner, B. F.	[50MEG/SCR]
Segrè, E.	[37PER/SEG], [39PER/SEG]
Seidel, A.	[82SEI]
Sekine, T.	[93LAK/SÀF]
Sekula, S. T.	[67SEK/KER]
Selig, H.	[61SEL/CHE], [62CLA/SEL], [62SEL/MAL], [63SEL/MAL], [67FRL/SEL], [68HOL/SEL], [70CLA/GOO], [71SEL/FRI], [74BIN/EL-], [76BIN/SEL], [78OSB/SCH], [86VAN/DAV]
Sergeev, V. V.	[94ANT/KRY]
Serizawa, H.	[98MIN/SER]
Shaikh, S. N.	[91ABR/COS]
Shakh, G. E.	[78SPI/KUZ], [80SHA/VAR]
Shannon, R. D.	[69ROG/SHA]
Shapovalov, M. P.	[88KOL/GOM2]
Sharpe, R. M.	[68BRA/SHA]
Shekhtman, V. S.	[81SPI/ANT]
Shepel'kov, S. V.	[73ZAI/KON], [74VIN/ZAI], [75SHE/KON], [77ZAI/KON], [78VIN/KON2], [78VIN/KON3], [83VIN/ZAI]
Sherman, R. L.	[59SHE]
Shilstein, S. S.	[84GLA/IRO], [85SHI/GLA]
Shimizu, M.	[63VAN/LAM]

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Author	References
Shishkov, N. V.	[73ZAI/KON2], [91ALE/BAR]
Shive, L. W.	[75COT/SHI]
Shmidt, V. S.	[86KOL/MAR]
Shock, E. L.	[88SHO/HEL], [89SHO/HEL], [89SHO/HEL2], [92SHO/OEL]
Shuh, D. K.	[95ALM/BRY]
Shukla, S. K.	[66SHU], [71SHU], [71SHU2], [78SHU]
Shunk, F. A.	[69SHU]
Shvedov, V. P.	[63SHV/KOT], [68KOT/PAV]
Sidorenko, G. V.	[91MIR/BOR]
Siegbahn, P. E. M.	[89LAN/BAU]
Siegel, M. D.	[88PHI/HAL]
Siegel, S.	[66SIE/NOR]
Sillén, L. G.	[64SIL/MAR], [71SIL/MAR]
Sills, R. J. C.	[68EDW/JON]
Silva, R. J.	[95SIL/BID]
Silverman, C.	[72HOD/SIL]
Silvester, L. F.	[76PIT/SIL], [77PIT/ROY], [78PIT/PET], [88PHI/HAL]
Simon, A.	[88DRO/KRE]
Simonov, A. E.	[87SPI/KUZ], [91KRY/GER]
Singh, R. N.	[81LIE/KRÜ], [83LIE/SIN]
Sinke, G. C.	[56STU/SIN]
Sinyakova, G. S.	[92SIN]
Sites, J. R.	[52SIT/BAL]
Skidan, B. S.	[91ALE/BAR]
Skosyrev, V. A.	[86ZAI/KRU3], [87ZAI/KRU5], [87ZAI/KRU6], [87ZAI/KRU7]
Skowronek, J.	[92PET/SKO]
Slavinskii, A. V.	[76ZAI/SLA]
Sleight, A. W.	[69ROG/SHA]
Smelov, V. S.	[86KOL/MAR]
Smith, H. M.	[59YOU/MAR]
Smith, J. F.	[87SMI], [89SMI]
Smith, Jr., W. T.	[52BOY/COB], [52COB/NEL], [52SMI/LIN], [53COB/OLI], [53COB/SMI], [53SMI/COB], [54NEL/BOY], [55CAR/SMI], [66LAV/STE]
Soga, T.	[81SAS/SOG]
Soldatov, A. A.	[85GER/ZEL]
Solomentsev, A. V.	[87ZAI/VEL], [87ZAI/VEL2]
Solomon, N. A.	[85ARO/HWA]
Somenkov, V. A.	[84GLA/IRO], [85SHI/GLA]
Spahiu, K.	[83SPA], [93ERI/NDA]
Spedding, F. H.	[74SPE/RAR]
Spies, H.	[81SPI/JOH], [84ABR/SPI], [85ABR/SPI]
Spirlet, J. C.	[94WAS/REB]

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Author	References
Spitsyn, V. I.	[59SPI/KUZ], [62KUZ/ZHD], [65SPI/KUZ], [70SPI/KUZ], [70ZHD/KUZ], [71SPI/GLI], [72KUZ/OBL], [73GLI/KUZ], [73ZEL/SUB], [75SPI/GRI], [75SPI/ZIN], [76SPI/KUZ], [77PIK/KRY], [77SPI/KUZ], [77SPI/KUZ2], [78KUZ/OBL], [78SPI/KUZ], [79KRY/PIK], [79SPI/PON], [80SPI/KUZ], [81SPI/ANT], [81SPI/BAI], [82KRY/KUZ], [82OBL/KUZ], [83KRY/KUZ], [83SPI/KRY], [84GOL/VEZ], [85SPI/KUZ], [86GER/GRI], [86GER/KRY], [86KRY/GRI], [86KRY/GRI2], [86KRY/KUZ], [86SPI/TAR], [87GER/GRI], [87KRY/GRI], [87KRY/GRI2], [87KRY/GRI3], [87KUZ/GER], [87SPI/KUZ], [88GER/KRJ], [88KRY/GRI], [88KRY/KUZ], [88SPI/BUK], [88SPI/KRY]
Sprinz, H.	[79KAD/LOR], [81KAD/LOR]
Srivastava, R. D.	[57KNO/TYR]
Stach, J.	[85ABR/SPI], [85KAD/LOR], [85KIR/STA], [86KIR/STA], [90KAD/LOR], [91HIL/HÜB]
Steele, R. M.	[66LAV/STE]
Steffen, A.	[78STE/BÄC]
Steigman, J.	[75STE/MEI], [78STE/MEI], [85ARO/HWA]
van Steijn, A. M. P.	[86KRO/STE]
Stepovaya, L. I.	[76SPI/KUZ]
Steventon, B. R.	[67EDW/JON]
Stewart, G. R.	[78STE/GIO], [82STE/COR]
Stokes, R. H.	[59ROB/STO]
Struchkov, Y. T.	[82STR/BAZ], [87KRY/GRI3], [88KRY/GRI], [90GRI/KRY], [94GRI/KRY]
Stull, D. R.	[56STU/SIN]
Stumm, W.	[81STU/MOR]
Stuve, J. M.	[76STU/FER]
Subbotina, N. A.	[73ZEL/SUB]
Sudarikov, B. N.	[72RAK/KOS]
Suglobov, D. N.	[91MIR/BOR]
Sukhih, A. I.	[91ALE/BAR]
Sukhikh, A. I.	[73ZAI/KON2], [74ZAI/KON], [74ZAI/KON2], [74ZAI/KON3], [74ZAI/KON4], [75ZAI/BEL], [75ZAI/KON], [76ZAI/KON], [76ZAI/KON2], [82ZAI/VEL], [82ZAI/VEL2]
Sullivan, J. C.	[78DEU/HEI], [88LIB/NOO], [92ROO/LEI]
Sunder, S.	[88VIK/GAR]
Sundrehagen, E.	[79SUN]
Surawski, H.	[77D'A/SUR]
Surazhskaya, M. D.	[81KOZ/LAR], [82KOZ/LAR], [82KOZ/SUR], [83KOZ/LAR], [83KOZ/LAR2], [85KOZ/SUR]
Suslov, Y. P.	[86SUS/RAM]
Sverjensky, D. A.	[89SHO/HEL2], [92SHO/OEL]
Swanson, R.	[82COT/DAV]
Synowietz, C.	[77D'A/SUR]
Syverud, A. N.	[85CHA/DAV]

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Author	References
Szalda, D. J.	[80TRO/DAV]
Szklarz, E. G.	[66GIO/SZK], [70GIO/SZK], [70GIO/SZK2], [81SZK/GIO], [82STE/COR]
Takahashi, H.	[84OMO/TAK]
Tanabe, S.	[83TAN/ZOD]
Tanger, IV, J. C.	[88TAN/HEL]
Tanner, L. E.	[86OKA/TAN]
Tarasov, V. P.	[86SPI/TAR], [86TAR/PET], [92TAR/KIR]
Tatsumi, K.	[90MAN/IAN]
Tatz, R.	[81DAV/JON2]
Taube, H.	[76ARM/TAU]
Taylor, J. R.	[82TAY]
Taylor, P.	[88VIK/GAR], [95BUR/CAM], [99JOB/TAY]
Tech, J. L.	[68BOZ/COR]
Teplinskiy, V. M.	[89ANT/BEL]
Teplov, A. A.	[83TEP/MIK]
Terry, A. A.	[63TER/ZIT]
Teterin, E. G.	[83TET/ZAI], [86TET/ZAI], [87ZAI/KRU3], [87ZAI/KRU4], [87ZAI/KRU7], [88ZAI/KRU]
Thümmler, F.	[85KLE/PAS]
Thakur, L.	[80THA/SAN]
Thiele, G.	[92HOL/PRE]
Thom, D.	[68BRA/SHA]
Thomas, J. A.	[91THO/DAV]
Thomas, R. W.	[80THO/DAV], [85THO/HEE], [88LIB/NOO]
Thomason, P. F.	[58THO], [60MIL/KEL]
Thompson, M.	[86THO/NUN]
Thornback, J. R.	[87BRO/NEW], [88BRO/NEW], [88BRO/NEW2], [87LAT/THO], [91RAR/RAN]
Thornley, R. F.	[85ANT/MER]
Thyer, A. M.	[93KEM/THY], [93KEM/THY2]
Tikhonov, M. F.	[80KOL/ZAI]
Titova, T. A.	[90BUK/TIT]
Titova, T. K.	[88SPI/BUK]
Tji, T. G.	[89HUI/TJI], [90TJI/VIN]
Tofe, A. J.	[80DEU/LIB]
Tomkins, I. B.	[68CAN/COL2], [68COL/TOM]
Torikachvili, M. S.	[89DAL/MAP]
Torstenfeld, B.	[79ALL/KIG]
Trémillon, B.	[78GRA/ROG], [79GRA/DEV]
Trainor, R. J.	[75TRA/BRO]
Trapp, C.	[89BOC/BRÜ]
Trapp, H. D.	[62VAN/LAM]
Trees, R. E.	[53KES/TRE]
Treher, E. N.	[86THO/NUN], [89TRE/FRA]

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Author	References
Trop, H. S.	[79COT/DAV], [79TRO/DAV], [80THO/DAV], [80TRO/DAV], [80TRO/JON], [81DAV/JON2], [82DAV/TRO]
Truffer-Caron, S.	[88TRU/IAN]
Trzebiatowski, W.	[62TRZ/RUD], [64TRZ/RUD]
Tsarenko, A. F.	[82AKO/KRI], [90AKO/KRI]
Turcotte, R. P.	[79BRA/HAR]
Turff, J. W.	[83LEV/OGD]
Tweed, C. J.	[87CRO/EWA]
Tyree, Jr., S. Y.	[57KNO/TYR]
Tyson, G. J.	[62MCD/TYS]
Unger, S. E.	[90LIN/MAL]
Usov, N. A.	[91ALE/BAR]
Van Ostenburg, D. O.	[62VAN/LAM], [63VAN/LAM]
Van Rongen, H. J. M.	[65VAN/KNO]
Vaal, M. J.	[76DEU/ELD]
Vakhrushin, A. Y.	[84ZAI/VAK], [87ROZ/ZAK]
Valentine, T. M.	[89GUP/ATK]
Vanderzee, C. E.	[74VAN/ROD], [80VAN/WAU]
Vankin, D.	[86VAN/DAV]
Varen, M.	[80SHA/VAR], [81SPI/BAI]
Varfolomeev, M. B.	[83VAR/ZAI]
Vasil'ev, V. P.	[62VAS]
Van den Berg, G. J.	[65VAN/KNO]
Van den Brand, J. A. G. M.	[81BRA/DAS], [82BRA/DAS]
Vedenov, A. A.	[91ALE/BAR]
Veits, I. V.	[82GLU/GUR]
Veleckis, E.	[64VEL/JOH]
Velichko, A. V.	[72ZAI/VEL], [72ZAI/VEL2], [73ZAI/KON2], [74ZAI/KON2], [74ZAI/KON3], [74ZAI/KON4], [75ZAI/KON], [77ZAI/KON2], [77ZAI/KON3], [78ZAI/KON], [78ZAI/VEL], [78ZAI/VEL2], [79ZAI/VEL], [82ZAI/VEL], [82ZAI/VEL2], [84ZAI/VEL], [86ZAI/VEL], [86ZAI/VEL2], [87ZAI/VEL], [87ZAI/VEL2], [91ALE/BAR]
Velikanova, T. Y.	[83ERE/VEL], [89ERE/VEL], [89VEL/ERE]
Venkatraman, M.	[86VEN/NEU]
Veres, À.	[93LAK/SÀF]
Vezhlivtsev, Y. V.	[84GOL/VEZ]
Vialard, E.	[84VIA/GER]
Vidal, M.	[89ALA/APP]
Vikis, A. C.	[88VIK/GAR]
Vink, H. A.	[90TJI/VIN]
Vinogradov, I. V.	[72ZAI/KON], [73ZAI/KON], [74VIN/ZAI], [74ZAI/KON5], [75SHE/KON], [78VIN/KON], [78VIN/KON2], [78VIN/KON3], [81VIN/KON], [83VIN/ZAI], [83ZAI/VIN], [84ZAI/VEL]
de Visser, C.	[76DES/VIS]
Vitorge, P.	[89RIG/ROB], [93GIF/VIT]

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Author	References
Vlasov, V. S.	[87ROZ/ZAK]
Voitovitch, R. F.	[67VOI/GOL]
Volden, H. V.	[92KIP/HER]
Volk, V. I.	[77VOL/KON]
Voltz, R. E.	[67VOL/HOL]
Voronin, Y. V.	[90PIR/POP]
de Vries, N.	[90VRI/COO]
Wagman, D. D.	[73HUL/DES], [82WAG/EVA], [89COX/WAG]
Wahren, M.	[79KAD/LOR], [81KAD/LOR], [82STR/BAZ], [92KAD/FIN]
Wajda, S.	[67JEŻ/WAJ]
Walford, L. K.	[63VEI/WAL], [64WAL]
Walker, C. T.	[94WAS/REB]
Wallace, R. M.	[85BIB/WAL]
Wang, J. Z.	[89BAL/WAN], [89WAN/BAL]
Wang, P.	[90ARC/WAN]
Wang, X.	[93LI/WAN]
Wanner, H.	[88WAN], [90WAN], [91RAR/RAN], [92GRE/FUG], [92GRE/WAN], [95SIL/BID], [98ÖST/WAN], [98WAN], [98WAN/ÖST], [98WAN/ÖST2]
Wassilopulos, M.	[65WAS], [66KEL/WAS]
Wastin, F.	[94WAS/REB]
Watson, R. E.	[81WAT/BEN]
Waugh, D. H.	[80VAN/WAU]
Weiss, A.	[77PIE/WEI]
Wendt, A.	[91PRE/WEN], [92WEN/PRE], [93WEN/PRE], [94WEN/PRE]
Whiffen, D. H. (chairman)	[79WHI]
White, Jr., H. J.	[87GAR/PAR]
White, W. B.	[64MUL/WHI], [83KHA/WHI], [84KHA/WHI]
Whitfield, M.	[79WHI2]
Whittle, R.	[80ELD/WHI], [80GLA/WHI]
Wiegers, G. A.	[96LAM/MEE]
Wildervanck, J. C.	[71WIL/JEL]
Wilkinson, C.	[67WIL]
Wilkinson, G.	[60COL/DAL], [88COT/WIL]
Williams, G. A.	[84BAL/BOA], [84BAL/BON], [84BAL/BON2], [85BAL/BON], [86BAL/BON], [90BAL/BOA], [91BAL/BOA], [91BAL/BOA2], [91BAL/COL], [92BAL/BOA], [93BAL/BOA]
Williams, M. J.	[71WIL/DEE]
Wilson, C. L.	[59MAG/SCO], [62AL-/MAG]
Wilson, G. M.	[85WIL/PIN]
Wilson, P. D.	[84GAR/WIL], [93KEM/THY], [93KEM/THY2]
Winkler, A.	[89BOC/BRÜ]
Winn, J. S.	[80BRE/WIN]
Winter, J.	[77RÖS/WIN]
Wittmann, A.	[65WIT/NOW]
Wolf, W.	[82LIV/WOL]

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Author	References
Wollert, R.	[93ABR/WOL], [93ABR/WOL2]
Woods, M.	[88LIB/NOO]
Wu, H.-F.	[96WU/BRE]
Wu, Y.	[93LI/WAN]
Xia, D. Y.	[95ZHU/ZHE]
Xiao, G.	[88XIA]
Yagi, M.	[84OMO/TAK]
Yamagishi, I.	[90YAM/KUB]
Yang, G. C.	[81HEI/YAN], [82YAN/HEI]
Yang, Q.	[93LI/WAN]
Yanovskii, A. I.	[87KRY/GRI3], [88KRY/GRI], [90GRI/KRY], [94GRI/KRY]
Yasnovitskaya, A. L.	[88ZIL/LEL]
Yates, G.	[68BRA/SHA]
Yoshihara, K.	[84OMO/TAK], [93LAK/SÀF]
Young, T. F.	[59YOU/MAR]
Yungman, V. S.	[82GLU/GUR]
Yurik, Y. K.	[94ANT/KRY]
Zachariasen, W. H.	[51ZAC]
Zaitseva, L. L.	[72ZAI/KON], [72ZAI/VEL], [72ZAI/VEL2], [73ZAI/KON], [73ZAI/KON2], [74VIN/ZAI], [74ZAI/KON], [74ZAI/KON2], [74ZAI/KON3], [74ZAI/KON4], [74ZAI/KON5], [75SHE/KON], [75ZAI/BEL], [75ZAI/KON], [76ZAI/KON], [76ZAI/KON2], [76ZAI/SLA], [77ZAI/KON], [77ZAI/KON2], [77ZAI/KON3], [78VIN/KON], [78VIN/KON2], [78VIN/KON3], [78ZAI/KON], [78ZAI/VEL], [78ZAI/VEL2], [79ZAI/VEL], [80KOL/ZAI], [81VIN/KON], [82ZAI/VEL], [82ZAI/VEL2], [83KRU/ZAI], [83TET/ZAI], [83VAR/ZAI], [83VIN/ZAI], [83ZAI/VIN], [84ZAI/VAK], [84ZAI/VEL], [86TET/ZAI], [86ZAI/KRU], [86ZAI/KRU2], [86ZAI/KRU3], [86ZAI/VEL], [86ZAI/VEL2], [87ZAI/KRU], [87ZAI/KRU2], [87ZAI/KRU3], [87ZAI/KRU4], [87ZAI/KRU5], [87ZAI/KRU6], [87ZAI/KRU7], [87ZAI/VEL], [87ZAI/VEL2], [88ZAI/KRU]
Zakharkin, B. S.	[87ROZ/ZAK]
Zakharov, E. N.	[90ZAK/BAG], [91ZAK/BAG]
Zamoshnikova, N. N.	[65SPI/KUZ]
Zavalishin, N. I.	[76ZAV/MAL], [76ZAV/MAL2]
Zaytzeva, L. L.	[91ALE/BAR]
Zegler, S. T.	[62DAR/ZEG]
Zelenkov, A. G.	[85GER/ZEL]
Zelentsov, V. V.	[73ZEL/SUB]
Zelverte, A.	[88ZEL]
Zharikov, O. V.	[89ANT/BEL]
Zhdanov, S. I.	[62KUZ/ZHD], [70SPI/KUZ], [70ZHD/KUZ]
Zheng, J. S.	[95ZHU/ZHE]
Zhou, W.	[93LI/WAN]
Zhu, Z. G.	[95ZHU/ZHE]
Zhuang, H. E.	[95ZHU/ZHE]

(Continued on next page)

Table VIII.1: (continued)

Author	References
Ziegler, M. L.	[91KAN/RAP], [93JOA/APO], [93JOA/APO2]
Zil'berman, B. Y.	[88ZIL/LEL]
Zinov'ev, V. E.	[75SPI/ZIN]
Zittel, H. E.	[63TER/ZIT]
Zodda, J. P.	[83TAN/ZOD]
Zotov, V. A.	[78ZAI/VEL], [78ZAI/VEL2]
de Zoubov, N.	[66ZOU/POU]
Zubieta, J.	[91ABR/COS]

Appendix A

Discussion of selected references

This appendix is comprised of discussions relating to a number of the key publications which contain experimental information cited in this review. These discussions are fundamental in explaining the accuracy of the data concerned and the interpretation of the experiments, but they are too lengthy or are related to too many different sections to be included in the main text. The notation used in this appendix is consistent with that used in the present book, and not necessarily with that used in the publication under discussion.

[45FLA/BLE]

Flagg and Bleidner did one of the earliest electrochemical characterisations of aqueous technetium, which was known only as "element 43" at that time. They found that the reduction potential was about 0.1 V relative to the SCE for electrodeposition of TcO_4^- from a solution of H_2SO_4 at pH = 2.36. They calculated a value of E° by assuming that TcO_4^- was being reduced to the metal by measuring the amount of technetium deposited on the electrode and the amount remaining in solution by a radiometric method. That is, for a 7 e^- reduction involving $8H^+/TcO_4^-$. It is now known that this reduction actually gives $TcO_2 \cdot xH_2O(s)$. Thus the correct standard potential from that study should be $E^\circ = 0.77$ V. However, because the concentration of TcO_4^- in their solutions, 10^{-12} M, was actually known only within a few orders of magnitude, this value of E° is uncertain by at least 0.03 V. In spite of that large uncertainty, it agrees well with the more direct determinations.

[52PAR/MAR]

Parker and Martin did not tabulate any experimental data for the solubility of $KTcO_4(cr)$ in their report, but instead just gave a plot of the molar concentrations of TcO_4^- against the reciprocal of the molar concentrations of K^+. The apparent solubility products (0.44 $mol^2 \cdot dm^{-6}$ at 27°C; 0.14 $mol^2 \cdot dm^{-6}$ at 7°C) were listed on that figure. They are equal to the slopes of the lines defined by the data points. These apparent solubility products can be represented by the equation

$$\ln K_s = \frac{-4809.3}{T} + 15.210$$

No uncertainty limits can be given, because this equation was based upon only two data points. At 298.15 K, this equation yields $K_s = 0.398$ $mol^2 \cdot dm^{-6}$, and the

corresponding solubility of $KTcO_4$(cr) is $\sqrt{K_s} = 0.63$ M, which agrees with two of the reported values [53COB/SMI, 57BUS/LAR].

The numbers given on the scales of their solubility plot indicate that K^+ was always in excess over TcO_4^- in their solutions, with a 4-fold to 62-fold mole ratio of these ions. Thus their solutions must have contained large amounts of an "inert" electrolyte such as KCl or KNO_3, but this "inert" electrolyte was not identified. This omission, together with the fact that numerical solubilities were not tabulated, means these results cannot be reextrapolated to yield thermodynamic solubility products or the solubility of $KTcO_4$(cr) in water. Consequently, the interpolated "solubility" of 0.63 M at 298.15 K pertains to some unknown ionic medium rather than pure water.

There are three pieces of evidence that suggest that the derived solubility for $KTcO_4$(cr) of 0.63 M is too high.

- First, solubilities of alkali metal $MClO_4$(cr) are fairly low and are of similar magnitude for $M^+ = K^+$, Rb^+, and Cs^+, and this is also true for $MReO_4$(cr). The reported solubility of $KTcO_4$(cr) is more than an order of magnitude larger than experimental solubilities of $CsTcO_4$(cr) and $RbTcO_4$(cr) [63KEL/KAN], which seems unlikely.

- Secondly, the solubility of aqueous $KReO_4$(cr) at 298.15 K is about 0.04 M [53COB/OLI], which is a factor of 16 lower than reported for $KTcO_4$(cr), whereas we expect them to be much closer.

- Thirdly, the solubilities of $KTcO_4$(cr) at 298.15 K determined by Busey and Bevan [60BUS/BEV] and by Neck *et al.* [98NEC/KÖN] are more precise and are mutually consistent with each other, but are lower by a factor of six than those derived from the study of Parker and Martin.

[52SIT/BAL]

The mass spectrometer study of Sites, Baldock and Gilpatrick has generally been described as giving the cracking pattern of NH_4TcO_4 [59AND, 59BOY2]. However, Sites, Baldock and Gilpatrick actually evaporated an aqueous ammonical solution of NH_4TcO_4 with H_2O_2(aq), and heated the residue to dryness at about 423 K. They stated (based on their mass spectrometric results) that this treatment produced both Tc_2O_7 and "$HTcO_4$". Samples of this "oxide" residue were heated to 353 to 433 K for the mass spectrometric measurements. They suggest that $HTcO_4$(g) could be a viable vapour species at these temperatures.

[53COB/SMI]

The following detailed calculation of the enthalpy of formation of Tc_2O_7(cr), derived from the heat of combustion of Tc(cr), is largely based on the report of Cobble, Smith, and Boyd. However, we also used some information from the more detailed presentation in Cobble's thesis [52COB], which allowed us to refine the analysis. Cobble, Smith and Boyd found it necessary to add some paraffin oil to their calorimeter as an

"accelerator" to improve combustion of the technetium metal. The results were then corrected for combustion of this oil and for ignition of the fuse. Even then, only 80 to 90% of the technetium burned in any experiment, so the residue of unburned technetium had to be weighed and corrected for. Hopefully, the "hotter" combustion produced by the burning oil helped keep the formation of lower oxides to a minimum.

Cobble, Smith and Boyd gave the temperature rises that occurred in their calorimeter (after correction for fuse ignition, paraffin oil combustion, and for side reaction formation of HNO_3) along with the amount of technetium burned and the heat capacity of their calorimeter. Thus, sufficient information was presented to allow a detailed recalculation of their data. The combustion of technetium metal produced concentrated $HTcO_4$, from solution of the Tc_2O_7(cr) in water produced by combustion of the paraffin oil. To yield aqueous concentrations of $HTcO_4$ that could more readily be converted to standard conditions, they added 2 cm^3 of water to the calorimeter. On the average, the final concentration of $HTcO_4$ in the calorimeter was 0.3 M.

Cobble, Smith and Boyd reported the results of 6 combustion experiments, for which the average temperature rise in the calorimeter was (0.9973 ± 0.0449) K per gram of technetium burned. The experimental heat capacity of their calorimeter was $5.8467\ \mathrm{kJ \cdot K^{-1}}$. Thus, $\Delta_r E = -(5.8309 \pm 0.2624)\ \mathrm{kJ \cdot g^{-1}}$, and $\Delta_r E_m = -(1153.4 \pm 51.9)\ \mathrm{kJ{\cdot}mol^{-1}}$ for formation of one mole of Tc_2O_7(cr). We used a corrected ΔT of 0.0571 K rather than 0.0572 K for their third experiment, based on their reported ΔT values for combustion of metal plus oil and for oil alone.

For the combustion of technetium to form Tc_2O_7(cr):

$$2\mathrm{Tc(cr)} + \frac{7}{2}\mathrm{O_2(g)} \quad \rightleftharpoons \quad \mathrm{Tc_2O_7(cr)}$$

there is a change of $-\frac{7}{2}$ moles of gas. Then, conversion of $\Delta_r E$ to $\Delta_r H$ involves $-\frac{7}{2}RT = -8.68\ \mathrm{kJ{\cdot}mol^{-1}}$ of Tc_2O_7(cr). This, together with a correction of $-0.68\ \mathrm{kJ{\cdot}mol^{-1}}$ [52COB] of the results from 30 atm to unit fugacity (1 bar) of O_2(g) yields $\Delta_r H_m = -(1162.8 \pm 51.9)\ \mathrm{kJ{\cdot}mol^{-1}}$. This experimental enthalpy change corresponds to the reaction:

$$2\mathrm{Tc(cr)} + \frac{7}{2}\mathrm{O_2(g)} + \mathrm{H_2O(l)} \rightleftharpoons 2\mathrm{HTcO_4}$$

where the solution concentration is at about 0.3 M. Cobble, Smith and Boyd found that diluting 0.3 M $HTcO_4$ to 0.0205 M resulted in the absorption of $1.17\ \mathrm{kJ{\cdot}mol^{-1}}$. Dilution of 0.0205 M $HTcO_4$ to infinite dilution was estimated by us to evolve $-0.21\ \mathrm{kJ{\cdot}mol^{-1}}$, from comparable data for $HClO_4$ [65PAR]. Thus, for infinite dilution as the final state, $\Delta_r H_m^\circ = -(1160.9 \pm 51.9)\ \mathrm{kJ{\cdot}mol^{-1}}$.

We have just calculated the enthalpy change for formation of $HTcO_4$ at infinite dilution from combustion of technetium metal in the presence of liquid water. However, we desire to compute the enthalpy of formation of crystalline Tc_2O_7(cr). These two enthalpies differ only by the negative of enthalpy of solution of Tc_2O_7(cr). Using the selected value of $\Delta_{sol} H_m^\circ$ from Section V.3.2.1, then

$$\Delta_f H_m^\circ(\mathrm{Tc_2O_7, cr, 298.15\ K}) \quad = \quad -(1114 \pm 52)\ \mathrm{kJ{\cdot}mol^{-1}}.$$

Our recalculated value $\Delta_f H^\circ_m = -1114$ kJ·mol^{-1} is in excellent agreement with the value given by Cobble, Smith and Boyd, $-(1113.4 \pm 10.9)$ kJ·mol^{-1}, with minor differences due to corrections to current atomic masses, and reanalysis of $\Delta_{sol} H^\circ_m$ data. However our assigned uncertainty of 52 kJ·mol^{-1} is 4.8 times larger than Cobble, Smith and Boyd's assigned uncertainty. Even assuming that they reported one standard deviation as opposed to us giving 95% confidence limits, the assigned errors still differ by a factor of 2.5. Nearly all of the uncertainty of $\Delta_f H^\circ_m$ of Tc_2O_7(cr) in Cobble, Smith and Boyd's study comes from the uncertainty in the temperature rise for their calorimeter due to combustion of technetium. They based their calculations on a average temperature rise of (0.998 ± 0.009) K · g^{-1} of technetium. We calculate a temperature rise of 0.9973 K · g^{-1} which agrees fairly well with their reported average temperature rise. However, from their tabulated values of ΔT per gram of technetium, we calculate a standard deviation of 0.0229 K · g^{-1} ($n - 1$ weighting) or 0.0209 K · g^{-1} (n weighting), and a mean deviation of 0.0203 K · g^{-1}. Whatever measure of precision was reported by Cobble, Smith and Boyd, it was much too low and thus so are their estimated uncertainties of $\Delta_f H^\circ_m$.

The first systematic investigation of the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode was reported by Cobble, Smith and Boyd. They prepared the hydrous oxide by two methods: by reduction with zinc metal of an aqueous solution of NH_4TcO_4 in HCl, or by electrodeposition from an acidic NH_4TcO_4 solution onto platinum gauze. The emf measurements were made with both types of electrode preparations at acidic pH values, but only the electrodes with $TcO_2 \cdot xH_2O$(s) electrolytically deposited onto platinum were used for alkaline solution experiments. The counter electrode was Ag/AgCl for experiments with acidic solutions ($HTcO_4$), and Hg/HgO for experiments with alkaline solutions (equal concentration of $NaTcO_4$ and NaOH). All potential measurements were done at (298.15 ± 0.05) K, and both types of cells contained a KCl-KNO_3 salt bridge.

For measurements with air-saturated solutions at low pH values, the two types of preparations of $TcO_2 \cdot xH_2O$(s) gave very similar potential readings from which Cobble, Smith and Boyd calculated an averaged value of 0.771 V for E° of Reaction (V.2). Cell potentials for the alkaline solution case, when converted by them into the same half cell reaction, gave $E^\circ = 0.792$ V. Cobble, Smith and Boyd recommended an averaged E° value of (0.782 ± 0.011) V, but they neglected the contribution of the liquid-junction potential on their measurements. Cobble, Smith and Boyd found that when N_2(g) was bubbled through their solutions at low pH values, the observed potentials slowly decreased. They assumed this emf drift was due to electrode poisoning or to catalytic reactions involving N_2(g).

Because flushing the solutions with N_2(g) or Ar(g) gave essentially identical redox potentials [55CAR/SMI, 75LIE/MÜN], the suggestion by Cobble, Smith and Boyd that N_2(g) caused electrode poisoning must be incorrect.

[53SMI/COB]

Smith, Cobble and Boyd reported the results of vapour pressure measurements for solid $Tc_2O_7 \cdot H_2O$(s) as a function of temperature up to about 360 K. Their results were given graphically and as a least-squares representation, but no actual numerical

data were listed. We note that the derived thermodynamic properties of Smith, Cobble and Boyd for "$HTcO_4$" differ from those of $Tc_2O_7 \cdot H_2O$(s) by a factor of 1/2. Smith, Cobble and Boyd also presented experimental vapour pressures for saturated solutions in equilibrium with solid $Tc_2O_7 \cdot H_2O$(s).

These vapour pressures were determined with an all-glass differential Bourdon gauge ("sickle gauge"). An all-glass system was necessary for these experiments because Tc(VII) is readily reduced to a lower oxidation state by stopcock grease and by Hg(l). A zero-point pressure correction for this gauge was obtained by cooling the system down to 273 K, and then determining the pressure required to return the gauge reading to zero. They consequently subtracted 0.00267 bar from all of their experimental pressure readings. Some experimental details were given in the published paper [53SMI/COB], and additional details can be found in the thesis [52COB] upon which that paper was based.

Their $Tc_2O_7 \cdot H_2O$(s) had been prepared in situ by distilling Tc_2O_7 into the lower part of the Bourdon gauge, and water vapour was then added through the vacuum line. The oxide became moist immediately, and excess water was removed with a vacuum pump while warming the apparatus slightly. Samples prepared in this manner were two-phase and contained some Tc_2O_7(cr). Because Tc_2O_7(cr) has very low vapour pressures in this temperature region, the observed pressures should be due essentially to H_2O(g) from the decomposition of $Tc_2O_7 \cdot H_2O$(s). Samples of saturated solution in contact with $Tc_2O_7 \cdot H_2O$(s) were prepared in a similar manner, except that the Tc_2O_7(cr) was allowed to absorb enough moisture to form both a solution phase and a solid phase.

Smith, Cobble and Boyd did not report the actual experimental vapour pressures, but they were given in Tables VII and VIII of Cobble's thesis [52COB]. Because that thesis is a rather inaccesible source of information, we give the detailed experimental temperatures and vapour pressures (after conversion of pressure units from mm of Hg to bar) in Table A.1. There is a small amount of physicochemical information about "$Tc_2O_7 \cdot H_2O$(s)" that provides some indirect information about its nature. First, the vapour pressures of solid "$Tc_2O_7 \cdot H_2O$(s)" and of saturated aqueous $HTcO_4$ are nearly equal over a wide temperature range, with vapour pressures of the aqueous solution being slightly higher. This presumably implies that the chemistries of these two systems are very similar. They noted that the vapour pressure of water above solid "$HTcO_4$(s)" was significantly higher than that above solid "$HReO_4$(s)", so solid "$HTcO_4$(s)" decomposed more readily. We expect that a $M_2O_7 \cdot H_2O$(s) should decompose (upon heating) more readily than a corresponding HMO_4(s). Inasmuch as "$HReO_4$(s)" is actually a hydrated oxide, this suggests that "$HTcO_4$(s)" may actually be $Tc_2O_7 \cdot H_2O$(s).

According to Cobble [52COB] and Smith, Cobble and Boyd [53SMI/COB], the vapour phase above $Tc_2O_7 \cdot H_2O$(s) results from the incongruent vaporisation process given by Eq. (V.26), *cf.* Section V.3.2.2.2, with H_2O(g) being the only significant vapour species even though their solid sample was a two-phase mixture of $Tc_2O_7 \cdot H_2O$(s) and Tc_2O_7(cr). We will now examine that assumption.

Vapour pressure measurements have been reported for Tc_2O_7(cr) from 362.2 to 391.2 K [52COB, 53SMI/COB]. They gave an equation for $\log_{10} p_{Tc_2O_7}$, based upon these data together with estimated heat capacities. That equation yields values of

Table A.1: Vapour pressures of water above $Tc_2O_7 \cdot H_2O$(s) and saturated $HTcO_4$ as a function of temperature.

T (K)	P_w [a] (bar)	f_w [b] (bar)	$\ln f_w$	Δf_w [c]
$Tc_2O_7 \cdot H_2O(s) \rightleftharpoons Tc_2O_7(cr) + H_2O(g)$				
291.8	0.00133[d]	0.00133	−6.623	−0.007
305.7	0.00320[d]	0.00320	−5.745	0.012
313.8	0.00507[d]	0.00507	−5.285	0.007
322.4	0.00793[i]	0.00793	−4.837	−0.014
330.6	0.01213[d]	0.01213	−4.412	−0.013
337.2	0.01760[i]	0.01759	−4.0403	0.033
341.5	0.02060[i]	0.02059	−3.883	−0.016
347.5	0.02773[d]	0.0277l	−3.586	0.003
353.8	0.03640[i]	0.03637	−3.314	−0.008
363.3	0.05526[d]	0.05521	−2.8966	0.003
H_2O(satd $HTcO_4$) $\rightleftharpoons H_2O$(g)				
312.9	0.00587[i]	0.00587	−5.138	0.074
324.5	0.00964[i]	0.00964	−4.642	−0.053
329.1	0.01247[d]	0.01247	−4.3848	−0.031
330.6	0.01420[i]	0.01419	−4.255	0.024
334.2	0.01573[i]	0.01572	−4.153	−0.052
337.0	0.01887[i]	0.01886	−3.9706	−0.005
339.5	0.02146[d]	0.02145	−3.842	0.004
344.7	0.02673[i]	0.0267l	−3.6226	−0.019
344.6	0.02706[i]	0.02704	−3.6103	−0.002
347.5	0.03100[i]	0.03098	−3.4744	0.002
351.0	0.03680[d]	0.03677	−3.303	0.016
355.8	0.04466[i]	0.04462	−3.1095	0.000
357.2	0.04813[d]	0.04809	−3.0347	0.015
361.0	0.05646[d]	0.05640	−2.8752	0.013
363.6	0.06286[d]	0.06279	−2.768	0.013

[a] Those pressures that were measured while the temperature was being increased are labelled (i), and those while the temperature was being decreased are labeled (d).

[b] Fugacity of water vapour as calculated from $f_w \approx p_w \exp\{B_2(T)p_w/RT\}$.

[c] Experimental value minus value from least-squares representation of the data.

$p_{Tc_2O_7}$ of 7.7×10^{-10}, 2.6×10^{-8}, 5.8×10^{-7}, 8.6×10^{-6}, and 5.3×10^{-5} bar at 290, 310, 330, 350, and 365 K, respectively. Comparison of these pressures to the decomposition pressures of $Tc_2O_7 \cdot H_2O$(s) in Table A.1 indicates that $p_{Tc_2O_7}$ is comparable in magnitude to the non-ideal vapour correction for the experiment at 363.3 K, but it is insignificant at all lower experimental temperatures. Thus, neglect of the contribution of Tc_2O_7(g) to the total vapour pressure is justified.

Sasahira *et al.* [94SAS/HOS] studied the liquid-vapour equilibrium of the $Tc_2O_7 + HNO_3 + H_2O$ system at temperatures from 336 to 363 K, with total technetium concentrations of 0.0023 to 0.023 M. The concentration of HNO_3 was adjusted to vary the water activity range between 1 and 0.4. Their equation is obviously not valid for saturated solutions of Tc_2O_7 in water, but it does allow us to roughly estimate that the partial vapour pressures of $TcO_3(OH)$(g) above the solutions studied by Smith, Cobble and Boyd [53SMI/COB] were of the order of 1×10^{-4} bar. This is insignificant compared to Smith and Cobble's experimental errors. Liquid-vapour equilibrium measurements for the chemically similar system $Re_2O_7 + H_2O$ [67BOL/PLO] likewise indicate that the partial vapour pressures of $ReO_3(OH)$(g) are extremely small at the temperatures and concentrations studied by Smith, Cobble and Boyd, and, by implication, so are those of $TcO_3(OH)$(g). Smith *et al.* [53SMI/COB] wrote the vaporisation reaction for the saturated solution as being

$$HTcO_4(\text{satd, aq}) \quad \rightleftharpoons \quad HTcO_4(s) + H_2O(g)$$

which, as written, is an unbalanced reaction. We will rewrite this reaction as

$$H_2O(\text{satd } HTcO_4) \quad \rightleftharpoons \quad H_2O(g).$$

For accurate thermodynamic calculations, the Gibbs energy change should be written in terms of the fugacity of water f_w, and not the vapour pressure p_w, although this distinction is frequently ignored due to the very small differences compared to the usual imprecision of such measurements. However, this correction will be made here.

For the purpose of converting vapour pressures to fugacities, it is convenient to represent the equation of state of the gas as a virial series in terms of the pressure. For the temperature and pressure range covered by the data in Table A.1 (291.8 to 363.6 K and 0.00133 to 0.06286 bar), only the second virial coefficient of water vapour is required for accurate calculations. To this very good approximation,

$$f_w \quad \approx \quad p_w \exp\{B_2(T)\, p_w / RT\}$$

where $B_2(T)$ is the second virial coefficient (which depends on temperature and not pressure). Values of $B_2(T)$ were calculated from the equation of state for water given by Le Fevre, Nightingale and Rose [75LE /NIG]. Typical values of $B_2(T)/RT$ are -0.0775, -0.0467, -0.0302, -0.0207, and -0.0148 bar^{-1}, respectively, at 273.15, 298.15, 323.15, 348.15, and 373.15 K.

Table A.1 contains values of p_w, f_w, and $\ln f_w$ for the experimental vapour pressures. At the lower temperatures, p_w and f_w are essentially equal, but at the higher temperatures f_w is up to (5 to 7)$\times 10^{-5}$ bar lower than p_w. This correction is significant relative to the three to four significant figures reported by Cobble [52COB], but may or may not be significant relative to the actual accuracy of the data.

We represent the fugacities of H_2O(g) above $Tc_2O_7 \cdot H_2O$(s) by the least-squares equation

$$\ln f_w = (12.2686 \pm 0.1480) - (5510.44 \pm 48.65)/T \quad \text{(A.1)}$$

with a correlation coefficient of -0.99992. Similarly, the vapour pressure of water above saturated aqueous $HTcO_4$ follows the least-squares equation

$$\ln f_w = (12.2278 \pm 0.3993) - (5457.05 \pm 136.28)/T \quad \text{(A.2)}$$

with a correlation coefficient of -0.99895. These correlation coefficients are very close to -1, which indicates both that linear equations give accurate representations of these experimental data, and that the heat capacities do not change significantly with temperature over the experimental interval. Vapour pressures for $Tc_2O_7 \cdot H_2O$(s) extend from 291.8 to 363.3 K, so the vapour pressure at 298.15 K can be accurately obtained by interpolation. Figure A.1 is a plot of the experimental vapour pressures and of Eqs. (A.1) and (A.2).

One approach to obtaining $\Delta_f G^\circ_m$ of $Tc_2O_7 \cdot H_2O$(s) would be to calculate it from $\Delta_{sol} G^\circ_m(Tc_2O_7 \cdot H_2O, s, 298.15\ K)$ and $\Delta_f G^\circ_m$ of TcO_4^-. The latter quantity is known. However, the derivation of $\Delta_{sol} G^\circ_m$ requires knowledge of the water activity a_{H_2O}, the molality of $HTcO_4$, and the activity coefficient of $HTcO_4$, all for the saturated solution.

A value of $a_{H_2O}(sat) = (0.073 \pm 0.044)$ was calculated at 298.15 K from our least-squares representation of the vapour pressure values of Cobble, Smith and Boyd for saturated solutions, Eq. (A.2) [52COB, 53SMI/COB]. Isopiestic measurements are available for aqueous $HTcO_4$ at 298.15 K from 0.10581 to 5.4404 mol $\cdot$ kg^{-1}, and they can be used to derive water activities and activity coefficients for $HTcO_4$ in this molality range [78BOY]. This molality range corresponds to water activities of $0.997 \geq a_{H_2O} \geq 0.710$.

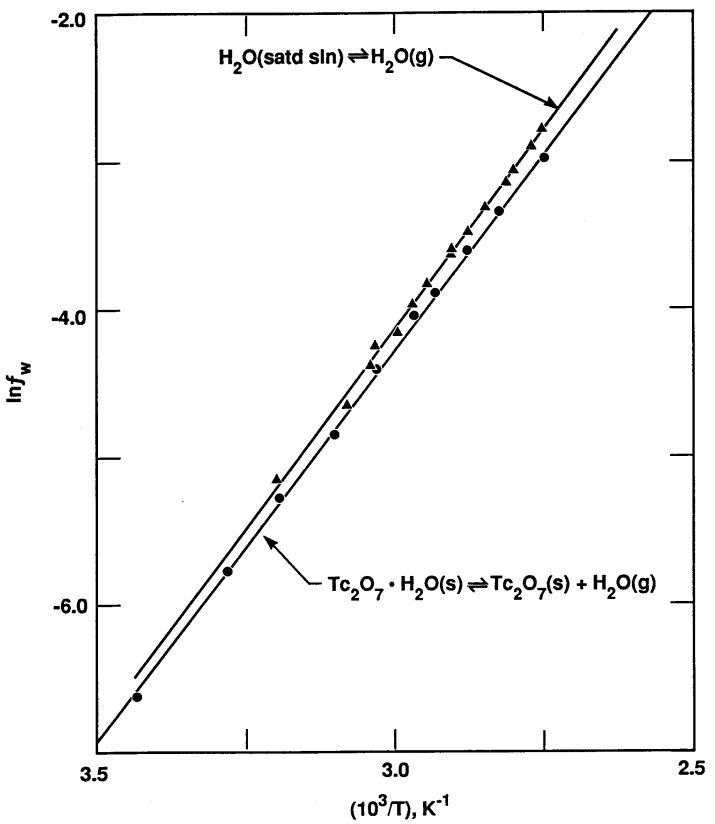
Unfortunately, the solubility of $Tc_2O_7 \cdot H_2O$(s) is unknown. However, vapour pressure results for the chemically similar system $Re_2O_7 \cdot H_2O$(s) [52SMI/LIN] imply that the saturated solutions contain about 45 to 50 mol% of Re_2O_7 and 55 to 50 mol% of H_2O. It is thus likely that the solubility of $Tc_2O_7 \cdot H_2O$(s) at 298.15 K is considerable. It is obvious that insufficient data are available to calculate an experimentally based value for $\Delta_{sol} G^\circ_m$ of $Tc_2O_7 \cdot H_2O$(s).

[55CAR/SMI]

The authors studied the redox potentials of the couple $TcO_4^-/TcO_2 \cdot xH_2O$(s) with the acidic solution cell and dilute solutions of $KTcO_4$ and H_2SO_4, by using the saturated calomel electrode (SCE) as counter electrode. Their $TcO_2 \cdot xH_2O$(s) electrodes were prepared by electrolytic deposition from aqueous $KTcO_4$-H_2SO_4 solutions using platinum foil, wire, or gauze, or a gold wire coil, as the substrait. All potential measurements were done at 297 K.

Experiments were performed for dilute mixtures of aqueous $KTcO_4$ and H_2SO_4, and the SCE compartment had the same concentration of H_2SO_4 as contained in the $KTcO_4$ solution compartment. Their emf values were reported for solutions that were

Figure A.1: Experimental values [52COB, 53SMI/COB] of the natural logarithm of the fugacity of $H_2O(g)$ above $Tc_2O_7 \cdot H_2O(s)$ (●) and saturated aqueous solution in equilibrium with $Tc_2O_7 \cdot H_2O(s)$ (▲). The curves represent the least-squares equations (bottom curve) $\ln f_w = (12.2686 \pm 0.1480) - (5510.44 \pm 48.65)/T$ and (top curve) $\ln f_w = (12.2278 \pm 0.3993) - (5457.05 \pm 136.28)/T$.



deaerated by flushing them with N_2(g) that had been deoxygenated by chemical methods. Cartledge and Smith found that the potentials of freshly-prepared electrodes of $TcO_2 \cdot xH_2O$(s) that were placed into solutions "...without prolonged exposure to solutions containing air became rapidly more noble for a time, and then slowly approached a steady (emf) value." They also found that switching from an atmosphere of N_2(g) to one of air caused the potential to increase (ennoble), but the rate of this potential shift depended on the metal substrait: after 20 minutes the coated gold electrode ennobled by 0.024 V, the platinum coil by 0.021 V, the platinum foil by 0.019 V, and the platinum gauze by 0.009 V. However, in each case the $TcO_4^-/TcO_2 \cdot xH_2O$(s) potentials were still changing with time.

They attributed the gradual approach of the potentials to constant values (after deaerating their solutions with N_2(g)) as being due to removal of the "more active oxygen." They did not explain what they meant by more "active oxygen". The redox potentials were unchanged when the N_2(g) was replaced by Ar(g). Presumably, their measurements in the absence of air are more reliable.

The experiments of Cartledge and Smith were done with solutions containing (1.037 to 1.815) $\times 10^{-3}$ M $KTcO_4$ and (0.5 to 2.0) $\times 10^{-3}$ M H_2SO_4 (pH = 2.49 to 3.10). They also reported a potential values for measurements with $KTcO_4$ alone (pH = 6.65). For the latter experiment, the potential never did reach a constant value but slowly increased with time, in contrast to lower pH values for which constant values of potential were obtained after an initial period of drift. They also found that for TcO_4^- concentrations below about 10^{-4} M, the rate of approach to equilibrium was too slow to give reliable measurements. Spectrophotometry was used to determine the concentrations of TcO_4^- at equilibrium. They reported that $E^\circ = (0.738 \pm 0.003)$ V from their measurements, but their measure of precision was not reported.

[59AND]

According to Anders, Fried and Hall [50FRI/HAL] reported that a volatile dark-purple oxide with oxygen-to-technetium mole ratios of 3.07 and 3.02 was obtained by reaction of technetium with O_2(g) at 673 to 1273 K. They also reported that treating this oxide with aqueous ammonia did not yield NH_4TcO_4, but it was produced when H_2O_2(aq) was added to the reaction mixture. The need for use of H_2O_2(aq) to get TcO_4^- indicates that the valence of technetium in the dark-purple oxide was < 7. This study provides the strongest evidence available for TcO_3(s). Unfortunately, the actual description of the experiments is limited because it appeared only in an abstract [50FRI/HAL], and no mention was made of the dark-purple $TcO_{3+\delta}$.

The formation of yellow Tc_2O_7(cr) by combustion of technetium metal has been reported by Herrell, Busey and Gayer [77HER/BUS]. They noted that the reaction mixture usually contains some red and black compounds as side products and suggested that the black coloured oxide was TcO_3(s) (and not red or purple coloured as assumed by other workers). They also suggested that the red oxide was Tc_2O_5(s). Given that TcO_2(cr) has been reported to be black coloured [54NEL/BOY], the black oxide in Herrell, Busey and Gayer's study may well have been TcO_2(cr).

Various experiments at the Atomic Energy of Canada, Ltd., using thermal decom-

position of NH_4TcO_4 (s) at 1023 K in ultrapure N_2 (g), yielded ~ 40 % of a volatile material that deposited on the cooler walls of the reaction vessel [98LEM]. This material was sometimes red coloured, and reacted rapidly with O_2 (g) and/or water.

Anders [59AND] reported that he had prepared a "pink substance" by oxidation of electrodeposited "TcO_2" by $NaClO_4$. Unfortunately, no experimental details were provided, so the valence in this compound is unknown. We note that electrodeposited TcO_2 is actually a hydrate $TcO_2 \cdot xH_2O$(s).

Anders [59AND] noted that there were early reports that NH_4TcO_4(cr) had a pink or reddish colour, although pure NH_4TcO_4(cr) is colourless. However, the colour of some technetium compounds and salts darkens with time due to radiolytic effects. For example, Vinogradov *et al*. [78VIN/KON3] noted that NH_4TcO_4(cr) stored for two to three months gradually became dark blue and then black, and Busey, Bevan and Gilbert [72BUS/BEV] reported that it "darkened upon standing." Similarly, $(CH_3)_4NTcO_4$, which was colourless when first prepared, gradually became yellowish-gray and finally dark gray [87GER/GRI]. These colour changes were due either to radiation damage to the crystals or most likely to radiolytic decomposition of the TcO_4^- ion. Vinogradov *et al*. [78VIN/KON3] noted that treatment of the dark-coloured NH_4TcO_4(cr) with H_2O_2(aq) and NH_3(aq) caused it to change to the colourless state; any reduced technetium would have been reoxidised back to pertechnetate. Inasmuch as $KTcO_4$(cr) does not undergo a colour change with time [78VIN/KON3], the presence of NH_4^+ or $(CH_3)_4N^+$ cations may be necessary to yield the dark-coloured species.

The purpose of this digression is to point out that a small amount of TcO_2(cr) dispersed in a pertechnetate salt matrix could conceivably appear pink or blueish under certain conditions, and thus by itself provides no evidence for another oxide such as TcO_3(s). Correspondingly, a small amount of TcO_2(cr) dispersed in yellow Tc_2O_7(cr) could possibly make it look pink. In this regard, Spitsyn *et al*. [88SPI/BUK] reported that the product of oxidation of technetium by O_2(g) was reddish coloured after sublimation, but when it was dissolved in water it exhibited the spectrum of TcO_4^-. Thus the major component of their "reddish oxide" must have been Tc_2O_7(cr).

[59BUS]

In 1959, Busey reported that $KTcO_4$ was reduced by aqueous HCl to form a singly oxygenated Tc(V) chloro species. The reduction was slow below about 6 M HCl, but was quite rapid in about 9 to 10 M HCl. For example, shortly after the $KTcO_4$ addition, there was 100% Tc(V) present in 11.86 M HCl, 61% in 8.90 M HCl, and 0.4% in 6.82 M HCl. Addition of H_3PO_2 to the HCl also produced Tc(V). In 12 M HCl, this Tc(V) species was slowly reduced to $TcCl_6^{2-}$. Photolysis of $TcCl_6^{2-}$ by solar radiation in 12 M HCl produced a different Tc(V) species.

In contrast, at 373 K, Jeżowska-Trzebiatowska and Baluka [65JEŻ/BAL] found that TcO_4^- was directly reduced to Tc(IV) by 12 M HCl, but they did observe Tc(V) for reactions at room temperature.

Ossicini, Saracino and Lederer [64OSS/SAR] did a chromatographic separation of the products of reaction of TcO_4^- with aqueous HCl and HBr (see also Ref. [64OSS/SAR] in this Appendix). In each system, an intermediate product of reduction

was found and was assumed to be a Tc(V) species, but no direct evidence was obtained for the valence of technetium. It was reported that TcO_4^- and $TcCl_6^{2-}$ reacted together slowly in 1.2 M HCl to form Tc(V)-oxychlorides [64OSS/SAR]. After 43 hours, 9% Tc(V) had formed, and this increased to 12% after 67 hours. Ossicini, Saracino and Lederer found that TcO_4^- was rapidly reduced by concentrated HCl at 373 K, but some Tc(V) was still present even after 4 hours. This conclusion conflicted with that of Jeżowska-Trzebiatowska and Baluka [65JEŻ/BAL].

At room temperature, Ossicini, Saracino and Lederer [64OSS/SAR] reported that TcO_4^- was reduced by concentrated HBr to Tc(IV) with a Tc(V) intermediate stage. No Tc(V) could be detected after one day reaction with "concentrated" HBr, nor with 80% HBr. With 60% HBr, no formation of Tc(V) was observed until after about one day, and with 40% HBr no reaction with TcO_4^- was observed at all in this time frame.

[60BUS]

Busey reported that zinc metal reduced TcO_4^- in aqueous HCl to produce Tc(III) chloro complexes. Presumably, O_2(g) was not completely excluded from his system since in its absence this reaction is known to produce $Tc_2Cl_8^{3-}$. The technetium in the present study was confirmed to be Tc(III) by using spectrophotometric titration with $Ce(SO_4)_2$. From changes in the ultraviolet spectrum of the solutions as a function of HCl concentration, Busey concluded that one technetium species predominated for 3 to 6 M HCl, and a different one predominated for 0.5 to 2 M HCl. Busey postulated that this spectroscopic change was due to the reaction

$$TcCl_4^- + H_2O(l) \quad \rightleftharpoons \quad TcCl_3(OH)^- + H^+ + Cl^-$$

By measuring the absorbancy at 265 nm for 0.5 to 6 M HCl, he obtained $K_c = 11\ \mathrm{mol^2 \cdot dm^{-6}}$ for this equilibrium reaction. This K_c value must be regarded with some scepticism. First, a more likely formula for the hydrolysed species is $TcCl_5(OH)^{3-}$. Secondly, the ionic strength was not held constant in these measurements, so this "K_c" value must have assimilated large changes in the activity coefficients that cannot be corrected for since the detailed experimental results were not tabulated. Consequently, we do not analyse this K_c value further.

[60COL/DAL]

The authors used polarography to study the reduction of TcO_4^- to Tc(IV) in 0.1 M KOH solution. They observed that the reduction occurred in two stages, corresponding to a two-electron reduction with a well-defined wave at $E_{1/2} = -0.85$ V, and a one-electron step with $E_{1/2} = -1.15$ V. We assume that the experiments were carried out at room temperature. The first value, which is not incompatible with later results obtained under similar conditions, seems to refer to the reduction potential of $TcO_4^- + 2e^- \rightarrow TcO_4^{3-}$. We use this value in our evaluation procedure.

[60MIL/KEL]

The long lived ^{99}Tc isolated from uranium fission product wastes was used. Polarograms were recorded of 10^{-4} M pertechnetate in different supporting electrolytes: 2 M and 10 M H_2SO_4, 4 M $HClO_4$, 0.1 M NaOH, 0.1 M NH_4Cl, 0.1 M KCl, a borate buffer of pH = 10, and a phosphate buffer of pH = 7. The measurements were done at room temperature which was reported to be (299.7 ± 1) K. In pH 7 buffer a linear relationship of i_d *vs.* $[TcO_4^-]$ has been shown over a concentration range of 0.1 to 1.1 ppm pertechnetate.

The observed potentials in 0.1 M NaOH, 0.1 M NH_4Cl (pH = 8.5), and 0.1 M KCl (pH 7-9) were all similar and lay around -0.8 V *vs.* SCE. The value in phosphate buffer (pH = 7) was more positive (-0.68 V), but in borate buffer (pH = 10) a well defined wave was found at $E_{1/2} = -0.79$ V. We assume that the ionic strength of the borate buffer was close to 0.1 M, as was reported for the phosphate buffer. We use the value of 0.8 V reported for NaOH, NH_4Cl and KCl solutions as one entry in the data evaluation procedure (see Table V.8), and the well defined value obtained from the borate buffer experiment also as one entry.

Miller, Kelley and Thomason also reported that the polarographic half wave potentials for reduction of TcO_4^- in an aqueous mixture of K_2HPO_4, KH_2PO_4, and $K_4P_2O_7$ at pH = 7 occurred at -0.68 and -1.35 V *vs.* SCE. The first wave was also present when $K_4P_2O_7$ was absent, but the second wave was there only in the presence of $K_4P_2O_7$. Russell and Cash [78RUS/CAS] reported that polarographic reduction of TcO_4^- at pH = 8.0 in a pyrophosphate solution at $I = 0.1$ M gave 3 e^- per technetium at -0.45 V and 4 e^- at -0.74 V. Anodic reoxidation after the first reduction wave gave 3 e^- per technetium at $+0.16$ V, and reoxidation after the second wave gave 1 e^- at -0.26 V and 4 e^- at $+0.24$ V. Similar potentials were obtained by cyclic voltammetry. Since the potentials from reduction and oxidation experiments are different, the electrochemical process is irreversible and yields no thermodynamic data. However, all these results together with other polarographic, cyclic voltammetric, coulometric, amperometric, and chemical experiments in 0.1 to 0.2 M pyrophosphate [63SAL/RUL, 78STE/MEI, 79RUS/CAS2], indicate that Tc(III) and Tc(IV) complexes were produced.

Additional polarographic experiments by Russell and Cash [79RUS/CAS] for the reduction of TcO_4^- in 0.1 M pyrophosphate solutions at pH = 7 confirm that the initial reduction was to a Tc(IV) complex followed by formation of Tc(III). Both the oxidation and reduction wave potentials were dependent on pH. Above about pH = 10, a 2 e^- reduction of TcO_4^- occurred to Tc(V) and 3 e^- to Tc(IV). However, the same type of 2 e^- and 3 e^- reductions occurred in non complexing media, so these waves in alkaline pyrophosphate solutions did not provide evidence for formation of a pyrophosphate complex.

[61HER/SCH]

In 1961, Herr and Schwochau reported preparation of "$Tl_3Tc(OH)_3(CN)_4$" which should contain Tc(IV). More details were given the following year [62SCH/HER].

This salt was prepared by dissolution of $TcO_2 \cdot xH_2O$(s) in aqueous alkaline cyanide solutions. Addition of Tl^+ salts yielded yellow-brown "$Tl_3Tc(OH)_3(CN)_4$" or "$Tl_3TcO(OH)(CN)_4$", as deduced from elemental analysis. They reported that this formulation was supported by electrical conductivity in water, and IR, visible, and UV spectra [62SCH/HER]. A study of the formation of the corresponding aqueous complex as a function of pH indicated that no cyanide complex formed below pH 5 to 6, and hydroxy cyanide complex formation was complete by pH = 9. Measurement of the light absorption (extinction coefficient) as a function of concentration gave information about the equilibrium

$$Tc(CN)_3(OH)_3^{2-} + CN^- \quad \rightleftharpoons \quad Tc(CN)_4(OH)_3^{3-} \qquad \text{(A.3)}$$

for which they determined K(A.3) $= (1.3 \pm 1.2) \times 10^8$ M^{-1} (presumably at 303 K) for ionic strengths around 10^{-5} M.

Trop, Jones and Davison [80TRO/JON] also reacted $TcO_2 \cdot xH_2O$(s) with aqueous KCN, and showed the pale greenish-yellow product was actually $K_2TcO(CN)_5 \cdot 4H_2O$ and not a $Tc(CN)_4(OH)_3^{3-}$ salt, using elemental analysis and IR and Raman spectroscopy. Reaction of $(NH_4)_2TcI_6$ with KCN in refluxing aqueous methanol in a N_2(g) atmosphere gave yellow-orange $K_4Tc(CN)_7 \cdot 2H_2O$. Its aqueous solutions were air-sensitive and decomposed to pale greenish-yellow $K_2TcO(CN)_5 \cdot 4H_2O$. This cyanide salt could be further hydrolysed in water in the absence of excess CN^- to form lemon-yellow potassium *trans*-dioxotetracyanotechnetate(V), $K_3TcO_2(CN)_4$. The $TcO_2(CN)_4^{3-}$ complex has since been studied by ^{99}Tc-NMR [82FRA/LOC]. These results suggest that Schwochau and co-workers [61HER/SCH, 62SCH/HER] actually had studied the Tc(V) complex $TcO(CN)_5^{2-}$ rather than the Tc(IV) complex "$Tc(OH)_3(CN)_4^{3-}$". Similarly, a claim by Colton for preparation of $Tc(CN)_6^{2-}$ salts by reaction of TcI_6^{2-} with CN^- in methanol (cited in the Gmelin Handbook [83ALL/BUR]) is apparently incorrect, since only $K_4Tc(CN)_7 \cdot 2H_2O$ has been isolated under these conditions [80TRO/JON].

[62KUZ/ZHD]

The reduction processes of TcO_4^- were investigated in 1 M $NaClO_4$ solution. The authors mention that they found analogous behaviour in 1 M Na_2SO_4 solution. According to the authors, this would mean that the same reduction processes occur in these aqueous media: in acidic solutions TcO_4^- is reduced to the tetravalent state, in acidic solutions a three-electron reduction of undissociated molecules of pertechnetic acid takes place, and in alkaline solutions the reduction proceeds to the pentavalent state and at more negative potentials to the hexavalent state.

It is not quite clear from this paper whether the authors used an SCE (as they mentioned on the potential axis in every figure) or a "normal calomel electrode" (as they stated in the text). The standard potential of the SCE and the "normal calomel electrode" differ by 0.039 V [61HIL/IVE]. They reported a half-wave potential of 0.87 V for the two-electron reduction of TcO_4^- in 1 M $NaClO_4$, but this obviously should read -0.87 V. If an SCE was used, then the potential *vs*. NHE is -0.63 V, and if a "normal

calomel electrode" was used, the potential *vs*. NHE is −0.59 V. However, this value seems to be an outlier anyway, since potentials reported in the later literature for 1 M solutions are in the range of −0.52 and −0.56 V. We do not consider this value in our data selection procedure.

[62SCH/AST]

Schwochau and Astheimer reported electrical conductances of aqueous $KTcO_4$ solutions at (298.15 ± 0.10) K for eight concentrations from 5.83×10^{-5} to 9.716×10^{-3} M. They extrapolated the equivalent conductances Λ to infinite dilution to obtain $\Lambda^\circ(KTcO_4, aq, 298.15\ K) = (129.0 \pm 0.5)\ S \cdot cm^2 \cdot equiv^{-1}$, from which they calculated $\Lambda^\circ(TcO_4^-, aq, 298.15\ K) = (55.5 \pm 0.5)\ S \cdot cm^2 \cdot equiv^{-1}$. They then used this limiting ionic conductance to calculate the tracer diffusion coefficient of aqueous TcO_4^- at infinite dilution. Their conductances were apparently reported in units of international ohms rather than absolute ohms. They evaluated the limiting ionic conductance graphically.

We reextrapolated these electrical conductances to infinite dilution by using the Debye-Hückel-Onsager limiting law as given by Equation 7.31 of Robinson and Stokes [59ROB/STO]. For an aqueous 1-1 electrolyte at 298.15 K, that Equation becomes $\Lambda = \Lambda^\circ - (0.2300\Lambda^\circ + 60.64) I_c^{\frac{1}{2}}$ for ionic strengths on the molar concentration scale. A plot of Λ against $I_c^{\frac{1}{2}}$ for aqueous $KTcO_4$ indicates the individual Λ are uncertain by about 0.5 $S \cdot cm^2 \cdot equiv^{-1}$. A least-squares analysis of the conductance data gives $\Lambda = (128.96 \pm 0.53) - (64.63 \pm 9.83) I_c^{\frac{1}{2}}$ for conductances in int-$S \cdot cm^2 \cdot equiv^{-1}$, with σ(fit) = 0.40. The correlation coefficient for this fit is −0.982. Taking the intercept, $\Lambda^\circ(TcO_4^-, aq, 298.15\ K) = (128.92 \pm 0.53)\ S \cdot cm^2 \cdot equiv^{-1}$ for conductances converted to absolute ohms. Using the ionic conductance of aqueous K^+ from Robinson and Stokes [59ROB/STO] then gives $\Lambda^\circ(TcO_4^-, aq, 298.15\ K) = (55.44 \pm 0.53)\ S \cdot cm^2 \cdot equiv^{-1}$. The calculated tracer diffusion coefficient then becomes $D^\circ(TcO_4^-, aq, 298.15\ K) = (1.48 \pm 0.01) \times 10^{-5}\ cm^2 \cdot s^{-1}$.

[62SCH/HER]

See comments under [61HER/SCH].

[63EAK/HUM]

The authors reported the preparation of a crystalline complex which they formulated as "$Tc(NH_2OH)_2(NH_3)_3(H_2O)Cl_2$". This empirical formula was based on chemical analysis and by determining the number of equivalents of ceric sulphate required to oxidise it to form TcO_4^-, and the presence of one molecule of water was assumed to give the technetium atom 6-coordination. This complex was prepared by reacting aqueous $(NH_4)_2TcCl_6$ with 2 M hydroxylamine-hydrochloride $NH_2OH \cdot HCl$ followed by evaporation to dryness. The solid was then extracted several times with diethylether, and subsequently dissolved in a minimal amount of H_2O(l) to which ammonia was

added until pH = 7. The result was a mixture, from which the above complex was isolated and purified by several dissolutions in water followed by precipitations with absolute ethanol. See comments under [76ARM/TAU].

[63LEF]

The aim of this investigation was to study the effect of γ-radiation from a radiocobalt source of 600 Ci on the TcO_4^-/TcO_2(s) couple in dilute solution. The ionising radiation was able to oxidise TcO_2(s) to TcO_4^-. The TcO_2(s) solutions in sulphuric acid were prepared by dissolving electrodeposited TcO_2(s) with concentrated sulphuric acid followed by dilution to the needed H_2SO_4 concentration, *i.e.*, 0.5 or 0.05 M. Both solutions, after centrifugation of the solid TcO_2(s), showed a technetium concentration of approximately 5×10^{-5} M - 5×10^{-4} M. This is orders of magnitude higher than the solubilities measured by Meyer *et al.* [91MEY/ARN2], from which one would, in addition, expect a large difference between 0.05 and 0.5 M H_2SO_4. The explanation is that TcO_2(s) was oxidised to TcO_4^- upon dissolution. Lefort [63LEF] showed by spectrophotometry that the equilibrated solutions contained TcO_4^- as the only technetium species. The equilibration process of the solutions was not experimentally followed. We note that electrodeposition of technetium from acidic solutions of TcO_4^- actually yields the hydrated dioxide $TcO_2 \cdot xH_2O$(s).

[63SAL/RUL]

Salaria, Rulfs and Elving studied the coulometric reduction of solutions of TcO_4^- in the presence of a mixture of 0.2 M Na_2CO_3, 0.1 M $NaHCO_3$, and 0.5 M KCl using a mercury pool cathode. The solutions were deoxygenerated before starting the reduction. The pH of the solution was 9.80 and a 3 e^- per technetium reduction was observed at -0.51 V; alkaline solutions of TcO_4^- containing KCl and KOH or K_2SO_4 and KOH at $I = 0.5$ M underwent 3 e^- reductions at a similar emf of -0.61 V, where these potentials are relative to the NHE. Coulometric reduction of TcO_4^- in carbonate solutions provided no direct evidence for complex formation between carbonate and Tc(IV) under these conditions.

They reported that TcO_4^- could be reduced electrolytically using coulometry, to give a precipitate of $TcO_2 \cdot xH_2O$(s). However, if the initial reduction of TcO_4^- was done in aqueous H_2SO_4 or HCl-KCl mixtures at more negative potentials, *e.g.*, -0.3 V for HCl-KCl at pH = 1.3, then a 4 e^- reduction occurred to form a solution of Tc(III). The two waves for reduction of TcO_4^- to Tc(III) or Tc(IV) were observed from pH $= -0.3$ to about 4, whereupon the reduction wave denoted by them as "II" disappeared abruptly, and their wave "I-A" decreased rapidly in intensity and was absent by pH = 5. This indicates that major changes occur around pH = 4 in the mechanisms for reduction of TcO_4^-. Salaria, Rulfs and Elving were able to generate a suspension of solid Tc(III) for pH < 4 by reduction of TcO_4^-, and they formulated that solid as "Tc_2O_3(s)".

[63SHV/KOT]

Shvedov and Kotegov performed electromigration experiments for aqueous $NaTcO_4$ and $KTcO_4$ solutions at 291 K. They reported values of the ionic mobilities and electrical conductances at 0.0005, 0.005, 0.01, and 0.02 M for $NaTcO_4$ and at 0.0005 and 0.02 M for $KTcO_4$. From these results they derived an ionic conductance of $\Lambda^\circ(TcO_4^-, \text{aq}, 291\ \text{K}) = 51.1\ \text{S} \cdot \text{cm}^2 \cdot \text{equiv}^{-1}$, but the method of extrapolation of data to infinite dilution was not described. We did not reextrapolate these results to infinite dilution because of the limited number of experimental points and because we are uncertain as to the reliability of the method, and neither they nor we assign an uncertainty to this value. However, it is given for completeness. They did similar measurements for aqueous $KReO_4$, and reported that their results agreed with literature data.

Shvedov and Kotegov also studied the concentration dependence of the mobilities of aqueous $NaTcO_4$ and $KTcO_4$ solutions from 0.0005 to 0.02 M at 291 K. These mobilities were determined by use of electrophoresis. They found that aqueous $NaTcO_4$ was completely dissociated in this molarity range, but that $KTcO_4$ was slightly associated. They reported that the dissociation constant:

$$K \quad = \quad [K^+][TcO_4^-]/[KTcO_4(\text{aq})]$$

was $(0.122 \pm 0.010)\ \text{mol} \cdot \text{dm}^{-3}$ in KNO_3 solutions, but it is not possible to assess the accuracy of this value for reasons given below. They cited agreement with a theoretically calculated value of $0.129\ \text{mol} \cdot \text{dm}^{-3}$ for K of $KTcO_4$(aq) as given by Cobble, Smith and Boyd [53COB/SMI]. However, Cobble, Smith and Boyd actually reported a solubility product rather than a dissociation constant, so the agreement of numerical values is accidental. Similarly, they obtained $K \approx 0.23\ \text{mol} \cdot \text{dm}^{-3}$ for $CsTcO_4$ in aqueous CsCl solutions.

The method of calculation used by Shvedov and Kotegov requires values of the mobility of the total electrolyte (an experimental quantity), the mobility of the anion, and activity coefficients for the ions. However, they took their activity coefficients "...from tables for a uni-univalent electrolyte at 18°C", but the electrolyte used as a surrogate for $KTcO_4$ was not mentioned. In addition, they assumed that the mobility of TcO_4^- in water could be equated to that of TcO_4^- in 0.02 M aqueous $NaNO_3$. Their calculations contained additional approximations in that the change in mobility of aqueous $KTcO_4$ with concentration was attributed solely to ionic association, and electrostatic contributions to the variation in mobility were neglected. In view of all of the above considerations, it is likely that the value of K reported by Shvedov and Kotegov is quite uncertain. In addition, since K was reported only at 291 K, it is not known how much it will change by 298.15 K.

Values of K have been reported for aqueous $KClO_4$, $RbClO_4$, and $CsClO_4$ at 298.15 K [70BUR/JUS], based upon high-precision measurements of electrical conductances from 0.002 to 0.003 up to 0.03 to 0.08 $\text{mol} \cdot \text{dm}^{-3}$. Their derived values of K are 1.1, 0.7, and 0.6 $\text{mol} \cdot \text{dm}^{-3}$ for $KClO_4$, $RbClO_4$, and $CsClO_4$, respectively. However, the lighter alkali metal perchlorates $LiClO_4$ and $NaClO_4$ appear to be essentially completely dissociated at these low molarities. This trend for the perchlorates is in rough agreement with that claimed for $NaTcO_4$ and $KTcO_4$ [63SHV/KOT], and

suggests that the value of K reported for $KTcO_4$ is meaningful even if highly uncertain. Because of this uncertainty, we will formally treat $KTcO_4$ as being completely dissociated for thermodynamic calculations. This is in agreement with the conventional thermodynamic treatments of alkali metal perchlorates and most other slightly associated electrolytes.

[63TER/ZIT]

The coulometric reduction of TcO_4^- in sodium tripolyphosphate ($Na_5P_3O_{10}$) solutions was investigated. At pH = 4.7 in an acetate-buffered solution, the colourless TcO_4^- ion was reduced to pink Tc(IV) followed by an orange mixture of Tc(IV) and Tc(III), and then it was finally reduced to a yellow Tc(III) solution. However, in a pH = 7.0 phosphate-buffered tripolyphosphate solution, the colour change was from colourless TcO_4^- to pink Tc(IV) followed by a grey mixture of Tc(IV) and Tc(III), and finally green Tc(III) was produced. Some further reduction of Tc(III) was also observed, but it was incomplete because this reduced species reacted with water or an ion. If the Tc(III) solution was allowed to sit in the presence of air, it became oxidised back to the pink Tc(IV) species.

Polarographic measurements were also reported. The half-wave potentials for the reduction of Tc(IV) to Tc(III) and the reoxidation of Tc(III) to Tc(IV) in pH = 4.7 acetate-buffered tripolyphosphate solution both occurred at −0.24 V so this redox process was reversible.

[64OSS/SAR]

The authors studied the hydrolysis of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ in aqueous HCl and HBr, respectively, using ion exchange chromatography on ion exchange paper. Studies were done of the hydrolysis of $TcCl_6^{2-}$ in 1.2 M HCl and $TcBr_6^{2-}$ in 0.9 M HBr at room temperature. They found that very little of the $TcBr_6^{2-}$ was still present after 24 hours, but that $TcCl_6^{2-}$ was still the predominant species after 139 hours. Based on the number of chromatographically separated technetium containing species and their rates of migration, they suggested that $TcBr_5^-$, $TcBr_4$(aq), $TcCl_5^-$ and $TcCl_4$(aq) species were the predominant neutral and anionic hydrolysed forms, and that other neutral and cationic species may have also been present in the bromide system. Their results indicated that $TcCl_6^{2-}$ was more stable than $TcBr_6^{2-}$ towards hydrolysis; (see also Ref. [59BUS] in this Appendix).

[65JØR/SCH]

Jørgensen and Schwochau studied the absorption spectra of aqueous solutions of TcX_6^{2-}, (X = F, Cl, Br, and I), from about 200 to 1200 nm. Although TcF_6^{2-} could be studied in water, solutions of relatively concentrated HX were required for the other three cases. They concluded that the tendency for hydrolysis to occur increased from chloride to bromide to iodide. In fact, hydrolysis of TcI_6^{2-} was rapid even in aqueous 57 mass-% iodine-free HI. Based on absorption spectra measurements for

$TcCl_6^{2-}$ in aqueous HCl and for $TcBr_6^{2-}$ in aqueous HBr as a function of temperature, Kawashima, Koyama and Fujinaga [76KAW/KOY] concluded that aquation of $TcBr_6^{2-}$ proceeded more rapidly and at lower temperatures than for $TcCl_6^{2-}$.

[65SPI/KUZ]

The paper deals with the problem of obtaining pure compounds of technetium from neutron-irradiated molybdenum metal and from the waste of plutonium production. It includes a study of the chemical and electrochemical properties of technetium.

Spitsyn *et al*. studied the electrodeposition of $TcO_2 \cdot xH_2O$(s) onto a platinum electrode. Solutions that were studied contained initially 2×10^{-5} M TcO_4^- in dilute aqueous H_2SO_4 at pH = 2.3, and TcO_4^- in aqueous $(NH_4)_2SO_4$ at pH = 5.6. By determining the fraction of TcO_4^- that had been plated out a a function of the applied cathodic potential, they were able to estimate that $E^\circ \approx 0.71$ V for the $TcO_4^-/TcO_2 \cdot xH_2O$(s) redox couple as given by Eq. (V.2).

[66LAV/STE]

Thermal decomposition of $(NH_4)_2TcF_6$(cr) in argon was studied by thermogravimetric analysis. A weight loss of 46.5% was observed. Reduction of this residue with H_2(g) to technetium metal at 773 K then gave an additional weight loss of 25.5%. These weight loss values are consistent with the initial residue being "TcNF(cr)". Powder pattern data indicated a hexagonal unit cell with $a = 5.98 \times 10^{-10}$ m and $c = 3.80 \times 10^{-10}$ m. This is in contrast (surprisingly) with ReNF(cr), which has a tetragonal unit cell.

Cowie, Lock and Ozog [70COW/LOC] argued that the X-ray evidence for "TcNF(cr)" was ambiguous. They stated that its lattice spacings were virtually identical to those of $(NH_4)_2ReF_6$(cr). They thus suggested that LaValle, Steele and Smith [66LAV/STE] actually had $(NH_4)_2TcF_6$(cr) and not TcNF(cr). However, their argument is somewhat weakened since the actual unit cell parameters (they gave $c = 4.79 \times 10^{-10}$ m for TcNF(cr), rather than the reported value of 3.80×10^{-10} m from LaValle, Steele and Smith) do not agree well. It must be acknowledged that more direct evidence for TcNF(cr) is desirable.

[67RUL/PAC2]

Rulfs, Pacer and Hirsch reported that when a 0.05 M solution of $HTcO_4$ was concentrated to 0.3 M, it became red coloured. They observed that this solution, if left in contact with the atmosphere, gradually formed a precipitate of black "TcO_2(s)" (presumably, hydrated), and a red solution remained. Addition of Ce(IV) caused the solution to become deeper red, as the "TcO_2(s) " was oxidised, and then colourless. If the oxidisable red species was assumed to contain Tc(VI), then up to 32% of the technetium was calculated to be present in this form, based on the amount of Ce(IV) consumed. They suggested that some Tc(VI) or Tc(V) formed in concentrated solutions of $HTcO_4$, possibly by reduction of $HTcO_4$ by dust or by traces of organic vapours in the air. The other possibility that they suggested was that concentrated solutions of $HTcO_4$ may

spontaneously decompose with evolution of O_2(g). In any case, it appears that the red colour of "$Tc_2O_7 \cdot H_2O$(s)" may be due to the presence of lower valence technetium species, and pure "$Tc_2O_7 \cdot H_2O$(s)" may possibly be colourless or yellow.

[68MÜN2]

In this careful study, various reduction processes were identified by using several different techniques. The reduction of TcO_4^- was investigated in solutions of 0.1 M NaOH containing 0.5 M of another inert salt ($NaClO_4$, sodium citrate, KSCN, and NaCl, respectively). Three reduction steps were identified and half-wave potentials *vs.* SCE reported: Tc(VII) + $2e^-$ → Tc(V): $E_{1/2} = -810$ mV; Tc(V) + e^- → Tc(IV): $E_{1/2} = -900$ mV, and Tc(IV) + e^- → Tc(III), $E_{1/2} = -1100$ mV, for the non-complexing media.

[68SCH/PIE]

Schwochau and Pieper reported preparation of a "Tc(V)" complex by reaction of $TcO_2 \cdot xH_2O$(s) or reduction of TcO_4^- in acidic thiocyanate solutions. They reported the preparation of salts with $(CH_3)_4N^+$ and Tl^+. One of these salts, "$(CH_3)_4NTc(NCS)_6$(cr)", was characterised by IR spectra and found to contain Tc-N bonds but not Tc-O bonds. A powder pattern X-ray study of this salt [73HAU/SCH] indicated a rhombohedral unit cell with $a = 8.84 \times 10^{-10}$ m and $\alpha = 82.9°$.

Schwochau, Astheimer and Schenk [73SCH/AST] further investigated the purported Tc(V)-SCN complex and its reduction product. Their elemental analyses indicated the two salts were yellow "$((CH_3)_4N)_2Tc(NCS)_6$" and violet "$(CH_3)_4NTc(NCS)_6$". Absorption, UV, and IR spectra were reported, as were molar electrical conductances for their solutions in acetonitrile. These conductance values indicated that $(CH_3)_4N^+$ salts behaved like 2:1 and 1:1 electrolytes, respectively, in that solvent. Their effective magnetic moments of the solid complexes at 293 K were 2.65 and 2.34 B.M., respectively.

Reinvestigation of technetium isothiocyanato solutions and salts by Trop *et al.* [80TRO/DAV] indicated that Schwochau and coworkers [68SCH/PIE, 73SCH/AST] were probably in error in assigning technetium valences of V and IV to the violet and yellow salts, respectively. Trop *et al.* [80TRO/DAV] prepared purple salts with the stoichiometries $(NH_4)_2Tc(NCS)_6$ and $(AsPh_4)_2Tc(NCS)_6$ which contain Tc(IV), and yellow to yellow-orange air-sensitive ($(n\text{-}C_4H_9)_4N)_3Tc(NCS)_6$(cr) and $(AsPh_4)_3Tc(NCS)_6$ which contain Tc(III). Both $(NH_4)_2TcBr_6$ and NH_4TcO_4 were reacted with NH_4SCN in methanol to prepare them, but H_2SO_4 was also added when NH_4TcO_4 was used, and air-free conditions were required to get Tc(III) salts. A detailed single-crystal X-ray structure determination for ($(n\text{-}C_4H_9)_4N)_3Tc(NCS)_6$(cr) showed it was cubic, with $a = (24.444 \pm 0.012) \times 10^{-10}$ m, $Z = 8$, and space group $P_a\bar{3}$. H_2O_2(aq) oxidised $Tc(NCS)_6^{3-}$ solutions to TcO_4^- and SCN^-. Addition of NO(g) to $Tc(NCS)_6^{3-}$ solutions in dichloromethane yielded $Tc(NCS)_6^{2-}$ solutions. The $Tc(NCS)_6^{2-}/Tc(NCS)_6^{3-}$ redox couple in acetonitrile was 1 e^- and reversible at −0.42 V. Since the purple species was obtained upon oxidation of the yellow species,

this confirmed that the violet-to-purple coloured solutions and solid complexes contained Tc(IV). Addition of Ce(IV) or thiocyanogen, $(NCS)_2$, to non-aqueous solutions of $Tc(NCS)_6^{3-}$ produced $Tc(NCS)_6^{2-}$ rapidly.

[69GOR/KOC]

The authors used electrophoretic mobility measurements to investigate the behaviour of Tc(IV) in aqueous solution at varying pH, 18°C and $I = 0.1$ M (KNO_3). They obtained a curve "mobility *vs*. pH" [69GOR/KOC, Figure 2] between pH 1 and 2.5. Their interpretation of this curve was that Tc(IV) was present as an ion with charge +2 at pH = 1, and as an ion with charge +1 at pH = 2. They proposed the following reactions:

$$TcO^{2+} + H_2O(l) \rightleftharpoons TcO(OH)^+ + H^+ \quad (A.4)$$

$$TcO(OH)^+ + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) + H^+ \quad (A.5)$$

with the constants ${}^*K$(A.4) $= (4.3 \pm 0.4) \times 10^{-2}$ and ${}^*K$(A.5) $= (3.7 \pm 0.4) \times 10^{-3}$. The pH scale in their Figure 2 shows that more than 90% of each of the Reactions (A.4) and (A.5) take place within a very narrow range of only 0.3 pH units. However, as investigations of similar equilibria with other diprotic acids show, the Equilibria (A.4) and (A.5) require, for monomeric species, a change of more than 1 pH unit for the same extent of deprotonation. Furthermore, the value $\log_{10}{}^*K$(A.5) $= -(2.43 \pm 0.05)$ would mean that at pH $= 2.43$ equal concentrations of $TcO(OH)^+$ and $TcO(OH)_2(aq)$ are present, but according to Figure 2 of [69GOR/KOC] the mobility is about zero at pH > 2.2, which means that no appreciable amount of ionic Tc species could be present in solution. This curve could only be explained if all involved species showed a nuclearity of 3 or larger and if the deprotonation reactions occurred in two distinct steps.

Other weak points of the paper under discussion are: (1) the use of an unknown technetium concentration; (2) the lack of precautions and control in order to avoid changes in the oxidation state of Tc; (3) the ionic strength of the solutions below pH 2 was larger than 0.1. Beneš and Glos [79BEN/GLO] showed that the method used by Gorski and Koch [69GOR/KOC] can give erroneous results if the mobilities measured are disturbed by a significant adsorption of the trace element on the walls of the apparatus or on the supporting porous medium. Consequently, adsorptions during electrophoresis should be kept as low as possible. It is known that hydrolysis is accompanied and often preceded by strong adsorption of trace elements on any available surface. The adsorption causes a decrease in the apparent mobility of the trace element in solution. For all these reasons it seems not appropriate to consider further the results of this paper.

[69KAN]

Kanchiku reported measurements of the absorption spectra of K_2TcCl_6(cr) dissolved in aqueous 0.1, 1.0, 3.0, 6.0, 8.0, and 12.0 M HCl at 293 K. He found that $TcCl_6^{2-}$ from K_2TcCl_6(cr) that had been dissolved in aqueous HCl was unaffected by UV light for HCl concentrations $\geq$ 12 M, but at lower HCl concentrations photochemical aquation

of $TcCl_6^{2-}$ occurred that took about 2 weeks to reach equilibrium at 293 K under constant irradiation. The amounts of the individual hydrolysis products varied with HCl concentration. However, solutions of K_2TcCl_6(cr) in 0.1 to 12 M HCl that were stored in the dark showed no spectroscopic changes with time and thus still contained $TcCl_6^{2-}$.

Solutions of $TcCl_6^{2-}$ in various concentrations of HCl were subjected to photochemical aquation for two weeks at 293 K, and the resulting chemical species were separated on ion exchange columns. The various eluted species were kept in the dark to prevent further photochemical reaction. These eluted fractions were analysed for technetium, generally by radioactive counting but sometimes by spectrophotometry, and for chloride. The charges on the complexes were obtained by ion exchange or electrophoresis. Kanchiku observed a chemical species with a charge of about −1.7 and a chloride-to-technetium mole ratio of 5.98 to 6.05, and Koyama, Kanchiku and Fujinaga [68KOY/KAN] observed a charge of about −1.8 and a chloride-to-technetium mole ratio of 6.046 to 6.077. This chemical species was obviously $TcCl_6^{2-}$. Another fraction that was eluted gave a charge of about −0.73 and chloride-to-technetium mole ratio of 5.23 to 5.27 [69KAN], and a charge of about −0.9 and chloride-to-technetium mole ratio of 5.024 to 5.040 [68KOY/KAN]. The formula $TcCl_5^-$ can thus be assigned. Koyama, Kanchiku and Fujinaga [68KOY/KAN] in their studies of the photochemical aquation of $TcCl_6^{2-}$, noted that solutions of yellow-coloured $TcCl_5^-$ became brownish if the pH was decreased below 1. They suggested that the reaction

$$TcCl_5^- + H_2O(l) \quad \rightleftharpoons \quad TcCl_5(OH)^{2-} + H^+$$

gave rise to this colour change. This is the same type of hydroxychloride as was formed by the reduction of TcO_4^- in HCl by using HI. Actually, an increase in pH seems more likely to produce acidic dissociation of this type rather than the claimed decreasing pH. Kanchiku [69KAN] also separated complexes with charges of 0 and +0.81, to which they tentatively assigned the formulas $TcCl_4$(aq) and $TcCl_3^+$. They could not be separated from the solution without being decomposed, which precluded the possibility of chemical analysis.

Similar experiments were performed for $TcBr_6^{2-}$ in 0.5 M H_2SO_4 at 323 K [76KAW/KOY], but aquation occurred rapidly enough that they quenched the reaction by cooling the solution in an ice bath. Ion exchange was used to separate the resulting chemical species; the first elution band contained both cationic and uncharged species. Chemical analysis of the isolated complex from the second band gave bromide-to-technetium mole ratios of 4.71 to 5.10, and from the third peak gave bromide-to-technetium ratios of 5.93 to 6.04. These two chemical species were thus $TcBr_5^-$ and $TcBr_6^{2-}$ [76KAW/KOY]. The photochemical aquation of K_2TcBr_6(cr) in aqueous 1 or 2 M HBr, $HClO_4$, and H_2SO_4 showed variations in the amount of individual products with the type of acid used [88COL/IAN]. A more detailed review of the photolysis of aqueous technetium solutions was published by Friedman [81FRI].

[69KIS/FEL]

The authors studied the reduction behaviour of TcO_4^- in alkaline solutions of I = 1 M, using chronoamperometric methods. Without gelatin, reduction from TcO_4^- to Tc(V)

occured directly:

$$TcO_4^- + 2e^- \quad \rightarrow \quad Tc(V) \tag{A.6}$$

When 0.005% gelatin or more was added, the mechanism shifted to a $1e^-$ reduction according to

$$TcO_4^- + e^- \quad \rightarrow \quad TcO_4^{2-} \tag{A.7}$$

Rard [83RAR] estimated, from the "apparent *n*" *vs*. potential curves, the aqueous reduction potential as E(A.7, I = 1 M) = $-(0.62 \pm 0.05)$ V, converted to refer to the NHE. From the curve "apparent *n*" *vs*. potential in the case of no addition of gelatin, Rard [83RAR] estimated E(A.6, I = 1 M) = -0.55 V.

[69MAJ/PAC]

Majumdar, Pacer and Rulfs determined the solubility of $Ba(TcO_4)_2$(s) at (293.2 ± 0.1) and (308.2 ± 0.1) K, by using a small-scale saturator column along with radiometric determination of the concentration of ^{99}Tc in the saturated solutions. They did similar solubility test experiments for aqueous NaCl, AgCl, and K_2CrO_4, and reported agreement to $\pm 0.8\%$ to $\pm 3.1\%$ with literature values for those solubilities. Based upon that information, we conservatively estimate that their solubilities for $Ba(TcO_4)_2$(s) are uncertain by $\pm 3\%$.

The solubility of $Ba(TcO_4)_2$(s) was studied at two temperatures. We represented this temperature dependence with the equation $\ln(4c_s^3) = A + BT^{-1}$ where $A = 44.249$ and $B = -14150.6\ K$. This concentration product is equivalent to a solubility product on the molarity scale but without activity coefficient corrections. We intend that this equation be used only for smoothing and interpolation of the experimental solubilities. We do not consider it to be reliable for calculation of enthalpies of solution, because of the fairly large uncertainty in the reported solubilities, and because of the neglect of activity coefficients.

In addition, the solubility of $Ba(TcO_4)_2$(s) is high enough that an estimated value of its activity coefficient would be fairly uncertain. Also, because only two temperatures were studied, it is difficult to estimate the reliability of the value of c_s at 298.15 K obtained by interpolation. Thus we do not reanalyse the $Ba(TcO_4)_2$(s) solubilities.

[70COW/LOC]

See comments under [66LAV/STE].

[71CAR2]

Cartledge used electrodes of technetium metal, or of gold or platinum onto which a layer of technetium was added. Those technetium covered electrodes in some cases were prepared by direct plating with technetium metal, whereas others were prepared by coating the electrodes with electrolytically generated "$Tc(OH)_4$(s)",

followed by drying the electrode and then reducing the surface with $H_2(g)$ to form technetium metal. The results of some related experiments were reported in a second paper [71CAR]. In some experiments the electrode was coated with a layer of "$Tc(OH)_4(s)$", which was then partially reduced to lower-valence hydrous oxides by cathodic polarisation.

Table A.2 contains the "corrosion potentials" reported by Cartledge for various redox couples involving technetium metal and various surface films of hydrous oxides. Although these measurements were performed in a laboratory whose temperature was controlled at 297 K, and not in a thermostatted temperature bath at 298.15 K, the temperature dependence of the emfs should be small enough that these values should be equal to those at 298.15 K within the precisions of the measurements. Cartledge used a saturated calomel electrode (SCE) as a reference electrode and adjusted the emfs by adding 0.245 V to convert them to potentials relative to the standard hydrogen electrode. According to Table VI of Hills and Ives [61HIL/IVE], a potential difference of (0.2445 ± 0.0001) V is appropriate for buffer solutions in contact with an SCE and (0.2450 ± 0.0001) V is appropriate for an acidic solution in contact with an SCE, in both cases when a salt bridge is present to reduce the contribution of the liquid junction potential, but a potential difference of (0.2412 ± 0.0002) V should be used when a salt bridge is absent. Cartledge described his measurements as having been performed in a large H-cell; presumably this cell contained a salt bridge.

Six of the corrosion potentials were only observed at a single pH value, whereas seven others were observed at two different pH values. However, two of the proposed "corrosion" reactions were observed at five different pH values, and another at seven. In addition, those potentials that were observed at more than one pH had the correct Nernstian slope of $0.059\ V \cdot pH^{-1}$, which indicates that these "corrosion" potentials represent reversible (or at least quasi-reversible) redox reactions. Thus they could be used to derive valid thermodynamic results for the hydrous oxides involved in these redox couple if the oxidised and reduced forms of technetium can be identified.

Given that oxygen was excluded from the cell it is unlikely that significant amounts of higher oxides or dissolved pertechnetate ions were formed. Cartledge thus postulated the formation of a number of hydrous surface oxides on his polarised electrodes which he formulated as $Tc(OH)(s)$, $Tc(OH)_2(s)$, $Tc(OH)_3(s)$, and $Tc(OH)_4(s)$, along with two mixed-valence hydrous oxides $Tc_3O_4(s)$ and $Tc_4O_7(s)$. He then attributed the 16 E° values in Table A.2 to various redox reactions involving these hydrous oxides. However, the potentials labeled (c), (d), (e), (f), (g), (l), and (p) in Table A.2 were detected at only a single pH. Thus there is no way of knowing if they really represent reversible or quasi-reversible redox reactions, or even if the corresponding extrapolations of these emfs to pH = 0 by Cartledge give meaningful E° results. Thus those potentials are rejected.

These redox couples involve solid state redox reactions for essentially insoluble hydrous oxides, and the only aqueous species that is involved in H^+. Consequently, only the pH dependence of the redox couples could be studied. Unfortunately, for this type of system, a reduction involving $1e^-$ and $1H^+$ can not be distinguished from another one involving $2e^-$ and $2H^+$, $3e^-$ and $3H^+$, or $4e^-$ and $4H^+$. Thus there is no direct evidence for the redox reactions that correspond to each of the redox couples.

Table A.2: Listing of the experimental "corrosion potentials" of Cartledge [71CAR2] and the pHs at which they were observed, along with his claimed reactions

E° / V[(a)] (experimental)	E° / V (normalised)	pHs	Reactions
a) 0.034 ±0.010	0.031	0.35, 2.05	$TcOH(s) + H^+ + e^- \rightleftharpoons Tc(s) + H_2O(l)$
b) 0.073 ±0.004	0.072	0.35, 3.65	$Tc(OH)_2(s) + 2H^+ + 2e^- \rightleftharpoons Tc(s) + 2H_2O(l)$
c) n.o.[(b)]	0.112		$Tc_3O_4(s) + 8H^+ + 8e^- \rightleftharpoons 3Tc(s) + 4H_2O(l)$
d) 0.114 ±?	0.113	3.65	$Tc(OH)_2(s) + H^+ + e^- \rightleftharpoons TcOH(s) + H_2O(l)$
e) 0.167 ±?	0.161	0.35	$Tc_3O_4(s) + 5H^+ + 5e^- \rightleftharpoons 3TcOH(s) + H_2O(l)$
f) 0.190 ±0.012	0.185	0.35	$Tc(OH)_3(s) + 3H^+ + 3e^- \rightleftharpoons Tc(s) + 3H_2O(l)$
g) 0.234 ±0.008	0.234	0.35	$Tc_3O_4(s) + 2H^+ + 2e^- + 2H_2O(s) \rightleftharpoons 3Tc(OH)_2(s)$
h) 0.264 ±0.010	0.262	0.35-5.40 (5)[(c)]	$Tc(OH)_3(s) + 2H^+ + 2e^- \rightleftharpoons TcOH(s) + 2H_2O(l)$
i) 0.296 ±0.012	0.294	0.35-6.75 (8)[(c)]	$Tc(OH)_4(s) + 2H^+ + 4e^- \rightleftharpoons Tc(s) + 4H_2O(l)$
j) 0.338 ±0.006	0.338	0.35, 2.05	$Tc_4O_7(s) + 10H^+ + 10e^- \rightleftharpoons 4TcOH(s) + 3H_2O(l)$
k) 0.382 ±0.004	0.382	0.35, 3.65	$Tc(OH)_4(s) + 3H^+ + 3e^- \rightleftharpoons TcOH(s) + 3H_2O(l)$
l) 0.411 ±?	0.414	0.35	$Tc(OH)_3(s) + H^+ + e^- \rightleftharpoons Tc(OH)_2(s) + H_2O(l)$
m) 0.516 ±0.014	0.518	0.35-5.40 (6)[(b)]	$Tc(OH)_4(s) + 2H^+ + 2e^- \rightleftharpoons Tc(OH)_2(s) + 2H_2O(l)$
n) 0.619 ±0.010	0.620	0.35, 3.65	$Tc(OH)_4(s) + H^+ + e^- \rightleftharpoons Tc(OH)_3(s) + H_2O(l)$
o) 0.661 ±0.008	0.657	0.35, 3.65	$3Tc(OH)_4(s) + 4H^+ + 4e^- \rightleftharpoons Tc_3O_4(s) + 8H_2O(l)$
p) 0.765 ±?	0.768	3.65	$3Tc(OH)_3(s) + H^+ + e^- \rightleftharpoons Tc_3O_4(s) + 5H_2O(l)$

(a) The experimental emfs were corrected to pH = 0 and referenced to the standard hydrogen electrode by Cartledge. The authors of this review assume that the uncertainties reported by Cartledge were estimated standard deviations, and therefore they were increased by a factor of 1.96 to convert them to 95% uncertainty limits.

(b) According to Cartledge, this expected potential was not observed. Actually, it falls so close to the potential for the reaction given immmediately below that it is impossible to be certain which of these emfs was actually observed.

(c) The numbers given in parentheses are the number of different pHs in this range where that potential was observed.

Cartledge noted that the Gibbs energy of formation per equivalent of metal, of a series of solid binary oxides of the same metal, frequently has a linear or nearly linear dependence on the average valence of the metal. By assuming that a similar linear relationship holds for the hydrous oxides of technetium, and using $\Delta_f G^\circ_m$ of Tc_2O_7(cr) and hydrated TcO_2(s) as "tie points" for the curve, he was able to estimate $\Delta_f G^\circ_m$ for various oxides of technetium with valences below seven. Once this was done, Cartledge was able to "explain" the observed "corrosion" potentials as being due to redox reactions involving TcOH(s), $Tc(OH)_2$(s), $Tc(OH)_3$(s), "$Tc(OH)_4$(s)", Tc_3O_4(s), and Tc_4O_7(s).

We note that even if the resulting average valences for the various hydrous oxides of technetium that were claimed by Cartledge [71CAR2] were correct, the chemical formulae are still uncertain. For example, the hydrous oxide of Tc(III) could be $Tc(OH)_3$(s), $Tc(OH)_3 \cdot xH_2O$(s), TcO(OH)(s), $TcO(OH) \cdot xH_2O$(s), or $Tc_2O_3 \cdot xH_2O$(s). There is no unambiguous criterion for distinguishing a hydroxide from a hydrated oxide in the absence of structural data.

There are several difficulties with the method of assigning valence states that was used by Cartledge. The first of these difficulties involves the assumption of a linear Gibbs energy relationship for technetium "oxides". Although it does hold for some systems, for others like FeO_q there is marked curvature. There is no information as whether or not it is applicable to hydrous oxides of technetium. In addition, the "tie points" used by Cartledge were Tc_2O_7(cr) and $TcO_2 \cdot xH_2O$(s). The use of a slope based upon one hydrated and one anhydrous oxide yields uncertainties in predicting $\Delta_f G^\circ_m$ for other hydrous oxides. Forcing the $\Delta_f G^\circ_m$ for the other hydrous oxides to fit on a linear or nearly linear curve effectively amounts to treating the valences of technetium in the oxides as least-squares variables.

Secondly, some of the "normalised" potentials derived by Cartledge [71CAR2, 71CAR] are so close together that ambiguity exists as to which redox reaction they actually refer to. For example, his calculated "normalised" values for the Tc_3O_4(s)/Tc(cr) and $Tc(OH)_2$(s)/TcOH(s) potentials only differ by 0.001 V, but the experimental emfs are uncertain by 0.004 to 0.014 V. Cartledge noted that the potential assigned by him to the Tc_4O_7(s)/TcOH(s) electrode could equally well be explained by assuming the lower valence hydrous oxide was $Tc(OH)_3$(s). This has also been discussed by Meyer, Arnold and Case [86MEY/ARN].

Thirdly, we note that Cartledge [71CAR] reported that he observed "halts" in the curves of potential against time when H_2 in the H_2-saturated solutions was displaced with He. These "halts" occurred at 0.01 to 0.02 V, which is too low to be accounted for in terms of redox reactions involving his postulated hydrous oxides.

One further consideration needs to be made. The experimental "corrosion" potentials were determined using polarised electrodes, and thus the experimental potentials may be shifted from the true equilibrium values. Consequently the observed potentials may differ from the correct values by several mV. This has serious ramifications on the accuracy of the derived $\Delta_f G^\circ_m$ for the various hydrous oxides. Meyer, Arnold and Case [86MEY/ARN] suggested that this polarisation was due to reduction of residual dissolved O_2(g) or radiolytically generated oxygen.

The purpose of this detailed discussion of Cartledge's corrosion potentials

[71CAR2, 71CAR] is to note that not all of his postulated hydrous oxides may be real, and that more detailed chemical information may cause some of them to be rejected in the future.

Six of the E° values of Cartledge were based on measurements at two pHs, one at five pHs, one at six pHs, and one at eight. Since the latter three potentials were observed at a variety of pHs, this suggests they probably represent valid redox potentials involving one or more of the more "stable" of the surface oxides. As indicated by the discussion in Section V.3, hydrous oxides of Tc(IV) are the most widely known and easily prepared of the bulk phase hydrous oxides, and thus a hydrous surface oxide of Tc(IV) is likely to be involved in at least some of these three redox reactions. However, as also discussed in that section, a hydrous oxide of Tc(III) is also known but which undergoes spontaneous disproportionation when the pH of the solution is increased above 3 or 4. Cartledge attributed the $E^\circ = 0.264 \pm 0.010$ V to a redox couple involving $Tc(OH)_3(s)$ and Tc(OH)(s). The potential "halts" giving rise to this redox couple were observed at pH = 0 35, 3.10, 4.03, 5.00, and 5.40. Given the instability of Tc(III) at these higher pH values, this assigned reaction seems doubtful to us.

Cartledge suggested that the redox potential of $E^\circ = (0.296 \pm 0.012)$ V, entry (i) of Table A.2, corresponds to the reduction of "$Tc(OH)_4(s)$" to Tc(cr):

$$Tc(OH)_4(s) + 4H^+ + 4e^- \quad \rightleftharpoons \quad Tc(cr) + 4H_2O(l)$$

This assignment was based on his observation that the value of $\Delta_f G^\circ_m(TcO_2 \cdot xH_2O, s, 298.15\ K)$ calculated from this potential was close to that calculated from the then available potential for the $TcO_4^-/TcO_2 \cdot xH_2O(s)$ redox couple. We repeated this calculation using our evaluated $\Delta_f G^\circ_m(TcO_2 \cdot 1.6H_2O, s, 298.15\ K)$ using the reaction:

$$TcO_2 \cdot 1.6H_2O(s) + 4H^+ + 4e^- \quad \rightleftharpoons \quad Tc(cr) + 3.6H_2O(l)$$

For this reaction, $\Delta_r G^\circ_m = -(95.20 \pm 8.4)$ kJ·mol^{-1}. This value yields $E^\circ = (0.2467 \pm 0.0218)$ V, which falls close to Cartledge's observed $E^\circ = (0.234 \pm 0.008)$ V, and $E^\circ = (0.264 \pm 0.010)$ V, entries (g) and (h) of Table A.2, and is in less than good agreement with his $E^\circ = (0.296 \pm 0.012)$ V. Clearly, the uncertainties in the calculated standard potentials are so large than no unique assignment of reactions can be made to the various E° values reported by Cartledge.

Because of these uncertainties we do not further analyse Cartledge's E° values. Furthermore, we consider some of the evidence for Cartledge's proposed lower-valence and mixed-valence hydrous oxides to be equivocal, especially for $Tc_3O_4(s)$ and $Tc_4O_7(s)$. There are several published thermodynamic data bases for technetium [74MAG/CAR, 80PAQ/REI, 83RAR, 85ISH, 85MAG/BLU, 86BRO] and several potential/pH diagrams [80PAQ/REI, 85ISH, 86BID/AVO, 86BRO] which include $\Delta_f G^\circ_m$ values calculated from the E° values of Cartledge. These potential/pH diagrams predict that $Tc_3O_4(s)$ can be a solubility limiting phase for the Tc-O_2-H_2O system under certain reducing conditions. However, in view of all of the available evidence, we consider $Tc_3O_4(s)$ to be a questionable compound. It is more likely that $TcO_2 \cdot xH_2O(s)$, $TcO_2(cr)$, and Tc(cr) are the actual solubility limiting phases under various reducing conditions.

[71SEL/FRI]

Vibrational peaks were observed for Tc_2O_7(g) at 185 and 957.3 cm^{-1} (strong or very strong); 60 cm^{-1} (medium-to-strong intensity); 178, 340, 357, and 955 cm^{-1} (medium intensity); and 466 cm^{-1} (very weak). Vibrational peaks at 60, 466, and 957.3 cm^{-1} were polarised. In addition, Selig and Fried showed that Re_2O_7(g) had a very similar Raman spectrum, with the same number of peaks and at similar frequencies and intensities, with the corresponding three peaks also being polarised.

All of the observed frequencies in the Raman spectrum for Tc_2O_7(g) were attributed by the authors to vibrational fundamentals and not overtones or combinational bands. Both liquid and gas phase Tc_2O_7 have fewer vibrational peaks than solid Tc_2O_7(cr); this implies that the symmetry of Tc_2O_7 in the fluid phases is greater than in the crystals. Selig and Fried assigned the vibrational fundamentals to δ(Tc-O-Tc) for 60 cm^{-1}; 178 and 185 cm^{-1} to the rocking mode ρ_r(-TcO_3); 340 and 357 cm^{-1} to δ(-TcO_3); 466 cm^{-1} to the symmetrical stretch ν_s(Tc-O-Tc); and 955 and 957.3 cm^{-1} to ν(TcO_3). No asymmetric stretching vibration of the Tc-O-Tc bridge was observed; it should appear in the IR spectrum which, unfortunately, has not been reported.

Baran [74BAR] reanalysed these published vibrational frequencies of Tc_2O_7(g) using a simplified molecular model with Tc_2O_7 being formally treated as a O_3TcO' molecule (the prime denotes the bridging oxygen) with C_{3v} point symmetry. Within the framework of this formalism the observed vibration at 60 cm^{-1} is no longer a fundamental, and the unobserved fundamental ν(Tc-O′) was estimated to occur at 633 cm^{-1}.

[71SPI/GLI]

Spitsyn, Glinkina and Kuzina studied the progressive hydrolysis of K_2TcOCl_5(cr) in 1.85, 3.7, and 5.5 M HCl at room temperature for up to 53 days, and changes in the absorption spectra were still occurring even after that time. Hydrolysis of K_2TcOCl_5(cr) in 3 M HCl was investigated both at room temperature and for heated samples. The resulting precipitate had a Tc:Cl ratio varying from 1:3.8 to 1:4.5. Oxidation with Ce^{4+} showed the technetium valence was Tc(V) in all cases. The varying Tc:Cl ratio, and the continuously changing spectra, suggested that a continuous series of hydroxyoxychlorides of Tc(V) was being formed. Crystals of the isolated solid had the approximate empirical composition $K_2TcOCl_4(OH)$(s). This crystalline substance was partially characterised by UV/VIS and IR spectroscopy.

An attempt was made to prepare this material by Baldas and co-workers [99BAL], and a substance was obtained which had an IR spectrum similar to that reported by Spitsyn *et al.* However, the IR features were identified as due to the presence of a pertechnetate salt, rather than a Tc(V) complex.

[73GUÉ/GUI]

An aqueous solution of $^{99m}TcO_4^-$ was reduced with 0.26 M $NaBH_4$ at pH = 9.5. Aliquots of this solution, after adding various amounts of $HClO_4$ and equilibrating for 15 minutes, were extracted with toluene to remove $TcO(OH)_2$(aq). The amount of extractable Tc(IV) decreased very rapidly in acidic solutions, and after 1 hour the distribution

coefficients decreased remarkably due to the oxidation of Tc(IV) to TcO_4^-. The authors mentioned the presence of radiocolloids at carrier-free concentration of Tc(IV). Guénnec and Guillaumont presented a rough estimate for the deprotonation reaction, $TcO(OH)^+ + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) + H^+$, of $\log_{10} K \approx -1$.

[74BAR]

See comments under [71SEL/FRI].

[74MAZ/MAG]

Convincing direct evidence for a Tc(III) hydrous oxide comes from the voltammetric reduction of TcO_4^- in O_2(g)-free (N_2(g)-purged) solutions [74MAZ/MAG]. Experiments were done on a platinum microelectrode, and the pH was varied from -0.5 to 14. The resulting electrode deposits were allowed to react with a 1 M H_2SO_4 solution containing Ce(IV), and dissolution occurred very slowly. The amount of excess Ce(IV) that remained after oxidation of the deposit to TcO_4^- was determined by back-titration with Fe^{2+}. Their experiments indicated that the brown-black electrode deposits contained only Tc(IV) for electrolysis done at pH > 3, but a mixture of Tc(IV) with a lower-valence hydrous oxide (presumably, of Tc(III)) was obtained at pH < 3. Similar oxidation state results were obtained if the electrode deposit was first dissolved in 3 to 10 M HCl and then oxidised with Ce(IV). These results indicate that a hydrous oxide of Tc(III) formed at low pH, but that it is probably unstable with regard to formation of Tc(IV) for pH > 3.

[74VIN/ZAI]

Vinogradov *et al*. reported the solubilities of $(NH_4)_2TcCl_6$(cr), K_2TcCl_6(cr), Rb_2TcCl_6(cr), and Cs_2TcCl_6(cr) in 3.0, 5.0, and 10 M aqueous HCl, and of $(NH_4)_2TcBr_6$(cr), K_2TcBr_6(cr), Rb_2TcBr_6(cr), and Cs_2TcBr_6(cr) in 3.5, 7.0, and 9.52 M aqueous HBr at 298 K. Solubility equilibrium was reached in one day for the chloride solids, and in one and a half days for the corresponding bromides. Photochemical aquation of the TcX_6^{2-} ions was probably not significant during the time frame of their experiments. The TcX_6^{2-} concentrations were determined spectrophotometrically, and that of NH_4^+ by Kjeldahl's method. None of the $TcBr_6^{2-}$ solids showed a variation in the solubility with HBr concentration, nor did those of K_2TcCl_6(cr) or Rb_2TcCl_6(cr) with HCl concentration for solubilities expressed on the molar concentration scale. Very slight trends were observed for $(NH_4)_2TcCl_6$(cr) and Cs_2TcCl_6(cr), but they were in opposite directions as a function of HCl concentration. However, since only three points were measured for each solid, and the trends are small, these trends may not be significant relative to the accuracy of the measurements. Plots were given of the variation of solubility of $(NH_4)_2TcCl_6$(cr) at 298.15 K in 10 M HCl with concentration of added NH_4Cl and for $(NH_4)_2TcBr_6$(cr) at 293.15 K in 7 M HBr with added NH_4Br. Addition of NH_4X caused a roughly 10-fold decrease in the solubility of $(NH_4)_2TcX_6$(cr).

The solid phases were not characterised. However, it is known that addition of stoichiometric amounts of MX salts to TcX_6^{2-} solutions gave a precipitate of unhydrated M_2TcX_6(cr) (see Section V.4.2.2.2), so it is safe to conclude that the solid phases in this solubility study were of this type. The nature of the solution phase is less certain. The absence of a variation of the molar solubilities on the concentration of X^- from HX indicates that fully-coordinated hexachlorotechnetium(IV) ions and hexabromotechnetium(IV) ions are the only or at least the predominant species in these HX solutions. However, the lack of variation of solubilities with H^+ concentration could indicate that either undissociated H_2TcX_6(aq), TcX_6^{2-}, or undissociated M_2TcX_6(aq) was the predominant dissolved species. It will obviously make a large difference in the extrapolation to infinite dilution, since $\sum_i z_i^2 = 0$ in the first and third cases but equals 6 in the second case.

If undissociated H_2TcX_6(aq) was produced upon dissolution of M_2TcX_6(cr) in aqueous HX, then the dissolution reaction would be

$$M_2TcX_6(cr) + 2H^+ \quad \rightleftharpoons \quad H_2TcX_6(aq) + 2M^+ \tag{A.8}$$

with a solubility constant of K_s(A.8) $= [H_2TcX_6(aq)][M^+]^2/[H^+]^2$. This strong dependence of K_s on H^+ was not observed, so this dissolution reaction is not considered to be tenable. The possiblity that undissociated M_2TcX_6(aq) was present in solution is also considered to be unlikely since alkali metal and ammonium salts are generally dissociated in aqueous solutions.

The remaining possibility for the solubility reaction is

$$M_2TcX_6(cr) \quad \rightleftharpoons \quad 2M^+ + TcX_6^{2-} \tag{A.9}$$

with a solubility constant of $K_{s,0}$(A.9) $= [M^+]^2[TcX_6^{2-}]$. The solubilities can be extrapolated to infinite dilution with the specific ion interaction approach, *cf*. Appendix C, which requires that the solubility and ionic strength are reported on the molal concentration scale. Vinogradov *et al*. however, gave their concentrations on the molar scale. Their solvents were 3.0 to 10 M HCl or 3.5 to 9.52 M HBr, and the molality-to-molarity ratio of dissolved M_2TcX_6(cr) will be the same as this ratio for the HX in that solution. These concentration scale conversions are done graphically by using the c (molarity) and m (molality) values tabulated by Morss for 0.10 to 6.83 mol $\cdot$ kg^{-1} HCl [76MOR] and the densities tabulated in Landolt-Börnstein [77D'A/SUR]. The Landolt-Börnstein densities are also used for aqueous HBr solutions. Densities in Landolt-Börnstein were given in tabular form at 273.15, 293.15, and 313.15 K, but not at 298.15 K. Since densities to only three significant figures are adequate for our concentration scale conversions, a simple linear interpolation to 298.15 K is used. The resulting saturation molalities m_s and solubility products are summarised in Table A.3.

Densities of aqueous HBr in Landolt-Börnstein extend only to 10.11 mol$\cdot$kg^{-1} (7.99 M). The molality of 9.52 M HBr is then estimated graphically from a plot of m/c against c extrapolated to higher c. Values based on this extrapolation are enclosed in parentheses.

Table A.3: Solubilities and solubility products for M_2TcX_6(cr) at 298.15 K in HX solutions from Vinogradov *et al*. [74VIN/ZAI].[(a)]

Ionic strength (mol · kg^{-1})	m_s (mol · kg^{-1})	$\log_{10} K_s$	$-6D$	$\log_{10} K_s - 6D = \log_{10} K_s^\circ$	
$(NH_4)_2TcCl_6(cr) \rightleftharpoons 2NH_4^+ + TcCl_6^{2-}$					
3.20 HCl	4.39×10^{-3}	−6.47	−1.48	−7.95	
5.56 HCl	4.56×10^{-3}	−6.42	−1.59	−8.01	
12.65 HCl	5.07×10^{-3}	−6.28	−1.71	−7.99	
				−7.98	(Average)
.....					
$K_2TcCl_6(cr) \rightleftharpoons 2K^+ + TcCl_6^{2-}$					
3.20 HCl	1.24×10^{-3}	−8.12	−1.48	−9.60	
5.56 HCl	1.31×10^{-3}	−8.05	−1.59	−9.64	
12.65 HCl	1.48×10^{-3}	−7.89	−1.71	−9.60	
				−9.61	(Average)
.....					
$Rb_2TcCl_6(cr) \rightleftharpoons 2Rb^+ + TcCl_6^{2-}$					
3.20 HCl	3.90×10^{-4}	−9.62	−1.48	−11.10	
5.56 HCl	4.11×10^{-4}	−9.56	−1.59	−11.15	
12.65 HCl	4.66×10^{-4}	−9.39	−1.71	−11.10	
				−11.12	(Average)
.....					
$Cs_2TcCl_6(cr) \rightleftharpoons 2Cs^+ + TcCl_6^{2-}$					
3.20 HCl	3.06×10^{-4}	−9.94	−1.48	−11.42	
5.56 HCl	3.23×10^{-4}	−9.87	−1.59	−11.46	
12.65 HCl	3.68×10^{-4}	−9.70	−1.71	−11.41	
				−11.43	(Average)
$(NH_4)_2TcBr_6(cr) \rightleftharpoons 2NH_4^+ + TcBr_6^{2-}$					
3.86 HBr	1.19×10^{-2}	−5.17	−1.52	−6.69	
8.56 HBr	1.31×10^{-2}	−5.05	−1.66	−6.71	
(12.7) HBr	(1.44×10^{-2})	(−4.92)	−1.72	(−6.64)	
				−6.68	(Average)
.....					
$K_2TcBr_6(cr) \rightleftharpoons 2K^+ + TcBr_6^{2-}$					
3.86 HBr	0.99×10^{-2}	−5.41	−1.52	−6.93	
8.56 HBr	1.09×10^{-2}	−5.29	−1.66	−6.95	

(Continued on next page)

Table A.3: (continued)

Ionic strength ($mol \cdot kg^{-1}$)	m_s ($mol \cdot kg^{-1}$)	$\log_{10} K_s$	$-6D$	$\log_{10} K_s - 6D = \log_{10} K_s^\circ$	
(12.7) HBr	(1.19×10^{-2})	(−5.17)	−1.72	(−6.89)	
				−6.92	(Average)
.....					
$Rb_2TcBr_6(cr) \rightleftharpoons 2Rb^+ + TcBr_6^{2-}$					
3.86 HBr	1.43×10^{-3}	−7.93	−1.52	−9.45	
8.56 HBr	1.49×10^{-3}	−7.88	−1.66	−9.54	
(12.7) HBr	(1.72×10^{-3})	(−7.69)	−1.72	(−9.41)	
				−9.47	(Average)
.....					
$Cs_2TcBr_6(cr) \rightleftharpoons 2Cs^+ + TcBr_6^{2-}$					
3.86 HBr	3.65×10^{-4}	−9.71	−1.52	−11.23	
8.56 HBr	3.76×10^{-4}	−9.67	−1.66	−11.33	
(12.7) HBr	(4.53×10^{-4})	(−9.43)	−1.72	(−11.15)	
				−11.24	(Average)

[(a)] The ionic strength (12.7 $mol \cdot kg^{-1}$) and m_s (equilibrium concentration of dissolved solid) values at the highest HBr concentration were converted from molar concentrations by graphical extrapolation of the m/c ratio against c for aqueous HBr.

Table A.3 contains the derived $\log_{10} K^\circ_{s,0}$(A.9) values for M_2TcX_6(cr). They show no significant variation with I_m, and the average values are recommended. The lack of a significant concentration dependence for these $\log_{10} K^\circ_{s,0}$(A.9) supports our chosen solubility reaction. However, we consider these $\log_{10} K^\circ_{s,0}$(A.9) values to be uncertain by at least ±1 since:

- the ionic strengths are quite high which makes the activity corrections less certain;
- in every case $\log_{10} K^\circ_{s,0}$(A.9) at the intermediate I_m is very slightly more negative than at the higher and lower I_m, which indicates that $\log_{10} K^\circ_{s,0}$(A.9) *vs.* I_m may have slight curvature.

It should be recalled that if the HX concentration is lowered sufficiently, hydrolytic precipitation of the technetium will generally occur.

[75BRA/BRA]

Polarographic measurements were made to study the reduction of $^{99}TcO_4^-$ in various media. Reduction to Tc(V) was observed in 0.1 M KOH, 0.1 M NaOH, 0.1 M KCl and 1 M $NaClO_4$ with a potential of $E_{1/2} = -0.8$ V *vs.* SCE. This process was followed by

catalytic evolution of hydrogen gas at more negative potentials. In 20% HCl solution (*i.e.*, about 6 M HCl) a three-electron reduction was observed, as was in 0.1 M KCN and 1 M sodium citrate with $E_{1/2} = -0.88$ V *vs.* the SCE, but the pH of this unbuffered solution was not reported. For Tc(V) and Tc(IV) the formation of hydrolysis products was proposed, which is in agreement with the results in acetonitrile at low amounts of water. In such concentrated HCl solutions, reduction of TcO_4^- occurs with partial formation of $TcCl_6^{2-}$ and other aqueous species. For a complete formation of $TcCl_6^{2-}$, concentrated HCl is needed, and several days are required at room temperature, see Section V.4.2.1.1. The conditions chosen are not appropriate for the measurements in acidic solution. The authors of this paper did not consider the large amount of literature existing on the behaviour of in aqueous HCl solutions [59BUS, 64RYA/POZ, 66SHU, 69KAN, 71SHU, 71SHU2]. Also, no mention was made concerning the calibration and standardisation of the pH and polarographic measurements.

[75COT/PED]

Cotton and Pedersen found that the half cell reaction

$$Tc_2Cl_8^{2-}(\text{aqueous ethanol}) + e^- \quad \rightleftharpoons \quad Tc_2Cl_8^{3-}(\text{aqueous ethanol})$$

occurred quasireversibly at 0.38 V in a mixture of 10 vol-% 12 M HCl and 90 vol-% ethanol. Since the lifetime of $Tc_2Cl_8^{2-}$ was found to be $\gg$300 s, it was clear that it could be possible to prepare other solid binuclear halides containing this anion.

Schwochau *et al.* [77SCH/HED] reported preparation of such a compound $((n\text{-}C_4H_9)_4N)_2Tc_2Cl_8$(s), using reduction of TcO_4^- by H_3PO_2 in aqueous O_2(g)-free HCl. However, Cotton *et al.* [81COT/DAN] reported that attempts to prepare that compound with reduction by H_3PO_2 gave solids containing $TcOCl_4^-$ ions instead.

Preetz and Peters [80PRE/PET2] reduced $TcCl_6^{2-}$ by using zinc in concentrated HCl, evaporated the solution and then extracted $ZnCl_2$ with diethylether, and obtained a residue. This residue was dissolved in dilute HCl with $(n\text{-}C_4H_9)_4NCl$ added, and the resulting mixture of $((n\text{-}C_4H_9)_4N)_2Tc_2Cl_8$ and $((n\text{-}C_4H_9)_4N)_3Tc_2Cl_8$ was extracted with CH_2Cl_2. These two compounds were separated by taking advantage of the greater solubility of $((n\text{-}C_4H_9)_4N)_2Tc_2Cl_8$ in acetone, relative to $((n\text{-}C_4H_9)_4N)_3Tc_2Cl_8$. This method of preparing $Tc_2Cl_8^{2-}$ was confirmed by Cotton *et al.* [81COT/DAN], who characterised the structure of this compounds. Since both Cotton *et al.* [81COT/DAN] and Schwochau *et al.* [77SCH/HED] reported the same structure type and very similar unit cell dimensions, their products must be identical. However, the details of preparation of $((n\text{-}C_4H_9)_4N)_2Tc_2Cl_8$(s) by reduction of $TcCl_6^{2-}$ with H_3PO_2 need to be more clearly defined.

[75LIE/MÜN]

The emf measurements of Liebscher and Münze were done at (298.15 ± 0.2) K using a cell arrangement quite similar to that of Cartledge and Smith [55CAR/SMI], except that Liebscher and Münze separated their cell compartments with a KCl salt bridge. Their electrode was prepared by electrodeposition of $TcO_2 \cdot xH_2O$(s) onto platinum, by

electrolytic reduction of TcO_4^- from a dilute solution of NH_4TcO_4 and H_2SO_4. They found that flushing the solutions with N_2(g) or Ar(g) to remove air during the emf measurements caused the observed cell potentials to decrease; these potentials slowly approached a steady value only after about 5 hours. This confirms earlier observations of the effect of deoxygenation on the cell potential [55CAR/SMI].

Liebscher and Münze varied the concentration of NH_4TcO_4 from 1.14×10^{-2} to 1.43×10^{-2} M, and the pH from 1.05 to 4.5. They did not report the concentrations of H_2SO_4 used in their individual solutions, but did state that they ranged from 5×10^{-4} to 0.05 M. However, because they reported the pH values, it was possible to estimate the concentrations of H_2SO_4 in their solutions. The three experiments for the pH range of 1.05 to 2.90 yielded derived E° values for the $TcO_4^-/TcO_2 \cdot xH_2O$(s) redox couple of 0.766 to 0.769 V. However, at pH = 3.85 this "standard" potential decreased to 0.745 V, and at pH = 4.5 it decreased further to 0.728 V. This decrease in E° at higher pH values was unexplained. They reported that their potentials had a Nernstian response with pH change for pH = 1.05 to 2.90.

[75MÜN/GRO]

Münze and Großmann studied the kinetics of the hydrolysis of $TcBr_6^{2-}$ in aqueous 0.001 to 3.0 M HBr. They reported that hydrolysis occurred by way of the reaction

$$TcBr_6^{2-} + 2H_2O(l) \quad \rightleftharpoons \quad TcO_2(s, \text{hydrated}) + 4H^+ + 6Br^-$$

The kinetics of this hydrolytic reaction were monitored by absorption spectra measurements, and the following rate equation was obtained:

$$-d[TcBr_6^{2-}]/dt \quad = \quad k[TcBr_6^{2-}]/[H^+]^2[Br^-]^6$$

No values of k were given, but for 9.35×10^{-5} mols of K_2TcBr_6 in 5 cm^3 of 0.01 M HBr, for example, after 90 minutes the hydrolysed species contained 3.58 OH^- per technetium (final pH = 1.13).

[76ARM/TAU]

A detailed study by Armstrong and Taube leaves no doubt that the complex prepared by Eakins, Humphreys and Mellish [63EAK/HUM] was actually *trans*-$[Tc(NH_3)_4(NO)(OH_2)]Cl_2$ rather than $[Tc(NH_2OH)_2(NH_3)_3(H_2O)]Cl_2$(s) as originally proposed. In most nitrosyl complexes the nitrosyl group is assigned a +1 charge, so they assumed their complex contained Tc(I). Armstrong and Taube followed Eakins, Humphreys and Mellish's [63EAK/HUM] method of preparation, except that they purified the complex by cation exchange using 1 M HCl as the eluting agent. The complex could be converted to a methanesulphonate solution by elution with methanesulphonic acid. Addition of solid NaBr or concentrated HBF_4 solutions then gave precipitates of the corresponding Br^- and BF_4^- salts. The trifloroacetate salt was prepared by ion exchange with the chloride salt.

Armstrong and Taube's results from potentiometric pH titration indicate that the H_2O in *trans*-$[Tc(NH_3)_4(NO)(OH_2)]^{2+}$ behaved as an acid with $pK_a = 7.3$ at I =

0.01 M and 298 K. At pH values above the end-point, solutions of the complex slowly decomposed in air. Solutions of the complex in 2 M $HClO_4$ or CF_3SO_3H, or in dilute HCl or HBr, appeared to be stable, but in 2 M HCl or HBr this complex underwent slow transformation to form a solid which had different colour than the Tc(I) aqueous complex. The solubility of the chloride complex in water was >0.03 M.

Oxidation of the Tc(I) complex by electrochemical or chemical methods in acidic solutions yielded the a complex of Tc(II), *trans*-$[Tc(NH_3)_4(NO)(OH_2)]Cl_3$. Results from cyclic voltammetry in 3.0 M trifluoromethanesulphonate indicated that water in this aqueous complex $Tc(NH_3)_4(NO)H_2O^{3+}$ behaved as an acid with $pK_a \approx 2.0$.

The $[Tc(NH_3)_4(NO)(OH_2)]^{3+}/[Tc(NH_3)_4(NO)(OH_2)]^{2+}$ redox couple in aqueous 3 M trifluoromethanesulphonate solution was reversible at 0.80 V for pH ≤ 2, but it was irreversible above pH = 2 [76ARM/TAU].

There is only a single approximate value for the acidic dissociation constant of H_2O complexed to *trans*-$[Tc(NH_3)_4(NO)(OH_2)]Cl_3$ and it is at the fairly high ionic strength of 3 M. Thus there are insufficient data to calculate a reliable value of K_a°. However, for the dissociation reaction

$$\textit{trans}\text{-}[Tc(NH_3)_4(NO)(OH_2)]^{2+} \rightleftharpoons \textit{trans}\text{-}[Tc(NH_3)_4(NO)OH]^{+} + H^{+} \qquad \text{(A.10)}$$

they reported that $\log_{10}K(\text{A.10}) = -7.3$ at an ionic strength of 0.01 M. At this low ionic strength, molarity and molality are essentially equal, and I_m is low enough that activity corrections can be made accurately. Thus, $\log_{10}K^\circ + 2D = -7.21$. Since no uncertainty was reported for $\log_{10}K$, and since only one ionic strength was studied, this review conservatively estimated that K° is uncertain by $\pm 3 \times 10^{-8}$ (50%). The obtained value is thus $\log_{10}K^\circ(\text{A.10}) = -(7.21 \pm 0.18)$

This value is not recommended by this review since only a single ionic strength was studied.

[76AST/SCH]

Polarographic and controlled-potential coulometric studies on permanganate, pertechnetate and perrhenate in water, acetonitrile, dimethyl sulfoxide and dimethylacetamide were performed. The potential measured in water for the reduction step Tc(VII) → Tc(V) was reported as $E_{1/2} = -0.84$ V *vs*. SCE at 298.15 K, *i.e*., −0.60 V *vs*. NHE. In aprotic solvents the oxidation state +VI is stabilised in all cases.

[76GAY/HER]

Gayer, Herrell and Busey purified their technetium metal by oxidation to Tc_2O_7(cr) with dry O_2(g), followed by purification of this Tc_2O_7 by sublimation, and, finally, reduction of it with H_2(g) to reform the metal. This metal was then ground to a fine powder for their solution experiments. Gayer, Herrell and Busey dissolved their technetium metal in aqueous solutions containing 0.15 M Ce(IV) perchlorate and 3.25 M $HClO_4$, with two enthalpy determinations. The metal was thereby oxidised to TcO_4^-.

They also performed similar solution experiments with mercury metal (gold as a catalyst), HgO (cr, yellow form), and Tc_2O_7(cr), each in this same solvent mixture. These results were combined in a thermodynamic cycle to yield results for the reaction:

$$2Tc(cr) + 7HgO(cr, yellow) \quad \rightleftharpoons \quad 7Hg(l) + Tc_2O_7(cr) \qquad (A.11)$$

for which $\Delta_r H^\circ_m$ (A.11) $= -(494.4 \pm 15.5)$ kJ·mol^{-1}, for one mole of Tc_2O_7(cr). We converted their reported standard deviation to 95% confidence limits. They used this result to derive the enthalpy of formation of Tc_2O_7(cr). Redoing this calculation gives: $\Delta_f H^\circ_m$ (Tc_2O_7, cr, 298.15 K) = $-(1127.6 \pm 15.5)$ kJ·mol^{-1}. We note that there is some uncertainty as to the correct numerical value of $\Delta_f H^\circ_m$(HgO, cr, yellow, 298.15 K), which is needed for the recalculation of $\Delta_f H^\circ_m$(Tc_2O_7, cr, 298.15 K) from the enthalpy of solution study of Gayer, Herrell and Busey [76GAY/HER]. We accepted their choice of $\Delta_f H^\circ_m = -90.46$ kJ·mol^{-1} for yellow HgO(cr) [82WAG/EVA]; the CODATA [89COX/WAG] (note 101) and NBS values [82WAG/EVA] of $\Delta_f G^\circ_m$ (HgO, cr, yellow, 298.15 K) are virtually identical.

Inasmuch as Gayer, Herrell and Busey obtained their HgO(cr) from the NBS, the NBS evaluation [82WAG/EVA] of $\Delta_f H^\circ_m$ (HgO, cr, yellow, 298.15 K) was accepted for reanalysis of results for Tc_2O_7(cr). However, if the experiment value of Vanderzee, Rodenburg and Berg [74VAN/ROD] proves to be correct, then the derived value of $\Delta_f H^\circ_m$ (Tc_2O_7, cr, 298.15 K) should be more negative by 2.6 kJ·mol^{-1}.

[77OWU/MAR]

A cation exchange distribution technique was used to determine the net charge of the technetium species produced by reduction of $^{99m}TcO_4^-$ with $SnCl_2$ in $HClO_4$ solutions. In the pH range 1.2 to 2.0 and in 10^{-4} to 10^{-2} M $Sn(ClO_4)_2$ solutions in nitrogen atmosphere, they found ^{99m}Tc concentrations between 10^{-9} and 10^{-7} M. The Tc(IV) species showed a charge of +2 per technetium, which could correspond to TcO^{2+} (or $Tc_2O_2^{4+}$) or $Tc(OH)_2^{2+}$. To demonstrate the validity of the method used, distribution experiments with the same resin system were carried out with trace ^{22}Na and ^{95}Zr species of known charge. Errors in the pH measurements seem excluded by direct determination of the H^+ ion concentrations via titration with standard sodium hydroxide. The results agree only partially with those of Meyer *et al*. [91MEY/ARN2], which implies that a Tc(IV) species of charge +2 can only exist (if at all) only at pH < 1.5.

[77SPI/KUZ]

Spitsyn *et al*. noted that hydrothermal reduction of $(Hpy)_2TcCl_6$(s) by molecular hydrogen in an autoclave produced different coloured solutions during reduction, depending on the HCl concentration used, but the final reduction product was always dark-brown $(Hpy)_3Tc_2Cl_8 \cdot 2H_2O$(s). The solution colours were blue in 7 M HCl, green in 5 to 6 M HCl, and brown in 4 to 4.5 M HCl. They accounted for these colour differences in terms of the formation of an intermediate species $TcCl_4(OH)_2^{2-}$ at lower HCl concentrations. The reverse process, decomposition of $Tc_2Cl_8^{3-}$ with changing HCl

concentrations, was studied in more detail both in the absence and presence of O_2(g) [80SPI/KUZ, 81KRY, 83KRY/KUZ].

Aqueous solutions of $Tc_2Cl_8^{3-}$ reacted with O_2-free HF(aq) and HI to form $Tc_2F_8^{3-}$ and $Tc_2I_8^{3-}$, respectively [81KRY]. Aqueous solutions of $Tc_2Cl_8^{3-}$ in concentrated HCl were gradually oxidised further to yellow $TcCl_6^{2-}$ by O_2(g) in air [70BRA/COT]. However, even in the absence of O_2(g), solutions of $Tc_2Cl_8^{3-}$ slowly decomposed to $TcCl_6^{2-}$ over a several day period [77SPI/KUZ2].

Spitsyn, Kuzina and Kryuchkov [80SPI/KUZ] studied aquation of $Tc_2Cl_8^{3-}$ in O_2-free HCl at different HCl concentrations. The solution colour at 293 K varied from azure blue in 5.0 to 9.0 M HCl, to turquoise green for 3.0 to 5.0 M HCl, to emerald green for 2.0 to 3.0 M HCl, to yellowish-green for 1.0 to 2.0 M HCl, to greenish-brown for 0.5 to 1.0 M HCl, and to dark brown in the absence of HCl at pH $\approx$ 10. Electrophoresis measurements indicated that the effective charge on the cluster varied from $-(3.0 \pm 0.8)$ in 5.0 to 9.0 M HCl to $+(3.4 \pm 1.4)$ at pH $= 10$, which indicates stepwise aquation with loss of chloride was occurring with increasing pH. The optical absorbance of these solutions was monitored as a function of pH and time. They saw evidence for little oxidation of the dimer in the absence of O_2(g), and proposed that the black solid that precipitated was $Tc_4O_5 \cdot xH_2O$(s). Magnetic susceptibilities gave an effective magnetic moment of 2.5 B.M., which indicates the presence of this hydrous oxide of a single unpaired electron. We note, however, if HCl can oxidise the hydrolysed species, then the average valence of technetium in this hydrous oxide could have been higher. Their proposed stepwise aquation of $Tc_2Cl_8^{3-}$ involved $Tc_2Cl_{8-x}(OH_2)_x^{x-3}$ intermediates [81KRY].

In the presence of O_2(g), decomposition of $Tc_2Cl_8^{3-}$ involved a more complex mechanism [81KRY, 83KRY/KUZ]. They suggested that competing processes occurred: acid induced aquation, disproportionation of the dimer with rupture of the Tc-Tc bond, and also oxidative addition of O_2(g) to the dimer with subsequent rupture of the Tc-Tc bond. It was also claimed that Tc(II) species and $TcCl_6^{2-}$ formed by disproportionation of $Tc_2Cl_8^{3-}$ for HCl concentrations >3 M in the absence of O_2(g) [83KRY/KUZ], and that $TcCl_6^{2-}$ and $TcOCl_4(OH)^{2-}$ formed in the presence of O_2(g) with $Tc_2O_2Cl_8^{3-}$ as a proposed intermediate species [81KRY]. If the concentration of HCl is reduced, the $TcCl_6^{2-}$ can undergo hydrolysis, and, at high enough pH values, $TcO_2 \cdot xH_2O$(s) should precipitate.

[77VOL/KON]

Volk, Konarev and Barabash reported values of the solubility of NH_4TcO_4(cr) in water and in aqueous NH_4NO_3, and of NH_4NO_3(cr) in water and in aqueous NH_4TcO_4, over the whole composition range at 298.2 K. They did not report how precisely they controlled their temperature.

The concentrations of NH_4^+ in the saturated solutions used by Volk, Konarev and Barabash were determined by them using the Kjeldahl method, and the concentrations of dissolved TcO_4^- by spectrophotometry or radiometry, but they did not identify which solutions were analysed for technetium by the individual methods. Concentrations of

NO_3^- in these solutions were obtained by difference, *i.e.*, charge balance between total NH_4^+ and the amount present as TcO_4^- salt. They did not estimate their experimental uncertainty. See also the discussion of [91RAR/MIL].

Their solubilities of NH_4TcO_4(cr) and NH_4NO_3(cr) were reported by them both in unit of per cent by mass and as moles of electrolyte per 100 g of solution. We calculated the molalities of NH_4TcO_4 and NH_4NO_3 from the per cent by mass values, by assuming that their technetium isotope was ^{99}Tc.

The thermodynamic solubility product for NH_4TcO_4(cr) on the molal concentration scale is given by:

$$K^\circ_{s,0} = m_{NH_4^+} \cdot m_{TcO_4^-} \cdot \gamma_{NH_4^+} \cdot \gamma_{TcO_4^-} = K_m \cdot \gamma_{NH_4^+} \cdot \gamma_{TcO_4^-}$$

where, in general, $m_{NH_4^+} > m_{TcO_4^-}$ because of the presence of NH_4NO_3 in the solutions. Corrections of the values of $\log_{10} K^\circ_{s,0}$ to infinite dilution are made using the SIT. If the contributions of the solubility of NH_4TcO_4 to the total ionic strength of the solutions were negligible compared to the contribution of NH_4NO_3, then the SIT equation for this system would have the following form:

$$\log_{10} K_{s,0} - 2D = \log_{10} K^\circ_{s,0} - \Delta\varepsilon I_m$$

In this case, the relatively large solubility of NH_4TcO_4 in water (0.594 mol·kg^{-1}) causes variations in the ionic strength I_m. However, we found this equation to be useful for a preliminary assessment of the precision of the solubility measurements.

Table A.4 contains a listing of the experimental solubility measurements, values of $K_{s,0}$, and $\log_{10} K_{s,0} - 2D$ at different total ionic strengths I_m. Figure A.2 is a plot of these $\log_{10} K_{s,0} - 2D$ values against I_m. An examination of Figure A.2 indicates that values of $\log_{10} K_{s,0} - 2D$ for experiments with $I_m \geq 6$ mol · kg^{-1} are fairly smooth, with a scatter of only ± 0.01 or $\pm$ 0.02 logarithmic units. Unfortunately, the values of that quantity with $I_m \leq 6$ mol · kg^{-1} are much more scattered, ± 0.05 to ± 0.15 log units, and this is the region most critical for the extrapolation to obtain $K^\circ_{s,0}$.

It is quite possible that this increased "scatter" is simply due to lower precision solubilities or is possibly due to systematic differences due to a change over in the method used for determining the concentration of TcO_4^- in the saturated solutions, but this cannot be concluded with any certainty because Volk, Konarev and Barabash did not indicate which method of analysis was used for any specific experiment.

If the solubility experiment with $I_m = 1.880$ mol · kg^{-1} is assumed to be an outlier (as appears to be the case), then the values of $\log_{10} K_{s,0} - 2D$ show a steady increase from infinite dilution to the highest molalities. We note that this quantity increases with ionic strength for the solubility $TlTcO_4$(cr) in various electrolytes (see Figure A.3 in this Appendix under Ref. [81MIK/MIŠ]), and hence the presumed behaviour of NH_4TcO_4(cr) in NH_4NO_3 solutions is reasonable. We therefore reject the solubility with $I_m = 1.880$ mol · kg^{-1}.

Unfortunately there is still some uncertainty in the extrapolation of solubilities for NH_4TcO_4(cr), because the values at $I_m = 0.594$ to 3.374 mol · kg^{-1} are somewhat scattered. We therefore did two least-squares fits to different combinations of the

Table A.4: Solubilities of aqueous mixtures of NH_4TcO_4 and NH_4NO_3 at 298.15 K [77VOL/KON]

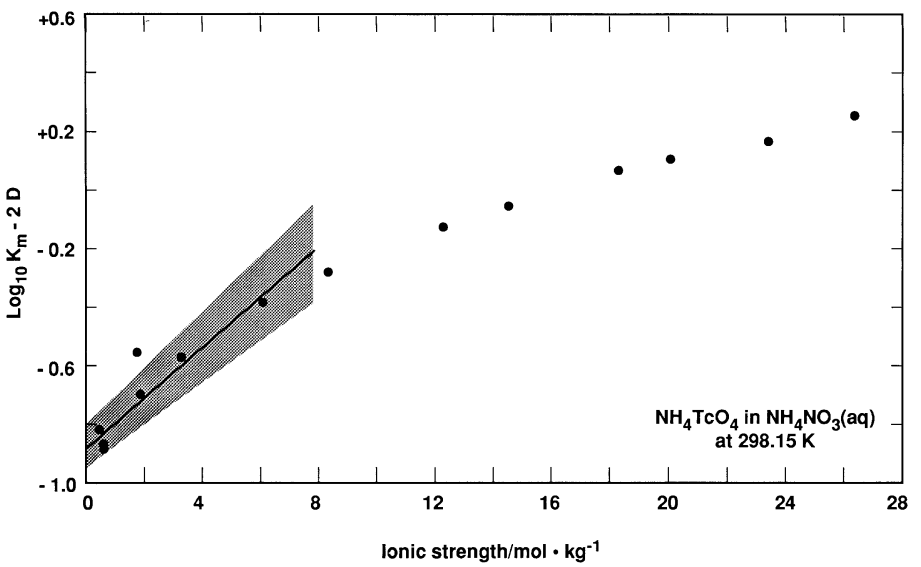
NH_4TcO_4[a] ($mol \cdot kg^{-1}$)	NH_4NO_3 ($mol \cdot kg^{-1}$)	I_m ($mol \cdot kg^{-1}$)	Solid phase	$K_{s,0}$[b] ($mol^2 \cdot kg^{-2}$)	$\log_{10} K_{s,0} - 2D$
0.594		0.594	NH_4TcO_4	0.352	−0.817
0.514	0.088	0.602	NH_4TcO_4	0.309	−0.875
0.438	0.271	0.709	NH_4TcO_4	0.311	−0.887
0.430	1.450	1.880	NH_4TcO_4	0.809	−0.549[c]
0.294	1.720	2.014	NH_4TcO_4	0.593	−0.689
0.251	3.123	3.374	NH_4TcO_4	0.845	−0.571
0.232	5.958	6.190	NH_4TcO_4	1.434	−0.379
0.224	8.207	8.431	NH_4TcO_4	1.890	−0.275
0.228	12.15	12.38	NH_4TcO_4	2.825	−0.120
0.238	14.40	14.64	NH_4TcO_4	3.482	−0.036
0.250	18.11	18.36	NH_4TcO_4	4.580	0.074
0.255	19.85	20.10	NH_4TcO_4	5.124	0.119
0.256	23.14	23.40	NH_4TcO_4	6.00	0.181
0.276	25.92	26.20	NH_4TcO_4	7.24	0.259
0.216	25.42	25.64	NH_4NO_3		
0.142	24.87	25.01	NH_4NO_3		
0.077	25.03	25.11	NH_4NO_3		
0.041	24.87	24.91	NH_4NO_3		
0.018	24.77	24.79	NH_4NO_3		
	24.69	24.69	NH_4NO_3		

[a] These molalities were calculated from the reported values of compositions in % by mass, by using 180.942 $g \cdot mol^{-1}$ for the molar mass of NH_4TcO_4 and 80.0434 $g \cdot mol^{-1}$ for NH_4NO_3

[b] $K_{s,0} = [NH_4^+][TcO_4^+]$, where concentrations are in $mol \cdot kg^{-1}$

[c] This point was given zero weight in the least-squares calculation.

Figure A.2: Plot of solubility data for NH_4TcO_4(cr) in aqueous solutions of NH_4NO_3 at 298.2 K [77VOL/KON]. Least-squares curve is shown for $\log_{10} K_{s,0} - 2D = \log_{10} K^\circ_{s,0} - \Delta\varepsilon I_m = -0.9013 \pm 0.0496 + (0.08824 \pm 0.01638) I_m$, from fit to results at $I_m = 0.594, 0.602, 0.709, 2.014, 3.374$, and $6.190\,\mathrm{mol \cdot kg^{-1}}$.



solubilities with $I_m \leq 6.190$ or 3.374 mol · kg^{-1}, which is the linear region in Figure A.2. First, including all these points yields $\log_{10} K^\circ_{s,0} = -(0.9013 \pm 0.0496)$, $\Delta\varepsilon = -(0.08824 \pm 0.01638)$ mol^{-1} · kg, and correlation coefficient 0.98253. Second, a fit with the values at $I_m = 0.594$ to 3.374 mol · kg^{-1} gives $\log_{10} K^\circ_{s,0} = -(0.9239 \pm 0.0538)$, $\Delta\varepsilon = -(0.10704 \pm 0.02946)$ mol^{-1} · kg, and correlation coefficient 0.97168. There is some variation between the $\log_{10} K^\circ_{s,0}$ values and between the $\Delta\varepsilon$ values from these two fits, but they agree within their uncertainty limits.

Attempts were made to extract a value for $\varepsilon(NH_4^+, TcO_4^-)$ by using the full form of the SIT, but the calculations show that the solubilities from this study are too scattered at the lower ionic strengths to allow a meaningful extraction of any ε values.

We accept the simple weighted average from the two fits without the point at $I_m = 1.880$ mol · kg^{-1}, $\log_{10} K^\circ_{s,0} = -0.9117$. The statistical uncertainty of 0.03645 for this value was doubled to 0.0729, because of the lack of experimental detail in the solubility study. This gives $K^\circ_{s,0} = (0.123 \pm 0.021)$ mol^2 · kg^{-2} for the thermodynamic solubility product of NH_4TcO_4(cr). All of the least-squares fits attempted, whether using the full form of SIT or with the selected ε I_m term agree within these uncertainty limits.

[78BOY2, 78BOY]

Boyd [78BOY2, 78BOY] reported isopiestic equilibrium molalities for aqueous $NaTcO_4$ from 0.10784 to 9.4640 mol·kg^{-1} and for aqueous $HTcO_4$ from 0.10581 to 5.4404 mol·kg^{-1}, both at 298.15 K, by using aqueous NaCl as the isopiestic reference standard. The stock solution of $HTcO_4$ was obtained from $KTcO_4$ solutions by ion exchange. $NaTcO_4$ solutions were produced from $HTcO_4$ by neutralisation with NaOH solution and evaporation. The concentration of the stock solution of $NaTcO_4$ was analysed to an accuracy of ± 0.1 % by precipitation of Pb_4AsTcO_4, and the reported accuracy for the isopiestic equilibration molalities was ± 0.1 %. Boyd reported the solubility as being 11.299 mol · kg^{-1}, but also gave 11.300 mol · kg^{-1} in his Figure 1. This minor difference is insignificant, but we assume the value given in the text was correct. Based upon that information, along with the familiarity of one of the present authors (Joseph A. Rard) with this method, we estimate that this solubility is uncertain by ±0.3%, and the recommended value is $m_s = (11.299 \pm 0.034)$ mol · kg^{-1}.

Boyd [78BOY] reported that a 5.44 mol · kg^{-1} solution of $HTcO_4$ was pink coloured, but that at lower molalities the solutions were colourless. He attributed the pink colour to "condensation equilibria" or to formation of undissociated $HTcO_4$.

[78OSB/SCH]

Osborne *et al*. calculated the entropy of TcF_6(g) from the entropy of the liquid at 320 K, together with the entropy of vaporisation of the liquid from their earlier vapour pressure study [62SEL/MAL].

The starting point for their calculations of the entropy of vaporisation from the equation of state was the Clapeyron equation for the variation of vapour pressure with

temperature,

$$\frac{\mathrm{d}p}{\mathrm{d}T} = \frac{\Delta S}{\Delta V}$$

where $\Delta S = (S_g - S_l)$ and $\Delta V = (V_g - V_l)$, ΔS and ΔV are molar quantities, subscript g denotes the gas, and subscript l the liquid. Thus,

$$\Delta S = \Delta V \frac{\mathrm{d}p}{\mathrm{d}T} = p\Delta V \frac{\mathrm{dln}\ p}{\mathrm{d}T}. \tag{A.12}$$

Their measured vapour densitites for unsaturated vapour at 298.15 K were used by them to calculate the second virial coefficient $B(T)$ of the virial equation of state

$$pV = RT + B(T)p$$

with $B(298.15\ \mathrm{K}) = -895\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$. They then assumed that $B(T)$ had an inverse square dependence on temperature as with the leading term in the Berthelot equation of state. This assumption is somewhat risky since $B(T)$ was measured at a single temperature. They evaluated $\mathrm{d}p/\mathrm{d}T$ from the vapour pressure equation of Selig and Malm [62SEL/MAL], and obtained $(V_g - V_l)$ from their approximate equations of state [78OSB/SCH]. This ΔS value from Eq. (A.12) was then added on to S°_m of the liquid, the resulting S_m was converted to 1 atm pressure of the vapour from the actual experimental vapour pressure, and a correction made for the non-ideal behaviour of the vapour. This review now repeats their type of calculation, but at 298.15 K rather than at 320 K where Osborne *et al.* did their calculations using TcF_6(cr, cubic) as the reference condensed phase. This should reduce the uncertainty, since the virial equation of state for the vapour now need only be valid right around 298.15 K.

Differentiation of the vapour pressure equation [62SEL/MAL] for TcF_6(cr, cubic) (Eq. (V.31) in Section V.4.1.2.1) gives

$$\frac{\mathrm{dln}\ p}{\mathrm{d}T} = \frac{5015.0}{T^2} - \frac{2.295}{T} = 0.04872\ \mathrm{K}^{-1}$$

at 298.15 K. Osborne *et al.* gave an approximate equation for the molar density ρ_m of TcF_6(cr, cubic) (from X-ray structure values) as

$$\rho_m = 0.01703 - 10^{-5}T$$

in $\mathrm{mol} \cdot \mathrm{cm}^{-3}$. Thus,

$$V_s = \frac{1}{\rho_m} = 71.2\ \mathrm{cm}^3 \cdot \mathrm{mol}^{-1}$$

at 298.15 K. Their assumed virial equation of state for the vapour can be rewritten as

$$V_g = \frac{RT}{p} + B(T) \tag{A.13}$$

where $B(T) = -895\ \text{cm}^3 \cdot \text{mol}^{-1}$ at 298.15 K. The smoothed vapour pressure of TcF_6(cr, cubic) at 298.15 K is 0.29876 bar. An ideal gas occupies 22414.1 $\text{cm}^3 \cdot \text{mol}^{-1}$ at 273.15 K and 1 atm pressure. For the real gas at 298.15 K and 0.29876 bar pressure, $V_g = 82080.3\,\text{cm}^3 \cdot \text{mol}^{-1}$ and thus $\Delta_{sub}V_m = 82009.1\,\text{cm}^3 \cdot \text{mol}^{-1}$. Then, Eq. (A.12) yields for the sublimation

$$\Delta_{sub}S_m = 119.37\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

This then gives $S_m(TcF_6, \text{g}, 298.15\ \text{K}) = 372.89\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the real gas from sublimation of TcF_6(cr, cubic). The entropy of TcF_6 at 0.29876 bar needs to be corrected for non-ideal behaviour and then extrapolated to unit fugacity at 1 bar pressure. The second correction is the entropy of isothermal compression for an ideal gas:

$$\begin{aligned}\Delta_r S^*_m &= -\int_{0.29876}^{1}\left(\frac{\partial V}{\partial T}\right)_p \mathrm{d}p = -\int_{0.29876}^{1}\left(\frac{R}{p}\right)\mathrm{d}p \\ &= R\ln(0.29876) = -10.04\,\text{J}\cdot\ \text{K}^{-1}\cdot\text{mol}^{-1}.\end{aligned}$$

The entropy of the real gas is now corrected for the slightly non-ideal behaviour of TcF_6 vapour:

$$\Delta_r S^{**}_m = \int_0^{0.29876}\left[\left(\frac{\partial V}{\partial T}\right)_p - \frac{R}{p}\right]\mathrm{d}p.$$

For their virial equation of state,

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p} + \left(\frac{\partial B(T)}{\partial T}\right)_p,$$

so

$$\Delta_r S^{**}_m = \int_0^{0.29876}\left(\frac{\partial B(T)}{\partial T}\right)_p \mathrm{d}p.$$

Virial coefficients are defined to be functions of temperature but not of pressure. Thus,

$$\Delta_r S^{**}_m = \left(\frac{\partial B(T)}{\partial T}\right)_p (0.29876)$$

Osborne *et al.* assumed $B(T)$ could be written as $-(79.6 \times 10^6)/T^2$, so

$$\left(\frac{\partial B(T)}{\partial T}\right)_p = 6.01\,\text{cm}^3 \cdot \text{mol}^{-1}\cdot\ \text{K}^{-1}$$

at 298.15 K and

$$\Delta_r S^{**}_m = 0.179\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

Although their temperature dependence of $B(T)$ was just an estimate, $\Delta_r S^{**}_m$ is small enough that very little uncertainty is introduced. There is also a very small correction for the change in the entropy of TcF_6(cr, cubic) from changing the pressure from 0.29876 to 1 bar, but since this change is $< 10^{-2}$ J $\cdot$ K^{-1} $\cdot$ mol^{-1} it is neglected.

The total ideal gas standard state entropy of TcF_6(g) is then S°_m (TcF_6, ideal gas, 298.15 K) = S_m(TcF_6, real gas) $+\Delta_r S^*_m + \Delta_r S^{**}_m$ = 363.03 J·K^{-1}·mol^{-1} which is within about 0.1% of Osborne *et al*'s. derived "experimental" value, after adjustment for the temperature differences. This review assumes the entropy of vaporisation is uncertain by 2%, $\Delta_r S^{**}_m$ by 50%, and S°_m of the condensed phase by 0.2%. Thus the uncertainty for S°_m (TcF_6, g, 298.15 K) is $\sqrt{(2.39)^2 + (0.09)^2 + (0.51)^2} = 2.44$ J· K^{-1}· mol^{-1}. The value resulting is thus

$$S^\circ_m \text{ (TcF}_6\text{, ideal gas, 298.15 K)} \quad = \quad (363.0 \pm 2.4) \text{ J· K}^{-1} \cdot \text{mol}^{-1}.$$

Osborne *et al*. also calculated the statistical thermodynamic entropy of TcF_6(g) using the vibration frequencies of Claassen *et al*. [70CLA/GOO]. Their calculated statistical entropy at 320 K was about 1% below their "experimental" entropy (which is consistent with the experimental value derived in this review). Somewhat surprising, a statistical entropy from Nagarajan and Brinkley [71NAG/BRI] using the same vibrational frequencies was about 10 J $\cdot$ K^{-1} $\cdot$ mol^{-1} lower than the statistical thermodynamic results of Osborne *et al*. and 14 J·K^{-1}·mol^{-1} below the experimentally based value derived in this review at 298.15 K. Clearly, one of these statistical calculations was done incorrectly. It appears likely that Nagarajan and Brinkley used an incorrect degeneracy for the ground state of TcF_6(g). The previous statistical thermodynamic entropies of Nagarajan [63NAG] are 25 J·K^{-1}·mol^{-1} lower than their later results at 298.15 K, but they were calculated with preliminary values of the vibrational frequencies [62CLA/SEL] rather than the later recommended values [70CLA/GOO] and probably were not calculated correctly.

Osborne *et al*. assumed the 1% discrepancy between their "experimental" and statistical thermodynamic entropies was due to inaccuracy in the estimated value of ν_6, and adjusted it to give better agreement.

This review recalculates the ideal gas thermodynamic properties of TcF_6(g) which are tabulated in Table V.17 (see Section V.4.1.3.1).

Fundamental constants were taken from Table II.7 (see Section II). The vibrational frequencies of Claassen *et al*. [70CLA/GOO] are used as reported by them. However, the Tc-F bond distance of 1.84×10^{-10} m recommended by [78OSB/SCH] is increased slightly to 1.85×10^{-10} m. A value of 1.8512×10^{-10} m was reported for Tc-F by Nagarajan [63NAG] based on use of an empirical correlation between stretching force constants and bond lengths. This value does agree with the average of the experimental Mo-F bond length $(1.82 \pm 0.02) \times 10^{-10}$ m [80BRE/LAM] and the Ru-F bond length of 1.8775×10^{-10} m (based on the same empirical correlation between force constants and bond length [64NAG]). On chemical grounds we expect the Tc-F bond length to be close to the Mo-F and Ru-F values.

A rigorous estimation of the uncertainties in the statistical thermodynamic values for TcF_6(g) is not possible, since ν_2, ν_5, and ν_6 are "estimated best values" or tentative

assignments, and not experimental [70CLA/GOO]. If this review makes the very conservative estimate that experimental vibrational frequencies are uncertain by 5 cm^{-1} and estimated values by 20 cm^{-1}, then it is calculated that S°_m is uncertain by about 5.5 $J \cdot K^{-1} \cdot mol^{-1}$ at 298 K and 6.3 at 1000 K. However, the calculated experimental value and derived statistical thermodynamic value of Table V.17 (see Section V.4.1.3.1) agree to 3.86 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ at 298.15 K, so the estimated uncertainty limits may be slightly too large. We consider the experimentally-based entropy for TcF_6(g) to be slightly more accurate than the statistical thermodynamic value.

The calculation of the experimentally-based value of $S^\circ_m(TcF_6, g, 298.15\ K) = (363.0 \pm 2.4)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ previously described, was performed by the same basic method used by Osborne *et al.* [78OSB/SCH] and which, in essence, is a second-law evaluation. However, since experimental heat capacities are available for TcF_6(cr, cubic), Table V.15 (see Section V.4.1.2.1), and statistical thermodynamic calculations are available for TcF_6(g), Table V.17 (see Section V.4.1.3.1), a third-law evaluation of the standard enthalpy of sublimation for TcF_6(cr, cubic) can be done. Third-law-based evaluations are generally more accurate than second-law-based evaluations of enthalpy changes.

Puigdomenech *et al.* [97PUI/RAR] have derived the third-law-based expression for the standard enthalpy of sublimation. For the case of TcF_6(g) being treated as a non-ideal gas, their equation becomes:

$$\begin{aligned}\Delta_{sub}H^\circ_m(TcF_6, cr, cubic, 298.15\ K) = T([G^\circ_m(TcF_6, cr, cubic, T) \\ -H^\circ_m(TcF_6, cr, cubic, 298.15\ K)]/T - [G^\circ_m(TcF_6, g, T) \\ -H^\circ_m(TcF_6, g, 298.15\ K)]/T) - RT\ln f \end{aligned} \quad (A.14)$$

where f is the fugacity of TcF_6(g). For convenience, we shall use the following shorthand notation

$$\begin{aligned}\sum \ = \ & [G^\circ_m(TcF_6, cr, cubic, T) - H^\circ_m(TcF_6, cr, cubic, 298.15\ K)] \\ & -[G^\circ_m(TcF_6, g, T) - H^\circ_m(TcF_6, g, 298.15\ K)]\end{aligned}$$

and, thus, Eq. (A.14) becomes

$$\Delta_{sub}H^\circ_m(TcF_6, cr, cubic, 298.15\ K) \ = \ T\left[\left(\sum /T\right) - R\ln f\right] \quad (A.15)$$

Values of $[G^\circ_m(TcF_6, cr, cubic, T) - H^\circ_m(TcF_6, cr, cubic, 298.15\ K)]/T$ were taken from Table V.15 (see Section V.4.1.2.1) and for $[G^\circ_m(TcF_6, g, T) - H^\circ_m(TcF_6, g, 298.15\ K)]/T$ were calculated using the vibrational frequencies and the interatomic distance given in footnote (a) of Table V.17 (see Section V.4.1.3.1), and they were adjusted for the differences between $H^\circ_m(298.15\ K)$ and $H^\circ_m(0\ K)$. The resulting values of $(\sum /T)$ are 0.10541_2, 0.10555_1, 0.10562_3, 0.10561_8, and $0.10558_8\ kJ \cdot K^{-1} \cdot mol^{-1}$, at the temperatures T = 268.335, 280.00, 298.15, 300.00 and 311.136 K, respectively. A graphical examination of these values of $(\sum /T)$ indicated that were precise to about $0.00006\ kJ \cdot K^{-1} \cdot mol^{-1}$ which is equivalent to an uncertainty for $\Delta_{sub}H^\circ_m(TcF_6, cr, cubic, 298.15\ K)$ of about $0.02\ kJ{\cdot}mol^{-1}$. Values of $(\sum /T)$ were

obtained by interpolation at each of the temperatures used for the sublimation vapour-pressure measurements for TcF_6(cr, cubic), by using a plot of $(\sum / T)$ against T.

Osborne *et al*. expressed the deviations of the vapour pressures of TcF_6(g) from ideal gas behaviour by use of the second virial coefficient $B(T)$, our Eq. (A.13). This equation is equivalent to a virial expansion of (pV/RT) as a function of pressure, with the expansion being truncated after the second virial term. To this approximation,

$$\ln f = \ln p + B(T)\, p/RT \tag{A.16}$$

Osborne *et al*. gave the expression $B(T) = -(79.6 \times 10^6 \mathrm{cm}^3 \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^2)/T^2$. Equation (A.16) then becomes

$$\ln f = \ln(p/bar) - (9.574 \times 10^5 \mathrm{K}^3 \cdot \mathrm{bar}^{-1})(p/T^3)$$

Thus, Eq. (A.15) can be written as

$$\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K}) = T\left[\left(\sum /T\right) - R\ln(p/bar) + 9.574 \times 10^5 \left(Rp/T^3\right)\right] \tag{A.17}$$

The detailed third-law evaluation of $\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K})$ for all of the vapour pressures reported by Selig and Malm [62SEL/MAL] for TcF_6(cr, cubic) is given in Table B.12 (Appendix B).

The third-law-based values of $\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K})$ show a very slight systematic trend with temperature of about 0.15 kJ·mol^{-1} for the 41.71 K experimental temperature range, with the calculated values decreasing slightly as the temperature increases. However, this dispersion is quite small and indicates that the thermodynamic data for TcF_6(g) and TcF_6(cr, cubic) are fairly consistent internally. The recommended average of the third-law-based values is $\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K}) = (34.536 \pm 0.094)$ kJ·mol^{-1}, which is somewhat smaller than the value of 36.0 kJ·mol^{-1} obtained from differentiation of Selig and Malm's [62SEL/MAL] vapour pressure equation, (Eq. (V.31) in Section V.4.1.2.1), at 298.15 K. The value obtained from the temperature derivative of the vapour-pressure equation is more uncertain because it relies heavily on the vapour pressure measurements around 298.15 K and on the quality of the least-squares fit in that temperature region. In contrast, the third-law-based value of $\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K}) = (34.536 \pm 0.094)$ kJ·mol^{-1} relies equally on all of the sublimation vapour pressure measurements for TcF_6(cr, cubic) and is a statistically better average. Thus the authors of this review recommend this third-law-based value. If the difference between fugacity and vapour pressure were neglected, then the third-law-based standard enthalpy of sublimation would be equal to $\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K}) = (34.514 \pm 0.116)$ kJ·mol^{-1}, which is only very slightly smaller than the value obtained by using Eq. (A.17). However, neglecting the difference between fugacity and vapour pressure does increase slightly the systematic trend in the calculated values of $\Delta_{sub}H^\circ_m(TcF_6, \text{cr, cubic, } 298.15\text{ K})$ with temperature from 0.15 to 0.19 kJ·mol^{-1} and the uncertainty of the mean values (95% confidence limits) from 0.094 to 0.116 kJ·mol^{-1}.

[78RUS/CAS]

Russell and Cash studied the polarographic reduction of TcO_4^- in various ionic media from pH = 1.0 to 13.0 with use of a dropping mercury electrode. In a pH = 9.8 carbonate solution, a 3 e^- per technetium reduction occurred at −0.51 V followed by an ill defined second wave at −0.86 V; half-peak potentials from cyclic voltammetry at the same pH gave the first reduction wave at −0.52 V. Reoxidation of the reduced technetium solutions with anodic sweep pulse polarography ocurred at −0.02 and +0.09 V from the first reduction wave and at −0.35 and −0.05 V from the second, and with cyclic voltammetry occurred at −0.31, −0.01, and +0.10 V. Inasmuch as the reduction and the oxidation potentials were numerically different in this study, the redox processes were irreversible. Since similar potentials were observed in carbonate solutions and in KOH and KCl, no evidence for complex formation with chloride or carbonate was obtained. They fixed the TcO_4^- concentration at 1.5×10^{-4} M and the ionic strength at 0.1 M.

See also the comments under [60MIL/KEL].

[78STE/BÄC]

Steffen and Bächmann used irradiation of uranium foil with thermal neutrons to produce various fission products, and studied their volatility in flowing O_2(g) at high temperatures. Two volatile oxides of technetium were observed, the lower temperature one was assumed to be TcO_2 and the higher temperature one "TcO_3" . They reported that TcO_3 was volatilised from the graphite crucible at 1773 K, but that it seemed to partially decompose at the lower chromatographic column temperatures. For example, separation of the volatile oxides by chromatography gave a 60% yield of "TcO_3" at 773 K, but only 7% "TcO_3" was obtained at 553 K. If the O_2(g) carrier gas was replaced by a O_2(g)-H_2O(g) mixture, then vapour phase transport occurred by formation of volatile $HTcO_4$. Based on the discussion in Section V.3.2.4.1, it is quite unlikely that TcO_2 was volatile under their experimental conditions.

[78STE/MEI]

Coulometric reduction of aqueous TcO_4^- at about −0.7 V in the presence of 0.2 M $Na_4P_2O_7$ at pH = 7.0 was investigated by Steigman, Meinken and Richards or at −0.61 V in 0.1 M $K_4P_2O_7$ with 0.1 M each of K_2HPO_4 and KH_2PO_4 at pH = 7.4 by Salaria, Rulfs, and Elving [63SAL/RUL]. These investigations indicated a 4 e^- reduction per Tc to Tc(III), although a 3 e^- reduction to Tc(IV) was obtained at −0.47 V [63SAL/RUL].

The reduced technetium pyrophosphate solution initially turned pink but then changed to light blue when the reduction was complete [78STE/MEI]. When air was bubbled through the solutions they turned pink and required 1.0 e^- per technetium for rereduction to Tc(III). Thus the light blue solution contained mostly Tc(III) and the pink solution Tc(IV). The light blue solution gradually turned darker blue upon standing, and when stored overnight under N_2(g) showed a pink surface layer with a build up of gas pressure. If this additional gas were H_2(g), it would indicate the blue

complex can reduce $H_2O(l)$. This reaction of Tc(III) to form spontaneously some Tc(IV) was generally observed, but one time their solution did remain blue for more than three days. Reduction of TcO_4^- with Sn^{2+} also gave this blue Tc(III) complex, and reduction of TcO_4^- with KI_3 gave the Tc(IV) complex.

Steigman, Meinken and Richards also reported coulometric reductions of TcO_4^- in 1 M $K_4P_2O_7$ at pH = 7 and obtained yellowish solutions. Two coulometric reductions of TcO_4^- gave 4.8 e^- and 4.4 e^- per technetium, respectively, which suggests partial formation of Tc(III) and Tc(II) occurred. Bubbling $O_2(g)$ through the yellowish solution gave no colour change, but rereduction of the product from the first coulombic reduction required 1.6 e^- per technetium. No change in absorption spectrum was observed with time for 20 days for coulometrically reduced technetium in 1 M pyrophosphate, but dilution of a 1 M $K_4P_2O_7$ solution of reduced technetium to 0.2 M showed extremely small and slow absorbance changes. These facts suggest that the complexes produced by reduction of TcO_4^- in 0.2 and 1 M $K_4P_2O_7$ either contained technetium in different oxidation states, that they were very slow to change to the blue species upon dilution, or both. Russell and Cash [79RUS/CAS2] performed amperometric titration of TcO_4^- in 0.1 M $Na_4P_2O_7$ at pH = 3.0, 7.0, and 12.0 with Sn^{2+}. These experiments gave 3 e^- reductions in each case [79RUS/CAS2].

Steigman, Meinken and Richards observed that light blue Tc(III) solutions that were produced by reduction of TcO_4^- in 0.2 M pyrophosphate gradually became darker blue with time, and they followed those changes with spectrophotometry using Sn^{2+} reduced technetium. They noted that these colour changes could have been due either to a structural rearrangement, a slow disproportionation reaction such as $2Tc(V) \rightarrow Tc(III) + TcO_4^-$, or a slow dimerisation of Tc(III). The last possibility seemed most likely to them and they found the calculated dimerisation kinetics to be approximately second order in the concentration of Tc(III).

[79BRA/HAR]

Borosilicate glass is usually prepared from about 60 mass-% SiO_2, 10 to 20% B_2O_3, and 5 to 20% Na_2O, along with lesser amounts of one or more of the following: CaO, Al_2O_3, Li_2O, ZnO, or TiO_2 [79BRA/HAR, 85ANT/MER, 89FRE/LUT].

Powdered samples of this glass are generally mixed with dried samples of reactor waste or simulated waste (technetium as $NaTcO_4$ or TcO_2), and then the mixture is vitrified at 1300 to 1500 K. Significant losses of technetium can occur in the presence of $O_2(g)$; Antonini, Merlini and Thornley [85ANT/MER] found that over 80% of technetium was lost in some cases when TcO_4^- salts were used, but smaller losses occurred when TcO_2 was used instead. This loss presumably occurred by volatilisation of Tc_2O_7, or sublimation of alkali metal pertechnetates. Closed systems should be used to reduce loss of technetium to the environment.

Bradley, Harvey and Turcotte [79BRA/HAR] dissolved reactor waste in 6 M HNO_3 with added HF(aq), and then wetted powdered borosilicate glass with this solution; the sample was vacuum dried and heated to 773 K to decompose the nitrate; and finally it was vitrified at around 1320 K. They found that technetium was concentrated on the internal surfaces of pores in the glass matrix, and that this technetium was apparently in

a water soluble form. Although Bradley, Harvey and Turcotte did not speculate about the chemical nature of this "soluble" technetium, others concluded that it was in the form of gaseous Tc_2O_7 [84KHA/WHI, 89FRE/LUT]. It seems to us, however, that it could have been present as a pertechnetate salt instead.

Antonini, Merlini and Thornley [85ANT/MER] prepared borosilicate glass by doping the powdered glass samples with NH_4TcO_4 or $TcO_2 \cdot xH_2O$(s). Samples were vitrified either under oxidising conditions or under reducing conditions. They used EXAFS to determine the chemical state of technetium in the glasses. Those glasses prepared under oxidising conditions contained TcO_2(cr) as a separate phase, whereas those samples prepared under reducing conditions contained both TcO_2(cr) and metallic Tc(cr) as separate phases.

Freude *et al*. [89FRE/LUT] prepared technetium-doped borosilicate glass under oxidising and reducing conditions by a procedure similar to that used by Antonini, Merlini and Thornley [85ANT/MER]. Redox potentials were measured for the borosilicate glass melts [89FRE/LUT] from 973 to 1373 K by using square-wave voltammetry with yttrium stabilised zirconia and platinum electrodes. Redox potentials were given graphically and corresponded to the Tc(VII)/Tc(IV) and Tc(IV)/Tc(0) couples. They found that borosilicate glass prepared under oxidising conditions was clear and colorless and apparently contained technetium as Tc(VII), whereas glass prepared under reducing conditions contained black particles that were apparently TcO_2(cr). This precipitation of TcO_2(cr) indicated that TcO_2(cr) has a low solubility in the borosilicate glass matrix. Thus, there is disagreement whether technetium occurred as Tc(VII) [79BRA/HAR, 89FRE/LUT] or Tc(IV) [85ANT/MER] in borosilicate glass prepared under oxidising conditions, but there is agreement that TcO_2(cr) and metallic technetium precipitated from such glass prepared under reducing conditions.

[79KAD/LOR]

Kaden *et al*. prepared a complex that they formulated as TcN_2L_2, which contained molecular dinitrogen, where L = $Ph_2PCH_2CH_2PPh_2$. It was prepared by reaction of L with $TcCl_4(PPh_3)_2$ and sodium amalgam in benzene under N_2(g). This complex formed yellow crystals with a strong IR absorption band at 2046 cm^{-1} due to N_2 (the $^{14}N^{15}N$ complex absorbed at 2014 cm^{-1}). It was "stable" in air for several hours. It was soluble in benzene and toluene but sparingly soluble in ethanol and hexane.

This complex was studied in more detail by Struchkov *et al*. [82STR/BAZ], who established that it is actually the hydride complex hydridobis(1,2-bis(diphenylphosphinoethane))dinitrogentechnetium(I), $HTc(N_2)L_2$(cr). Crystals were grown from *n*-hexane, and X-ray diffraction established that it crystallised in the monoclinic space group $P2_1/n$ with $a = (11.090 \pm 0.006) \times 10^{-10}$ m, $b = (24.550 \pm 0.010) \times 10^{-10}$ m, $c = (16.379 \pm 0.008) \times 10^{-10}$ m, $\beta = (96.02 \pm 0.04)°$, and $Z = 4$. The technetium atom was octahedrally coordinated with the hydridic hydrogen being *trans* to the N_2 group; the presence of a hydridic hydrogen was supported by ^{1}H-NMR measurements.

[79RUS/CAS]

See comments under [60MIL/KEL].

[79SUN]

The author found that electrophoretic mobility measurements of ^{99}Tc(IV) in solutions of similar pH values to those used by Gorski and Koch [69GOR/KOC] gave no reproducible results. However, he was able to measure the UV absorption spectra of Tc(IV) solution at pH < 4. Unfortunately, the experimental temperature was not reported. An increase of the temperature in the cuvettes by action of light could change the speciation of the solution. The experiments were performed in an atmosphere of highly purified nitrogen gas which was bubbled through all solutions used. Contrary to [91MEY/ARN2], no controlled atmosphere box was used. Therefore, the amount of Tc(VII) should be similar or larger with respect to the solutions obtained in that paper. The use of common cuvettes for spectroscopic measurements is practically impossible without contamination of the solution with oxygen. Since the concentration of TcO_4^- is not known, no reliable equilibrium constant can be expected from this work.

Preliminary measurements in solutions of 1 M $HClO_4$ ($[Tc]_t$) $= 1.2 \times 10^{-4}$ M), 0.05 M $HClO_4$ + 0.15 M $NaClO_4$ ($[Tc]_t$) $= 2.33 \times 10^{-5}$ M), and 0.025 M $HClO_4$ + 0.175 M $NaClO_4$ ($[Tc]_t$) $= 2.75 \times 10^{-6}$ M) in the wavelength range from 190 to 300 nm resulted in an isosbestic point near 250 nm [79SUN, Figure1]. Sundrehagen attributed these total technetium concentration to equilibrium mixtures of various hydrolysed forms of Tc(IV). From the results of Meyer *et al*. [91MEY/ARN2] the Tc(IV) solubilities at the acid concentrations used in [79SUN] should be 5×10^{-5} M, 2×10^{-6} M, and 8×10^{-8} M, respectively. This indicates that the solutions prepared by Sundrehagen [79SUN] could be oversaturated. This could also signify that some Tc(IV) could have been present as solid or colloid without taking part in the equilibria. Another possibility is that the solution in fact was clear and that a large fraction of Tc was present as Tc(VII). This assumption agrees with the values of the optical densities [81FRI]. The advantage of using $NaClO_4$ as inert salt is that complexes with the perchlorate ion are either non-existent or very weak. On the other hand, perchlorate favours the oxidation to Tc(VII) in acidic solutions [88COL/IAN]. Data processing gave equilibrium constants for the protonation, as well as for the dimerisation, of $TcO(OH)_2$(aq), but some results are odd, such as the standard deviation of the molar absorptivity of $TcO(OH)^+$, which is larger than the actual value: $\epsilon = (497 \pm 559)$ M^{-1} cm^{-1}. As said above, since the amount of Tc(VII) was not measured, the result of this work cannot be considered for quantitative calculations.

[80BEH/RIN]

The authors studied the vaporisation of Tc, contained in a TaC effusion cell, from 2051 to 2348 K with a quadrupole mass-spectrometer, using Ag and Au as standards. This requires an estimate of the relative cross-sections of Ag, Au and Tc, which [80BEH/RIN] estimated introduces an uncertainty of 50% in the vapour pressures. This alone contributes an uncertainty of about 10 $kJ \cdot mol^{-1}$ to the value

of $\Delta_f H^\circ_m$(Tc, g, 298.15 K). Six separate runs, comprising in total 162 data points, were carried out. Tc^+(g) was the only important peak in the mass-spectrum, although minor peaks due to TcO_n^+(g) species ($n = 1, 2, 3$) (and some impurity atoms) were observed in the early stages of heating the samples. The results of the normal second and third law analyses, using the selected thermal functions for Tc are shown in Table V.4. Again, the very large differences in the second and third law enthalpies of reaction and the related fact that the experimental entropy of vaporisation is as small as (97.0 ± 2.9) J·K^{-1}·mol^{-1}, compared to that calculated at the mid-range temperature $\Delta_{sub}S^\circ_m(2200\ K) = S^\circ_m(Tc, g, 2200\ K) - S^\circ_m(Tc, cr, 2200\ K) = 143.7$ J·K^{-1}·mol^{-1} (Tables B.1 and B.2), immediately throw doubt as to whether the measured pressures correspond to a simple sublimation process.

Behrens and Rinehart discussed and dismissed various possible reasons for the discrepancies and suggest that their pressures may be "somewhat too low" due to reaction of Tc(g) with the effusion cell, despite the fact that interaction of Tc with the cell was earlier ruled out, on the grounds that one run was carried out specifically under conditions to minimise such interaction, but gave Tc pressures similar to other runs. However, they earlier indicated that a Tc sample heated in a new TaC crucible at 1940 K for 2 hours and then heated to 2264 K showed no Tc^+(g) signal from the orifice, indicating severe reaction with the TaC. These findings confirm the conclusion from the very low entropy of reaction, that the reaction being studied by Behrens and Rinehart was probably not simple sublimation of Tc(cr).

[80PAC]

Pacer reported three values for the solubility of Ph_4AsTcO_4(cr) at 297.2 to 298.2 K, by using radiometric determination of the concentrations of ^{99}Tc in TcO_4^-. Equilibration times ranged from seven to twelve days. The resulting solubilities ranged from 2.89×10^{-5} to 3.02×10^{-5} M and exhibited no obvious variation with temperature or time. The average solubility from those experiments is $c_s = (2.94 \pm 0.14) \times 10^{-5}$ M.

The solubility of Ph_4AsTcO_4(cr) is low enough that for solutions in water the molality can be related to molarity by the density of pure water. Thus the measurements of Pacer yield $m_s = (2.949 \pm 0.14) \times 10^{-5}$ mol · kg^{-1}. This molality is low enough that the activity coefficient can be estimated from the specific ion interaction equation, $\gamma_\pm = 0.9937$. The resulting thermodynamic solubility product is $K^\circ_m = (8.59 \pm 0.82) \times 10^{-10}$ mol^2 · kg^{-2}.

We note that Parker and Martin [52PAR/MAR] measured solubilities for Ph_4AsTcO_4(cr) in solutions of Ph_4AsCl at a mole ratio of 1 to 17. Results were just given graphically, and the temperature range was about 285 to about 325 K. Under these conditions the solubility of Ph_4AsTcO_4(cr) was constant at about 5 mg · dm^{-3} from about 285 to 325 K, which corresponds to a molar concentration of 9×10^{-6} M.

For the results of Parker and Martin [52PAR/MAR], $[TcO_4^-] = 9 \times 10^{-6}$ M, $[Ph_4As^+] = 18[TcO_4^-] = 1.62 \times 10^{-4}$ M, and $I_c = 1.62 \times 10^{-4}$ M. The same type of calculation as above yields $m_{TcO_4^-} = 9 \times 10^{-6}$ mol · kg^{-1}, $m_{Ph_4As^+} = 1.625 \times 10^{-4}$ mol · kg^{-1}= I_m, and $\gamma_\pm = 0.9854$. Consequently, $K^\circ_m = 14 \cdot 10^{-10}$ mol^2 · kg^{-2}

from that study.

The value of K°_m derived from the study of Parker and Martin [52PAR/MAR] is about 65% larger than the value derived from the study of Pacer [80PAC]. We consider this agreement to be satisfactory, because only a rough value of the solubility could be estimated from the graph of Parker and Martin and K°_m from that study is uncertain by about 50%. We recommend the value of K°_m from the study of Pacer, because numerical solubilities were given and the experimental conditions were well defined.

[80PAQ/REI]

Paquette, Reid and Rosinger listed values of S°_m and $\Delta_f G^\circ_m$ both for TcO_2(cr) and $Tc(OH)_4$(cr). Inasmuch as both of these $\Delta_f G^\circ_m$ are based on emf studies for the same hydrous oxide, the inclusion of both solid phases in thermodynamic calculations would give erroneous results.

[80SPI/KUZ]

These authors and later Kryuchkov [81KRY] studied the hydrolysis of the $Tc_2Cl_8^{3-}$ ion in aqueous HCl. They reported that for concentrations of HCl >3 M, in the presence of air, this ion underwent oxidation and disproportionation. However, if the HCl concentration was < 3 M, then this ion underwent stepwise hydrolysis with, ultimately, precipitation of "$Tc_4O_5 \cdot xH_2O$(s)". They gave this formula based upon chemical analysis, but did not provide any details. We don't know if they analysed their precipitate for the presence or absence of chloride to make sure they did not actually have an oxychloride of technetium, as this was not stated. They determined that the effective magnetic moment of this "$Tc_4O_5 \cdot xH_2O$(s)", by use of the Faraday method, was (2.50 ± 0.08) B.M., which is comparable to ~2 B.M. reported for various solid salts of $Tc_2Cl_8^{3-}$ and which falls in the observed range for a dinuclear technetium compound with a Tc-Tc multiple bond containing one unpaired electron. The Tc $3d_{5/2}$ binding energy of 255.9 eV for this hydrous oxide falls in the range for Tc(2.5), Tc(III), and Tc(IV) compounds [82GER/KRY].

[80TRO/JON]

See comments under [61HER/SCH].

[81DAV/JON2]

Davison *et al*. have prepared a Tc(V) complex with isothiocyanate, but it is an oxopentakis(isothiocyanato)technetate(V) complex. They prepared it by using ligand substitution of $(n\text{-}C_4H_9)_4NTcOCl_4$ with NH_4SCN in methanol. Subsequent addition of $Ph_4AsCl \cdot H_2O$ yielded fine bright red crystals of $(AsPh_4)_2TcO(NCS)_5$. Elemental analysis, optical spectroscopy in acetonitrile, and IR spectra of the complex in solid KBr were used to partially characterise this salt. Addition of excess KSCN to solutions of $TcO(NCS)_5^{2-}$ in acetonitrile gave complete reduction to a $Tc(NCS)_6^{2-}$ and $Tc(NCS)_6^{3-}$

mixture within 24 hours. Small amounts of self-ionisation of $TcO(NCS)_5^{2-}$ also yielded enough free SCN^- to produce slow autoreduction of this complex even in the absence of excess SCN^-. Addition of $AgNO_3$ to $TcO(NCS)_5^{2-}$ solutions produced a $Ag_2TcO(NCS)_5$-AgSCN mixture, with partial reduction to $Tc(NCS)_6^{2-}$ also occurring.

[81IAN/KOS]

Ianovici *et al*. compared the absorption maxima for $TcCl_6^{2-}$ and $TcCl_5^-$. The $TcCl_6^{2-}$ has a maximum at 338 to 340 nm [65JØR/SCH, 68KOY/KAN, 81IAN/KOS], and $TcCl_5^-$ has absorption maxima at 320 or ∼330 nm [68KOY/KAN, 81IAN/KOS] and 235 nm [69KAN, 81IAN/KOS]. There is another absortion maximum for $TcCl_6^{2-}$ at 234 to 240 nm [65JØR/SCH, 69KAN]. Although these absorption maxima occur at similar frequencies for $TcCl_6^{2-}$ and $TcCl_5^-$, there are enough subtle differences in their spectra, and large enough differences in their extinction coefficients, that these two species can be spectroscopically distinguished. The absorption spectra of $TcCl_4$(aq) and $TcCl_3^+$ exhibit much greater differences from each other and from $TcCl_6^{2-}$ and $TcCl_5^-$ [69KAN], and those for $TcBr_6^{2-}$ and $TcBr_5^-$ also show major differences from each other [76KAW/KOY, 88COL/IAN].

[81MIK/MIŠ]

Mikulaj, Mišianiková and Macášek reported solubilities of $TlTcO_4$(cr) in water at 298.15 K, along with those of $TlTcO_4$(cr) in solutions of HNO_3, $LiNO_3$, $NaNO_3$, NH_4NO_3, and $Ca(NO_3)_2$ up to quite high ionic strengths. Their experimental solubilities are tabulated in Table A.5. They stated that their solubilities were determined radiometrically for $^{99}TcO_4^-$, with an overall error of 2% or less. However, they only allowed fifty minutes for their solutions to reach equilibrium, which does not seem to us to be long enough to reach complete saturation. In fact, their reported solubility of $TlTcO_4$(cr) in water, 0.002116 M, is about 13% below the solubility reported by Keller and Kanellakopulos [63KEL/KAN]. In all cases, addition of HNO_3 or nitrate salts caused a significant "salting in" of $TlTcO_4$(cr) which suggests that much of the Tl^+ is being complexed as $TlNO_3$(aq).

Table A.5: Solubilities of $TlTcO_4$(cr) in aqueous solutions of different electrolytes at 298.15 K [81MIK/MIŠ].

Major electrolyte	I_c (mol · dm^{-3})	c_s (mol · dm^{-3})	K_c (mol^2 · dm^{-6})	$\log_{10} K_c - 2D_c$ [(a)]
$TlTcO_4$	0.002116	0.002116	4.477×10^{-6}	−5.393
HNO_3	0.10	0.002665	7.102×10^{-6}	−5.367
	0.30	0.003147	9.904×10^{-6}	−5.311
	0.50	0.003494	1.221×10^{-5}	−5.263
	1.0	0.004215	1.777×10^{-5}	−5.158
	2.0	0.005178	2.681×10^{-5}	−5.034

(Continued on next page)

Table A.5: (continued)

Major electrolyte	I_c (mol · dm^{-3})	c_s (mol · dm^{-3})	K_c (mol^2 · dm^{-6})	$\log_{10} K_c - 2D_c$ [(a)]
	3.0	0.006044	3.653×10^{-5}	−4.928
	4.0	0.006494	4.217×10^{-5}	−4.885
	5.0	0.006994	4.822×10^{-5}	−4.840
	6.0	0.007310	5.344×10^{-5}	−4.807
	7.0	0.007820	6.115×10^{-5}	−4.757
	8.0	0.007753	6.011×10^{-5}	−4.771
$LiNO_3$	1.0	0.003881	1.506×10^{-5}	−5.230
	2.0	0.004464	1.993×10^{-5}	−5.163
	3.0	0.005294	2.803×10^{-5}	−5.043
	4.0	0.006436	4.142×10^{-5}	−4.893
	6.0	0.007551	5.702×10^{-5}	−4.778
$NaNO_3$	0.10	0.002404	5.779×10^{-6}	−5.457
	0.50	0.003193	1.020×10^{-5}	−5.342
	1.0[(b)]	0.004292	1.842×10^{-5}	−5.143
	2.0[(b)]	0.005954	3.545×10^{-5}	−4.912
	2.5[(b)]	0.006482	4.202×10^{-5}	−4.855
	3.0	0.007153	5.117×10^{-5}	−4.782
	3.5	0.007666	5.877×10^{-5}	−4.732
	4.0	0.008612	7.417×10^{-5}	−4.640
	5.0	0.008445	7.132×10^{-5}	−4.670
NH_4NO_3	0.1	0.002664	7.097×10^{-6}	−5.368
	0.5	0.003567	1.272×10^{-5}	−5.245
	1.0	0.004218	1.779×10^{-5}	−5.158
	2.0	0.005495	3.020×10^{-5}	−4.982
	2.5	0.007218	5.210×10^{-5}	−4.761
	3.0	0.008057	6.492×10^{-5}	−4.679
	3.5	0.009313	8.673×10^{-5}	−4.563
	4.0	0.01097	1.203×10^{-4}	−4.429
	5.0	0.01221	1.491×10^{-4}	−4.350
$Ca(NO_3)_2$	0.3	0.002911	8.474×10^{-6}	−5.379
	0.9	0.003475	1.208×10^{-5}	−5.317
	1.5	0.003948	1.559×10^{-5}	−5.247
	3.0	0.004902	2.403×10^{-5}	−5.110
	6.0	0.005733	3.287×10^{-5}	−5.018
	9.0	0.008219	6.755×10^{-5}	−4.727
	12.0	0.01007	1.014×10^{-4}	−4.564

[(a)] The Debye-Hückel constant in molar units is given by $A_c = A\sqrt{\rho^\circ}$, where ρ° is the density of the solvent. For water at 298.15 K, $A_c = A/\sqrt{0.997045} = 0.50985$ mol$^{-1/2}$ · dm$^{3/2}$ at 298.15 K

(continued on next page)

(footnotes continued)

(b) For each electrolyte added to the $TlTcO_4$ solutions, the published data were presented in the order of increasing concentration. However, for $NaNO_3$ solutions, the reported concentrations of 1.0, 2.0, and 2.5 mol · dm^{-3} $NaNO_3$ were out of sequence whereas those of $TlTcO_4$ in those solutions were in sequence. By examination of their derived activity coefficient in their Figure V7, we concluded that their $NaNO_3$ molarities were transposed in their Table A.1 but that their $TlTcO_4$ molalities were reported correctly.

The ionic strengths due to those added electrolytes in the solutions used by Mikulaj, Mišianiková and Macášek range from 0.1 to 12.0 M, which is 47 to 5600 times as large as the concentration of $TlTcO_4$ in these solutions. Thus $TlTcO_4$ makes only a minor contribution to the total ionic strengths, which are mainly determined by the concentration of the other electrolyte added to the solution. Consequently, it is possible to convert the reported molar solubilities of $TlTcO_4$(cr) to molality units, simply by multiplying c_s by the (m/c) ratio of the added electrolyte. However, the molar concentrations of the added electrolyte were only reported to one or two significant figures, whereas those of $TlTcO_4$ were given to four significant figures, and such a conversion would result in a decrease in precision of derived quantities. It should be more accurate to extrapolate the molar solubility product K_c to infinite dilution to obtain K_c° , and then convert this value to $K_{s,0}^\circ$ by use of the density of water.

The concentration product for the formation of saturated solutions is given by $K_c = [Tl^+][TcO_4^-] = c_s^2$, where c_s is the molar concentration of $TlTcO_4$ in the saturated solution. The specific ion interaction equation (SIT) as applied to this system is given by

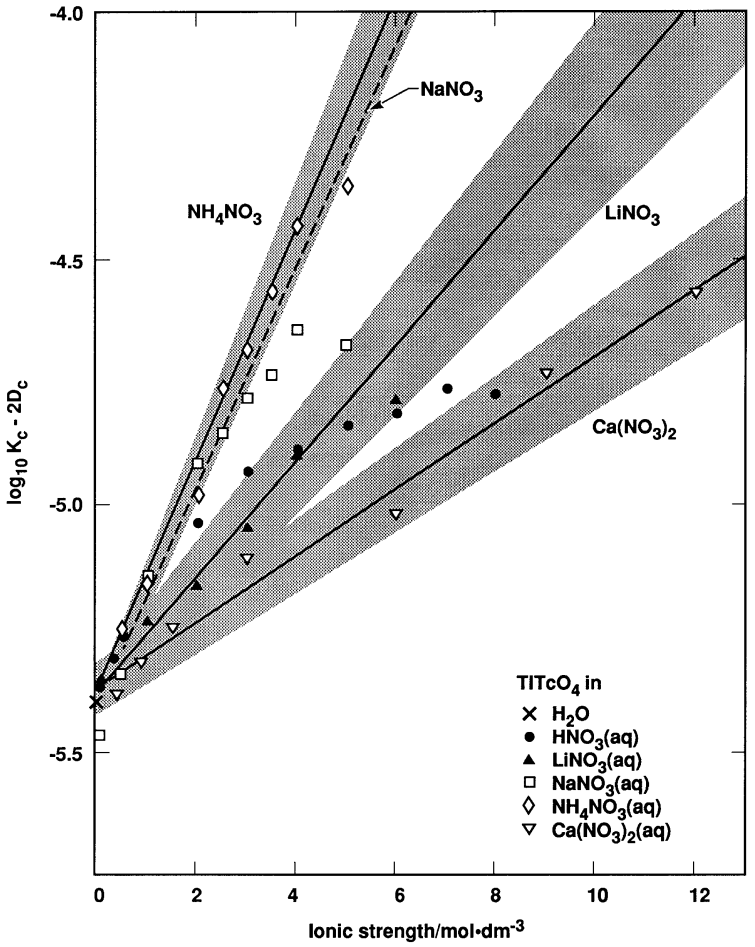
$$\log_{10} K_c - 2D_c \quad = \quad \log_{10} K_c^\circ - \Delta\varepsilon_c I_c \tag{A.18}$$

where D_c is the Debye-Hückel term with ionic strengths expressed on the molarity concentration scale.

Figure A.3 is a plot of $\log_{10} K_c - 2D_c$ against I_c for solubilities of $TlTcO_4$(cr) in various nitrate solutions, as recalculated by us from the experimental values of Mikulaj, Mišianiková and Macášek. Examination of this plot indicates that $\log_{10} K_c - 2D_c$ for $TlTcO_4$(cr) is a linear function of I_c over the whole concentration range for solutions in $Ca(NO_3)_2$, but there is a definite curvature for this type of plot for solutions in HNO_3 with $I_c > 1$ M, and there is probably also some curvature for solutions in $NaNO_3$ with $I_c > 3$ M. However, for saturated solutions of $TlTcO_4$ in $LiNO_3$ or NH_4NO_3, this type of plot is linear except for the single highest ionic strength. In those two cases it is not clear whether those singular points are due to scatter or represent the beginning of curvature in these plots.

The plot of $\log_{10} K_c - 2D_c$ for the solubility of $TlCO_4$(cr) as a function of the stoichiometric ionic strength is linear for concentrations of aqueous $HNO_3 \leq 1$ M, but it becomes non-linear at higher concentrations. This is not surprinsing given that nitric acid is incompletely dissociated except at low concentrations, and thus at higher concentrations the actual ionic concentrations of H^+ and NO_3^- are no longer identical to their stoichiometric concentrations. Examinations of Figures 2 and 3 of Young, Maranville and Smith [59YOU/MAR] indicates that at most 1 or 2% of the HNO_3 in an aqueous

Figure A.3: Plot of solubility data for $TlTcO_4$(cr) in water and aqueous nitrate solutions at 298.15 K [81MIK/MIŠ]. Parameters for the least-squares equations $\log_{10} K_c - 2D_c = \log_{10} K_c^\circ - \Delta\varepsilon I_c$ can be found in Table A.6, based upon fits for the linear region of the curves. Least-square curves for $TlTcO_4$ in NH_4NO_3 or HNO_3 coincide. Uncertainty limits are not plotted for solubilities in solutions with $NaNO_3$ or HNO_3, because of overlap with uncertainty limits for NH_4NO_3 solutions.



solution is associated for concentrations $\leq$1 M and this is small enough that it does not preclude the solubility of $TlTcO_4$(cr) from being represented accurately by the specific ion interaction model. However, at higher concentrations, HNO_3 is appreciably associated, ca. 18% at 5 M and 50% at 10 M, and consequently the plot of $\log_{10} K_c - 2D_c$ for the solubility of $TlTcO_4$(cr) as a function of the stoichiometric ionic strength is appreciably curved at higher concentrations of HNO_3.

Our major interest in these solubilities is to derive the limiting value of K_c at infinite dilution. We therefore determine $\Delta\varepsilon_c$ of Eq. (A.18) separately for each added electrolyte, with use of their [81MIK/MIŠ] solubility of pure $TlTcO_4$(cr) in each case. These fits were restricted to the range of I_c for which $\log_{10} K_c - 2D_c$ is a linear function of I_c. The resulting correlation coefficients for these fits are 0.9862 to 0.9977, and they are given in Table A.6 along with the least-squares parameters.

Table A.6: Parameters for ionic strength dependence of solubility of $TlTcO_4$(cr) at 298.15 K in solutions of various electrolytes [81MIK/MIŠ].

Major electrolyte	Range of I_c (mol · dm^{-3})	$\log_{10} K_c^\circ$	$\Delta\varepsilon_c$ (mol · dm^3)	Correlation coefficient
HNO_3	0.002 – 1.0	-5.388 ± 0.009	-0.2351 ± 0.0181	0.9977
$LiNO_3$	0.002 – 4.0	-5.382 ± 0.040	-0.11875 ± 0.0163	0.9927
$NaNO_3$	0.002 – 3.0	-5.423 ± 0.058	-0.2284 ± 0.0336	0.9862
NH_4NO_3	0.002 – 4.0	-5.392 ± 0.033	-0.2379 ± 0.0141	0.9968
$Ca(NO_3)_2$	0.002 – 12.0	-5.375 ± 0.038	-0.06859 ± 0.00648	0.9931

The selected value for $\log_{10} K_{s,0}^\circ$ is the statistically weighed average of the intercepts for these five least-squares fits, $\log_{10} K_c^\circ = -(5.388 \pm 0.008)$. This value is readily converted to the molal concentration scale by $\log_{10} K_{s,0}^\circ = \log_{10} K_c^\circ - 2\log_{10} d^\circ = -(5.385 \pm 0.008)$, where d° is the density of pure water in kg/dm^3.

The corresponding value of $K_{s,0}^\circ$ is $(4.12 \pm 0.08) \times 10^{-6}$ mol^2 · kg^{-2}.

[81RAJ/MAC]

In Table A.7, the rate constant values reported by Rajec and Macášek [81RAJ/MAC] and by Kawashima, Koyama and Fujinaga [76KAW/KOY] for the aquation (forward reactions, k_{aq}) and anation (reverse reactions, k_{an}) of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ are given. Both studies were done at $I = 4.0$ M solutions of Cl^- or Br^-. Kawashima, Koyama and Fujinaga [76KAW/KOY] reported results for $TcCl_6^{2-}$ from 348.2 to 363.2 K and from 313.2 to 327.7 K for $TcBr_6^{2-}$ (see comments under Ref. [65JØR/SCH] in this Appendix), and Rajec and Macášek studied $TcCl_6^{2-}$ at 298 K [81RAJ/MAC]. In both cases concentrations of technetium species were determined by spectrophotometry.

Rajec and Macášek did their measurements in 4.0 M HCl only, whereas Kawashima, Koyama and Fujinaga [76KAW/KOY] kept I = 4.0 M but replaced variable amounts of HX with LiX, NaX, or KX where X^- denotes Cl^- or Br^- . In all cases, the observed rate constant k_{obs} depended on the HX concentration, but only for LiX solutions of HX was the variation linear in the H^+

Table A.7: Experimental kinetic parameters and equilibrium constants for the aquation of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ at various temperatures.

T (K)	Ionic medium	k_{aq} or k'_{aq} ($mol^{-1} \cdot dm^3 \cdot s^{-1}$)[(a)]	k_{an} ($mol^{-1} \cdot dm^3 \cdot s^{-1}$)	$K^{(b)}{}_c$ (M)	Reference
$TcCl_6^{2-} \rightleftharpoons TcCl_5^- + Cl^-$					
348.2	4.0 M	$(1.18 \pm 0.14) \times 10^{-4}$	$(9.16 \pm 0.97) \times 10^{-5}$	1.29(1.25)	[76KAW/KOY]
353.7	HCl+LiCl	$(2.48 \pm 0.29) \times 10^{-4}$	$(1.93 \pm 0.21) \times 10^{-4}$	1.28(1.29)	
357.7	or	$(3.80 \pm 0.42) \times 10^{-4}$	$(2.87 \pm 0.28) \times 10^{-4}$	1.32(1.33)	
363.2	$HCl+HClO_4$	$(9.07 \pm 0.91) \times 10^{-4}$	$(6.52 \pm 0.65) \times 10^{-4}$	1.39(1.39)	
298	4.0 M HCl	$(4.05 \pm 0.22) \times 10^{-5}$	$(3.22 \pm 0.18) \times 10^{-5}$	1.26(1.25)	[81RAJ/MAC]
$TcBr_6^{2-} \rightleftharpoons TcBr_5^- + Br^-$					
313.2	4.0 M	$(2.77 \pm 0.19) \times 10^{-4}$	$(3.65 \pm 0.18) \times 10^{-4}$	0.759(0.756)	[76KAW/KOY]
318.2	HBr+LiBr	$(5.62 \pm 0.38) \times 10^{-3}$	$(6.23 \pm 0.37) \times 10^{-3}$	0.902(0.901)	
323.2	or	$(1.19 \pm 0.08) \times 10^{-3}$	$(1.20 \pm 0.06) \times 10^{-3}$	0.992(1.02)	
327.7	$HBr+HClO_4$	$(2.17 \pm 0.13) \times 10^{-3}$	$(1.88 \pm 0.09) \times 10^{-3}$	1.15(1.14)	

(a) These units are for the study of Kawashima, Koyama and Fujinaga [76KAW/KOY]; the correct units for k_{aq} from Rajec and Macášek [81RAJ/MAC] are s^{-1}. The difference arises because Ref. [81RAJ/MAC] reported measurements in pure HCl, whereas Ref. [76KAW/KOY] gave measurements in HCl+LiCl or HBr+LiBr, and they observed a catalytic effect of H^+. Values of k_{aq} from the earlier study [76KAW/KOY] should be multipled by 4.0 M for a direct comparison with values from the later study [81RAJ/MAC].

(b) The first value of K_c is computed from the ratio of k_{aq}/k_{an}. Values in parentheses were reported by these authors from spectroscopic determination of equilibrium concentrations in HCl or HBr solutions.

molarity. Similar measurements at 4.0 M H^+ with variable amounts of X^- ($HClO_4$ was used to control ionic strength) also gave a linear variation for k_{obs}. Thus,

$$k_{obs} = k_{aq}[H^+] + k_{an}[X^-] = k'_{aq} + k_{an}[X^-]$$

where k'_{aq} is the type of rate constant reported in Ref. [81RAJ/MAC].

Kawashima, Koyama and Fujinaga [76KAW/KOY] prepared their solutions by dissolution of K_2TcX_6(cr) in aqueous HCl, and stored their solutions in the dark except for brief illumination for the spectrophotometric measurements. Thus photochemical aquation should have been minimised, (see [69KAN]) and their kinetic parameters should approximate to those for the thermal reactions. In contrast, Rajec and Macášek [81RAJ/MAC] prepared their $TcCl_6^{2-}$ by electrolytic reduction of $TcOCl_5^{2-}$, apparently without excluding light from their solutions. Thus, as noted by those authors [81RAJ/MAC], their kinetic parameters contained catalytic and photochemical contributions. Huber, Heineman and Deutsch [87HUB/HEI] found that reduction of $TcCl_6^{2-}$ (in a mixture of 2.0 M HCl and 2.0 M NaCl) to Tc(III) followed by reoxidation to Tc(IV) during a four minute cyclic voltammetric cycle was sufficient to produce an equilibrated mixture of $TcCl_6^{2-}$ with the pentachloro complex of Tc(IV). Inasmuch as partial reduction of Tc(IV) may have occurred in the experiments of Rajec and Macàšek, their kinetic parameters may largely represent catalytic effects of Tc(III). This is supported by their observation that their kinetic parameters are several orders of magnitude larger than obtained by extrapolation of Kawashima, Koyama and Fujinaga's values to 298.15 K.

Kawashima, Koyama and Fujinaga [76KAW/KOY] did their equilibrium constant measurements with spectrophotometry, and additional results are obtained by this review from equating their rates of aquation and anation reactions, Table A.7, and they are in good agreement. They performed equilibrium constant measurements in I = 4.0 M Cl^- or Br^- solutions, with $[H^+]$ ranging from 1 to 4 M, and either Li^+, Na^+, or K^+ were present to maintain the proper ionic strength. Replacing H^+ with Li^+ had no effect on the value of the measured equilibrium constants, whereas replacing H^+ with Na^+ or K^+ caused the apparent equilibrium constant to increase. This presumably occurred because of changes in activity coefficients and water activities with composition. The equilibrium constant values reported by Kawashima, Koyama and Fujinaga were based only on their measurements in 4.0 M HCl or HBr and not in the mixed electrolyte solutions. It is not clear from the experimental description given in this paper whether the solutions were prepared to take into account the variation of the ionic strength with changes in temperature, or whether the ionic strengths of 4.0 M refer to the room temperature values only.

Rajec and Macášek [81RAJ/MAC] also studied the kinetics of electrolytic reduction of $TcOCl_5^{2-}$ in 4.0 M HCl at 298 K by using simultaneous coulometry and UV-visible spectrophotometry. The observed reaction sequence was

$$TcOCl_5^{2-} + 2H^+ + e^- \rightleftharpoons TcCl_5^- + H_2O(l)$$

followed by

$$TcCl_5^- + Cl^- \rightleftharpoons TcCl_6^{2-}$$

It is also possible that some of the $TcOCl_5^{2-}$ was directly reduced in a single step of the type

$$TcOCl_5^{2-} + 2H^+ + Cl^- + e^- \quad \rightleftharpoons \quad TcCl_6^{2-} + H_2O(l)$$

[82PAQ/LIS]

Paquette, Lister and Lawrence reported that spectroscopic evidence was obtained by them for complex formation between carbonate ions and both Tc(III) and Tc(IV). They noted in the absence of carbonate, a solution of 5×10^{-4} M Tc(III) disproportionated to yield Tc(IV) if pH $>$ 4, and Tc(IV) hydrous oxide precipitated around pH $=$ 4; in contrast, when carbonate was present, both the precipitation of Tc(IV) and the disproportionation of Tc(III) could be suppressed up to higher pH. This provides significant evidence for complex formation between technetium and carbonate, but no experimental details were provided nor were any experimental values given. Some of the details were provided in a later study [85PAQ/LAW].

A detailed study was done of the redox behaviour of technetium in HCO_3^- solutions at pH $=$ 8 [85PAQ/LAW]. The ionic strength was maintained at $I = 1$ M using sodium trifluoromethanesulfonate, and the HCO_3^- concentration was maintained at 0.5 to 1.0 M by use of $NaHCO_3$ and pressurisation with CO_2(g). The technetium concentration was generally 1.2×10^{-4} M, so the total carbonate-to-technetium ratios in their solutions were 4167 to 8333. Coulometric reduction indicated that a 4.1 e^- per technetium reduction of TcO_4^- occurred between -0.76 to -0.82 V vs SCE. The TcO_4^- solution was colourless, but upon reduction it rapidly turned pink and then pale blue. The pale blue Tc(III) solution was easily oxidised by O_2(g) in air to reform the pink species, and coulometric rereduction required 0.9 e^- per technetium. Thus the pink species contained Tc(IV).

They did a very careful study of the redox behaviour of the Tc(IV)/Tc(III) couple in carbonate solutions using spectroelectrochemistry with an optically transparent vitreous carbon electrode [85PAQ/LAW]. The redox potential was reversible or at least quasi-reversible at pH $=$ 8 in 0.5 M HCO_3^- with a formal reduction potential of -0.625 V vs. SCE. By varying the carbonate concentrations and pH, they showed that these Tc(III) and Tc(IV) complexes contained the same number of carbonate ligands, whereas the Tc(III) complex had one more hydroxide than the Tc(IV) complex. Thus the redox reaction can be written as

$$Tc(CO_3)_q(OH)_n^{4-n-2q} + H_2O(sln) + e^- \rightleftharpoons Tc(CO_3)_q(OH)_{n+1}^{3-(n+1)-2q} + H^+$$

where $n + q > 4$. However, since the values of n and q were unknown, no equilibrium constant was derived by the authors.

[82STR/BAZ]

See comments under [79KAD/LOR].

[83LEE/BON]

Lee and Bondietti studied the precipitation of technetium sulphide from an aqueous solution of 10^{-5} M NH_4TcO_4 with 1.9×10^{-4} to 1.50×10^{-3} M Na_2S at pH = 8.5. The extent of precipitation increased from 3 mass-% for 1.9×10^{-4} M Na_2S to 31 mass-% for 1.50×10^{-3} M Na_2S, for solutions equilibrated for five days. They described their black precipitate of technetium sulphide as being "insoluble in both acid and alkaline solution in the absence of strong oxidants". A sample of solution and precipitate prepared by reacting 3×10^{-4} M aqueous NH_4TcO_4 with 6×10^{-2} M Na_2S at pH = 8.5 was aged for one month at 343 K followed by seven months at 298 K. After that time, the precipitate was removed, washed, and then dried at 343 K for one day. The resulting particles typically were about 50 pm in diameter, they were roughly circular and plate-like in shape, and they were amorphous towards X-ray and electron diffraction. Chemical analysis by neutron activation yielded a composition of $TcS_{3.23}$(s) (or $Tc_2S_{6.5}$(s)), which is in approximate agreement with the expected composition of Tc_2S_7(s). However, we note that this analysis is equally compatible with a formulation TcS_3(s).

[83MIL]

The author did a fairly extensive investigation of the electrochemical behaviour of TcO_4^- in tripolyphosphate solutions. The tripolyphosphate concentration was generally fixed at 0.100 M, and the pH was controlled by an acetate buffer (0.05 to 0.1 M) for pH = 3 to 5 and by either ammonia (0.05 to 0.1 M) or borate (0.02 M) for pH = 9.5 to 11. The solution pH values were adjusted with addition of small amounts of HCl, H_2SO_4, or NaOH. A variety of different technetium tripolyphosphate (TPP) complexes were produced depending on differences in experimental conditions: bulk (coulometric) electrolysis of TcO_4^-, polarographic reduction of TcO_4^-, or ligand exchange with $TcBr_6^{2-}$.

Miller found that bulk electrolysis of TcO_4^- in acidic TPP solutions at pH = 4.0 to 4.8 produced an air sensitive Tc(III) complex that could be oxidised to a Tc(IV) species that was stable towards both oxidation and reduction. No direct reaction occurred between freshly-prepared Tc(III) and TcO_4^-. However, coulometrically prepared Tc(IV) species gradually underwent hydrolysis in both acidic and alkaline solutions, and these hydrolysed species could be reduced in irreversible pH-dependent processes. The hydrolysis products were different for hydrolysis under acidic or alkaline conditions, possibly because protonation of coordinated TPP may have occurred at lower pH values. The hydrolysis reaction for pH = 3 to 6 followed the rate equation

$$-\mathrm{d}[\mathrm{Tc(IV)}, \mathrm{unhyd}]/\mathrm{d}t \quad = \quad k[\mathrm{Tc(IV)}, \mathrm{unhyd}][\mathrm{OH}^-]$$

where $k = 580\ \mathrm{mol}^{-1} \cdot \mathrm{dm}^3 \cdot \mathrm{min}^{-1}$ and "unhyd" denotes the unhydrolysed Tc-TPP complex. A different and possibly dimeric Tc(III) complex was produced by polarographic reduction of TcO_4^- in TPP solutions. It could be reoxidised nearly reversibly to a possibly dimeric Tc(IV) complex.

Ligand exchange of H_2TcBr_6 solutions containing NH_4^+ with TPP was also studied, and the resulting technetium complexes were separated by gel permeation chromatography. A mixture was obtained, from which a 1:1 Tc-TPP complex was isolated, and it appeared to be polymeric. Its behaviour was distinct from those of the Tc(IV)-TPP complexes produced by electrochemical reduction of TcO_4^- in TPP solutions.

[83SPI/KRY]

Spitsyn, Kryuchkov and Kuzina studied the reduction of TcO_4^- in aqueous HNO_3 with hydrazine. At HNO_3 concentrations of < 1.0 M, hydrazine reduced TcO_4^- with precipitation of Tc(IV) and Tc(V) hydrous oxides (note: there is very little supporting evidence for a Tc(V) oxide). In solutions of > 8 M HNO_3, hydrazine concentrations of up to 1 M did not reduce TcO_4^-, which is partly due to precipitation of $N_2H_4 \cdot 2HNO_3$. However, at various HNO_3 concentrations, high concentrations of both N_2H_4 and TcO_4^- reacted explosively to form a complex. This "fairly stable" complex was isolated in solid form, and identified as $TcO(NO_3)_3 \cdot H_2O$(s). No details of its identification were provided.

[84KOL/GOM]

The kinetics of the hydrolysis of $TcOCl_5^{2-}$ have been studied in aqueous HCl using spectrophotometry as have the oxidation of this species by HNO_3 [84KOL/GOM2] and HNO_2 [84KOL/GOM3]. In each case, a rapid equilibrium of the type (A.19) or (A.20) was invoked in order to explain the observed reaction kinetics.

$$TcOCl_5^{2-} + H_2O(l) \rightleftharpoons TcO_2Cl_4^{3-} + 2H^+ + Cl^- \qquad \text{(A.19)}$$

$$TcOCl_5^{2-} + 2H_2O(l) \rightleftharpoons TcOCl_4(OH)_2^{3-} + 2H^+ + Cl^- \qquad \text{(A.20)}$$

It is impossible to distinguish between these alternate reactions solely on the basis of their kinetic data, so it is not known whether the intermediate species was a hydroxyoxy- or a dioxy-complex of tetrachlorotechnetium(V). There are possibly other equilibrium reactions that are consistent with the reaction kinetics data. The equilibrium constant at 298.15 K for the above reaction (no matter which reaction is correct) is $K = 0.05$ mol$^3 \cdot$ dm^{-9} at an ionic strength of $I = 1$ M [84KOL/GOM], $K = 0.06$ mol$^3 \cdot$ dm^{-9} at $I = 2$ M, and $K = 0.1$ mol$^3 \cdot$ dm^{-9} at $I = 3$ M [84KOL/GOM3].

One way to explicitly include the activity of water in the equilibrium constants is to define the mixed concentration-activity products

$$K\,(\text{A.19}) = \frac{[TcO_2Cl_4^{3-}][H^+]^2[Cl^-]}{[TcOCl_5^{2-}]a_{H_2O}}$$

and

$$K\,(\text{A.20}) = \frac{[TcOCl_4(OH)_2^{3-}][H^+]^2[Cl^-]}{[TcOCl_5^{2-}]a_{H_2O}^2}$$

These two equilibrium constants are related by

$$K\,(\text{A.20}) \quad = \quad \frac{K\,(\text{A.19})}{a_{H_2O}} \tag{A.21}$$

This equality is based on the recognition that $[TcO_2Cl_4^{3-}] = [TcOCl_4(OH)_2^{3-}]$ because they are just two different ways of formally denoting the same chemical species. The equilibrium constants given in references [84KOL/GOM, 84KOL/GOM3] apparently do not contain these water activity factors.

The major solute constituent in each of the solutions studied by Koltunov and Gomonova [84KOL/GOM, 84KOL/GOM3] is HCl, and thus the ratios of molality to molarity for HCl, given in Table II.5, are used to convert ionic strengths and equilibrium constants to the molality scale. The reported ionic strengths of 1, 2 and 3 M are equivalent to 1.02, 2.08 and 3.2 mol·kg^{-1}, respectively. The values of aH$_2$O for HCl solutions are calculated from the osmotic coefficients tabulated by Robinson and Stokes [59ROB/STO], and are a_{H_2O} = 0.9625, 0.9141 and 0.8526 at 1.02, 2.08 and 3.20 mol·kg^{-1}, respectively.

Using these conversion factors and a_{H_2O} values yields K(A.19) = 0.055 and K(A.20) = 0.057 at I_m = 1.02 mol·kg^{-1}, K(A.19) = 0.073 and K(A.20) = 0.80 at I_m = 2.08 mol·kg^{-1}, and K(A.19) = 0.12 and K(A.20) = 0.17 at I_m = 3.20 mol·kg^{-1}. The units of both K(A.19) and K(A.20) are mol^3·kg^{-3}.

The specific ion interaction equation for K(A.19) and K(A.20) has the following form

$$\log_{10}K^\circ = \log_{10}K - 8D + \varepsilon\ I_m \tag{A.22}$$

where D is the Debye-Hückel term, *cf* Appendix C. Least-squares evaluations of the parameters of Eq. (A.22) for K°(A.19) and K°(A.20) indicated that e was not statistically significant for either case, and it was consequently set equal to zero for the calculations repeated. Eq. (A.22) then yields $\log_{10}K^\circ$(A.19) $= -(2.90 \pm 0.16)$ and $\log_{10}K^\circ$(A.20) $= -(2.86 \pm 0.19)$. Eq. (A.21) implies that K° (A.19) = K°(A.20). Thus $\log_{10}K^\circ = -(2.9 \pm 0.2)$. Since there is some uncertainty about the exact equilibrium reaction occurring for this system, we can not recommend the derived value at this time.

[84RUS/BIS]

Russell and Bischoff investigated the ionic charge on technetium pyrophosphate complexes at various pH values. They prepared their solutions by reaction of tracer amounts of $^{99m}TcO_4^-$ in 0.15 M NaCl with 0.01 M $Na_4P_2O_7$ that had been previously adjusted to pH = 7.0 with acetic acid. To this solution was added a small amount of a solution of 0.5 M $SnCl_2$ in 2 M HCl; the solutions were aged 10 minutes before the chromatographic experiments were started. They performed their ion-exchange experiments at pH = 3.7 to 4.8 and at pH = 6.0 to 7.5 on two different ion-exchange systems.

They found that the two principal technetium pyrophosphate complexes, which were separated by ion-exchange chromatography, tended to decompose below pH =

3.7 unless a small amount of DTPA (diethylenetetramine pentaacetic acid) was added to the solutions. Chromatographic retention times were the same for these solutions and for samples eluted a second time with a solution of 0.1 M $Na_4P_2O_7$ and 0.1 M KNO_3 at pH = 7.0. The identical retention times imply that the technetium pyrophosphate complexes were not altered by the presence of DTPA.

[85ANT/MER]

See comments under [79BRA/HAR].

[85ARO/HWA]

Aronson *et al*. studied changes in the electronic spectrum of $TcCl_6^{2-}$ in several different ionic media. They found that a solution of $((n\text{-}C_4H_9)_4N)_2TcCl_6$ was "stable" in aqueous 25 mol·kg^{-1} choline chloride, and that its spectrum was similar to that of $TcCl_6^{2-}$ in concentrated HCl. However, spectroscopic measurements for $((n\text{-}C_4H_9)_4N)_2TcBr_6$ in 10 mol·kg^{-1} $(n\text{-}C_4H_9)_4NBr$ showed that $TcBr_6^{2-}$ was much less stable in this medium and 70% of it decomposed within 18 hours, but addition of 0.12 M HBr to that solution stabilised it for several days.

[85KOL/GOM]

Koltunov and Gomonova studied the reproportionation of TcO_4^- and $TcCl_6^{2-}$. A preliminary experiment indicated that no detectible reaction occurred between TcO_4^- and $TcCl_6^{2-}$ below room temperature, but at 353 K the reaction occured at a significant rate. The reaction kinetics were studied at ionic strengths of 1 to 4 M and from 348 to 363 K using spectrophotometry, with most experiments at 353 K. The observed reaction was

$$2TcCl_6^{2-} + TcO_4^- + 3Cl^- + 2H^+ \quad \rightleftharpoons \quad 3TcOCl_5^{2-} + H_2O(l)$$

The reaction kinetics at 353 K were first order in [Tc(IV)] at $I = 1$ and 2 M, but were one-tenth order in both $[TcO_4^-]$ and $[H^+]$ at $I = 2$ M and were independent of both of their concentrations at $I = 1$ M.

[85PAQ/LAW]

See comments under [82PAQ/LIS].

[85SPI/KUZ]

A mixed valence oxychloride of technetium was reported. The original references are not available to us, but it was described in some detail by Spitsyn *et al*.

$K_3Tc_2O_2Cl_8(s)$ can be prepared by refluxing $K_3Tc_2Cl_8 \cdot 2H_2O(s)$ in methyl ethyl ketone in the presence of air. This solid was sparingly soluble in organic solvents, but it dissolved readily in aqueous solutions of inorganic acids. It was rather resistant to oxidation and reduction both in the solid phase and in solution, but decomposition was

relatively more rapid in the presence of complexing agents. When $K_3Tc_2O_2Cl_8$(s) was added to concentrated aqueous HCl, the initial decomposition was to form equivalent amounts of $TcCl_6^{2-}$ and $TcOCl_5^{2-}$. This supports their claim that the solid was a mixed-valence Tc(IV,V) compound.

[86FLI/LAN]

Flint and Lang prepared $Cs_2TcBr_{6-x}Cl_x$(s) in Cs_2SnCl_6(s) by reaction of Cs_2TcCl_6(s) with a small amount of concentrated HBr, adding the mixture to a large excess of $SnCl_4$ in aqueous HCl, and precipitating the Cs_2SnCl_6(s) with excess CsCl in HCl. These authors also obtained luminescence spectra of these solids under blue or ultraviolet excitation at low (but unspecified) temperatures; these spectra were analysed in terms of all the ten possible $[TcCl_nBr_{6-n}]^{2-}$ species except the facial $[TcCl_3Br_3]^{2-}$ isomer.

Wendt and Preetz [92WEN/PRE] made a more extensive investigation of the luminiscence spectra of these phases at 10 K using Cs_2SnBr_6(s) and Cs_2TcCl_6(s) as well as Cs_2SnCl_6 as host lattices and suggest somewhat different assignments of the luminiscence bands for the eight mixed isomers, including $fac-[TcCl_3Br_3]^{2-}$. The same authors had previously described [91PRE/WEN] the preparation and substantial separation of the individual isomers of the $((n\text{-}C_4H_9)_4N)_2Tc(Cl, Br)_6$ series of compounds, by ligand exchange in HCl or HBr acids at room temperature, followed by ion-exchange chromatography on diethylaminocellulose. They also measured the infrared and Raman spectra of these compounds, and compared the experimental vibrational frequencies with those calculated from a normal-coordinate analysis. They found that due to the different trans-effect of the Cl and Br ligands, the Tc-Br bonds are strengthened and the Tc-Cl bonds weakened on the asymmetric Cl-Tc-Br axes as compared with those on symmetrical X-Tc-X axes.

[86MEY/ARN]

Meyer, Arnold and Case found that measurable amounts of TcO_4^- were present in saturated solutions of Tc(IV) in contact with $TcO_2 \cdot xH_2O$(s) even though the experiments were performed in a glove box in an argon atmosphere containing $< 0.7 \times 10^{-6}$ mass fraction of O_2(g). Meyer, Arnold and Case (their Figures 1 and 2) even found that under these conditions the equilibrium concentrations of TcO_4^- generally exceeded those of Tc(IV) in both acidic and alkaline solutions. It is probable that some of this oxidation of Tc(IV) involved chemical species produced in small amounts by the radiolysis of water, as some of the ^{99}Tc underwent radioactive decay.

Meyer, Arnold and Case determined redox potentials at pH $= 1.9$ for variable concentrations of TcO_4^- of about 2×10^{-6}, 2×10^{-5} and 2×10^{-4} M. Results were presented graphically. By assuming that Reaction (V.2) was reversible, and using the value of Cartledge and Smith [55CAR/SMI] of $E^\circ = 0.738$ V, they predicted values of E as a function of the TcO_4^- concentration that were within a few mV of the experimental points. This confirms the general reliability and consistency of cell potential measurements involving the $TcO_4^-/TcO_2 \cdot xH_2O$(s) electrode.

[86SPI/TAR]

Nuclear quadrupole coupling constants (QCC) were reported for ^{99}Tc in a variety of pertechnetate salts with monovalent cations [86SPI/TAR, 86TAR/PET]. The $LiTcO_4$ was the only salt with a QCC of zero; this implies that the ^{99}Tc is in a completely symmetrical environment. Values of QCC for the other salts ranged from 1.25 to 5.2 MHz. There appears to be a rough correlation of QCC values with the crystallographic unit cell size; crystals with smaller unit cells (and, presumably, shorter cation-to-pertechnetate distances) tend to have larger values of QCC.

The nuclear quadrupole coupling constant of ^{99}Tc in "$Tc_2O_7 \cdot H_2O$(s)" or "$Tc_2O_7 \cdot xH_2O$(s)" is considerably larger than for alkali metal pertechnetates [86SPI/TAR, 86TAR/PET], although the structural significance of this is not entirely unambiguous. The unit cell of "$Tc_2O_7 \cdot H_2O$(s)" or "$Tc_2O_7 \cdot xH_2O$(s)" was reported in these studies to be orthorhombic, but no details were given nor was the space group reported.

Kirkpatrick [88KIR] tabulated values of QCC for ^{17}O in a variety of inorganic and organic oxides containing M-O-M or M-O-M′ bonds. Values of QCC were small for highly ionic bonds but were large for predominately covalent bonds. The QCC for "$Tc_2O_7 \cdot H_2O$(s)" [86SPI/TAR, 86TAR/PET], ∼10 MHz, was much larger that for any of the pertechnetate salts. If the same type of correlation holds between QCC and degree of ionic character for ^{99}Tc as for ^{17}O, then the larger value of QCC for "$Tc_2O_7 \cdot H_2O$(s)" implies that highly covalent bonds and not ionic bonds are present which then implies that this compound is more probably a hydrated oxide rather than being pertechnetic acid. Alternatively, the large QCC value could simply indicate that the technetium atoms are in a highly asymmetric environment. Also see the discussion of reference [98GUE] which suggests that "$Tc_2O_7 \cdot H_2O$(cr)" may possible have an ionic structure. Unit cell parameters have been determined for "$Tc_2O_7 \cdot H_2O$" at 196 K in the laboratory of K.E. Guerman [98GUE2]. However, the detailed structured of this compound was not solved.

[86TAR/PET]

See comments under [86SPI/TAR].

[86VAN/DAV]

Vankin, Davidov and Selig studied the intercalation of TcF_6 and other metal hexafluorides into graphite. These authors noted that some compounds of this type showed metal-like conductivities. The graphite used in this study was highly oriented pyrolytic graphite, HOPG. This HOPG had essentially single crystal properties along the crystallographic *c*-axis, but exhibited some mosiac spread along the *a*-axis. Both HOPG and its intercalation compounds exhibited strongly anisotropic properties. These intercalation compounds generally formed spontaneously when MF_6 and HOPG were brought into contact.

Intercalation of MF_6 into graphite occurred by way of the reaction

$$n\mathrm{C(HOPG)} + \mathrm{MF_6(l?)} \quad \rightleftharpoons \quad (\mathrm{C}_n^{x+})(\mathrm{MF}_6^-)_x(\mathrm{MF_6})_{1-x}\mathrm{(s)}$$

where x is the degree of charge transfer from carbon to the MF_6. The authors cited a literature estimate that the electron affinity of MF_6 should exceed about 500 $\mathrm{kJ{\cdot}mol^{-1}}$ for spontaneous intercalation to occur.

Vankin, Davidov and Selig observed that when HOPG came in contact with TcF_6, the electrical conductivity of the intercalation compound rapidly increased to about 7 times that of HOPG, and the d-plane spacing became 11.46×10^{-10} m (stage-II). Upon further exposure to TcF_6, the d-plane spacing decreased to 8.12×10^{-10} m and the conductivity dropped to that or below that of HOPG (stage-I). Parameters were reported for the temperature dependence of the electrical conductivities of stage-I (C_9TcF_6) and stage-II ($C_{20}TcF_6$), based on measurements from about 10 to 280 K.

Their ESR measurements of stage-I $C_{10}TcF_6$ at 4 K showed a clearly resolved ten-line spectrum, which was similar to that for ^{99}Tc(VI) compounds. However, the effective magnetic moment of this same sample was 0.7 B.M., which fell between that of TcF_6 (0.45 B.M.) and TcF_6^- in alkali metal MTc^vF_6 (2.25 to 2.51 B.M.). These results led them to an estimated value of $x = 0.06$ for the degree of charge transfer, which they felt was unrealistically low. However, based on a linear correlation of the d-plane spacing with the degree of charge transfer for MF_6 in HOPG, they estimated that a degree of charge transfer of $x \approx 1$ was more likely for the technetium case.

[87HUB/HEI]

Huber, Heineman and Deutsch investigated the redox behaviour of TcX_6^{2-} in aqueous HX-NaX mixtures, where $X^- = Cl^-$ or Br^-. Typical experimental compositions were (1 to 3) $\times 10^{-3}$ M Tc(IV), 2.0 M HX, and 2.0 or 3.0 M NaX. These electrochemical measurements were done with thin-layer and bulk solution cyclic voltammetry, thin-layer coulometry, and thin-layer spectropotentiostatic measurements relative to a saturated NaCl calomel electrode. The reversible redox reactions occurred by the general unbalanced reaction (in H_2O)

$$\mathrm{Tc(IV)} + \mathrm{e^-} \quad \rightleftharpoons \quad \mathrm{Tc(III)} + n_h\mathrm{H^+} + n_x\mathrm{X^-}$$

where Tc(IV) denotes the hexahalo complex or a mixed aquo-halide complex. Their least-squares analysis of the emf results indicated that $n_h = (1.2 \pm 0.2)$ and $n_x = (2.7 \pm 0.2)$ for the chloride system, and $n_h = (1.6 \pm 0.6)$ and $n_x = (5.9 \pm 1.0)$ for the bromide system. Based on the known equilibrium constants, the Tc(IV) solutions under these conditions are known to be mixtures of TcX_6^{2-} and TcX_5^-. However, for Tc(III) the electrochemical results indicate that $TcCl_3(OH)^-$ and $TcCl_3(OH)_2^{2-}$ are the predominant species in the chloride system, and $Tc(OH)^{2+}$ and $Tc(OH)_2^+$ predominate for the bromide system. Thus the tendency for aquation and hydrolysis of Tc(III) halide complexes is greater for the bromide system than for the chloride, as was found to be the case for Tc(IV).

[87LIE/BAU2]

Lieser *et al*. prepared TcO_2(cr) by thermal decomposition of NH_4TcO_4(cr) in flowing N_2(g) at 1073 K, and the resulting TcO_2(cr) was then placed in a sealed quartz ampoule and annealed at 1133 K for 14 hours. This produced a well-crystallised sample of TcO_2(cr), which was used for aqueous solubility experiments. In this study, they found that relative dissolution rates per gram of TcO_2(cr) in 0.1 M $NaNO_3$ in the presence of air were independent of the amount of TcO_2(cr) used in the solubility experiments, but the absolute rates did depend on the surface area per gram of TcO_2(cr). This implies that the rate limiting step for the dissolution of TcO_2(cr) involved a reaction at its surface. In addition, they found that for aqueous solutions with low concentrations of Cl^- the rate of oxidation of TcO_2(cr) by oxygen was the rate limiting step, and this oxidation rate was proportional to the aqueous concentration of oxygen. They also found that in the presence of oxygen, oxidative dissolution of TcO_2(cr) occurred, with more than 99% of the dissolved technetium then being present as TcO_4^-.

Lieser *et al*. also studied the dissolution of TcO_2(cr) under anaerobic (low oxygen) conditions. They found that the relative dissolution rate was (2.34 ± 0.09) ppm $\cdot$ d^{-1} under aerobic conditions ($E_h = (0.475 \pm 0.015)$ V), but was < 0.02 ppm $\cdot$ d^{-1} under anaerobic conditions ($E_h = (0.300 \pm 0.015)$ V). They attributed the initial dissolution of a small amount of TcO_2(cr) under anaerobic conditions as being due to the action of oxygen sorbed on the TcO_2(cr), but the oxidation state of this dissolved technetium is not known. For this dissolution experiment under anaerobic conditions at pH $= (5.7 \pm 0.1)$, 3 mg of TcO_2(cr) was placed in 100 cm^3 of 0.1 M $NaNO_3$. This TcO_2(cr) had previously been washed free of soluble impurities. The resulting concentration of technetium due to dissolution of 3 ppm TcO_2(cr) is equivalent to 7×10^{-10} M.

The solubility study of Lieser *et al*. was described in detail, and their TcO_2(cr) was well characterised. However, it is possible to interpret their solubility measurements for TcO_2(cr) under anaerobic conditions in different ways. One of these interpretations was given by Lieser *et al*., *viz*., that the initial dissolution involved residual aqueous oxygen and resulted in the formation of TcO_4^-, whereas the dissolution of TcO_2(cr) without oxidation is so slow that saturation is never reached for aqueous Tc(IV). Another possibility is that the 3 ppm initial dissolution was sufficient to produce a saturated solution of Tc(IV) in equilibrium with either TcO_2(cr) or a partially hydrated surface oxide.

[87LIE/BAU]

Lieser and Bauscher studied the sorption behaviour of technetium from various groundwaters onto various wet sediments as a function of applied potential. They found that for experiments performed at pH $= (7.0 \pm 0.5)$, the sorption of technetium decreased by nearly a factor of 10^4 as the potential was changed from negative to positive values. The most rapid change in sorption occurred at (0.170 ± 0.060) V, but at higher and lower potential values the sorption was nearly independent of pH. We assume, as they did, that this sorption change was due to reduction of TcO_4^- to Tc(IV); Tc(IV) is known to be more strongly sorbed than TcO_4^-. The redox potential needs to be

corrected to pH = 0 to yield the standard potential for Reaction (V.2), thus yielding $E^\circ = (0.722 \pm 0.072)$ V. Given the approximate nature of this type of measurement, the derived value is in excellent agreement with the direct experimental values cited in Section V.2.1.

[87MEY/ARN]

Meyer and coworkers [87MEY/ARN, 89MEY/ARN] studied the solubility of $TcO_2 \cdot xH_2O$(s) as a function of pH in various electrolyte solutions (mainly HCl or NaCl solutions). Solubilities of $TcO_2 \cdot xH_2O$(s) in solutions of NaCl at concentrations of NaCl between 0.05 and 2.6 M and at pH = 6.9 to 9.3 showed no significant variation with either variable. However, solubility measurements were also made in 0.01 M $NaHCO_3$ plus Na_2CO_3 at pH = 9.74 [87MEY/ARN] and at pH = 9.54 and 9.70 [89MEY/ARN] and in synthetic basaltic groundwater containing HCO_3^- at pH = 9.27 to 9.43. These solubilities are consistent with solubilities at these same pH values in NaCl-NaOH solutions, and no evidence was obtained for carbonate or chloride complexes under those conditions.

[87NEC/KAN]

Neck and Kanellakopulos [87NEC/KAN] reported their densities of aqueous $NaTcO_4$ in g·mL^{-1} at 298.15 K for five concentrations from 0.0982 to 0.3101 mol·dm^{-3}. From these data they derived the value $\overline{V}_2^\circ(TcO_4^-, \text{aq}, 298.15\ \text{K}) = (45.9 \pm 1.0)\ \text{cm}^3 \cdot \text{mol}^{-1}$. However, their densities were only determined to $\pm 1 \times 10^{-4}$ g · mL^{-1}, which gives uncertainties of the apparent molar volume V_ϕ of ± 0.63 cm^3 · mol^{-1} at c = 0.3101 mol · dm^{-3} to ± 1.98 cm^3 · mol^{-1} at c = 0.0982 mol · dm^{-3}. In addition, they only determined the $NaTcO_4$ concentrations to a precision of $\pm 0.5\%$ by a radiometric method, which contributes further to the uncertainty of V_ϕ. It is clear that extrapolation of their V_ϕ to infinite dilution to obtain $V_\phi^\circ = \overline{V}_2^\circ$ will have considerable uncertainty. Neck and Kanellakopulos reported using a molar mass of 185.99 g · mol^{-1} in their calculations, which may be a typographical error since it differs by 0.10 g · mol^{-1} from a value of 185.8937 g · mol^{-1} calculated using current IUPAC "atomic weights". Apparent molar volumes V_ϕ were calculated from the reported densities and concentrations. An attempt was made to extrapolate these values to infinite dilution using the extended Debye-Hückel (Redlich-Meyer) equation, $V_\phi = V_\phi^\circ + A_v\sqrt{I_m} + B_v I_m$, where A_v is the Debye-Hückel limiting slope for volumes and B_v is a salt-specific empirical parameter. The apparent molar volume values were too scattered to yield an unique value of V_ϕ° by least-squares analysis. Using a combination of fits to various subsets of this data set and empirical extrapolations, this review derives an estimated value of $V_\phi^\circ(NaTcO_4, \text{aq}, 298.15\ \text{K}) = (46.3 \pm 1.5)\ \text{cm}^3 \cdot \text{mol}^{-1}$ from this study.

[88GER/KRJ]

German *et al*. studied the solubility of *n*-tetrabutylammonium pertechnetate in aqueous solutions of $LiNO_3$, HNO_3, $(n\text{-}C_4H_9)_4NOH$, and $LiNO_3$-HNO_3 mixtures at 293.15 K using radiometric determination of the concentration of ^{99}Tc. The solubility of $(n\text{-}C_4H_9)_4NTcO_4$(cr) was unaffected by the presence of $LiNO_3$, it increased with the concentrations of HNO_3, but it decreased with increasing concentrations of $(n\text{-}C_4H_9)_4NOH$. This increase in solubility with addition of HNO_3 is due, at least in part, to tying up some of the TcO_4^- as undissociated $HTcO_4$, whereas the decrease in solubility with addition of $(n\text{-}C_4H_9)_4NOH$ is largely a "common ion effect." The increase in solubility of $(n\text{-}C_4H_9)_4NTcO_4$(cr) in mixtures of $LiNO_3$ and HNO_3 at $I_c = 5.00$ M is virtually identical to the solubility increase in HNO_3 alone, at the actual concentration of HNO_3.

In contrast to the "salting in" effect of HNO_3 on the solubility of $(n\text{-}C_4H_9)_4NTcO_4$(cr), the presence of $(n\text{-}C_4H_9)_4NOH$ caused a reduction of its solubility. They found that the reduction of the concentration of TcO_4^- upon addition of different concentrations of $(n\text{-}C_4H_9)_4NOH$ was less than expected from solubility product considerations, and they attributed this effect to the formation of undissociated species of the type $(n\text{-}C_4H_9)_4NTcO_4$(aq). By neglecting activity coefficient corrections, they obtained a formation constant for these ion pairs: $K_c = (15 \pm 6)\ M^{-1}$. Because of the variable ionic strength and the neglect of activity coefficients, this equilibrium constant should be considered uncertain.

[88LIB/NOO]

Libson *et al*. described a red salt of Tc(III) that contains the $NO_3 \cdot HNO_3^-$ anion, which is a nitrate ion solved with a molecule of nitric acid. No experimental details were given for the preparation of *trans*-$[TcCl_2(dppe)_2]NO_3 \cdot HNO_3$(cr), where dppe denotes the 1,2-bis(diphenylphosphino) ethane ligand. It is quite likely that it was prepared by ligand exchange with *trans*-$[TcCl_2(dppe)_2]Cl$ in concentrated HNO_3. This *trans*-$[TcCl_2(dppe)_2]NO_3 \cdot HNO_3$(cr) crystallised in the triclinic space group $P\bar{1}$ with $a = (10.083 \pm 0.004) \times 10^{-10}$ m, $b = (11.119 \pm 0.008) \times 10^{-10}$ m, $c = (12.767 \pm 0.002) \times 10^{-10}$ m, $\alpha = (71.80 \pm 0.02)°$, $\beta = (73.68 \pm 0.02)°$, $\gamma = (69.35 \pm 0.02)°$, and $Z = 1$.

[88VIK/GAR]

Very few experimental details are available for the solubility study of Paquette and Lawrence, which is summarised in this report by Vikis *et al.*, and the experimental solubilities were only presented graphically. The only real experimental information concerning that solubility study was that their TcO_2(cr) had been prepared by thermal decomposition of NH_4TcO_4(cr) and that their amorphous $TcO_2 \cdot xH_2O$(am) had been prepared by titration of an aqueous acidic Tc(IV) solution with NaOH.

Vikis *et al*. gave a plot of the logarithm of the solubility of TcO_2(cr) as a function of pH at 298 K; at pH = 5.7 this curve yields a solubility of $\sim 2 \times 10^{-8}$ M. This solubility is about a factor of 30 higher than the total solubility obtained by Lieser *et al*. [87LIE/BAU2] for TcO_2(cr) at this same pH. The report by Vikis *et al*. also contained

a plot of the solubility of freshly precipitated amorphous $TcO_2 \cdot xH_2O$(s) as a function of pH. The solubility of their TcO_2(cr) was lower than that of $TcO_2 \cdot xH_2O$(s) in acidic solutions, but was higher in alkaline solutions.

The higher solubilities for TcO_2(cr) than for $TcO_2 \cdot xH_2O$(s) at high pH values and the reverse order for their solubilities at lower pH is clearly not thermodynamically consistent. Three main possibilities exist as to what could have caused such an inversion. First, it is possible that the aqueous speciation of Tc(IV) was not the same for measurements with TcO_2(cr) and for $TcO_2 \cdot xH_2O$(s) due to kinetic factors such as slow hydrolysis or gradual colloid formation. Secondly, it is possible that the nature of the solid phase changed with pH due to precipitation of a second phase that incorporated anions or cations from the unspecified electrolytes used to adjust the pH of the solutions. The third possibility is that one or both of those solubility studies is in error such as from failure to adequate correct for the presence of TcO_4^- in the solution, or failure to completely remove colloidal material.

In this paper, two graphical representations of Tc solubility measurements are shown, one using freshly precipitated TcO_2(am), the other using crystalline TcO_2(cr) obtained by thermal decomposition of ammonium pertechnetate. The solubilities of these Tc(IV) oxide phases were measured as a function of pH between pH values of 5 and 12. The shape of the solubility curves are similar, showing a minimum in near-neutral solutions. The solubility of the crystalline Tc(IV) oxide appears even somewhat higher than that of the amorphous phase in neutral and alkaline solutions. The results are not compatible with the measurements of Meyer *et al*. [91MEY/ARN2]. In addition, the authors state that they were unable to obtain reliable data in acidic solution, "due to the formation of a more insoluble compound with the acids used". Burnett and Jobe [97BUR/JOB] tabulate the solubilities of Paquette and Lawrence for TcO_2(cr) in their Table 3. They list 13 solubilities for the pH range of 4.26 to 10.97.

[89BAL/BOA]

Baldas, Boas and Bonnyman hydrolysed Cs_2TcNCl_5(s) by dissolving it in water to yield a brown precipitate. This precipitate was coagulated by heating, washed twice with dilute HNO_3 and then separated by being centrifuged. This solid was subsequently dried under vacuum over solid KOH to yield black pitch-like flakes of nitridotechnetic(VI) acid.

Approximately 99% of the chloride was removed during the rinsing and washing of the precipitate, so the nitridotechnetic(VI) acid was essentially chloride free. It had the IR peak at 1054 cm^{-1} corresponding to the Tc-N triple bond. Analysis for technetium gave a technetium mass fraction corresponding to an empirical composition of H_3NO_3Tc. They noted that this could correspond either to $TcN(OH)_3$, $TcN(O)(OH)(OH_2)$, or $Tc_2N_2O_3 \cdot 3H_2O$. However, they concluded that it must be a polymeric form of one of these formulas, based in part on its low solubility in water. Additional evidence for a polymeric nature came from the continual change in magnetic moment with the increase in extent of hydrolysis of the chloride salt.

Baldas *et al*. [90BAL/BOA] further investigated the properties of this "nitridotechnetic(VI) acid". A sample of it that was dissolved in 1 M toluene-*p*-sulphonic acid

(Hpts), CF_3SO_3H, or CH_3SO_3H gave an air-stable yellow solution after setting for half an hour, and paper electrophoresis of the solution at 600 V in 0.5 M acid solution indicated all of the technetium was present as a single cationic species. In 1 M CF_3SO_3H the UV-visible spectrum of this species exhibited maxima at 251 and 295 nm. Solutions of this species at 2×10^{-3} M technetium in 1 M Hpts, CF_3SO_3H, or CH_3SO_3H, that were frozen, exhibited no ESR signal at 130 K.

They [90BAL/BOA] added 1.5 equivalents of sodium diethyldithiocarbamate $Na_2S_2CNEt_2 \cdot 3H_2O$ in 1 M K_2HPO_4 to a yellow solution of this cation in 1 M Hpts. Extraction of the resulting solution with CH_2Cl_2 followed with separation by silica gel chromatography gave a 37% yield of yellow-coloured Tc(VI) complex $[\{Tc^{VI}N(S_2CNEt_2)\}_2(\mu\text{-}O)_2](cr)$ together with 15% of the previously known $Tc^{V}N(S_2CNEt_2)_2$. The first of these products was characterised by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction. It crystallised in the triclinic space group $P\bar{1}$ with $a = (8.069 \pm 0.004) \times 10^{-10}$ m, $b = (9.224 \pm 0.004) \times 10^{-10}$ m, $c = (14.017 \pm 0.006) \times 10^{-10}$ m, $\alpha = (107.77 \pm 0.04)°$, $\beta = (102.05 \pm 0.04)°$, $\gamma = (93.80 \pm 0.04)°$, and $Z = 2$. It contains a di(μ-oxo) bridged dimer of technetium, with the technetium atoms 0.65×10^{-10} m above the "S_2" and "O_2" basal planes. The Tc-O-Tc bond angles were $(81.8 \pm 0.2)°$ and $(82.1 \pm 0.2)°$, and some metal-metal interaction was likely. Based on this structural information, they formulated the yellow-coloured aqueous cation as being $\{TcN(OH_2)_3\}_2(\mu\text{-}O)_2^{2+}$. They later reported that $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2]$ melted with decomposition at 486 K [91BAL/BOA].

A salt of "nitridotechnetic(VI) acid" has also been reported [91BAL/BOA]. Baldas *et al.* hydrolysed $Cs_2(TcNCl_5)$ in water, and the resulting "nitridotechnetic(VI) acid" was added to a solution of 1 mol $\cdot$ kg^{-1} CsOH. This solution was diluted to about one third of the original concentration and then filtered. The addition of ethanol to the yellow-brown coloured solution gave a yellow powdery precipitate. This solid was dried under a vacuum and then chemically analysed for Tc, C, H, and N. A small amount of carbon was detected, which indicates that a trace of ethanol was retained by the precipitate. The IR spectrum of this salt in a KBr pellet had peaks at 639, 734, 1046, and 1628 cm^{-1}, along with a broad band at 2800 to 3600 cm^{-1}. Addition of $Na(S_2CNEt_2)$ to an alkaline solution of the "nitridotechnetic(VI) acid" gave the previously characterised $[\{TcN(S_2CNEt_2)\}_2(\mu\text{-}O)_2](cr)$. The UV-visible spectrum of the corresponding aqueous cation showed similarities to the known cation $(H_2O)_3Mo(\mu\text{-}O)_2Mo(OH_2)_3^{2+}$. This Tc compound was subsequently shown [92BAL/BOA] to crystallise with a triclinic cell, space group P1. This dimeric Tc(VI) complex is best described as two edge-sharing square pyramids, with Tc-N and Tc-Tc distances of $(1.623 \pm 0.004) \times 10^{-10}$ m and $(2.543 \pm 0.001) \times 10^{-10}$ m. The related Tc(V) complex $As(C_6H_5)_4[TcN(S_2CNEt_2)(SCOCOS)]$, containing the thio-oxalate ligand, is monomeric, with a monoclinic cell, space group $P2_1/n$, in which the technetium atom has square pyramidal geometry with a Tc-N distance of $(1.54 \pm 0.02) \times 10^{-10}$ m.

In view of all of this information, they [91BAL/BOA] formulated the solid salt as $Cs_2[(HO)_2NTc(\mu\text{-}O)_2TcN(OH)_2]$, and the "nitridotechnetic(VI) acid" as $[(H_2O)(HO)NTc(\mu\text{-}O)_2Tc(OH)(OH_2)]$. However, they noted that the true formulas could actually be polymers of these proposed dimers.

Baldas, Boas and colleagues [93BAL/BOA2, 93BAL/BOA] have further studied

the de-dimerisation reactions of this "nitridotechnetic acid" [{TcN(OH)(OH_2)}$_2(\mu$-O$)_2$] by ESR, visible and ultra-violet spectroscopy in a number of oxo-acids of sulphur and phosphorus. They proposed a sequence of reactions for increasing concentrations of HL, the co-ordinating acid. High acidity and the presence of strongly co-ordinating anions favour the formation of the monomeric forms, which may be written generically as $TcNL_4^-$, but almost certainly contain both $TcNL_5^{2-}$ and $TcNL_4(OH_2)^-$ species; the halide complexes seem particularly stable. These monomeric species can easily be monitored, since they are are ESR-active and have an intense absorption peak in their U-V spectrum at 266-300 nm. The dimeric species, which are ESR-silent and have intense absorption bands in the visible region of 470-580 nm, have been identified with very weakly coordinating acids. They were studied in H_2SO_4, H_3PO_4, $H_4P_2O_7$, NH_2SO_3H (sulfamic acid), and various sulphonic acids RSO_3H, including those with R = CF_3, CH_3, and *p*-CH_3-C_6H_4. Baldas *et al*. [93BAL/BOA] prepared and made X-ray structure determinations on the solids $[As(C_6H_5)_4]_2(TcNX_2)_2(\mu - O)_2]$, X = Cl, Br. They do not give the details of the symmetry or lattice parameters of the unit cells, but do give the structure of the $[(TcNCl_2)_2(\mu - O)_2]^{2-}$ ion in the chloro-complex. The bond distances are Tc-Tc = $(2.579 \pm 0.002) \times 10^{-10}$ m, Tc-N = $(1.650 \pm 0.0016) \times 10^{-10}$ m, average Tc-Cl = 2.396×10^{-10} m. Many of the properties of these Tc(VI)N-complexes mirror those of the isoelectronic Mo(V)O-oxo species, particularly the formation of stable monomeric and dimeric μ-oxo and di(μ-oxo) species.

[89BOC/BRÜ]

Bock *et al*. investigated the sorption of technetium on several iron and sulphide minerals: stibnite (Sb_2S_3), pyrrhotite (FeS), pyrite (FeS_2), galena (PbS), and loellingite ($FeAs_2$). Technetium was initially present at about 10^{-6} M as TcO_4^-, and the measurements were done in a bicarbonate-type groundwater. After two weeks, more than 95% of the technetium was immobilised on the minerals, although, in most cases, equilibrium was not achieved for 6 to 12 weeks. Both FeS and Sb_2S_3 reached equilibrium within two weeks, and absorbed essentially all of the technetium. The authors suggested that all of these minerals would make favorable backfill materials for a nuclear waste repository.

[89FRE/LUT]

See comments under [79BRA/HAR].

[89GUP/ATK]

The authors measured the solubility of Tc(IV) oxide under conditions of a cementitious near-field of a radioactive waste repository, *i.e*., they used saturated $Ca(OH)_2$ solutions at pH = 12.5. They applied a "bias potential" to investigate the Tc solubility as a function of the reduction potential, and they monitored the concentration of the dissolved Tc by using β-counting (with a detection limit of 2×10^{-8} M) or inductively coupled

plasma-mass spectrophotometry (ICP-MS, with a detection limit of 10^{-9} M, and with an uncertainty of ±5%). The concentration of Tc was found to be independent of the bias potential. Solutions equilibrated for one day or longer generally had Tc concentrations ranging between 3×10^{-8} and 2×10^{-7} M, which corresponds roughly to the value extrapolated to pH = 12.5 from [92ERI/NDA]. The authors concluded that the cathodic reduction of TcO_4^- to Tc(IV) oxide was not reversible, and that therefore the redox conditions could not be controlled by electrochemical means. Also, using H_2(g) and $Fe(OH)_2$(s), it was not possible to obtain the expected Tc concentrations. This seems to be due to the slow kinetics of the hydrogen oxidation in the first case. In the other case, it was not established whether reduction of TcO_4^- occurred at the surface of the ferrous hydroxide particles rather than in homogeneous solution. This could also be correlated to the inertness of Tc(IV).

[89MEY/ARN]

See comments under [87MEY/ARN].

[90BAL/BOA]

See comments under [89BAL/BOA].

[90BAL/BOA2]

Baldas *et al*. reported that the reaction of aqueous KCN with a solution of $(AsPh_4)TcNCl_4$ in acetonitrile initially became purple-red and then bright yellow. Aqueous $AsPh_4Cl$ was added to the solution, and the mixture was evaporated under reduced pressure to dryness over solid KOH. The resulting yellow material was washed with cold water to remove KCl, KCN, and excess $AsPh_4Cl$, but the amount of water was kept to a minimum because of the solubility of the yellow nitrido complex. This material was partially characterised by elemental analysis for technetium, by IR spectroscopy, and by ESR spectroscopy at 130 K. The recrystallised material melted at 506 to 507 K.

A single-crystal X-ray diffraction study established that the complex was $[(AsPh_4)]_2[TcN(CN)_4(OH_2)] \cdot 5H_2O$(cr). It crystallised in the monoclinic space group $P2_1/n$ with $a = (17.107 \pm 0.010) \times 10^{-10}$ m, $b = (19.965 \pm 0.014) \times 10^{-10}$ m, $c = (15.473 \pm 0.010) \times 10^{-10}$ m, $\beta = (101.70 \pm 0.04)°$, and $Z = 4$. The crystals contain discrete $AsPh_4^+$ cations and $TcN(CN)_4(OH_2)^{2-}$ anions, with the nitrido nitrogen and coordinated water being *trans* to each other. The absence of an ESR signal for a polycrystalline sample of this material indicates that the diamagnetic anion contained Tc(V). However, solutions of Cs_2TcNCl_5 or nitridotechnetic(VI) acid in concentrated aqueous HCl and KCN turned deep-purple coloured, and exhibited ESR spectra corresponding to partial formation of two of the following Tc(VI) species: $TcNCl_3(CN)^-$, $TcNCl_2(CN)_2^-$, or $TcNCl(CN)_3^-$. After longer reaction times with HCl, only $TcNCl_4^-$ was observed.

[90PIL]

In this study, the solubility of Tc(IV) hydrous oxide was followed at high pH and under reducing conditions, reached by addition of sodium dithionite in the presence of three different cement types. The experimental setup was designed to simulate the cementitious near-field of a radioactive waste repository, and leachates containing organic decomposition products were added as well. Under reducing conditions, the solubility of Tc(IV) oxide was found to be around 10^{-7} M. Variation of the pH from 7.0 to 12.7 or modification of the solid-liquid separation method had little effect on the results, while the Tc solubility increased by a factor of about 10 in the presence of organic degradation products. For solutions containing 10^{-3} M sodium dithionate and with Eh ≤ -0.16 V, the technetium concentration varied between 1.2×10^{-8} and 5.9×10^{-7} M. If no sodium dithionite was used, the solubility of Tc(IV) oxide was generally 50-100 times larger.

[91BAL/BOA]

See comments under [89BAL/BOA].

[91MEY/ARN]

The most recent and most detailed redox potential measurements for the TcO_4^- / $TcO_2 \cdot xH_2O$(s) couple were reported by Meyer and co-workers. They presented their detailed results in two separate reports [88MEY/ARN, 89MEY/ARN], and summarised their experimental values in a journal article [91MEY/ARN]. Five series of experimental measurements were reported; three in which the concentration of TcO_4^- was varied, and two in which the pH was varied. All experiments were performed in an argon-filled glove box containing a mass fraction of $< 0.7 \times 10^{-6}$ O_2(g).

These experiments were done with aqueous mixtures of NH_4TcO_4 and HCl. Five series of experiments were done, three of these series using the same electrode, for a total of 23 emf points. In three of their series, the pH was held approximately constant at 2.27 to 2.35 by making the solutions 5×10^{-3} M in HCl, and the NH_4TcO_4 concentration was varied from 9.11×10^{-5} to 3.51×10^{-3} M. In each of the other two series of experiments the concentrations of NH_4TcO_4 were held approximately constant at about $(0.9 - 1.2) \times 10^{-4}$ or 1.1×10^{-3} M and the pH was varied from 1.90 to 3.99. The HCl concentrations in these latter two series of measurements were not reported, but this information was supplied to us by Meyer [91MEY].

These series of potential measurements by Meyer *et al.* involved three different electrodes of $TcO_2 \cdot xH_2O$(s), prepared by electrodeposition of TcO_4^- onto platinum mesh at pH $= 2$ and at a potential of $+0.0445$ V. A SCE was used as the counter electrode. They found that if either or both the concentration of TcO_4^- or the pH of the solutions was changed, then it took some time (not specified) for the potential to return to a constant value (or at least a steady state). For example, at lower pH values (pH ≈ 2) about four hours were required for the emf to become constant, whereas at higher pH values (pH ≈ 4) about one day was necessary. However, for concentrations

of TcO_4^- of 10^{-4} M or lower, steady potentials were never obtained due to continuous drift.

A saturated calomel electrode (SCE) was used as the counter electrode in all three of those studies, and all of these cells contained a salt bridge or liquid junction. Completely reliable corrections can not be made for liquid-junction potentials. However, Hills and Ives [61HIL/IVE] recommended an apparent "$E°$" value of (0.2450 ± 0.0001) V (their table VI) for the SCE in contact with an acidic solution at the liquid junction. We will accept that value for our recalculations, in order to put the experimental redox potentials on a consistent basis.

Meyer *et al*. found that the $TcO_4^-/TcO_2 \cdot xH_2O$(s) couple had an approximately Nernstian response with change in pH or TcO_4^- concentration. They recommended that $E° = (0.747 \pm 0.004)$ V at (298.15 ± 0.1) K, based on their measurements with $> 9 \times 10^{-4}$ M TcO_4^-.

[91MEY/ARN2]

This paper summarises the results of several reports from Oak Ridge National Laboratory, USA [86MEY/ARN, 87MEY/ARN, 88MEY/ARN, 89MEY/ARN]. The Tc(IV) oxide was prepared by precipitation upon purified sand with a 30% excess of hydrazine, or by electrodeposition on a platinum mesh electrode in acidic or basic solutions. The concentrations of total technetium and Tc(IV) (after separation of TcO_4^- by solvent extraction) in the equilibrated solutions over the solid oxide were determined daily by liquid scintillation counting of the β-activity of ^{99}Tc. Extraction to determine Tc(VII) was done with tetraphenylarsonium chloride in chloroform. It is remarkable that the amount of Tc(VII) was always considerably larger than that of Tc(IV), although all operations were carried out within a controlled atmosphere box containing argon and < 1 ppm oxygen (see also Section V.2.1). This indicates that the equilibria involving Tc(IV) can be evaluated only if the amount of Tc(VII) is also exactly known. This condition was never fulfilled in any of the previous studies on Tc(IV) equilibria in aqueous solution, and they are therefore to be discarded. The solubility measurements of $TcO_2 \cdot xH_2O$(s) at a fixed applied potential show a gradual increase of both Tc(IV) and Tc(VII) concentrations until a steady value was obtained after about 12 days [91MEY/ARN2, Figure 1]. Solutions with pH values between 0 and 10 containing HCl and NaCl as inert electrolytes, sometimes containing $NaHCO_3$ and Na_2CO_3, have been used. The Tc solubility is not strongly dependent on the ionic strength and the chloride concentration in near-neutral solutions of 0.05 to 2.6 M NaCl [91MEY/ARN2, Figure 4]. The solubilities of the Tc(IV) oxide from different precipitates lie between 10^{-9} and 10^{-8} M for solutions with pH > 2 . The average value of 19 solubilities measured between pH values 5 and 9.5 (*i.e*., the pH range in which no side reactions such as protonation or deprotonation of $TcO(OH)_2$(aq) occur) is $(3.6 \pm 2.1) \times 10^{-9}$ M (1σ uncertainty). We consider this value as the most representative one for the solubility of $TcO_2 \cdot xH_2O$(s).

The Tc(IV) oxide prepared by precipitation on purified sand was used to measure the solubility of $TcO_2 \cdot xH_2O$(s) as a function of pH between pH = 0 and 10 [91MEY/ARN2, Figure 3]. The strong increase of the solubility observed in the four

experimental points at pH < 3 can be explained with the formation of protonated species. In these solutions, HCl was used to obtain pH values between 3 and 0. The ionic strength was not maintained constant but varied between 0.01 and 1 M. The questionable values reported by Gorski and Koch [69GOR/KOC] were used by the authors to quantify the protonation of $TcO(OH)_2(aq)$ according to the reactions:

$$TcO^{2+} + H_2O(l) \rightleftharpoons TcO(OH)^+ + H^+ \quad (A.23)$$

$$TcO(OH)^+ + H_2O(l) \rightleftharpoons TcO(OH)_2(aq) + H^+ \quad (A.24)$$

The reported constants, $\log_{10}{}^{*}K$(A.23) = −1.37 and $\log_{10}{}^{*}K$(A.24) = −2.43, seem plausible at first sight, because at pH < 1.5 the increase in the Tc(IV) solubility is of two orders of magnitude per pH unit, indicating that the predominant species in solution could be TcO^{2+}, since

$$[TcO^{2+}] = \frac{[TcO(OH)_2(aq)][H^+]^2}{K(A.23)K(A.24)} = \text{const} \times [H^+]^2 \quad (A.25)$$

However, pH measurements were performed even at very low pH values in spite of the large liquid junction potentials under such conditions, *e.g.*, 16.6 mV in the case of 1 M HCl and 3.4 mV in the case of 0.1 M HCl [63MIL]. In addition, the use of chloride as a background anion was unfortunate, because in chloride solutions the presence of various chloride and chloride-hydroxide complexes should be expected, see for example [69KAN] and Section V.3. Due to the lack of data, no quantitative estimation or correction is possible. In this context it should be added that equilibria with $TcCl_6^{2-}$ [69KAN] have been investigated without rigorous exclusion of oxygen. Hence, it is almost certain that TcO_4^- was present, which increases the difficulties of interpreting the results obtained. When using Tc(IV) oxides obtained from other procedures, large changes in the amount of dissolved Tc(IV) are observed. For example, in the case of electrodeposited Tc(IV) oxide [91MEY/ARN2, Figure 5], an increase of the solubility is not observed unless the pH is lower than 1, and below pH = 1 large differences in the solubility are observed. The data interpretation in strongly acidic solutions is thus doubtful. While the first protonation reaction of $TcO(OH)_2(aq)$ seems well established, the second one is uncertain, and we can only give a limiting value for Reaction (A.23): $\log_{10}{}^{*}K$(A.23) > −1.5. For the first protonation reaction we estimate, based on the three points at pH values 3.01, 2.16 and 1.27 [91MEY/ARN2, Figure 3], $\log_{10}{}^{*}K$(A.24) = −(2.5 ± 0.3).

[91POW]

This paper describes a model for the heat capacity of Tc(cr), *cf.* Section V.1.1.2. The author's expressions for the contributions to the heat capacity (*cf.* Section V.1.1.2) are:

$$C_L = \text{Deb}C_p(\theta/T)$$

where $\text{Deb}C_p$(u) is the normal Debye function for heat capacity, with θ_0 = 445 K

$$C_d = \alpha^2 V T/\beta$$

where C_d is the contribution to the heat capacity from lattice dilation, and where α, the coefficient of thermal expansion, β, the isothermal coefficient of compressibility, and V are defined functions of T. Also,

$$C_e/R = 5.17 \times 10^{-4}\, T$$

where C_e is the electronic contribution to the heat capacity. Powers also included a contribution due to the formation of thermal vacancies, C_{vac}, given by:

$$C_{vac}/R = (E_v/RT)^2 \exp(-E_v/RT)$$

with $E_v/R = (15100 \pm 1500)$ K. The value for the constant Debye temperature used is that derived by Trainor and Brodsky [75TRA/BRO] from heat capacity measurements from 3 to 15 K, and the value of E_v/R was taken from Spitsyn *et al.* [75SPI/ZIN].

[91RAR/MIL]

Rard and Miller used the following equation for osmotic coefficient,

$$\phi = 1 - \frac{A^*|Z_+Z_-|}{I_m}[(1 + 1.5\sqrt{I_m}) - 2\ln(1 + 1.5\sqrt{I_m}) - (1 + 1.5\sqrt{I_m})^{-1}] + \sum_{i=4}^{p} A_{i-3} \cdot m^{i/4}$$

with a sequential series in $m^{1/4}$ starting with m. They found that a quarter power series in molality gave much better fits than integral or half integral power fits. At 298.15 K, $A^* = 0.34733$ mol$^{-1/2} \cdot$ kg$^{1/2}$. The corresponding activity coefficient form of this equation is

$$\ln \gamma_\pm = -\frac{A'|Z_+Z_-| \cdot \sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \sum_{i=4}^{p} \frac{(i/4 + 1)}{i/4} A_{i-3} \cdot m^{i/4}$$

where $A' = 1.1722$ mol$^{-1/2} \cdot$ kg$^{1/2}$ at 298.15 K. Four coefficients were required for $HTcO_4$ and seven for $NaTcO_4$. Table A.8 contains values of water activity a_{H_2O} and mean molal activity coefficient $\gamma_\pm$ as reported by Rard and Miller. Rard and Miller based their evaluation on a reanalysis of the isopiestic measurements of Boyd [78BOY2, 78BOY]. This reanalysis was necessary because Boyd's smoothed quantities for $NaTcO_4$ are inconsistent with his experimental data. The more recent isopiestic measurements of Könnecke *et al.* [97KÖN/NEC] are in very good agreement with Rard and Miller's derived values.

Boyd [78BOY2] also determined the saturation molality of $NaTcO_4$ at 298.15 K. We plotted the ϕ and $\gamma_\pm$ values of Rard and Miller [91RAR/MIL], and extrapolated these curves to estimate the values of these properties for the saturated solution. These estimated values are also included in Table A.8. They yield a water activity of 0.6442 ± 0.0079 for the saturated solution.

Table A.8: Water activities and mean molal activity coefficients for $HTcO_4$ and $NaTcO_4$ solutions at 298.15 K[(a)].

Molality mol · kg^{-1}		a_{H_2O}	$\gamma\pm$	a_{H_2O}	$\gamma\pm$
		$HTcO_4$		$NaTcO_4$	
0.1		0.99666	0.7681	0.99669	0.7455
0.2		0.99338	0.7239	0.99348	0.6937
0.3		0.99009	0.7009	0.99034	0.6605
0.4		0.98677	0.6871	0.98726	0.6350
0.5		0.98342	0.6785	0.98424	0.6141
0.6		0.98004	0.6733	0.98127	0.5963
0.7		0.97661	0.6704	0.97835	0.5808
0.8		0.97314	0.6694	0.97545	0.5672
0.9		0.96961	0.6699	0.97258	0.5552
1.0		0.96604	0.6716	0.96973	0.5444
1.5		0.94726	0.6954	0.95560	0.5050
2.0		0.92661	0.7408	0.94141	0.4809
2.5		0.90365	0.8080	0.92700	0.4656
3.0		0.8780	0.9004	0.91234	0.4559
3.5		0.8495	1.024	0.8974	0.4499
4.0		0.8178	1.186	0.8823	0.4466
4.5		0.7832	1.399	0.8669	0.4453
5.0		0.7456	1.678	0.8513	0.4458
5.5				0.8354	0.4477
6.0				0.8193	0.4509
6.5				0.8030	0.4551
7.0				0.7865	0.4601
7.5				0.7701	0.4655
8.0				0.7540	0.4708
5.4404		0.7103	1.996		
8.4913				0.7387	0.4753
11.299	(satd $NaTcO_4$)			$0.6442 \pm 0.0.0079$[(b)]	0.53 ± 0.02[(b)]
–	(satd $HTcO_4$)	0.073			

(a) Values of water activities and activity coefficients are from Rard and Miller [91RAR/MIL], which are based upon a reanalysis of the isopiestic molalities of Boyd [78BOY2, 78BOY]. The exception is the water activity of aqueous $HTcO_4$ in equilibrium with solid $Tc_2O_7 \cdot H_2O$(s), which was taken from the present reanalysis of vapour pressures of Cobble *et al.* [52COB, 53SMI/COB].

(b) Obtained by graphical extrapolation of the lower-molality data.

[91ZAK/BAG]

Zakharov *et al*. studied the electrolytic reduction of aqueous NH_4TcO_4 at pH = 1 onto a nickel substrate at current densities of 7 and 12 $A \cdot dm^{-2}$. The electrode deposits were examined by X-ray diffraction and were found to be a mixture of a crystalline phase and an amorphous phase. Their reported unit cell parameters for this deposit were $a = b = (2.973 \pm 0.002) \times 10^{-10}$ m and $c = (3.444 \pm 0.002) \times 10^{-10}$ m. However, their reported value of $c = (3.444 \pm 0.002) \times 10^{-10}$ m is probable a typographical or translation error for $(4.444 \pm 0.002) \times 10^{-10}$ m, and their value of $a = (2.973 \pm 0.002) \times 10^{-10}$ m is probably a partially transposed value for $a = (2.793 \pm 0.002) \times 10^{-10}$ m; these two changes give c/a = (4.444/2.793) = 1.591, which agrees exactly with their reported ratio. The value for a is comparable to values determined for the known hydrides of technetium, which range from 2.801×10^{-10} m to 2.838×10^{-10} m, but is distinctly larger than $a = 2.735 \times 10^{-10}$ m to 2.743×10^{-10} m for Tc(cr) as reported in Table V.1. Zakharov *et al*. reported that the maximum hydrogen content of their deposits corresponded to $TcH_{\leq 0.27}$(cr). Annealing of these electrode deposits for 1 hour at 473 K or 10 minutes at 773 K was sufficient to drive off this hydrogen, and resulted in crystalline material with unit cell parameters corresponding to those for pure Tc(cr).

[92EL-/GER]

El-Wear, German, and Peretrukhin studied the absorption of $NaTcO_4$ from aqueous solutions onto various natural minerals and rocks (*i.e*., sandstone, feldspar, bauxite, basalt, megrele, phosphorite, peat, pyrite, and kaoline), on several synthetic inorganic minerals and rocks (mostly oxides), and on some organic absorbents. Absorption experiments were done with 60-80 mesh particles for 4 to 20 days at pH = 1.27, for 1 to 13 days at pH = 6.46, and for 1 to 7 days at pH = 12.7 for the synthetic minerals, and for 1 to 2 days for several natural minerals at pH = 6. By far the best synthetic-mineral absorbent was CdS(cr) (the only synthetic sulphide examined) and the best of the natural-mineral absorbents was sandstone followed closely by a feldspar. Somewhat surprisingly, natural pyrite (FeS_2(cr)) was not a particularly good absorbent for technetium under their experimental conditions at pH $\approx$ 6. El-Wear, German, and Peretrukhin suggested that the greater amount of absorption of technetium by the CdS(cr) occurred because of formation and precipitation of Tc_2S_7(s), although this identification seems to be based solely on the black colour of the precipitate. This tentative identification of the precipitate as Tc_2S_7(s) is plausible, but it does conflict with the assertion of Zhuang *et al*. [95ZHU/ZHE] that Tc(IV) is formed under similar conditions.

El-Wear, German, and Peretrukhin also studied the solubility of Tc_2S_7(s) in water. They prepared this compound by reaction of an aqueous solution containing "equimolar amounts" of aqueous Na_2S and $NaTcO_4$ for 0.5 hours with stirring. (It is possible that they meant "stoichiometric amounts" rather than "equimolar amounts"). This precipitate was centrifuged for 0.5 hours at 8000 r.p.m., rinsed with distilled water, and the process was repeated for a total of ten times. Distilled water was added to the washed precipitate for the solubility experiment; after 5 hours the solution had

became violet coloured due to formation of some unknown intermediate species. After stirring of the solution for 3 days the solution was colourless and the pH had dropped from pH ≈ 7 to pH = 2.35. These authors stated that "the solution was centrifuged and the solubility of the precipitate was measured to be 0.257 g/L." They claimed that the dissolution occurred by way of the reversible reaction:

$$Tc_2S_7(s) + 8H_2O(l) \rightleftharpoons 2H^+ + 2TcO_4^- + 7H_2S \qquad (A.26)$$

However, they did not indicate which phase, gas or aqueous, contained the H_2S. They also did not indicate whether the $HTcO_4$ and H_2S were detected experimentally or whether Reaction (A.26) was assumed.

El-Wear, German, and Peretrukhin did not describe how the solubility was determined, but it probably was done by β^- counting since that method was used in their absorption studies. They also did not describe any temperature control or precautions to exclude oxygen.

We have corresponded K.E. Guerman (different transliteration of German) who provided [96GUE] additional details about the $Tc_2S_7(s)$ solubility determination [92EL-/GER]. The solubility experiment was performed at 25°C in a glove box. Approximately 1 g of $Tc_2S_7(s)$ was added along with distilled water to a 20 cm^3 container having at most 1 cm^3 "head" space. This container was sealed for the duration of the experiments, except for being opened on five occasions for about 20 seconds each time. The first time, after 4 hours, was to remove a sample for recording of the ultra violet-visible spectrum, and the remaining times after 3, 8, 14, and 21 days were to remove 50μL samples for solubility determinations. Given the length of time that this solution was allowed to equilibrate; it is likely that the reported concentration of technetium is close to the equilibrium solubility or at least is a steady state value. Furthermore, the amount of time the solution was exposed to atmospheric air was restricted. However, the extent of oxidation of the $Tc_2S_7(s)$ by atmospheric oxygen is unknown.

As noted by Guerman [96GUE], the measured concentration of technetium represents not only the amount present as TcO_4^- but also other dissolved species. Guerman suggested that these species possibly include various Tc(VII) oxysulphides formed by hydrolysis of $Tc_2S_7(s)$ and/or the complex TcS_4^-. However, since none of these species was actually isolated, the identity of these other dissolved species is uncertain.

The experimental solubility of $Tc_2S_7(s)$ in water [92EL-/GER] is 6.1×10^{-4} mol · dm^{-3}. One of the products of Reaction (A.26) is $H_2S(aq)$. This $H_2S(aq)$ is a weak acid which will be essentially undissociated at pH = 2.35. At this low concentration molarity and molality are near equal. Assuming that Reaction (A.26) achieves thermodynamic equilibrium during the solubility experiments and that all of the H_2S remains in solution, the saturated solution will contain 0.0012 mol · kg^{-1} of H^+, the total concentration of technetium will be 0.0012 mol · kg^{-1}, and 0.0043 mol · kg^{-1} of $H_2S(aq)$ will be present. An upper bound for K°_m(A.26) can be calculated by using these concentrations and assuming that all of the dissolved technetium is present as TcO_4^-. It will also be assumed that activity coefficients of the pertechnetic acid and water in this solution will be nearly equal to those in solutions of a solution of pure $HTcO_4$ at 298.15 K, thus they can be calculated from the equation of Rard and Miller [91RAR/MIL] to be

$\gamma_{\pm} = 0.913$ and $a_{H_2O} \approx 1$. The activity coefficient of H_2S(aq) will be set equal to unity since it is an uncharged species. The thermodynamic equilibrium constant for Reaction (A.26) is thus

$$K^{\circ}_{m}(\text{A.26}) \quad \leq \quad 5 \times 10^{-29}\ \text{mol}^9 \cdot \text{kg}^{-9}$$

The calculated standard Gibbs energy of formation of Tc_2S_7(s) is $\Delta_f G^{\circ}_m$ (Tc_2S_7, s, 298.15 K) $<$ +267 kJ·mol^{-1}. Given that Tc_2S_7(s) can be synthesised readily at room temperature, a positive Gibbs energy of formation is totally unrealistic. It is equally obvious that the correct value of K°_m(A.26) must be considerably smaller for $\Delta_f G^{\circ}_m(Tc_2S_7, \text{s}, 298.15\ \text{K})$ to have a negative value. This type of calculation will yield a negative value of $\Delta_f G^{\circ}_m(Tc_2S_7, \text{s}, 298.15\ \text{K})$ only if $K^{\circ}_m(\text{A.26}) < 8 \times 10^{-76}\ \text{mol}^9 \cdot \text{kg}^{-9}$.

The above calculation was done by assuming that (1) all of the H_2S(aq) remained dissolved in the solution, (2) oxidation of H_2S(aq) to elemental sulphur or to oxysulphur anions by the dissolved oxygen was negligible, and (3) all of the technetium was present as TcO_4^-. The first assumption will be valid only if the solution was enclosed in a sealed container with no "head" space. Given that there was up to 1 cm^3 "head" space, some of the H_2S would have partitioned into the vapour phase and some of that lost when the container was opened for sampling. There was also an unknown amount of oxidation of the H_2S by residual oxygen, and an unknown fraction (and quite possible most) of the technetium present in chemical forms other than TcO_4^-. None of these factors can be quantified, but all three would act to reduce the experimental value of K°_m(A.26). The recent observations of Kunze *et al.* [96KUN/NEC] suggest that a fine colloid containing technetium may also be present in such solutions.

[92ERI/NDA]

The authors investigated the solubility of $TcO_2 \cdot xH_2O$(s) in slightly acidic and alkaline aqueous solution, without inert salt, in the absence and presence of CO_2(g). The experiments were carried out in a glove box that was flushed with argon containing less than 0.5 ppm oxygen to minimise oxidation of Tc(IV). The desired p_{CO_2} was reached with CO_2/N_2 gas mixtures and by varying the alkalinity by adding appropriate amounts of Na_2CO_3. The Tc(IV) oxide was prepared by electroreduction and precipitation on a platinum mesh electrode from a 5×10^{-4} M aqueous solution of TcO_4^- by applying an electrode potential of -250 mV *vs.* SCE. After measurement of the pH, the quantities of Tc(VII) and Tc(IV) were determined in each solution. Solution samples were taken daily until constant ^{99}Tc concentration was found.

In the absence of CO_2(g), the solubility of $TcO_2 \cdot xH_2O$(s) was independent of pH in the range $6 <$ pH < 9.5. From the increase of the solubility at pH > 9.5, the authors concluded the formation of a hydrolysis product according to

$$TcO_2 \cdot xH_2O(\text{s}) + (2 - x)\ H_2O(\text{l}) \quad \rightleftharpoons \quad TcO(OH)_3^- + H^+ \qquad \text{(A.27)}$$

with $\log_{10}{}^{*}K(\text{A.27}) = -(19.06 \pm 0.24)$.

In the presence of CO_2(g), the solubility of $TcO_2 \cdot xH_2O$(s) increased with increasing values of p_{CO_2}. Eriksen *et al.* worked with CO_2 partial pressures of 0.1, 0.3, 0.5

and 1 bar. In addition, a slight solubility increase at constant p_{CO_2} was observed at pH > 8. The authors interpreted these observations by proposing the formation of the following two mixed hydroxide-carbonate complexes

$$\begin{aligned} TcO_2 \cdot xH_2O(s) + (1-x)H_2O(l) \quad &+ \quad CO_2(g) \\ &\rightleftharpoons \quad TcCO_3(OH)_2(aq) \qquad \text{(A.28)} \\ TcO_2 \cdot xH_2O(s) + (2-x)\ H_2O(l) \quad &+ \quad CO_2(g) \\ &\rightleftharpoons \quad TcCO_3(OH)_3^- + H^+ \qquad \text{(A.29)} \end{aligned}$$

From a least squares fitting exercise they found $\log_{10} K(\text{A.28}) = -(7.09 \pm 0.08)$ and $\log_{10}{}^{*}K(\text{A.29}) = -(15.35 \pm 0.07)$. These uncertainties are no doubt underestimated (they represent the 1σ standard deviation) because they are based on only a small number of experimental points. This is especially true for $\log_{10}{}^{*}K$(A.29), see [92ERI/NDA, Figure 1].

This study was performed with care but the temperature of the experiments was not reported. In a subsequent report [93ERI/NDA], which contains tables of experimental values, it is indicated that the experiments were carried out at "ambient" temperature. The values are accepted by this review with increased uncertainties. Table A.1 of their appendix contains 10 experimental solubilities for the pH range 6.05 to 12.1 in the absence of carbonate and Table A.4 contains 11 solubilities for pH = 6.24 to 8.56 in the presence of carbonate.

[92KAD/FIN]

Kaden *et al*. have shown that the dinitrogen ligand in $HTc(N_2)(dppe)_2$ (where dppe denotes the 1,2-bis(diphenylphosphino) ethane ligand) can be exchanged in organic solvents under rather mild conditions with carbon monoxide, acetonitrile, and organic phosphite ligands. They thus prepared hydrido compounds that were formulated as $HTc(CO)(dppe)_2$, $HTc(CH_3O)_3P(dppe)_2$, $HTc(tert\text{-}C_4H_9NC)(dppe)_2$, etc., along with some non-hydridic salts of the type $TcL(CH_3CN)(dppe)_2^+PF_6^-$.

[92PET/SKO]

A method for the preparation of mixed valency halides was described by Peters, Skowronek and Preetz. They first prepared $(n\text{-}C_4H_9)_4NTcOCl_4(s)$ by the repeated reaction of $(n\text{-}C_4H_9)_4NTcO_4(s)$ with concentrated HCl, followed by recrystallisation from dichloromethane/*n*-hexane or other solvents. When this compound was reacted with $(n\text{-}C_4H_9)_4NBH_4$ in tetrahydrofuran, the solvent removed and the residue agitated in a stream of HCl(g) and air, the resulting $((n - C_4H_9)_4N)_2Tc_2Cl_8(s)$ could be crystallised from diethylether at 243 K. The yield depended critically on the details of the exposure to air, but could be as high as 85%. After being converted to $((n\text{-}C_4H_9)_4N)_2Tc_2Br_8(s)$ by ligand exchange with HBr in CCl_2H_2, this Tc(VI) compound was further reduced with $(n\text{-}C_4H_9)_4NBH_4$ in acetone, to give a 70% yield of $((n\text{-}C_4H_9)_4)_3Tc_2Cl_8(s)$. The tricaesium compound can also be prepared by precipitation with CsBr. The same authors measured the well-resolved vibrational

structure of the Raman spectrum of $Cs_3Tc_2Cl_8$(s) in a CsBr disk at 6 K. The fact that the origin of this band is at 5970 cm^{-1}, very close to the value of 5900 cm^{-1} found for the $Tc_2Cl_8^{3-}$ ion [81COT/DAN] suggests that this excitation is predominantly that of the Tc-Tc bond.

[92ROO/LEI]

These authors studied spectrophotometrically the kinetics of the displacement of the H_2O ligand in the *trans*-$TcO(H_2O)(CN)_4^-$ ion by the NCS^- ligand in a 1 M KNO_3 solvent at pH 1 to 4.5 at temperatures from 276.15 to 298.15 K. The first acidic dissociation constant of the *trans*-$TcO(H_2O)(CN)_4^-$ ion was inferred to be $10^{(-2.90\pm0.05)}$ at 298.15 K from a non-linear fitting of the kinetic data as a function of pH. Equilibria involving the mono-protonated $TcO(OH)(CN)_4^{2-}$ ion are difficult to measure since it rapidly dimerises to the $Tc_2O_3(CN)_8^{4-}$ ion.

Additional data on the kinetics of proton transfer reactions of these tetracyanotechnetates are described in further papers by Roodt and his colleagues. Roodt *et al.* [94ROO/LEI] report limiting values for the rate constants at 298.15 K for the forward and reverse reactions in the equilibria:

$$TcO(H_2O)(CN)_4^- \rightleftharpoons TcO(OH)(CN)_4^{2-} + H^+$$

$$TcO(OH)(CN)_4^{2-} \rightleftharpoons TcO_2(CN)_4^{3-} + H^+$$

and the proton exchange reaction

$$TcO(OH)(CN)_4^{2-} + Tc^*O_2(CN)_4^{3-} \rightleftharpoons Tc^*O(OH)(CN)_4^{2-} + TcO_2(CN)_4^{3-}$$

NMR techniques based on ^{13}C and ^{17}O were used, the total metal concentrations being 0.2 mol $\cdot$ kg^{-1} with a supporting electrolyte of 1.0 to 1.4 mol $\cdot$ kg^{-1} KNO_3. It should be noted that the exchange rates constants were derived somewhat indirectly by comparison with computer simulations of the pH dependence of the species distribution according to possible reaction schemes. Similar studies on the oxygen exchange kinetics from 281.25 to 308.15 K in 1.2 to 2.4 mol $\cdot$ kg^{-1} KNO_3, again using NMR techniques with ^{17}O, by Roodt *et al.* [95ROO/LEI] were interpreted in terms of the rate law

$$2R = k_{aq}[TcO(OH_2)(CN)_4^-] + k_{OH}[TcO(OH)(CN)_4^{2-}]$$

where R denotes the rate of exchange of ^{17}O labeled H_2O from the bulk phase with coordinated (unlabeled) water coordinated to the complex ion.

Values of k_{OH} were determined, but those for k_{aq} had to be estimated from similar experiments on the corresponding Re(V) ions, reported in the same reference.

[92SIN]

Sinyakova made a detailed comparison of the properties of the higher oxides of technetium with those of the higher oxides of rhenium and with the higher oxides of some

of the platinum group metals and of molybdenum. She argued that some properties of technetium oxides can been explained by considering the vapour phase oxide at high temperatures to be $TcO_4(g)$ which, upon being cooled to room temperature, undergoes the following reactions

$$2TcO_4(g) \rightarrow Tc_2O_8(s?) \rightarrow Tc_2O_7(s) + \text{“}O(g)''$$

The authors of this review found Sinyakova's discussion hard to follow and some of the arguments to be unconvincing. In view of the mass spectrometric measurements described in reference [93GIB], which detected no technetium oxide with a higher valence than $Tc_2O_7(g)$, the existence of $TcO_4(g)$ is quite unlikely.

[93BAL/BOA2]

See comments under [89BAL/BOA].

[93BAL/BOA]

See comments under [89BAL/BOA].

[93GIB]

Gibson investigated the mass spectrometry of a solid oxide of technetium (of undefined composition) in the presence of $O_2(g)$ and $H_2O(g)$ at low pressures of $\sim$ 10 Pa at temperatures of about 873 to 1373 K. By consideration of the ion intensities as a function of ionising electron energies of 20 to 70 eV, Gibson inferred that the dominant (parent) vapour species were $Tc_2O_5(g)$, $Tc_2O_7(g)$, $TcO_3(g)$, $TcO_3(OH)(g)$, and $TcO_2(OH)_3(g)$. These vapour species were detectable above about 873 K, and were present in greatest amounts between about 1173 and 1273 K.

[93JOA/APO]

Joachim *et al*. dissolved the hydridotris(3,5-dimethylpyrazolyl) borato complex $HB(3,5\text{-}(CH_3)_2C_3N_2)_3Tc(CO)_3$ in tetrahydrofuran (THF), flushed the solution with $N_2(g)$, and irradiated the solution with mercury lamp UV light. From this solution they isolated an air-stable solid compound in 10-15% yield, which was recrystallised from a mixture of hexane and methylene chloride. It was characterised by IR, UV, and ^1H NMR spectroscopy, mass spectrometry, and single crystal X-ray crystallography. These measurements indicated that the compound was $[\{HB(3,5\text{-}(CH_3)_2C_3N_2)_3\}Tc(CO)_2]_2(\mu\text{-}N_2)$(cr). It crystallised in the monoclinic space group C2/c with $a = (20.322 \pm 0.012) \times 10^{-10}$ m, $b = (14.547 \pm 0.008) \times 10^{-10}$ m, $c = (14.270 \pm 0.010) \times 10^{-10}$ m, and $Z = 4$. In this structure the monomer units $\{HB(3,5\text{-}(CH_3)_2C_3N_2)_3\}Tc(CO)_2$ are bridged by the N_2 group.

[93MER/SCH]

Mercier and Schrobilgen reported that the dissolution of Tc_2O_7(cr) in anhydrous HF, in which it was only sparingly soluble, resulted in a two-phase liquid system, with the lower layer consisting of a yellow coloured liquid and the upper layer being a pale yellow HF(l) solution. By using ^{99}Tc NMR spectroscopy, they established that both layers contained TcO_3F. The probable formation reaction was

$$Tc_2O_7(cr) + 4HF(l) \rightarrow 2TcO_3F + H_3O^+ + HF_2^-$$

Addition of excess XeF_6 to this solution resulted in precipitation of microcrystalline TcO_2F_3(cr). They proposed a rather complicated mechanism for the formation of TcO_2F_3(cr), which was based on ^{129}Xe and ^{19}F NMR measurements during the course of the reaction, and on the known chemical reactions of XeF_6 in HF(l) solutions containing some water. Single crystals of TcO_2F_3(cr) were grown by slow cooling of a solution of Tc_2O_7(cr) in HF(l), containing XeF_6 with a XeF_6/Tc_2O_7 mole ratio of 5 to 1. This TcO_2F_3(cr) was characterised by Raman spectroscopy and single crystal X-ray crystallography. It crystallised in the triclinic space group P $\bar{1}$ with $a = (7.774 \pm 0.006) \times 10^{-10}$m, $b = (7.797 \pm 0.002) \times 10^{-10}$m, $c = (11.602 \pm 0.006) \times 10^{-10}$m, $\alpha = (89.41 \pm 0.04)°$, $\beta = (88.63 \pm 0.06)°$, $\gamma = (84.32 \pm 0.04)°$, and Z = 8.

[94BUR/BRY]

Burrell, Bryan, and Kubas dissolved $TcCl(dppe)_2$ (where dppe denotes the 1,2-bis(diphenylphosphino) ethane ligand) in tetrahydrofuran (THF) and then flushed the solution with N_2(g). After 12 hours, $(Si(CH_3)_3)_2O$ was added and a yellow solid precipitated. Based on ^{1}H NMR and infrared spectroscopic measurements, along with elemental analysis for C, H, and N, they formulated the complex as being $TcCl(N_2)(dppe)_2$(s).

[94ROO/LEI]

See comments under [92ROO/LEI].

[94WEN/PRE]

Wendt and Preetz have obtained solids of Tc(IV) containing the $Tc_2Br_9^-$ [93WEN/PRE], $Tc_2Br_{10}^{2-}$ and $Tc_2Cl_{10}^{2-}$ anions [94WEN/PRE]. The tetraethylammonium nonabromo compound was prepared by reacting solutions of tetraethylammonium hexabromotechnetate $(N(C_2H_5)_4)_2TcBr_6$(s) with trifluoroacetic acid at room temperature for 30 minutes. It is easily soluble in acetonitrile. The infrared spectrum was measured in polyethylene pellets at room temperature, and the Raman spectrum at 80 K using a krypton laser. By analogy with the similar compounds containing the $Pt_2Br_9^-$ anion, whose structure has been determined [92HOL/PRE], the spectra were interpreted assuming D_{3h} symmetry (face-linked octahedra) for the $Tc_2Br_9^-$ ion.

The nine observed vibration frequencies agreed well with those calculated from a normal-coordinate analysis, using distances of 2.42×10^{-10} m and 2.52×10^{-10} m for the terminal and bridging Tc-Br bonds, the same distances as in the Pt compound [92HOL/PRE].

The decahalo- species also were prepared by reacting solutions of the tetraethylammonium hexahalotechnetate $(N(C_2H_5)_4)_2TcX_6(s)$ with trifluoroacetic acid at room temperature

$$2[N(C_2H_5)_4]_2TcX_6(s) + 2CF_3COOH \rightleftharpoons [N(C_2H_5)_4]_2Tc_2X_{10}(s) + 2HX + 2[N(C_2H_5)_4]CF_3COO$$

For the bromocomplex, it is imperative to stop the reaction after an appropriate time (20 minutes for the conditions used by [94WEN/PRE]) to avoid formation of the $Tc_2Br_9^-$ species discussed above. In common with other Tc(IV) halocomplexes, these compounds are sensitive to light. The infra-red and Raman spectra were measured at 80 K. By analogy with the similar osmium(IV) compounds, whose crystal structures have been determined [84COT/DUR, 84KRE/HEN], the $Tc_2Cl_{10}^{2-}$ anions in the technetium compounds were assumed to consist of edge-linked octahedra, with D_{2h} symmetry. A normal-coordinate analysis based on a general force field has been performed for the $Tc_2X_{10}^{2-}$ anions, using the interatomic distances in the similar $(n\text{-}C_4H_9)_4N]_2Os_2X_{10}(s)$ compounds [84COT/DUR, 84KRE/HEN], (M-Cl = (2.301 to 2.411)$\times 10^{-10}$ m, M-Br = (2.448 to 2.544)$\times 10^{-10}$ m). The observed frequencies (14 for the chloride, 10 for the bromide) agree very well with the calculated values.

[95BUR/CAM]

Burnett *et al*. prepared their crystalline $TcO_2(cr)$ by thermal decomposition of purified $NH_4TcO_4(cr)$ in an atmosphere of flowing ultra-high-purity $N_2(g)$. They heated the sample at 348 K

for 1 to 2 hours in a micro-tube furnace, followed by 16 hours at 1023 K. For the chemical analyses, samples of the presumed $TcO_2(cr)$ were allowed to react with an excess of standard Ce(IV) for two days (because of slow oxidation kinetics), followed by back-titration of the excess Ce(IV) with a standard solution of Fe(II) sulfate. The amount of technetium present was determined by β^- liquid scintillation counting with comparison to reference solutions. The mass fraction of Tc determined by oxidation with Ce(IV) was 0.727 ± 0.029 (18 samples titrated) and 0.727 ± 0.036 (28 samples used) for β^- liquid scintillation counting. This compares to a mass fraction of 0.75556 calculated for $^{99}TcO_2(cr)$, which is within the experimental uncertainty limits of the experimental values. They also noted that their experimental results could be slightly low because of problems with static charge buildup on the $TcO_2(cr)$ samples as they were being weighed on their microbalance; this static problem gives high apparent masses and thus low mass fractions.

Burnett *et al*. studied the enthalpy of formation of $TcO_2(cr)$ using solution calorimetry. Dissolution was done by oxidation of the $TcO_2(cr)$ with solutions of Ce(IV) perchlorate, and all such solutions were prepared so as to correspond to the compositions used by Gayer, Herrell, and Busey [76GAY/HER] for their study of the enthalpy

of oxidation of Tc(cr). Burnett *et al*. found that the oxidative dissolution reaction was quite slow, but that samples ground to a fine powder dissolved more readily. Thus all of their enthalpy of dissolution experiments involved TcO_2(cr) that was sieved through a 355 μm mesh. The enthalpies of solution were performed in an isoperibol calorimeter and were monitored for about 1.5 hours in each experiment.

They did 17 dissolution enthalpy measurements using different samples of TcO_2(cr). Re-averaging of their dilution enthalpies and converting their reported uncertainties to 95% confidence limits gives $\Delta_{sol}H_m$(V.28) $= -(132.6 \pm 15.8)$ kJ·mol^{-1} if the calculation is done using the mass of each sample of TcO_2(cr) as determined by direct weighing, and $\Delta_{sol}H_m$(V.28) $= -(138.5 \pm 11.3)$ kJ·mol^{-1} if the mass of each sample of TcO_2(cr) was determined by β^- liquid scintillation counting. Burnett *et al*. had difficulties with the accuracy of their weighings of the TcO_2(cr) because of static charge buildup and, consequently, they considered the β^- liquid scintillation counting results to be more accurate. We accept their assessment.

Burnett *et al.* also prepared hydrated amorphous "TcO_2" samples by hydrolysis of an initially acidic solution of $(NH_4)_2TcCl_6$ or $(NH_4)_2TcBr_6$ with excess NaOH. Analysis of such "TcO_2(am)" for water content using a coulometric titration with Karl-Fischer reagent gave 0.46 H_2O per technetium, which is much lower that the water content for samples of $TcO_2 \cdot xH_2O$(am) produced from electrolytic or chemical reduction of TcO_4^-. In addition, the mass fraction of technetium in the "TcO_2(am)" produced by hydrolytic precipitation of TcX_6^{2-} was much lower than expected, indicating that part of the Tc in such "TcO_2(am)" is in an oxidation data greater than +4. This information demonstrates that "TcO_2(am)" prepared by hydrolysis of TcX_6^{2-} salts is heterogeneous and chemically-different from samples prepared by chemical or electrochemical reduction of TcO_4^-. Thus thermodynamic data measured for samples of "TcO_2(am)" prepared by these different methods should not be combined in a thermodynamic calculation.

Cartledge [71CAR2] stated that a sample of the hydrous technetium oxide produced by cathodic deposition from an alkaline TcO_4^- solution, after being dried at 383 K in air, gave the same electron diffraction pattern as the product of hydrolysis of K_2TcCl_6. However, the hydrolysis conditions were not described nor were the electron diffraction patterns given. Because of the lack of information about the experimental conditions, there is no way to know if the resulting hydrous oxide is chemically equivalent to that prepared by Burnett *et al.* [95BUR/CAM]. Furthermore, the drying of the hydrous oxide in air at 383 K may have reduced the water content of the original precipitate and caused partial oxidation of the technetium. In contrast, Meyer *et al.* [89MEY/ARN] dried their samples of hydrous oxide over a molecular sieve in an argon atmosphere at 303 K, which is far less likely to have resulted in further oxidation of the technetium.

[95ROO/LEI]

See comments under [92ROO/LEI].

[95ZHU/ZHE]

Zhuang *et al*. studied the flow of a solution containing both $NH_4^{99}TcO_4$, with an activity of 2×10^7 Bq · dm^{-3}, and 0.1 M NH_3(aq) through columns of crushed natural stibnite Sb_2S_3(cr) (which contained some Si and trace amounts of Al, Ca, K, and W), crushed granite, and mixtures of 5% Sb_2S_3(cr) + 95% granite and 10% Sb_2S_3(cr) + 90% granite. The granite was mainly composed of plagioclase and orthoclase feldspars, hornblende, biotite, and quartz, with a small amount of magnetite. As little as 10% Sb_2S_3(cr) was found to be sufficient to significantly retard the flow of TcO_4^-, but the extent of retention of ^{99}Tc depended on the flow rate. At a linear flow rate of 3 cm · h^{-1} 23 to 28% of the TcO_4^- was eluted, whereas at a linear flow rate of 0.43 cm · h^{-1} essentially all of the ^{99}Tc was retained for 100% Sb_2S_3(cr). For the 10% Sb_2S_3(cr) + 90% granite packed column, partial retention of the ^{99}Tc was observed only at the slower flow rate, whereas none occurred for pure granite at either rate. Zhuang *et al*. suggested that absorption occurred by way of reduction of the TcO_4^- to Tc(IV), but the chemical form of this reduced technetium was not identified.

[96NGU/PAL]

This is an extended abstract of a study of the solubility of $TcO_2 \cdot xH_2O$(am) and TcO_2(cr) over the pH range of 1 to 13 at 298.15 K, and at ionic strength $I = 0.1$ mol·dm^{-3}, using NaCl to adjust the ionic strength. Samples of $TcO_2 \cdot xH_2O$(am) were prepared by the reduction of TcO_4^- at room temperature using hydrazine, and those of TcO_2(cr) by dehydration of this amorphous dioxide at 1173 K for 2 days under a 1 bar atmosphere of argon. For solutions with pH < 4 and with pH > 11, a minimum of 15 days was required to reach solubility equilibrium, whereas a minimum of 30 days was necessary for $4 <$ pH < 11.

Saturated solutions were ultrafiltered to remove suspended material and extracted to remove TcO_4^-, before analysing the resulting filtrates for their Tc(IV) concentrations by measuring their β decay activities. Presumably, the solubility experiments were performed in an inert atmosphere of argon, but this is never stated.

The authors interpreted the pH dependencies of their solubilities in terms the formation of the following aqueous species : $Tc(OH)_2^{2+}$, $Tc(OH)_3^+$, $Tc(OH)_4$(aq), and $Tc(OH)_5^-$. These formula are equivalent to the formula TcO^{2+}, $TcO(OH)^+$, $TcO(OH)_2$(aq) and $TcO(OH)_3^-$ assumed for the present review. However, the resulting hydrolysis constants were not reported nor were the solubilities. The authors did report the following information :

1. The $TcO_2 \cdot xH_2O$(am) solubility was constant (and at a minimum) at about 10^{-8} mol·dm^{-3} for $3 <$ pH < 10.

2. The solubility of TcO_2(cr) was constant at about $10^{-8.5}$ in this same pH range.

3. At higher acidities (pH < 3) and higher alkalinities (pH > 12), the solubilities of TcO_2(cr) were about two orders of magnitude below those of $TcO_2 \cdot xH_2O$(am). This is surprising to us since their reported solubilities for the same

two solid phases only differed by a factor of three in the intermediate pH range of $3 < pH < 10$. We decline to speculate on the cause of these differences because we do not have access to all of their experimental details or to the measured solubilities.

The solubilities of this study for $TcO_2 \cdot xH_2O$(am) are in fairly good agreement with the concordant values of Meyer and Arnold [91MEY/ARN2] and Eriksen *et al.* [92ERI/NDA, 93ERI/NDA], both obtained with $TcO_2 \cdot xH_2O$(s) samples prepared by electrolytic reduction of TcO_4^-, with the present solubilities [96NGU/PAL] being higher by a factor of 2 to 3. Such minor differences can easily be due to differences in hydration or in degree of partial crystallinity resulting from the different methods of preparation of $TcO_2 \cdot xH_2O$(s).

Solubilities reported for TcO_2(cr) are far less concordant, with variations of about three orders of magnitude. See the discussions of references [87LIE/BAU2] and [97BUR/JOB] for information about the other solubility determinations.

[97BUR/JOB]

Burnett and Jobe studied the kinetics of dissolution of TcO_2(cr) as a function of pH at a constant ionic strength of 0.1 M and at the temperature 298.15 K. Results were reported at eight different nominal pHs ranging from 0.9 to 13.0. At each pH, the technetium concentrations were determined at eight to ten different times ranging from 156 to 8009 hours. The relative proportions of Tc(IV) and Tc(VII) were determined at pH = 0.9 and 1.8 using extraction of TcO_4^- by Ph_4AsCl in chloroform, and this same proportion was assumed to apply at the higher pHs. No extractions were done at the higher pHs. As noted by the authors, there is a possibility that anionic complexes of Tc(IV), such as $TcO(OH)_3^-$, might co-extract with the TcO_4^-, thereby giving erroneously low values for the total concentration of Tc(IV). However, as also noted by these authors, the potential at which the TcO_4^-/Tc(IV) redox reaction occurs decreases as the pH increases, which means that the true TcO_4^-/Tc(IV) concentration ratio may be larger at higher pHs than observed at pH < 4. This implies that the procedure used by Burnett and Jobe may underestimate the concentration of TcO_4^- and thus overestimate the concentrations of Tc(IV), thus yielding solubilities of TcO_2(cr) that are too large for solutions with pH > 4.

Molar concentrations of Tc(IV), C(t), were determined as functions of the sampling time t, and were related to the equilibrium solubility C(sat.) by the Nernst expression

$$C(t) = C(sat.)\{1 - \exp(-k_{diss}t)\}$$

where k_{diss} is the first order dissolution rate constant. This k_{diss} depends, in principal, on the ratio of the surface area of the solid phase to the volume of the solution phase in contact with the solid. The equilibrium solubility parameter C(sat.) is a least-squares fitting parameter. At six of the investigated pHs the increases in the Tc(IV) concentrations with time were in general agreement with this exponential approach to saturation. However, for the experiments at a nominal pH = 4.0, the measured concentrations of

Tc(IV) increased only during the first four samplings (174.8 to 668.4 hours) but then began a rapid decrease. Also, for the experiments at the nominal pH = 13.0, the Tc(IV) concentrations showed the expected initial rapid increase with time, but then changed to slower increases. This behaviour is not consistent with the above dissolution rate equation. The authors suggested that this anomalous behaviour at pH = 13.0 was either due to a change in the dissolution mechanism or the formation of a less soluble solid phase than TcO_2(cr), possibly a double oxide such as Na_2TcO_3(s).

The minimum solubilities obtained in this study were C(sat.) $= 1.2 \cdot 10^{-8}$ M at nominal pH = 4.0 (at which pH the dissolution data are less reliable) and C(sat.) $= 7 \cdot 10^{-7}$ to $1.4 \cdot 10^{-6}$ M for the nominal pH range of 1.8 to 9.0. They noted that their derived solubilities are in general agreement with those of Paquette and Lawrence for TcO_2(cr), which are described under the discussion of reference [88VIK/GAR]. However, the reported solubilities are also slightly higher than those reported for the amorphous hydrated dioxide $TcO_2 \cdot xH_2O$(s) [91MEY/ARN2, 92ERI/NDA, 96NGU/PAL], which generally fall in the range C(sat.) $= 1 \cdot 10^{-9}$ to $8 \cdot 10^{-9}$ M for pH = 3 to 9. The solubilities of Burnett and Jobe are also considerably higher and discrepant from other reported values for TcO_2(cr): C(sat.) $= 7 \cdot 10^{-10}$ M in $I = 0.1$ M $NaNO_3$ [87LIE/BAU2] and C(sat.) $= 3 \cdot 10^{-9}$ M in I = 0.1 M NaCl at pH = 3 to 10 [96NGU/PAL]. Crystalline metal dioxides are generally significantly less soluble than their corresponding amorphous hydrous dioxides, not more soluble.

Burnett and Jobe argued that synthesis of $TcO_2 \cdot xH_2O$(s) from TcO_4^-, by electrodeposition on a platinum electrode, does not yield simply an amorphous hydrated oxide of Tc(IV). Instead, electrodeposition form an acidic solution may yield either a mixture of Tc(III) and Tc(IV) hydrous oxides or substoichiometric (mixed valence) oxides. They also noted that the hydrous oxide prepared by hydrolysis of $(NH_4)TcCl_6$(s) "...was not entirely in the +4 state." See Table V.13 which summarises the preparation methods used for the various solubility studies. They further suggested that a Tc(V) hydrous oxide may be the thermodynamically stable phase at alkaline pHs, rather than a Tc(IV) hydrous oxide.

Reduction of TcO_4^- by hydrazine at acidic pHs is known to yield Tc(IV) hydrous oxides. See the discussion in Section V.3.2.5.1. Solubilities of $TcO_2 \cdot xH_2O$(s) prepared using hydrazine [91MEY/ARN2, 96NGU/PAL] agree well with solubilities determined for samples obtained by electrodeposition at acidic pHs [91MEY/ARN2, 93ERI/NDA]. Thus this review disagrees with the assertion of Burnett and Jobe, and concludes that hydrous oxides precipitated by electrodeposition at acidic pHs is $TcO_2 \cdot xH_2O$(s), but with variable degrees of hydration. We do agree with Burnett and Jobe that hydrous oxide prepared by electrodeposition at alkaline pHs are chemically distinct with lower solubilities [91MEY/ARN]. However, at this time it is not certain whether these hydrous oxides prepared at alkaline pHs different in the average valence of the technetium from those prepared at acidic pHs, or whether they difference only in their degree of hydration and/or degree of crystallinity.

[97COU]

The objective of this recent thesis, which we obtained shortly before finishing the final draft, was to investigate the redox mechanisms of technetium in aqueous solution using a mercury electrode. This is an interesting study, in which three-dimensional polarography was applied in order to extend the timescale of the experiments. The author proposed a mechanistic model for the reduction of Tc(VII) to Tc(0). The experiments were carried out in an acetate buffer of a constant concentration of 0.1 M, usually at pH = 4.6. The influence of pH, which is a crucial parameter for the speciation of technetium, was investigated by performing measurements at pH = 3.1, 1.9 and 1, respectively. While the ionic strength of a 0.1 M acetate buffer at pH = 4.6 is about 0.05 M, at pH = 3.1 it is only about 0.003 M due to the increased proportion of undissociated acetic acid. In order to obtain lower pH values, Courson added perchloric acid to a 0.1 M acetic acid solution. Hence, the ionic strength is about 0.014 M at pH=1.9 and 0.13 M at pH=1. The author took care to maintain the total acetate concentration at 0.1 M, but he failed to maintain a constant ionic strength. The activity coefficients are thus not kept constant. In addition, acetate is likely to form complexes with Tc(III) and Tc(IV) and may thus influence the redox behaviour of technetium in the experiments of Courson, especially since the concentration of deprotonated acetate ion varied with pH. The author did not extract any thermodynamic data from his measurements. For the reasons mentioned above, it is not possible to extract values of E° from the reported information.

[98GUE2]

Boyd [78BOY2] determined the solubility of sodium pertechnetate at (298.15±0.01) K to be 11.299 $mol \cdot kg^{-1}$ using the isopiestic method. Although Boyd added $NaTcO_4$(cr) to a reservoir solution at the beginning of this experiment, isopiestic equilibrations are typically at least several days in duration, which should have been ample time for the $NaTcO_4$(cr) to convert to the possibly hydrated equilibrium solid phase. German *et al.* [87GER/KRY] reported that one of the polymorphic forms of $NaTcO_4 \cdot 4H_2O$(cr) is the equilibrium solid phase in contact with a saturated aqueous solution at 298.15 K. However, crystals of this substance exposed to laboratory air gradually effloresce with loss of some of the waters of hydration.

The only other published solubilities are those of Guerman *et al.* [93GER/GRU] for $NaTcO_4 \cdot 4H_2O$(cr), 1.7 M at 282 K and 1.48 M at 293 K. These values imply that this hydrate has retrograde solubility, at least over this temperature interval, and that the solubility has a very large temperature coefficient. Extrapolation of these two values to estimate the solubility of this tetrahydrate at 298.15 K yields a solubility about an order of magnitude smaller than that reported by Boyd [78BOY2]. We do not expect extrapolation of the lower temperature solubilities [93GER/GRU] to yield a very accurate value for the solubility at 298.15 K since

- These solubilities are available at only two temperatures, and,
- $NaTcO_4 \cdot 4H_2O$(cr) undergoes a polymorphic crystalline transformation begin-

ning around 298 K [93GER/GRU] which will change the temperature dependence of the solubility.

K.E. Guerman (the same person as K.E. German) volunteered to perform additional solubility measurements at 298.15 K to resolve the apparent inconsistency between these two solubility studies. The following paragraphs summarise the preliminary results obtained by Dr. Guerman.

A saturated solution of $NaTcO_4$ was prepared by boiling an unsaturated solution until crystals formed from the solution, followed by cooling of the solution and crystals to room temperature. However, these crystals redissolved by the next morning, thus indicating either the initial precipitate was metastable at 298.15 K or that this phase has a retrograde solubility with a large temperature dependence. However, four days later some new crystals spontaneously precipitated from this same solution. Based on a visual inspection of the crystal shape, these crystals appear to be the lower-temperature crystalline form of $NaTcO_4 \cdot 4H_2O$(cr).

A separate saturated solution was prepared by addition of 0.5 cm^3 of bidistilled water to 10 g of anhydrous $NaTcO_4$(s). A 0.2 cm^3 sample of this solution was removed for analysis, after equilibrating this solution and crystals for 7 days at (298.15 ± 0.2) K. This solution had a molality of 12.6 $mol \cdot kg^{-1}$ and a density of 1.890 $g \cdot cm^{-3}$, which yields a molar concentration of 7.13 M. This preliminary solubility value supports the solubility reported by Boyd [78BOY2]. Additional solubility determinations are planned.

[98GUE]

A reddish-black compound with the stoichiometry "$Tc_2O_7 \cdot H_2O$(cr)" has been known for many years [53SMI/COB]. However, since no structural information is available, it is not known if this substance is really hydrated Tc_2O_7, or whether it is $HTcO_4$ (which differs in its empirical formula from $Tc_2O_7 \cdot H_2O$ only by a factor of 1/2), or whether it has a polymeric structure. K.E. Guerman and his colleagues at the Institute of Physical Chemistry of the Russian Academy of Sciences in Moscow, Russia, have an ongoing program of characterising this substance, and the following description is based on their experiments.

Red coloured crystals of "$Tc_2O_7 \cdot H_2O$" or "$HTcO_4$" were prepared by K.E. Guerman, V.G. Maksimov, S.V. Kryutchkov, and L.I. Belyaeva using two different methods. The first method involved adding water to Tc_2O_7(s) and the second method involved removal of water from an aqueous solution of $HTcO_4$ using $Mg(ClO_4)_2$(s) as a desiccant. The $HTcO_4$ solution was obtained by cation exchange of a $KTcO_4$ solution using a DOWEX-1 resin in its hydrogen form.

An X-ray structural determination by M.S. Grigoriev and colleagues [93GRI/KRY] showed that this substance crystallised in the triclinic space $P\bar{1}$ with (at room temperature) $a = (11.26 \pm 0.02) \times 10^{-10}$ m, $b = (12.87 \pm 0.02) \times 10^{-10}$ m, $c = (14.16 \pm 0.04) \times 10^{-10}$ m, $\alpha = (71.0 \pm 0.2)°$, $\beta = (69.1 \pm 0.2)°$, and $\gamma = (74.1 \pm 0.2)°$. The detailed structure has not been solved, but it is probable that the unit cell contains 8 technetium atoms.

Recent ^{99}Tc NMR measurements by K.E. Guerman and V.P. Tarasov indicate that the crystal structure of this substance contains equal amounts of Tc in two non-equivalent environments. From this evidence they speculated that the technetium may be present in both anionic and cationic forms.

Occasionally, attempts to prepare "$Tc_2O_7 \cdot H_2O$(cr)" yielded white rather than red crystals. The nature of this white substance is unknown, but it is possibly a more hydrated form of Tc_2O_7.

[99JOB/TAY]

The authors of reference [95BUR/CAM] have obtained the unit cell parameters for TcO_2(cr) from their X-ray structural study, and kindly supplied that information to this review in advance of publication. Because of pseudo-symmetric relation between the unit cell parameters, $a \sim c \sim (2/\sqrt{3})b$, the least-squares analysis of the diffraction lines had multiple relative minima. Depending on the initial estimates for the unit cell parameters, convergence was obtained to different local minima with significantly different unit cell dimensions. By using a large number of different initial estimates of the unit cell dimensions, an absolute minimum was obtained by this "trial and error" approach. The analysis definitely established that the space group of TcO_2(cr) is $P2_1/c$, in agreement with the claim in reference [55MAG/AND], and yielded the dimensions $a = (5.6872 \pm 0.012) \times 10^{-10}$m, $b = (4.7635 \pm 0.0014) \times 10^{-10}$m, $c = (5.5195 \pm 0.0012) \times 10^{-10}$m, and $\beta = (121.59 \pm 0.02)^\circ$. These are probably the most accurate set of parameters for TcO_2(cr).

Because of the pseudo-symmetric relationship between the unit cell parameters, it was also possible to refine the unit cell parameters of TcO_2(cr) in the space group $P2_1/n$, which is a redundant variant of space group $P2_1/c$. However, this analysis yielded two alternative set of unit cell parameters: $a = (5.6872 \pm 0.0012) \times 10^{-10}$m, $b = (4.7635 \pm 0.0014) \times 10^{-10}$m, $c = (5.4704 \pm 0.0012) \times 10^{-10}$m, and $\beta = (120.74 \pm 0.02)^\circ$; or $a = (5.4704 \pm 0.0012) \times 10^{-10}$m, $b = (4.7635 \pm 0.0014) \times 10^{-10}$m, $c = (5.5195 \pm 0.0012) \times 10^{-10}$m, and $\beta = (117.67 \pm 0.02)^\circ$.

Appendix B

Tables of thermodynamic functions

B.1 Thermal functions of Tc(cr) below 298.15 K

The only measurements of the heat capacity of technetium at low temperatures are those of Trainor and Brodsky [75TRA/BRO] from 3 to 15 K; the actual experimental values of heat capacity were given only as a small graph. The methodology of [89FER/GRI] should be valid down to temperatures of about 0.3 θ^{S}, about 100 K for technetium. Calculations have shown that the correlation upon which the simple relation (V.1) has been based is valid down to at least 100 K, using recent data for S°_{m} (T) for the six pairs of elements Zr/Hf to Pd/Pt (excluding Tc/Re). We have therefore extended the calculations of Fernández Guillermet and Grimvall [89FER/GRI] down to 100 K (below which they begin to be less accurate), and calculated "first-pass" values of S°_{m} and by fitting, $C^{\circ}_{p,m}$, down to these temperatures. The thermal functions in the remaining interval between 15 K [75TRA/BRO] and 100 K have been estimated somewhat arbitrarily by fitting reasonable values of $C^{\circ}_{p,m}$ (T) and S°_{m} (T) in this range to a polynomial in T such that S°_{m} and $dS^{\circ}_{m}/dT = C^{\circ}_{p,m}/T$ are continuous at 15 K and a temperature not far removed from 100 K, (finally selected to be 115 K), the values at 15 K being taken from Trainor and Brodsky [75TRA/BRO]. This automatically gives a set of functions consistent with the selected data at 298.15 K. The derived value of $H^{\circ}_{m}(298.15\ K) - H^{\circ}_{m}(0\ K)$from this analysis is 4994 J · mol^{-1}, very close to that estimated by [88KRI], 4952 J · mol^{-1}. The lower value of 4269 J · mol^{-1} from Powers [91POW] is, like his value of $S^{\circ}_{m}(298.15\ K) - S^{\circ}_{m}(0\ K)$, likely to be too small due to the use of an inappropriate constant Debye temperature. The final values of the thermal functions of Tc(cr, l) are given in Table B.1.

B.2 Thermodynamic functions of Tc(hcp, liq) and Tc(g)

The thermodynamic functions of Tc(hcp, liq) and Tc(g) are given in Tables B.1 and B.2 and thermodynamic functions for the vaporisation of Tc(hcp, liq) are given in Table B.3. For practical calculations, the Gibbs energies of sublimation and vapor-

Table B.1: Thermodynamic functions of Tc(hcp, l).

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	S°_{m} ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$H^\circ_{\mathrm{m}}(T) - H^\circ_{\mathrm{m}}(0\ \mathrm{K})$ ($\mathrm{J \cdot mol^{-1}}$)	$-[G^\circ_{\mathrm{m}}(T) - H^\circ_{\mathrm{m}}(0\ \mathrm{K})]/T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)
7.86	0.044	0.037	0.215	0.010
15.00	0.165	0.091	0.847	0.035
25.00	0.934	0.332	5.9	0.096
50.00	5.070	2.087	75.0	0.586
75.00	11.095	5.254	275.5	1.582
100.00	16.391	9.229	624.1	2.988
125.00	18.715	13.151	1064.5	4.635
150.00	20.549	16.737	1557.0	6.357
200.00	22.711	22.976	2644	9.757
250.00	24.031	28.196	3815	12.937
298.15	24.879	32.506	4994	15.757
300.00	24.904	32.660	5040	15.861
400.00	25.955	39.982	7587	21.014
500.00	26.657	45.853	10220	25.414
600.00	27.219	50.764	12914	29.241
700.00	27.711	54.998	15661	32.625
800.00	28.164	58.728	18455	35.659
900.00	28.592	62.070	21293	38.411
1000.00	29.002	65.104	24173	40.931
1100.00	29.398	67.887	27093	43.257
1200.00	29.784	70.461	30052	45.418
1300.00	30.160	72.860	33049	47.437
1400.00	30.527	75.109	36084	49.335
1500.00	30.888	77.227	39155	51.124
1600.00	31.241	79.232	42261	52.819
1700.00	31.587	81.136	45403	54.429
1800.00	31.927	82.951	48578	55.963
1900.00	32.261	84.687	51788	57.430
2000.00	32.588	86.350	55030	58.835
2100.00	32.910	87.948	58305	60.183
2200.00	33.226	89.486	61612	61.480
2300.00	33.535	90.970	64950	62.730
2400.00	33.839	92.403	68319	63.937
2430.00(cr)	33.929	92.824	69336	64.291
2430.00(l)	47.000	106.524	102626	64.291
2500.00	47.000	107.859	105916	65.492
2600.00	47.000	109.702	110616	67.158
2700.00	47.000	111.476	115316	68.766
2800.00	47.000	113.185	120016	70.322
2900.00	47.000	114.835	124716	71.829
3000.00	47.000	116.428	129416	73.289

isation,

$$\mathrm{Tc(cr, hcp)} \quad \rightleftharpoons \quad \mathrm{Tc(g)} \tag{B.1}$$

$$\mathrm{Tc(l)} \quad \rightleftharpoons \quad \mathrm{Tc(g)} \tag{B.2}$$

can be expressed to well within their uncertainty by the following equations:

$$\Delta_r G^\circ_m(\text{B.1}, 298.15 \text{ to } 2430 \text{ K}) \quad = \quad (673.292 - 0.144192T) \text{ kJ·mol}^{-1}$$

$$\Delta_r G^\circ_m(\text{B.2}, 2430 \text{ to } 3000 \text{ K}) \quad = \quad (632.665 - 0.127483T) \text{ kJ·mol}^{-1}$$

Table B.2 contains ideal gas statistical thermodynamic values for Tc(g). The sources for the energy levels are discussed in Section V.1.2.1.

Table B.2: Ideal gas thermodynamic functions of Tc(g).

Part I.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	S°_m ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$-[G^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})$ ($\mathrm{J \cdot mol^{-1}}$)
0	0.000	0.000	Infinite	-6197
10	20.786	110.481	709.460	-5989
25	20.786	129.528	356.647	-5677
50	20.786	143.936	247.102	-5158
100	20.786	158.344	199.534	-4119
200	20.786	172.752	182.954	-2040
298.15	20.795	181.052	181.052	0
300	20.796	181.181	181.052	38
400	20.916	187.175	181.869	2122
500	21.364	191.882	183.417	4232
600	22.293	195.851	185.166	6411
700	23.679	199.387	186.949	8706
800	25.356	202.656	188.710	11156
900	27.101	205.744	190.433	13780
1000	28.715	208.685	192.112	16572
1100	30.058	211.487	193.747	19513
1200	31.062	214.148	195.337	22572
1300	31.719	216.662	196.882	25714
1400	32.062	219.027	198.380	28906
1500	32.148	221.244	199.831	32118
1600	32.037	223.316	201.235	35329
1700	31.791	225.251	202.592	38521
1800	31.461	227.059	203.901	41684
1900	31.091	228.751	205.165	44812
2000	30.712	230.336	206.384	47902
2100	30.352	231.825	207.561	50955
2200	30.027	233.230	208.696	53974
2300	29.751	234.558	209.792	56962
2400	29.531	235.819	210.850	59926
2430	29.478	236.186	211.161	60811
2500	29.374	237.021	211.873	62870
2600	29.282	238.172	212.863	65803
2700	29.255	239.276	213.821	68729
2800	29.292	240.340	214.749	71656
2900	29.392	241.370	215.649	74589
3000	29.552	242.369	216.523	77536
3100	29.767	243.341	217.373	80502
3200	30.035	244.290	218.199	83491
3300	30.351	245.219	219.004	86510
3400	30.711	246.131	219.788	89563
3500	31.109	247.026	220.554	92654
3600	31.540	247.909	221.301	95786
3700	32.001	248.779	222.032	98963
3800	32.486	249.639	222.748	102187
3900	32.991	250.489	223.448	105461
4000	33.510	251.331	224.135	108786

Table B.2: (continued)

Part II.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	S°_{m} ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$-[G^\circ_{\mathrm{m}}(T) - H^\circ_{\mathrm{m}}(0\ \mathrm{K})]/T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$H^\circ_{\mathrm{m}}(T) - H^\circ_{\mathrm{m}}(0\ \mathrm{K})$ ($\mathrm{J\cdot mol^{-1}}$)
0	0.000	0.000	Infinite	0
10	20.786	110.481	89.695	207
25	20.786	129.528	108.741	519
50	20.786	143.936	123.149	1039
100	20.786	158.344	137.557	2078
200	20.786	172.752	151.965	4157
298.15	20.795	181.052	160.265	6197
300	20.796	181.181	160.393	6236
400	20.916	187.175	166.375	8319
500	21.364	191.882	171.021	10430
600	22.293	195.851	174.836	12608
700	23.679	199.387	178.095	14904
800	25.356	202.656	180.963	17354
900	27.101	205.744	183.546	19977
1000	28.715	208.685	185.914	22770
1100	30.058	211.487	188.113	25711
1200	31.062	214.148	190.173	28770
1300	31.719	216.662	192.115	31912
1400	32.062	219.027	193.953	35103
1500	32.148	221.244	195.700	38316
1600	32.037	223.316	197.362	41526
1700	31.791	225.251	198.946	44719
1800	31.461	227.059	200.458	47882
1900	31.091	228.751	201.903	51010
2000	30.712	230.336	203.286	54100
2100	30.352	231.825	204.609	57153
2200	30.027	233.230	205.879	60171
2300	29.751	234.558	207.097	63160
2400	29.531	235.819	208.268	66123
2430	29.478	236.186	208.610	67008
2500	29.374	237.021	209.394	69068
2600	29.282	238.172	210.479	72000
2700	29.255	239.276	211.525	74927
2800	29.292	240.340	212.535	77853
2900	29.392	241.370	213.512	80787
3000	29.552	242.369	214.457	83734
3100	29.767	243.341	215.373	86699
3200	30.035	244.290	216.262	89689
3300	30.351	245.219	217.126	92708
3400	30.711	246.131	217.966	95761
3500	31.109	247.026	218.783	98851
3600	31.540	247.909	219.580	101984
3700	32.001	248.779	220.357	105160
3800	32.486	249.639	221.117	108385
3900	32.991	250.489	221.859	111658
4000	33.510	251.331	222.585	114983

Table B.3: Thermodynamic functions for the reaction Tc(hcp, l) $\rightleftharpoons$ Tc(g).

T (K)	$\Delta_r H^\circ_m$ ($kJ \cdot mol^{-1}$)	$\Delta_r S^\circ_m$ ($J \cdot K^{-1} \cdot mol^{-1}$)	$\Delta_r G^\circ_m$ ($kJ \cdot mol^{-1}$)
298.15	675.00	148.546	630.71
500.00	674.02	146.029	600.99
1000.00	672.39	143.582	528.81
1500.00	672.96	144.017	456.93
2000.00	672.86	143.987	384.89
2430.00(cr, hcp)	671.47	143.362	323.10
2430.00(l)	638.18	129.662	323.10
2500.00	636.95	129.662	314.04
3000.00	628.11	125.939	250.29

B.3 Gaseous technetium ions

B.3.1 $Tc^+(g)$

Green *et al.* [60GRE/POL] have given values for the two functions $(G^\circ_m(T) - H^\circ_m(0\ K))/T$ and $(H^\circ_m(T) - H^\circ_m(0\ K))$ for $Tc^+(g)$ at selected temperatures up to 50 kK, calculated from the 33 energy levels given by Moore [58MOO]. We have extended these calculations using the same energy levels and give all the thermal functions for this species up to 6000 K in Table B.4. Since there are relatively few levels characterised, the calculated values above this temperature will be less precise, although, again this error is trivial compared with the uncertainty in the enthalpy of formation. The enthalpy of formation of this species is calculated from the ionisation potential from [58MOO] ($(58700 \pm 100)\ cm^{-1}$) (uncertainty estimate by the present reviewer) giving for

$$\begin{aligned} Tc(g) &\rightleftharpoons Tc^+(g) + e^-(g) \\ \Delta_r H^\circ_m(0\ K) &= (702.2 \pm 1.2)\ kJ \cdot mol^{-1} \end{aligned}$$

The difference in $H^\circ_m(298.15\ K) - H^\circ_m(0\ K)$ for this reaction is $6.2\ kJ \cdot mol^{-1}$, giving $\Delta_r H^\circ_m(298.15\ K) = (708.4 \pm 1.2)\ kJ \cdot mol^{-1}$, and finally

$$\begin{aligned} \Delta_f H^\circ_m(Tc^+, g, 298.15\ K) &= \Delta_f H^\circ_m(Tc, g, 298.15\ K) + (708.4 \pm 1.2)\ kJ \cdot mol^{-1} \\ &= (1383^{+12}_{-40})\ kJ \cdot mol^{-1} \end{aligned}$$

When combined the standard entropy from Table B.4,

$$S^\circ_m(Tc^+, g, 298.15\ K) = (182.333 \pm 0.1)\ J \cdot K^{-1} \cdot mol^{-1}$$

this gives

$$\Delta_f G^\circ_m(Tc^+, g, 298.15\ K) = (1322.383\ ^{+12}_{-40})\ kJ \cdot mol^{-1}$$

Table B.4: Thermodynamic functions of $Tc^+(g)$.

Part I.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	S°_m ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$-[G^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})$ ($\mathrm{J \cdot mol^{-1}}$)
0	0.000	0.000	Infinite	-6197
10	20.786	111.763	710.720	-5989
25	20.786	130.809	357.920	-5677
50	20.786	145.217	248.380	-5158
100	20.786	159.625	200.813	-4118
200	20.786	174.033	184.234	-2040
298.15	20.786	182.333	182.333	0
300	20.786	182.461	182.333	38
400	20.793	188.442	183.148	2117
500	20.845	193.086	184.689	4198
600	21.018	196.899	186.415	6290
700	21.387	200.164	188.151	8408
800	21.984	203.056	189.837	10575
900	22.792	205.690	191.454	12812
1000	23.754	208.140	193.001	15138
1100	24.797	210.453	194.484	17566
1200	25.847	212.656	195.907	20098
1300	26.838	214.764	197.277	22733
1400	27.725	216.787	198.599	25462
1500	28.476	218.726	199.876	28273
1600	29.078	220.584	201.113	31152
1700	29.530	222.361	202.311	34084
1800	29.841	224.058	203.472	37054
1900	30.025	225.677	204.599	40048
2000	30.099	227.219	205.692	43055
2100	30.081	228.688	206.752	46065
2200	29.988	230.085	207.781	49069
2300	29.838	231.415	208.780	52060
2400	29.644	232.681	209.750	55035
2500	29.418	233.887	210.691	57988
2600	29.171	235.036	211.606	60918
2700	28.912	236.132	212.494	63822
2800	28.647	237.179	213.357	66700
2900	28.381	238.179	214.196	69551
3000	28.119	239.137	215.011	72376
3200	27.619	240.935	216.576	77949
3400	27.163	242.596	218.058	83427
3600	26.761	244.137	219.465	88818
3800	26.415	245.574	220.802	94135
4000	26.125	246.922	222.074	99388
4200	25.888	248.190	223.288	104588
4400	25.701	249.390	224.448	109747
4600	25.560	250.529	225.557	114872
4800	25.460	251.615	226.620	119973
5000	25.396	252.653	227.641	125058
5200	25.365	253.648	228.622	130134
5400	25.362	254.605	229.567	135206
5600	25.384	255.528	230.478	140281
5800	25.426	256.419	231.357	145361
6000	25.487	257.282	232.207	150452

Table B.4: (continued)

Part II.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	S°_m ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$-[G^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(0\ \mathrm{K})]/T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(0\ \mathrm{K})$ ($\mathrm{J \cdot mol^{-1}}$)
0	0.000	0.000	Infinite	0
10	20.786	111.763	90.977	207
25	20.786	130.809	110.023	519
50	20.786	145.217	124.431	1039
100	20.786	159.625	138.839	2078
200	20.786	174.033	153.247	4157
298.15	20.786	182.333	161.546	6197
300	20.786	182.461	161.675	6235
400	20.793	188.442	167.655	8314
500	20.845	193.086	172.294	10396
600	21.018	196.899	176.086	12487
700	21.387	200.164	179.298	14606
800	21.984	203.056	182.090	16772
900	22.792	205.690	184.568	19010
1000	23.754	208.140	186.804	21336
1100	24.797	210.453	188.850	23763
1200	25.847	212.656	190.742	26296
1300	26.838	214.764	192.510	28930
1400	27.725	216.787	194.172	31660
1500	28.476	218.726	195.745	34471
1600	29.078	220.584	197.240	37350
1700	29.530	222.361	198.665	40281
1800	29.841	224.058	200.029	43251
1900	30.025	225.677	201.337	46245
2000	30.099	227.219	202.593	49252
2100	30.081	228.688	203.801	52262
2200	29.988	230.085	204.964	55266
2300	29.838	231.415	206.085	58258
2400	29.644	232.681	207.167	61232
2500	29.418	233.887	208.212	64186
2600	29.171	235.036	209.222	67115
2700	28.912	236.132	210.199	70019
2800	28.647	237.179	211.144	72897
2900	28.381	238.179	212.059	75749
3000	28.119	239.137	212.945	78574
3200	27.619	240.935	214.639	84147
3400	27.163	242.596	216.236	89624
3600	26.761	244.137	217.743	95016
3800	26.415	245.574	219.171	100332
4000	26.125	246.922	220.525	105585
4200	25.888	248.190	221.813	110786
4400	25.701	249.390	223.039	115944
4600	25.560	250.529	224.210	121069
4800	25.460	251.615	225.329	126171
5000	25.396	252.653	226.401	131256
5200	25.365	253.648	227.430	136332
5400	25.362	254.605	228.419	141404
5600	25.384	255.528	229.371	146478
5800	25.426	256.419	230.288	151559
6000	25.487	257.282	231.174	156650

The standard state for the gaseous electron is that conventionally used in thermodynamic tables [85CHA/DAV], so that the thermal functions are those of a Boltzmann gas with the electron mass, with a ground state quantum weight of 2, and $\Delta_f H^\circ_m(T) = \Delta_f G^\circ_m(T) = 0$ for all temperatures. These are not, of course, correct at 298.15 K and 1 bar pressure (where the electron behaves as a Fermi-Dirac gas), but are correct for the common situations of an electron gas pressure less than 10^{-6} bar above ~5 K [85CHA/DAV]. Thus

$$S^\circ_m(e^-, g, 298.15\,K) = (20.979 \pm 0.013)\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

B.3.2 Tc^-(g)

Hotop and Lineberger [85HOT/LIN] have estimated the electron affinity of Tc(g) to be (0.55 ± 0.20) eV, from the correlation of the *s*-electron binding energies of the 4*d* transition elements with number of *d*-electrons, given by Figure 17 of the paper by Feigerle et al. [81FEI/COR]. The appreciable uncertainty in this value is due to the paucity of measured electron affinities with 6 or 7 *d*-electrons required for the comparison. (Of the six elements Mn, Fe, Tc, Ru, Re and Os only that of Fe has been measured). The estimated electron affinity corresponds to $\Delta_r H_m$(B.3, 0 K) = −(53 ± 19) kJ·mol^{-1} for the reaction

$$Tc(g) + e^-(g) \rightleftharpoons Tc^-(g) \qquad (B.3)$$

There are no spectroscopic data from which the entropy and other thermal functions of Tc^-(g) can be derived, but the change in the enthalpy of reaction B.3 between 0 and 298.15 K can be estimated to be $\Delta_r H_m$(B.3, 298.15 K) − $\Delta_r H_m$(B.3, 0 K) = −6.2 kJ·mol^{-1}, with negligible uncertainty, from the value for the corresponding reaction involving Mo (and many other elements, [85CHA/DAV]). Thus the selected value for the enthalpy of formation of Tc^-(g) is

$$\Delta_f H_m(Tc^-, g, 298.15\,K) = (616^{+22}_{-44})\ kJ{\cdot}mol^{-1} \qquad (B.4)$$

B.4 Tables of thermodynamic functions of Tc_2O_7(cr,l)

Table B.5 contains a more extensive listing of the heat capacities, enthalpies, and Gibbs energies of formation for Tc_2O_7(cr) from 298.15 to 392.7 K and for Tc_2O_7(l) from 392.7 to 650.00 K. The thermodynamic functions for the reaction 2Tc(cr) + 3.5O_2(g) ⇌ Tc_2O_7(cr, l) are given in Table B.6. See Section V.3.2.1.2 for a detailed discussion of these calculations.

Table B.5: Thermodynamic functions of Tc_2O_7(cr, l).

T (K)	$C^\circ_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	S°_m ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$H^\circ_m(T) - H^\circ_m(298\ K)$ ($J \cdot mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(298\ K)]/T$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)
298.15	160.39	192.00	0.0	192.00
300.00	160.80	192.99	297.1	192.00
350.00	170.41	218.53	8587.5	194.00
392.70(cr)	177.10	238.54	16010.0	197.77
392.70(liq)	250.00	350.58	60011.0	197.77
400.00	250.00	355.19	61835.0	200.60
450.00	250.00	384.63	74335.0	219.44
500.00	250.00	410.97	86835.0	237.30
550.00	250.00	434.80	99335.0	254.19
600.00	250.00	456.55	111835.0	270.16
650.00	250.00	476.56	124335.0	285.28

Table B.6: Thermodynamic functions for the reaction $2Tc(cr) + 3.5O_2(g) \rightleftharpoons Tc_2O_7$(cr, l).

T (K)	$\Delta_r C^\circ_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$\Delta_r H^\circ_m$ ($kJ{\cdot}mol^{-1}$)	$\Delta_r S^\circ_m$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$\Delta_r G^\circ_m$ ($kJ{\cdot}mol^{-1}$)
298.15	7.818	-1126.50	-591.04	-950.280
300.00	8.147	-1126.49	-590.99	-949.187
350.00	15.481	-1125.88	-589.15	-919.680
392.70	20.117	-1125.12	-587.10	-894.566
392.70	93.017	-1081.12	-475.05	-894.565
400.00	92.661	-1080.44	-473.34	-891.104
450.00	90.226	-1075.87	-462.57	-867.713
500.00	87.831	-1071.42	-453.19	-844.824
550.00	85.513	-1067.09	-444.93	-822.475
600.00	83.293	-1062.87	-437.58	-800.316
650.00	81.184	-1058.75	-431.00	-778.604

B.5 Tables of thermodynamic functions of TcO(g)

As discussed in Section V.3.3.2, there are no definitive measurements on the spectrum of TcO(g) from which its molecular parameters can be derived, but various values of these appear in the literature, both from an experimental study which may refer to TcO(g) [77CHE], and *a priori* calculations and estimates. These are given in Table B.7. Table B.8 gives our own independent estimates, shown in bold, of the relevant parameters based on those of the surrounding elements, taken from the comprehensive survey on gaseous monoxides by Pedley and Marshall [83PED/MAR], with an additional experimental value for MoO(g). Some of these values, enclosed in parentheses, are themselves estimates. The values in bold in Table B.8 are seen to be in reasonable agreement with those in Table B.7 and are the preferred values.

The calculated thermal functions are given in detail in Table B.9.

Table B.7: Molecular parameters for TcO(g)

Method	ω (cm^{-1})	$r \times 10^{10}$ (m)	Reference
Ab initio (approximation 1a)	795	1.772	[89LAN/BAU]
Ab initio (approximation 1b)	766	1.776	[89LAN/BAU]
Ab initio (approximation 2)	877	1.745	[89LAN/BAU]
Experimental[(a)]	935±25		[77CHE]
Estimation	854	1.783	[66SCH]

[(a)] Probably TcO(g), but could be TcN(g).

Table B.8: Comparison of molecular parameters for MO(g) for 3d, 4d and 5d transition metals

Compound	ω (cm^{-1})	ωx (cm^{-1})	$r \times 10^{10}$ (m)
CrO	898	6.8	1.618
MnO	840	4.8	1.769
FeO	881	4.6	1.626
MoO	(950) 894[(a)]		1.73
TcO	**900** ±50	4	**1.78**±0.05
RuO	855		1.70
WO	1055	3.85	1.658
ReO	900		1.834
OsO	785		1.85

[(a)] Experimental value from [79BAT/GRU].

Table B.9: Ideal gas thermal functions for TcO(g)

Part I.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	S°_{m} ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$-[G^\circ_{\mathrm{m}}(T) - H^\circ_{\mathrm{m}}(298.15\ \mathrm{K})]/T$ ($\mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$)	$H^\circ_{\mathrm{m}}(T) - H^\circ_{\mathrm{m}}(298.15\ \mathrm{K})$ ($\mathrm{J \cdot mol^{-1}}$)
0	0.000	0.000	Infinite	-8823
10	29.149	144.812	998.221	-8534
25	28.552	169.363	495.243	-8147
50	29.105	191.531	338.923	-7369
100	29.109	211.706	270.849	-5914
200	29.671	231.982	246.913	-2986
298.15	31.256	244.109	244.109	0
300	31.288	244.302	244.109	57
400	32.889	253.531	245.357	3269
500	34.085	261.006	247.762	6621
600	34.927	267.299	250.508	10074
700	35.520	272.731	253.304	13598
800	35.949	277.503	256.036	17173
900	36.267	281.757	258.662	20785
1000	36.511	285.591	261.166	24424
1100	36.705	289.080	263.548	28085
1200	36.867	292.281	265.811	31764
1300	37.012	295.238	267.962	35458
1400	37.152	297.986	270.010	39166
1500	37.296	300.554	271.961	42888
1600	37.453	302.966	273.824	46626
1700	37.631	305.241	275.606	50380
1800	37.837	307.398	277.313	54153
1900	38.076	309.450	278.951	57948
2000	38.351	311.410	280.525	61769
2100	38.664	313.289	282.041	65620
2200	39.016	315.095	283.503	69503
2300	39.408	316.838	284.914	73424
2400	39.838	318.524	286.280	77386
2500	40.303	320.160	287.602	81393
2600	40.802	321.750	288.885	85448
2700	41.329	323.300	290.131	89554
2800	41.881	324.813	291.343	93715
2900	42.453	326.292	292.523	97931
3000	43.041	327.741	293.673	102206

Table B.9: (continued)

Part II.

T (K)	$C^\circ_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	S°_m ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(0\,K)]/T$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$H^\circ_m(T) - H^\circ_m(0\,K)$ ($J \cdot mol^{-1}$)
0	0.000	0.000	Infinite	0
10	29.149	144.812	115.914	288
25	28.552	169.363	142.321	676
50	29.105	191.531	162.461	1453
100	29.109	211.706	182.618	2908
200	29.671	231.982	202.798	5836
298.15	31.256	244.109	214.516	8823
300	31.288	244.302	214.699	8880
400	32.889	253.531	223.299	12092
500	34.085	261.006	230.116	15444
600	34.927	267.299	235.803	18897
700	35.520	272.731	240.699	22421
800	35.949	277.503	245.007	25996
900	36.267	281.757	248.859	29608
1000	36.511	285.591	252.343	33247
1100	36.705	289.080	255.527	36908
1200	36.867	292.281	258.458	40587
1300	37.012	295.238	261.175	44281
1400	37.152	297.986	263.707	47989
1500	37.296	300.554	266.079	51711
1600	37.453	302.966	268.310	55449
1700	37.631	305.241	270.416	59203
1800	37.837	307.398	272.411	62976
1900	38.076	309.450	274.307	66771
2000	38.351	311.410	276.114	70592
2100	38.664	313.289	277.839	74443
2200	39.016	315.095	279.492	78326
2300	39.408	316.838	281.078	82247
2400	39.838	318.524	282.603	86209
2500	40.303	320.160	284.073	90216
2600	40.802	321.750	285.492	94271
2700	41.329	323.300	286.864	98377
2800	41.881	324.813	288.192	102538
2900	42.453	326.292	289.480	106754
3000	43.041	327.741	290.732	111029

B.6 Tables of thermodynamic functions of $Tc_2O_7(g)$

See Tables B.10 and B.11. The origin of the vibration fundamentals and the molecular parameters are discussed in Section V.3.3.3.

B.7 Tables of enthalpy of sublimation of TcF_6(cr, cubic)

See Table B.12. A detailed discussion of the calculation of these values can be found in Appendix A, under reference [78OSB/SCH].

Table B.10: Vibration frequencies for Tc_2O_7(g), where vs = very strong, s = strong, m = medium, ms = medium strong, mw = medium weak, w = weak, and p = polarised.

Mode	Calculated			Observed	
	Frequency cm^{-1}	Intensity	Depolarisation Ratio[(a)]	Frequency cm^{-1}	Intensity
1	**985**				
2	958	100	0.005	**957**.3	vs, p
3	955	4	0.15	**955**	m
4	**955**				
5	**955**	3			
6	**955**	3			
7	**852**				
8	467	9	0.005	**466**	vw, p
9	**358**				
10	357		0.28	**357**	m
11	**350**				
12	340	5		**340**	m
13	**340**	4			
14	**340**		0.55		
15	**302**				
16	187	33	0.40	**185**	m
17	**185**	9			
18	184	7		**178**	m
19	60	15	0.37	**60**	ms, p
20	**58**	10	0.56		
21	**38**				

(a) The calculated depolarisation ratio is not given when greater than 0.7.

Table B.11: Ideal gas thermodynamic functions for Tc_2O_7(g)

Part I.

T (K)	$C^\circ_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	S°_m ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(298.15\ K)]/T$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$H^\circ_m(T) - H^\circ_m(298.15\ K)$ ($J \cdot mol^{-1}$)
0	0.000	0.000	Infinite	-29456
50	57.877	264.665	808.961	-27214
100	82.710	312.178	549.338	-23715
200	122.333	382.959	449.337	-13275
298.15	146.736	436.641	436.641	0
300	147.119	437.550	436.644	271
400	164.342	482.388	442.640	15899
500	176.005	520.398	454.489	32954
600	183.888	553.230	468.273	50974
700	189.320	582.010	482.508	69651
800	193.167	607.555	496.573	88786
900	195.966	630.477	510.199	108249
1000	198.054	651.237	523.281	127955

Table B.11: (continued)

Part II.

T (K)	$C^\circ_{p,m}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	S°_m ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$-[G^\circ_m(T) - H^\circ_m(0\,K)]/T$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$H^\circ_m(T) - H^\circ_m(0\,K)$ ($J \cdot mol^{-1}$)
0	0.000	0.000	Infinite	0
50	57.877	264.665	219.829	2241
100	82.710	312.178	254.772	5740
200	122.333	382.959	302.054	16180
298.15	146.736	436.641	337.843	29456
300	147.119	437.550	338.455	29728
400	164.342	482.388	368.999	45355
500	176.005	520.398	395.575	62411
600	183.888	553.230	419.178	80431
700	189.320	582.010	440.427	99107
800	193.167	607.555	459.752	118242
900	195.966	630.477	477.470	137706
1000	198.054	651.237	493.825	157412

Table B.12: Third-law evaluation of the standard enthalpy of sublimation of TcF_6(cr, cubic) at 298.15 K from the vapour pressures of Selig and Malm [62SEL/MAL].

T (K)	p (bar)	$-R \ln f$ ($kJ \cdot K^{-1} \cdot mol^{-1}$)	$\sum / T$ ($kJ \cdot K^{-1} \cdot mol^{-1}$)	$\Delta_{sub}H^\circ_m(TcF_6, cr\ cubic, 298.15\ K)$ ($kJ{\cdot}mol^{-1}$)
268.32	0.058608	0.023611	0.10544	34.627
268.71	0.059928	0.023427	0.10544	34.628
269.88	0.064461	0.022822	0.10545	34.618
269.98	0.064821	0.022776	0.10545	34.618
272.00	0.073127	0.021776	0.10546	34.608
272.20	0.074261	0.021648	0.10546	34.599
273.15	0.078380	0.021201	0.10547	34.600
274.08	0.082886	0.020738	0.10548	34.594
274.54	0.084553	0.020572	0.10548	34.606
275.12	0.087899	0.020251	0.10548	34.591
275.69	0.091326	0.019934	0.10548	34.575
276.12	0.093046	0.019779	0.10549	34.589
277.31	0.100165	0.019169	0.10550	34.572
278.52	0.107324	0.018597	0.10550	34.563
279.25	0.110924	0.018323	0.10551	34.580
280.08	0.116444	0.017921	0.10551	34.571
281.32	0.124590	0.017361	0.10552	34.569
282.17	0.130509	0.016977	0.10552	34.565
284.16	0.145641	0.016069	0.10553	34.554
286.12	0.161600	0.015209	0.10554	34.549
286.49	0.165066	0.015034	0.10554	34.543
288.12	0.179652	0.014334	0.10555	34.541
289.12	0.189491	0.013892	0.10556	34.536
290.10	0.199037	0.013487	0.10556	34.535
291.05	0.209383	0.013068	0.10557	34.530

(Continued on next page)

Table B.12: (continued)

T (K)	p (bar)	$-R \ln f$ (kJ · K^{-1} · mol^{-1})	$\sum / T$ (kJ · K^{-1} · mol^{-1})	$\Delta_{sub}H^{\circ}_{m}$(TcF$_6$, cr cubic, 298.15 K) (kJ·mol^{-1})
293.06	0.231821	0.012227	0.10557	34.522
294.59	0.250899	0.011575	0.10558	34.513
296.05	0.270111	0.010966	0.10559	34.506
297.53	0.290376	0.010369	0.10559	34.501
297.79	0.293709	0.010275	0.10559	34.503
298.19	0.298909	0.010130	0.10560	34.510
299.22	0.315707	0.009680	0.10560	34.494
299.96	0.325573	0.009426	0.10560	34.503
300.51	0.335706	0.009174	0.10560	34.491
301.98	0.360104	0.008596	0.10561	34.488
302.60	0.369170	0.008391	0.10561	34.497
302.64	0.370370	0.008365	0.10561	34.493
302.71	0.371170	0.008347	0.10561	34.496
302.72	0.371436	0.008341	0.10561	34.495
303.44	0.385702	0.008031	0.10561	34.483
304.10	0.396501	0.007804	0.10562	34.492
304.19	0.397301	0.007787	0.10562	34.497
304.28	0.399834	0.007735	0.10562	34.492
304.96	0.413833	0.007452	0.10562	34.482
305.90	0.430765	0.007122	0.10562	34.488
305.93	0.431031	0.007117	0.10562	34.490
306.92	0.454096	0.006689	0.10563	34.473
308.16	0.478494	0.006259	0.10563	34.480
309.16	0.498759	0.005918	0.10563	34.486
310.03	0.520757	0.005564	0.10564	34.477

B.8 Tables of thermodynamic functions of TcS(g)

The molecular parameters calculated by Langhoff *et al.* [89LAN/BAU], which are summarised in Table B.13 have been used to compute the thermal functions of TcS(g), (see Table B.14). An anharmonicity correction of $\omega_e \times x_e = 1.5$ cm^{-1} (estimated from known values for transition metal monosulphides, Huber and Herzberg [79HUB/HER]), was used for all the electronic states, with the results given in Table B.14. The ground state was predicted to be $^6\Sigma$ by Langhoff *et al.* [89LAN/BAU].

Table B.13: Calculated molecular parameters for TcS(g) from Langhoff *et al.* [89LAN/BAU].

State	Term value (cm^{-1})	Statistical weight	ω (cm^{-1})	r $\times 10^{10}$ (m)
$^6\Sigma$	0	6	492	2.168
$^4\Pi$	9420	8	541	2.118
$^6\Pi$	12100	12	387	2.250
$^4\Delta$	14200	8	485	2.164
$^4\Pi$	19900	8	511	2.188

Table B.14: Ideal gas thermodynamic functions of TcS(g).

Part I.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	S°_m ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$-[G^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})]/T$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(298.15\ \mathrm{K})$ ($J \cdot mol^{-1}$)
0	0.000	0.000	Infinite	-9290
100	29.470	221.369	285.121	-6375
200	32.360	242.633	259.085	-3290
298.15	34.474	255.990	255.990	0
500	36.259	274.326	259.978	7173
1000	37.281	299.872	274.242	25629
1500	37.689	315.063	285.483	44368
2000	38.563	326.006	294.306	63398
2500	40.348	334.785	301.550	83087
3000	42.887	342.358	307.733	103873

Part II.

T (K)	$C^\circ_{p,\mathrm{m}}$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	S°_m ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$-[G^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(0\ \mathrm{K})]/T$ ($J{\cdot}K^{-1}{\cdot}mol^{-1}$)	$H^\circ_\mathrm{m}(T) - H^\circ_\mathrm{m}(0\ \mathrm{K})$ ($J \cdot mol^{-1}$)
0	0.000	0.000	Infinite	0
100	29.470	221.369	192.220	2914
200	32.360	242.633	212.635	5999
298.15	34.474	255.990	224.831	9290
500	36.259	274.326	241.398	16463
1000	37.281	299.872	264.952	34919
1500	37.689	315.063	279.290	53658
2000	38.563	326.006	289.661	72688
2500	40.348	334.785	297.834	92377
3000	42.887	342.358	304.636	113164

Appendix C

Ionic strength corrections[†]

Thermodynamic data always refer to a selected standard state. The definition given by IUPAC [82LAF] is adopted in this review as outlined in Section II.3.1. According to this definition, the standard state for a solute B in a solution is a hypothetical solution, at the standard state pressure, in which $m_B = m^\circ = 1\,\mathrm{mol}\cdot\mathrm{kg}^{-1}$, and in which the activity coefficient γ_B is unity. However, for many reactions, measurements cannot be made accurately (or at all) in dilute solutions from which the necessary extrapolation to the standard state would be simple. This is invariably the case for reactions involving ions of high charge. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of sufficiently high concentration, ensuring that activity factors are reasonably constant throughout the measurements. This appendix describes and illustrates the method used in this review for the extrapolation of experimental equilibrium data to zero ionic strength.

The activity factors of all the species participating in reactions in high ionic strength media must be estimated in order to reduce the thermodynamic data obtained from the experiment to the state $I = 0$. Two alternative methods can be used to describe the ionic medium dependence of equilibrium constants:

- One method takes into account the individual characteristics of the ionic media by using a medium dependent expression for the activity coefficients of the species involved in the equilibrium reactions. The medium dependence is described by virial or ion interaction coefficients as used in the Pitzer equations [73PIT] and in the specific ion interaction theory.

- The other method uses an extended Debye-Hückel expression in which the activity coefficients of reactants and products depend only on the ionic charge and the ionic strength, but it accounts for the medium specific properties by introducing ionic pairing between the medium ions and the species involved in the equilibrium reactions. Earlier, this approach has been used extensively in marine chemistry, *cf.* Refs. [79JOH/PYT, 79MIL, 79PYT, 79WHI2].

The activity factor estimates are thus based on the use of Debye-Hückel type equations. The “extended" Debye-Hückel equations are either in the form of specific ion

[†]This Appendix contains essentially the text written by Grenthe and Wanner [92GRE/WAN] which was also printed in the uranium NEA–TDB review as Appendix B [92GRE/FUG]. The equations presented here are an essential part to the review procedure and are required to use the selected thermodynamic values. The main differences between this Appendix and the one in Grenthe *et al.* [92GRE/FUG] are: Table C.1, Eq. (C.11) and Sections C.1.2 and C.1.4. The contents of Tables C.3 and C.4 have also been revised.

interaction methods or the Davies equation [62DAV]. However, the Davies equation should in general not be used at ionic strengths larger than 0.1 mol · kg^{-1}. The method preferred in the NEA Thermochemical Data Base review is a medium-dependent expression for the activity coefficients, which is the specific ion interaction theory in the form of the Brønsted-Guggenheim-Scatchard approach. Other forms of specific ion interaction methods (the Pitzer and Brewer "B-method" [61LEW/RAN] and the Pitzer virial coefficient method [79PIT]) are described in the NEA Guidelines for the extrapolation to zero ionic strength [92GRE/WAN].

The specific ion interaction methods are reliable for intercomparison of experimental data in a given concentration range. In many cases this includes data at rather low ionic strengths, $I = 0.01$ to 0.1 M, *cf.* Figure C.1, while in other cases, notably for cations of high charge ($\geq +4$ and ≤ -4), the lowest available ionic strength is often 0.2 M or higher, see for example Figures V.12 and V.13 in [92GRE/FUG]. It is reasonable to assume that the extrapolated equilibrium constants at $I = 0$ are more precise in the former than in the latter cases. The extrapolation error is composed of two parts, one due to experimental errors, the other due to model errors. The model errors seem to be rather small for many systems, less than 0.1 units in $\log_{10} K^\circ$. For reactions involving ions of high charge, which may be extensively hydrolysed, one cannot perform experiments at low ionic strengths. Hence, it is impossible to estimate the extrapolation error. This is true for all methods used to estimate activity corrections. Systematic model errors of this type are not included in the uncertainties assigned to the selected data in this review.

It should be emphasised that the specific ion interaction model is *approximate*. Modifying it, for example by introducing the equations suggested by Ciavatta [90CIA, Eqs. (8–10)] (*cf.* Section C.1.4), would result in slightly different ion interaction coefficients and equilibrium constants. Both methods provide an internally consistent set of values. However, their absolute values may differ somewhat. Grenthe *et al.* [92GRE/FUG] estimate that these differences in general are less than 0.2 units in $\log_{10} K^\circ$, *i.e.*, approximately 1 kJ·mol^{-1} in derived $\Delta_f G^\circ_m$ values.

C.1 The specific ion interaction equations

C.1.1 Background

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for electrostatic, non-specific long-range interactions. At higher concentrations short range, non-electrostatic interactions have to be taken into account. This is usually done by adding ionic strength dependent terms to the Debye-Hückel expression. This method was first outlined by Brønsted [22BRØ2, 22BRØ], and elaborated by Scatchard [36SCA] and Guggenheim [66GUG]. The two basic assumptions in the specific ion interaction theory are described below.

Assumption 1: The activity coefficient γ_j of an ion j of charge z_j in the solution of

ionic strength I_m may be described by Eq. (C.1).

$$\log_{10}\gamma_j = -z_j^2 D + \sum_k \varepsilon_{(j,k,I_m)} m_k \tag{C.1}$$

D is the Debye-Hückel term:

$$D = \frac{A\sqrt{I_m}}{1 + Ba_j\sqrt{I_m}} \tag{C.2}$$

where I_m is the molal ionic strength:

$$I_m = \frac{1}{2}\sum_i m_i z_i^2$$

A and B are constants which are temperature and pressure dependent, and a_j is an ion size parameter ("distance of closest approach") for the hydrated ion j. The Debye-Hückel limiting slope, A, has a value of $(0.509 \pm 0.001)\,\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ at 25°C and 1 bar, (*cf.* Section C.1.2). The term Ba_j in the denominator of the Debye-Hückel term has been assigned a value of $Ba_j = 1.5\,\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$ at 25°C and 1 bar, as proposed by Scatchard [76SCA] and accepted by Ciavatta [80CIA]. This value has been found to minimise, for several species, the ionic strength dependence of $\varepsilon_{(j,k,I_m)}$ between $I_m = 0.5$ m and $I_m = 3.5$ m. It should be mentioned that some authors have proposed different values for Ba_j, ranging from $Ba_j = 1.0$ [35GUG] to $Ba_j = 1.6$ [62VAS]. However, the parameter Ba_j is empirical and as such correlated to the value of $\varepsilon_{(j,k,I_m)}$. Hence, this variety of values for Ba_j does not represent an uncertainty range, but rather indicates that several different sets of Ba_j and $\varepsilon_{(j,k,I_m)}$ may describe equally well the experimental mean activity coefficients of a given electrolyte. The ion interaction coefficients at 25°C listed in Tables C.3 through C.5 have thus to be used with $Ba_j = 1.5\,\mathrm{kg}^{1/2}\cdot\mathrm{mol}^{-1/2}$.

The summation in Eq. (C.1) extends over all ions k present in solution. Their molality is denoted m_k, and the specific ion interaction parameters, $\varepsilon_{(j,k,I_m)}$, in general depend only slightly on the ionic strength. The concentrations of the ions of the ionic medium is often very much larger than those of the reacting species. Hence, the ionic medium ions will make the main contribution to the value of $\log_{10}\gamma_j$ for the reacting ions. This fact often makes it possible to simplify the summation $\sum_k \varepsilon_{(j,k,I_m)} m_k$ so that only ion interaction coefficients between the participating ionic species and the ionic medium ions are included, as shown in Eqs. (C.4) to (C.8).

Assumption 2: The ion interaction coefficients $\varepsilon_{(j,k,I_m)}$ are zero for ions of the same charge sign and for uncharged species. The rationale behind this is that ε, which describes specific short-range interactions, must be small for ions of the same charge since they are usually far from one another due to electrostatic repulsion. This holds to a lesser extent also for uncharged species.

Eq. (C.1) will allow fairly accurate estimates of the activity coefficients in mixtures of electrolytes if the ion interaction coefficients are known. Ion interaction coefficients for

simple ions can be obtained from tabulated data of mean activity coefficients of strong electrolytes or from the corresponding osmotic coefficients. Ion interaction coefficients for complexes can either be estimated from the charge and size of the ion or determined experimentally from the variation of the equilibrium constant with the ionic strength.

Ion interaction coefficients are not strictly constant but may vary slightly with the ionic strength. The extent of this variation depends on the charge type and is small for 1:1, 1:2 and 2:1 electrolytes for molalities less than 3.5 m. The concentration dependence of the ion interaction coefficients can thus often be neglected. This point was emphasised by Guggenheim [66GUG], who has presented a considerable amount of experimental material supporting this approach. The concentration dependence is larger for electrolytes of higher charge. In order to accurately reproduce their activity coefficient data, concentration dependent ion interaction coefficients have to be used, *cf.* Lewis, Randall, Pitzer and Brewer [61LEW/RAN], Baes and Mesmer [76BAE/MES], or Ciavatta [80CIA]. By using a more elaborate virial expansion, Pitzer and co-workers [73PIT, 73PIT/MAY, 74PIT/KIM, 74PIT/MAY, 75PIT, 76PIT/SIL, 78PIT/PET, 79PIT] have managed to describe measured activity coefficients of a large number of electrolytes with high precision over a large concentration range. Pitzer's model generally contains three parameters as compared to one in the specific ion interaction theory. The use of the theory requires the knowledge of all these parameters. The derivation of Pitzer coefficients for many complexes such as those of the actinides would require a very large amount of additional experimental work, since few data of this type are currently available.

The way in which the activity coefficient corrections are performed in this review according to the specific ion interaction theory is illustrated below for a general case of a complex formation reaction. Charges are omitted for brevity.

$$m\mathrm{M} + q\mathrm{L} + n\mathrm{H_2O(l)} \quad \rightleftharpoons \quad \mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n + n\mathrm{H}^+$$

The formation constant of $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, ${}^*\beta_{q,n,m}$, determined in an ionic medium (1:1 salt NX) of the ionic strength I_m, is related to the corresponding value at zero ionic strength, ${}^*\beta^\circ_{q,n,m}$, by Eq. (C.3).

$$\begin{aligned} \log_{10}{}^*\beta_{q,n,m} \quad = \quad & \log_{10}{}^*\beta^\circ_{q,n,m} + m\log_{10}\gamma_\mathrm{M} + q\log_{10}\gamma_\mathrm{L} + n\log_{10}a_{\mathrm{H_2O}} \\ & - \log_{10}\gamma_{q,n,m} - n\log_{10}\gamma_{\mathrm{H}^+} \end{aligned} \tag{C.3}$$

The subscript (q,n,m) denotes the complex ion $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$. If the concentrations of N and X are much greater than the concentrations of M, L, $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$ and H^+, only the molalities m_N and m_X have to be taken into account for the calculation of the term $\sum_k \varepsilon_{(j,k,I_m)} m_k$ in Eq. (C.1). For example, for the activity coefficient of the metal cation M, γ_M, Eq. (C.4) is obtained at 25°C and 1 bar.

$$\log_{10}\gamma_\mathrm{M} \quad = \quad \frac{-z_\mathrm{M}^2 0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} + \varepsilon_{(\mathrm{M,X},I_m)} m_\mathrm{X} \tag{C.4}$$

Under these conditions, $I_m \approx m_\mathrm{X} = m_\mathrm{N}$. Substituting the $\log_{10}\gamma_j$ values in Eq. (C.3) with the corresponding forms of Eq. (C.4) and rearranging leads to

$$\log_{10}{}^*\beta_{q,n,m} - \Delta z^2 D - n\log_{10}a_{\mathrm{H_2O}} \quad = \quad \log_{10}{}^*\beta^\circ_{q,n,m} - \Delta\varepsilon I_m \tag{C.5}$$

where, at 25°C and 1 bar:

$$\Delta z^2 = (mz_{\mathrm{M}} - qz_{\mathrm{L}} - n)^2 + n - mz_{\mathrm{M}}^2 - qz_{\mathrm{L}}^2 \quad \text{(C.6)}$$

$$D = \frac{0.509\sqrt{I_m}}{1 + 1.5\sqrt{I_m}} \quad \text{(C.7)}$$

$$\Delta\varepsilon = \varepsilon_{(q,n,m,\mathrm{N\ or\ X})} + n\varepsilon_{(\mathrm{H,X})} - q\varepsilon_{(\mathrm{N,L})} - m\varepsilon_{(\mathrm{M,X})} \quad \text{(C.8)}$$

Here $(mz_{\mathrm{M}} - qz_{\mathrm{L}} - n)$, z_{M} and z_{L} are the charges of the complex $\mathrm{M}_m\mathrm{L}_q(\mathrm{OH})_n$, the metal ion M and the ligand L, respectively.

Equilibria involving H_2O(l) as a reactant or product require a correction for the activity of water, $a_{\mathrm{H_2O}}$. The activity of water in an electrolyte mixture can be calculated as

$$\log_{10} a_{\mathrm{H_2O}} = \frac{-\phi \sum_k m_k}{\ln(10) \times 55.51} \quad \text{(C.9)}$$

where ϕ is the osmotic coefficient of the mixture and the summation extends over all solute species k with molality m_k present in the solution. In the presence of an ionic medium NX in dominant concentration, Eq. (C.9) can be simplified by neglecting the contributions of all minor species, *i.e.*, the reacting ions. Hence, for a 1:1 electrolyte of ionic strength $I_m \approx m_{\mathrm{NX}}$, Eq. (C.9) becomes

$$\log_{10} a_{\mathrm{H_2O}} = \frac{-2m_{\mathrm{NX}}\phi}{\ln(10) \times 55.51}. \quad \text{(C.10)}$$

Values of osmotic coefficients for single electrolytes have been compiled by various authors, *e.g.*, Robinson and Stokes [59ROB/STO]. The activity of water can also be calculated from the known activity coefficients of the dissolved species. In the presence of an ionic medium $\mathrm{N}_{\nu_+}\mathrm{X}_{\nu_-}$ of a concentration much larger than those of the reacting ions, the osmotic coefficient can be calculated according to Eq. (C.11) (*cf.* Eqs. (23-39), (23-40) and (A4-2) in [61LEW/RAN]).

$$1 - \phi = \frac{A\ln(10)|z_+z_-|}{I_m(Ba_j)^3}\left[1 + Ba_j\sqrt{I_m} - 2\log_{10}(1 + Ba_j\sqrt{I_m}) - \frac{1}{1 + Ba_j\sqrt{I_m}}\right] - \ln(10)\,\varepsilon_{(\mathrm{N,X})}m_{\mathrm{NX}}\left(\frac{\nu_+\nu_-}{\nu_+ + \nu_-}\right) \quad \text{(C.11)}$$

where ν_+ and ν_- are the number of cations and anions in the salt formula ($\nu_+z_+ = \nu_-z_-$), and in this case

$$I_m = \frac{1}{2}|z_+z_-|m_{\mathrm{NX}}(\nu_+ + \nu_-)$$

The activity of water is obtained by inserting Eq. (C.11) into Eq. (C.10). It should be mentioned that in mixed electrolytes with several components at high concentrations, it may be necessary to use Pitzer's equation to calculate the activity of water. On the other hand, $a_{\mathrm{H_2O}}$ is near constant in most experimental studies of equilibria in dilute aqueous

solutions, where an ionic medium is used in large excess with respect to the reactants. The medium electrolyte thus determines the osmotic coefficient of the solvent.

In natural waters the situation is similar; the ionic strength of most surface waters is so low that the activity of $H_2O(l)$ can be set equal to unity. A correction may be necessary in the case of seawater, where a sufficiently good approximation for the osmotic coefficient may be obtained by considering NaCl as the dominant electrolyte.

In more complex solutions of high ionic strengths with more than one electrolyte at significant concentrations, *e.g.*, $(Na^+, Mg^{2+}, Ca^{2+})(Cl^-, SO_4^{2-})$, Pitzer's equation (*cf.* [92GRE/WAN]) may be used to estimate the osmotic coefficient; the necessary interaction coefficients are known for most systems of geochemical interest.

Note that in all ion interaction approaches, the equation for mean activity coefficients can be split up to give equations for conventional single ion activity coefficients in mixtures, *e.g.*, Eq. (C.1). The latter are strictly valid only when used in combinations which yield electroneutrality. Thus, while estimating medium effects on standard potentials, a combination of redox equilibria with $H^+ + e^- \rightleftharpoons \frac{1}{2} H_2(g)$ is necessary (*cf.* Example C.3).

C.1.2 Ionic strength corrections at temperatures other than 298.15 K

Values of the Debye-Hückel parameters A and B in Eqs. (C.2) and (C.11) are listed in Table C.1 for a few temperatures at a pressure of 1 bar below 100°C and at the steam saturated pressure for $t \geq 100$°C. The values in Table C.1 may be calculated from the static dielectric constant and the density of water as a function of temperature and pressure, and are also found for example in Refs. [74HEL/KIR, 79BRA/PIT, 81HEL/KIR, 84ANA/ATK, 90ARC/WAN].

The term Ba_j in the denominator of the Debye-Hückel term D, *cf.* Eq. (C.2), has been assigned in this review a value of $1.5\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$ at 25°C and 1 bar, *cf.* Section C.1.1. At temperatures and pressures other than the reference and standard state, the following possibilities exist:

- The value of Ba_j is calculated at each temperature assuming that ion sizes are independent of temperature and using the values of B listed in Table C.1.

- The value of Ba_j is kept constant at $1.5\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$. Due the variation of B with temperature, *cf.* Table C.1, this implies a temperature dependence for ion size parameters. Assuming that ion sizes are in reality constant, then it is seen that this simplification introduces an error in D which increases with temperature and ionic strength (this error is less than ± 0.01 at $t \leq 100$°C and $I < 6$ m, and less than ± 0.006 at $t \leq 50$°C and $I \leq 4$ m).

- The value of Ba_j is calculated at each temperature assuming a given temperature variation for a_j and using the values of B listed in Table C.1. For example, in the aqueous ionic model of Helgeson *et al.* [88TAN/HEL, 88SHO/HEL, 89SHO/HEL, 89SHO/HEL2] ionic sizes follow the relation: $a_j(T)$

Table C.1: Debye-Hückel constants as a function of temperature at a pressure of 1 bar below 100°C and at the steam saturated pressure for $t \geq 100$°C. The uncertainty in the A parameter is estimated by this review to be ± 0.001 at 25°C, and ± 0.006 at 300°C, while for the B parameter the estimated uncertainty ranges from ± 0.0003 at 25°C to ± 0.001 at 300°C.

t (°C)	p (bar)	A $(\mathrm{kg}\cdot\mathrm{mol}^{-1})^{\frac{1}{2}}$	$B \times 10^{-10}$ $(\mathrm{kg}^{\frac{1}{2}}\cdot\mathrm{mol}^{-\frac{1}{2}}\cdot\mathrm{m}^{-1})$
0	1.00	0.491	0.3246
5	1.00	0.494	0.3254
10	1.00	0.498	0.3261
15	1.00	0.501	0.3268
20	1.00	0.505	0.3277
25	1.00	0.509	0.3284
30	1.00	0.513	0.3292
35	1.00	0.518	0.3300
40	1.00	0.525	0.3312
50	1.00	0.534	0.3326
75	1.00	0.564	0.3371
100	1.013	0.600	0.3422
125	2.32	0.642	0.3476
150	4.76	0.690	0.3533
175	8.92	0.746	0.3593
200	15.5	0.810	0.365
250	29.7	0.980	0.379
300	85.8	1.252	0.396

$= a_j(298.15\,\mathrm{K}, 1\,\mathrm{bar}) + |z_j| g(T, p)$ [90OEL/HEL], where $g(T, p)$ is a temperature and pressure function which is tabulated in [88TAN/HEL, 92SHO/OEL], and is approximately zero at temperatures below 175°C.

The values of $\varepsilon_{(j,k,I_m)}$ obtained with the methods described in Section C.1.3 at temperatures other than 25°C will depend on the value adopted for Ba_j. As long as a consistent approach is followed, values of $\varepsilon_{(j,k,I_m)}$ absorb the choice of Ba_j, and for moderate temperature intervals (between 0 and 200°C) the choice $Ba_j = 1.5\,\mathrm{kg}^{1/2} \cdot \mathrm{mol}^{-1/2}$ is the simplest one and is recommended by this review.

The variation of $\varepsilon_{(j,k,I_m)}$ with temperature is discussed by Lewis, Randall, Pitzer and Brewer [61LEW/RAN], Millero [79MIL], Helgeson *et al.* [81HEL/KIR, 90OEL/HEL], Giffaut *et al.* [93GIF/VIT] and Grenthe and Plyasunov [97GRE/PLY]. The absolute values for the reported ion interaction parameters differ in these studies due to the fact that the Debye-Hückel term used by these authors is not exactly the same. Nevertheless, common to all these studies is the fact that values of $(\partial\varepsilon/\partial T)_p$ are usually $\leq 0.005\,\mathrm{kg} \cdot \mathrm{mol}^{-1} \cdot \mathrm{K}^{-1}$ for temperatures below 200°C. Therefore, if values of $\varepsilon_{(j,k,I_m)}$ obtained at 25°C are used in the temperature range 0 to 50°C to perform ionic strength corrections, the error in $(\log_{10}\gamma_j)/I_m$ will be ≤ 0.13. It is clear that in order to reduce the uncertainties on solubility calculations at $t \neq 25°$, studies on the variation of $\varepsilon_{(j,k,I_m)}$-values with temperature should be undertaken.

C.1.3 Estimation of ion interaction coefficients

C.1.3.1 Estimation from mean activity coefficient data

Example C.1:

The ion interaction coefficient $\varepsilon_{(\mathrm{H^+,Cl^-})}$ can be obtained from published values of $\gamma_{\pm,\mathrm{HCl}}$ *vs.* m_{HCl}.

$$\begin{aligned} 2\log_{10}\gamma_{\pm,\mathrm{HCl}} &= \log_{10}\gamma_{\mathrm{H^+}} + \log_{10}\gamma_{\mathrm{Cl^-}} \\ &= -D + \varepsilon_{(\mathrm{H^+,Cl^-})} m_{\mathrm{Cl^-}} - D + \varepsilon_{(\mathrm{Cl^-,H^+})} m_{\mathrm{H^+}} \\ \log_{10}\gamma_{\pm,\mathrm{HCl}} &= -D + \varepsilon_{(\mathrm{H^+,Cl^-})} m_{\mathrm{HCl}} \end{aligned}$$

By plotting $\log_{10}\gamma_{\pm,\mathrm{HCl}} + D$ *vs.* m_{HCl} a straight line with the slope $\varepsilon_{(\mathrm{H^+,Cl^-})}$ is obtained. The degree of linearity should in itself indicate the range of validity of the specific ion interaction approach. Osmotic coefficient data can be treated in an analogous way.

C.1.3.2 Estimations based on experimental values of equilibrium constants at different ionic strengths

Example C.2:

Equilibrium constants are given in Table C.2 for the reaction

$$\mathrm{UO_2^{2+}} + \mathrm{Cl^-} \quad \rightleftharpoons \quad \mathrm{UO_2Cl^+}. \tag{C.12}$$

Table C.2: The preparation of the experimental equilibrium constants for the extrapolation to $I = 0$ with the specific ion interaction method at 25°C and 1 bar, according to Reaction (C.12). The linear regression of this set of data is shown in Figure C.1.

I_m	$\log_{10}\beta_1(\text{exp})^{(a)}$	$\log_{10}\beta^{(b)}_{1,m}$	$\log_{10}\beta_{1,m} + 4D$
0.1	−0.17±0.10	−0.174	0.264 ± 0.100
0.2	−0.25±0.10	−0.254	0.292 ± 0.100
0.26	−0.35±0.04	−0.357	0.230 ± 0.040
0.31	−0.39±0.04	−0.397	0.220 ± 0.040
0.41	−0.41±0.04	−0.420	0.246 ± 0.040
0.51	−0.32±0.10	−0.331	0.371 ± 0.100
0.57	−0.42±0.04	−0.432	0.288 ± 0.040
0.67	−0.34±0.04	−0.354	0.395 ± 0.040
0.89	−0.42±0.04	−0.438	0.357 ± 0.040
1.05	−0.31±0.10	−0.331	0.491 ± 0.100
1.05	−0.277±0.260	−0.298	0.525 ± 0.260
1.61	−0.24±0.10	−0.272	0.618 ± 0.100
2.21	−0.15±0.10	−0.193	0.744 ± 0.100
2.21	−0.12±0.10	−0.163	0.774 ± 0.100
2.82	−0.06±0.10	−0.021	0.860 ± 0.100
3.5	0.04±0.10	−0.021	0.974 ± 0.100

(a) Equilibrium constants for Reaction (C.12) with assigned uncertainties, corrected to 25°C where necessary.

(b) Equilibrium constants corrected from molarity to molality units, as described in Section II.2.

The following formula is deduced from Eq. (C.5) for the extrapolation to $I = 0$:

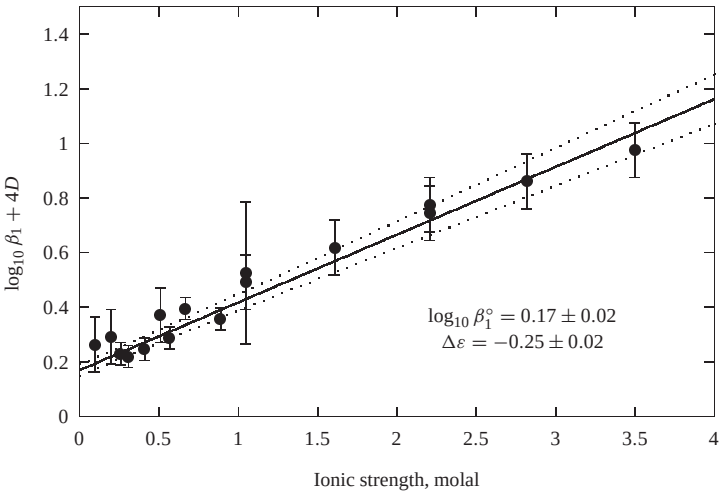
$$\log_{10}\beta_1 + 4D \quad = \quad \log_{10}\beta_1^\circ - \Delta\varepsilon\, I_m \tag{C.13}$$

The linear regression is done as described in Appendix D. The following results are obtained:

$$\begin{aligned} \log_{10}\beta_1^\circ &= 0.170 \pm 0.021 \\ \Delta\varepsilon(\text{C.12}) &= -(0.248 \pm 0.022)\ \text{kg}\cdot\text{mol}^{-1} \end{aligned}$$

The experimental data are depicted in Figure C.1, where the dashed area represents the uncertainty range that is obtained by using the results in $\log_{10}\beta_1^\circ$ and $\Delta\varepsilon$ and correcting back to $I \neq 0$.

Figure C.1: Plot of $\log_{10}\beta_1 + 4D$ *vs.* I_m for Reaction (C.12), $UO_2^{2+} + Cl^- \rightleftharpoons UO_2Cl^+$ at 25°C and 1 bar. The straight line shows the result of the weighted linear regression, and the dotted lines represent the uncertainty range obtained by propagating the resulting uncertainties at $I = 0$ back to $I = 4$ m.



Example C.3:

When using the specific ion interaction theory, the relationship between the redox potential of the couple UO_2^{2+}/U^{4+} in a medium of ionic strength I_m and the corresponding quantity at $I = 0$ should be calculated in the following way. The reaction in the galvanic cell

$$\text{Pt} \mid \text{H}_2(\text{g}) \mid \text{H}^+ \parallel \text{UO}_2^{2+}, \text{U}^{4+} \mid \text{Pt}$$

is

$$UO_2^{2+} + H_2(g) + 2\,H^+ \quad \rightleftharpoons \quad U^{4+} + 2\,H_2O(l). \tag{C.14}$$

For this reaction

$$\begin{aligned} \log_{10} K^\circ &= \log_{10}\left(\frac{a_{U^{4+}} \times a_{H_2O}^2}{a_{UO_2^{2+}} \times a_{H^+}^2 \times f_{H_2}}\right), \\ \log_{10} \mathrm{K}^\circ &= \log_{10} K + \log_{10} \gamma_{U^{4+}} - \log_{10} \gamma_{UO_2^{2+}} - 2\log_{10} \gamma_{H^+} \\ &\quad - \log_{10} \gamma_{f,H_2} + 2\log_{10} a_{H_2O}, \end{aligned}$$

$f_{H_2} \approx p_{H_2}$ at reasonably low partial pressure of $H_2(g)$, $a_{H_2O} \approx 1$, and

$$\begin{aligned} \log_{10} \gamma_{U^{4+}} &= -16D + \varepsilon_{(U^{4+},ClO_4^-)} m_{ClO_4^-} \\ \log_{10} \gamma_{UO_2^{2+}} &= -4D + \varepsilon_{(UO_2^{2+},ClO_4^-)} m_{ClO_4^-} \\ \log_{10} \gamma_{H^+} &= -D + \varepsilon_{(H^+,ClO_4^-)} m_{ClO_4^-}\,. \end{aligned}$$

Hence,

$$\begin{aligned} \log_{10} K^\circ &= \log_{10} K - 10D \\ &\quad + \left(\varepsilon_{(U^{4+},ClO_4^-)} - \varepsilon_{(UO_2^{2+},ClO_4^-)} - 2\varepsilon_{(H^+,ClO_4^-)}\right) \mathrm{m}_{ClO_4^-}\,. \end{aligned} \tag{C.15}$$

The relationship between the equilibrium constant and the redox potential is

$$\ln K = \frac{nF}{RT} E \tag{C.16}$$

$$\ln K^\circ = \frac{nF}{RT} E^\circ. \tag{C.17}$$

E is the redox potential in a medium of ionic strength I, E° is the corresponding standard potential at $I = 0$, and n is the number of transferred electrons in the reaction considered. Combining Eqs. (C.15), (C.16) and (C.17) and rearranging them leads to Eq. (C.18).

$$E - 10D\left(\frac{RT\ln(10)}{nF}\right) = E^\circ - \Delta\varepsilon m_{ClO_4^-}\left(\frac{RT\ln(10)}{nF}\right) \tag{C.18}$$

For $n = 2$ in the present example and $T = 298.15$ K, Eq. (C.18) becomes

$$E[\mathrm{mV}] - 295.8D = E^\circ[\mathrm{mV}] - 29.58\Delta\varepsilon m_{ClO_4^-}$$

where

$$\Delta\varepsilon = \left(\varepsilon_{(U^{4+},ClO_4^-)} - \varepsilon_{(UO_2^{2+},ClO_4^-)} - 2\varepsilon_{(H^+,ClO_4^-)}\right).$$

C.1.4 On the magnitude of ion interaction coefficients

Ciavatta [80CIA] made a compilation of ion interaction coefficients for a large number of electrolytes. Similar data for complexations of various kinds were reported by Spahiu [83SPA] and Ferri, Grenthe and Salvatore [83FER/GRE2]. These and some other data for 25°C and 1 bar have been collected and are listed in Section C.3.

It is obvious from the data in these tables that the charge of an ion is of great importance for the magnitude of the ion interaction coefficient. Ions of the same charge type have similar ion interaction coefficients with a given counter-ion. Based on the tabulated data, Grenthe *et al*. [92GRE/FUG] proposed that it is possible to estimate, with an error of at most ± 0.1 in ε, ion interaction coefficients for cases where there are insufficient experimental data for an extrapolation to $I = 0$. The error that is made by this approximation is estimated to ± 0.1 in $\Delta\varepsilon$ in most cases, based on comparison with $\Delta\varepsilon$ values of various reactions of the same charge type.

Ciavatta [90CIA] has proposed an alternative method to estimate values of ε for a first or second complex, ML or ML_2, in an ionic media NX, according to the following relationships,

$$\varepsilon(\text{ML, N or X}) \approx (\varepsilon_{(\text{M,X})} + \varepsilon_{(\text{L,N})})/2 \tag{C.19}$$

$$\varepsilon(\text{ML}_2\text{, N, or X}) \approx (\varepsilon_{(\text{M,X})} + 2\varepsilon_{(\text{L,N})})/3 \tag{C.20}$$

Ciavatta obtained [90CIA] an average deviation of $\pm 0.05\,\text{kg} \cdot \text{mol}^{-1}$ between ε-estimates according to Eqs. (C.19) and (C.20) and the ε-values at 25°C obtained from ionic strength dependency of equilibrium constants.

C.2 Ion interaction coefficients *versus* equilibrium constants for ion pairs

It can be shown that the virial type of activity coefficient equations and the ionic pairing model are equivalent provided that the ionic pairing is weak. In these cases the distinction between complex formation and activity coefficient variations is difficult or even arbitrary unless independent experimental evidence for complex formation is available, *e.g.*, from spectroscopic data, as is the case for the weak uranium(VI) chloride complexes. It should be noted that the ion interaction coefficients evaluated and tabulated by Ciavatta [80CIA] were obtained from experimental mean activity coefficient data without taking into account complex formation. However, it is known that many of the metal ions listed by Ciavatta form weak complexes with chloride and nitrate ion. This fact is reflected by ion interaction coefficients that are smaller than those for the non-complexing perchlorate ion, *cf*. Table C.3. This review takes chloride and nitrate complex formation into account when these ions are part of the ionic medium and uses the value of the ion interaction coefficient $\varepsilon_{(M^{n+},\text{ClO}_4^-)}$ as a substitute for $\varepsilon_{(M^{n+},\text{Cl}^-)}$ and $\varepsilon_{(M^{n+},\text{NO}_3^-)}$. In this way, the medium dependence of the activity coefficients is described with a combination of a specific ion interaction model and an ion pairing model. It is evident that the use of NEA recommended data with ionic strength

correction models that differ from those used in the evaluation procedure can lead to inconsistencies in the results of the speciation calculations.

It should be mentioned that complex formation may also occur between negatively charged complexes and the cation of the ionic medium. An example is the stabilisation of the complex ion $UO_2(CO_3)_3^{5-}$ at high ionic strength, see for example Section V.7.1.2.1.d (page 322) in the uranium review [92GRE/FUG].

C.3 Tables of ion interaction coefficients

Tables C.3 through C.5 contain the selected specific ion interaction coefficients used in this review, according to the specific ion interaction theory described. Table C.3 contains cation interaction coefficients with Cl^-, ClO_4^- and NO_3^-, Table C.4 anion interaction coefficients with Li^+, with Na^+ or NH_4^+ and with K^+. The coefficients have the units of $kg \cdot mol^{-1}$ and are valid for 298.15 K and 1 bar. The species are ordered by charge and appear, within each charge class, in standard order of arrangement, *cf.* Section II.1.7.

In some cases, the ionic interaction can be better described by assuming ion interaction coefficients as functions of the ionic strength rather than as constants. Ciavatta [80CIA] proposed the use of Eq. (C.21) for cases where the uncertainties in Tables C.3 and C.4 are $\pm 0.03\,kg \cdot mol^{-1}$ or greater.

$$\varepsilon \quad = \quad \varepsilon_1 + \varepsilon_2 \log_{10} I_m$$

For these cases, and when the uncertainty can be improved with respect to the use of a constant value of ε, the values ε_1 and ε_2 given in Table C.5 should be used.

It should be noted that ion interaction coefficients tabulated in Tables C.3 through C.5 may also involve ion pairing effects, as described in Section C.3. In direct comparisons of ion interaction coefficients, or when estimates are made by analogy, this aspect must be taken into account.

Table C.3: Ion interaction coefficients $\varepsilon_{j,k}$ for cations j with $k = Cl^-$, ClO_4^- and NO_3^-, taken from Ciavatta [80CIA, 88CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table C.5. The coefficients $\varepsilon_{(M^{n+},Cl^-)}$ and $\varepsilon_{(M^{n+},NO_3^-)}$ reported by Ciavatta [80CIA] were evaluated without taking chloride and nitrate complexation into account, as discussed in Section C.2.

j $k \rightarrow$ $\downarrow$	Cl^-	ClO_4^-	NO_3^-
H^+	0.12 ± 0.01	0.14 ± 0.02	0.07 ± 0.01
NH_4^+	-0.01 ± 0.01	$-0.08 \pm 0.04^{\dagger}$	$-0.06 \pm 0.03^{\dagger}$
H_2gly^+	-0.06 ± 0.02		
Tl^+		$-0.21 \pm 0.06^{\dagger}$	
$ZnHCO_3^+$	0.2[(a)]		
$CdCl^+$		0.25 ± 0.02	
CdI^+		0.27 ± 0.02	
$CdSCN^+$		0.31 ± 0.02	
$HgCl^+$		0.19 ± 0.02	
Cu^+		0.11 ± 0.01	
Ag^+		0.00 ± 0.01	$-0.12 \pm 0.05^{\dagger}$
YCO_3^+		0.17 ± 0.04[(b)]	
UO_2^+		0.26 ± 0.03[(c)]	
UO_2OH^+		-0.06 ± 3.7[(c)]	0.51 ± 1.4[(c)]
$(UO_2)_3(OH)_5^+$	0.81 ± 0.17[(c)]	0.45 ± 0.15[(c)]	0.41 ± 0.22[(c)]
UF_3^+	0.1 ± 0.1[(d)]	0.1 ± 0.1[(d)]	
UO_2F^+	0.04 ± 0.07[(e)]	0.29 ± 0.05[(c)]	
UO_2Cl^+		0.33 ± 0.04[(c)]	
$UO_2ClO_3^+$		0.33 ± 0.04[(d)]	
UO_2Br^+		0.24 ± 0.04[(d)]	

(Continued on next page)

[(a)] Taken from Ferri *et al.* [85FER/GRE].

[(b)] Taken from Spahiu [83SPA].

[(c)] Evaluated in the uranium review [92GRE/FUG], using $\varepsilon_{(UO_2^{2+},X)} = (0.46 \pm 0.03)\ kg \cdot mol^{-1}$, where X = Cl^-, ClO_4^- and NO_3^-, *cf.* Section C.2.

[(d)] Estimated in the uranium review [92GRE/FUG].

[(e)] Taken from Riglet, Robouch and Vitorge [89RIG/ROB], where the following assumptions were made: $\varepsilon_{(Np^{3+},ClO_4^-)} \approx \varepsilon_{(Pu^{3+},ClO_4^-)} = 0.49\ kg \cdot mol^{-1}$ as for other (M^{3+}, ClO_4^-) interactions, and $\varepsilon_{(NpO_2^{2+},ClO_4^-)} \approx \varepsilon_{(PuO_2^{2+},ClO_4^-)} \approx \varepsilon_{(UO_2^{2+},ClO_4^-)} = 0.46\ kg \cdot mol^{-1}$.

Table C.3: (continued)

j $k\rightarrow$ $\downarrow$	Cl^-	ClO_4^-	NO_3^-
$UO_2BrO_3^+$		0.33 ± 0.04[(d)]	
$UO_2IO_3^+$		0.33 ± 0.04[(d)]	
$UO_2N_3^+$		0.3 ± 0.1[(d)]	
$UO_2NO_3^+$		0.33 ± 0.04[(d)]	
UO_2SCN^+		0.22 ± 0.04[(d)]	
NpO_2^+		0.25 ± 0.05[(e)]	
PuO_2^+		0.17 ± 0.05[(e)]	
$Am(OH)_2^+$		0.17 ± 0.04[(f)]	
AmF_2^+		0.17 ± 0.04[(f)]	
$AmSO_4^+$		0.22 ± 0.08[(g)]	
$AmCO_3^+$		0.17 ± 0.04[(f)]	
$AlOH^{2+}$	0.09[(h)]	0.31[(h)]	
$Al_2CO_3(OH)_2^{2+}$	0.26[(h)]		
Pb^{2+}		0.15 ± 0.02	$-0.20 \pm 0.12^\dagger$
Zn^{2+}		0.33 ± 0.03	0.16 ± 0.02
$Zn_2CO_3^{2+}$	0.35 ± 0.05[(a)]		
Cd^{2+}			0.09 ± 0.02
Hg^{2+}		0.34 ± 0.03	$-0.1 \pm 0.1^\dagger$
Hg_2^{2+}		0.09 ± 0.02	$-0.2 \pm 0.1^\dagger$
Cu^{2+}	0.08 ± 0.01	0.32 ± 0.02	0.11 ± 0.01
Ni^{2+}	0.17 ± 0.02		
Co^{2+}	0.16 ± 0.02	0.34 ± 0.03	0.14 ± 0.01
$FeOH^{2+}$		0.38[(b)]	
$FeSCN^{2+}$		0.45[(b)]	
Mn^{2+}	0.13 ± 0.01		
$YHCO_3^{2+}$		0.39 ± 0.04[(b)]	
UO_2^{2+}	0.21 ± 0.02[(i)]	0.46 ± 0.03	0.24 ± 0.03[(i)]
$(UO_2)_2(OH)_2^{2+}$	0.69 ± 0.07[(c)]	0.57 ± 0.07[(c)]	0.49 ± 0.09[(c)]

(Continued on next page)

(f) Estimated in the NEA-TDB review on americium thermodynamics [95SIL/BID].

(g) Evaluated in the NEA-TDB review on americium thermodynamics [95SIL/BID].

(h) Taken from Hedlund [88HED].

(i) These coefficients were not used in the NEA-TDB uranium review [92GRE/FUG] because they were evaluated by Ciavatta [80CIA] without taking chloride and nitrate complexation into account. Instead,

Table C.3: (continued)

j $k\rightarrow$ $\downarrow$	Cl^-	ClO_4^-	NO_3^-
$(UO_2)_3(OH)_4^{2+}$	0.50 ± 0.18[c]	0.89 ± 0.23[c]	0.72 ± 1.0[c]
UF_2^{2+}		0.3 ± 0.1[d]	
USO_4^{2+}		0.3 ± 0.1[d]	
$U(NO_3)_2^{2+}$		0.49 ± 0.14[j]	
$AmOH^{2+}$		0.39 ± 0.04[f]	
AmF^{2+}		0.39 ± 0.04[f]	
$AmCl^{2+}$		0.39 ± 0.04[f]	
AmN_3^{2+}		0.39 ± 0.04[f]	
$AmNO_2^{2+}$		0.39 ± 0.04[f]	
$AmNO_3^{2+}$		0.39 ± 0.04[f]	
$AmH_2PO_4^{2+}$		0.39 ± 0.04[f]	
$AmSCN^{2+}$		0.39 ± 0.04[f]	
Mg^{2+}	0.19 ± 0.02	0.33 ± 0.03	0.17 ± 0.01
Ca^{2+}	0.14 ± 0.01	0.27 ± 0.03	0.02 ± 0.01
Ba^{2+}	0.07 ± 0.01	0.15 ± 0.02	-0.28 ± 0.03
Al^{3+}	0.33 ± 0.02		
Fe^{3+}		0.56 ± 0.03	0.42 ± 0.08
Cr^{3+}	0.30 ± 0.03		0.27 ± 0.02
La^{3+}	0.22 ± 0.02	0.47 ± 0.03	
$La^{3+} \rightarrow Lu^{3+}$		$0.47 \rightarrow 0.52$[b]	
U^{3+}		0.48 ± 0.08[j]	
UOH^{3+}		0.48 ± 0.08[j]	
UF^{3+}		0.48 ± 0.08[d]	
UCl^{3+}		0.59 ± 0.10[j]	
UBr^{3+}		0.52 ± 0.10[d]	
UI^{3+}		0.55 ± 0.10[d]	
UNO_3^{3+}		0.62 ± 0.08[j]	

(Continued on next page)

Grenthe *et al.* used $\varepsilon_{(UO_2^{2+},X)} = (0.46 \pm 0.03)$ kg · mol^{-1}, for X = Cl^-, ClO_4^- and NO_3^-.

[j]Evaluated in the uranium review [92GRE/FUG] using $\varepsilon_{(U^{4+},ClO_4^-)} = (0.76 \pm 0.06)$ kg · mol^{-1}.

Table C.3: (continued)

$j \quad k \rightarrow$ $\downarrow$	Cl^-	ClO_4^-	NO_3^-
Am^{3+}		0.49 ± 0.03[f]	
Be_2OH^{3+}		0.50 ± 0.05[k]	
$Be_3(OH)_3^{3+}$	0.30 ± 0.05[k]	0.51 ± 0.05[k]	0.29 ± 0.05[k]
$Al_3CO_3(OH)_4^{4+}$	0.41[h]		
$Fe_2(OH)_2^{4+}$		0.82[b]	
$Y_2CO_3^{4+}$		0.80 ± 0.04[b]	
Pu^{4+}		1.03 ± 0.05[e]	
Np^{4+}		0.82 ± 0.05[e]	
U^{4+}		0.76 ± 0.06[d]	
Th^{4+}	0.25 ± 0.03		0.11 ± 0.02
$Al_3(OH)_4^{5+}$	0.66[h]	1.30[h]	

[k] Taken from Bruno [86BRU], where the following assumptions were made: $\varepsilon_{(Be^{2+},ClO_4^-)} = 0.30\ kg \cdot mol^{-1}$ as for other $\varepsilon_{(M^{2+},ClO_4^-)}$, $\varepsilon_{(Be^{2+},Cl^-)} = 0.17\ kg \cdot mol^{-1}$ as for other $\varepsilon_{(M^{2+},Cl^-)}$, and $\varepsilon_{(Be^{2+},NO_3^-)} = 0.17\ kg \cdot mol^{-1}$ as for other $\varepsilon_{(M^{2+},NO_3^-)}$.

Table C.4: Ion interaction coefficients $\varepsilon_{j,k}$ for anions j with k = Li^+, Na^+ and K^+, taken from Ciavatta [80CIA, 88CIA] unless indicated otherwise. The uncertainties represent the 95% confidence level. The ion interaction coefficients marked with † can be described more accurately with an ionic strength dependent function, listed in Table C.5.

j $k\rightarrow$ $\downarrow$	Li^+	Na^+	K^+
OH^-	$-0.02 \pm 0.03^{\dagger}$	0.04 ± 0.01	0.09 ± 0.01
F^-		0.02 ± 0.02 [a]	0.03 ± 0.02
HF_2^-		-0.11 ± 0.06 [a]	
Cl^-	0.10 ± 0.01	0.03 ± 0.01	0.00 ± 0.01
ClO_3^-		-0.01 ± 0.02	
ClO_4^-	0.15 ± 0.01	0.01 ± 0.01	
Br^-	0.13 ± 0.02	0.05 ± 0.01	0.01 ± 0.02
BrO_3^-		-0.06 ± 0.02	
I^-	0.16 ± 0.01	0.08 ± 0.02	0.02 ± 0.01
IO_3^-		-0.06 ± 0.02 [b]	
HSO_4^-		-0.01 ± 0.02	
N_3^-		0.0 ± 0.1 [b]	
NO_2^-	$0.06 \pm 0.04^{\dagger}$	0.00 ± 0.02	-0.04 ± 0.02
NO_3^-	0.08 ± 0.01	$-0.04 \pm 0.03^{\dagger}$	$-0.11 \pm 0.04^{\dagger}$
$H_2PO_4^-$		$-0.08 \pm 0.04^{\dagger}$	$-0.14 \pm 0.04^{\dagger}$
HCO_3^-		0.00 ± 0.02 [d]	
SCN^-		0.05 ± 0.01	-0.01 ± 0.01
$HCOO^-$		0.03 ± 0.01	
CH_3COO^-	0.05 ± 0.01	0.08 ± 0.01	0.09 ± 0.01
$SiO(OH)_3^-$		-0.08 ± 0.03 [a]	
$Si_2O_2(OH)_5^-$		-0.08 ± 0.04 [b]	
$B(OH)_4^-$		$-0.07 \pm 0.05^{\dagger}$	
$UO_2(OH)_3^-$		-0.09 ± 0.05 [b]	
$UO_2F_3^-$		0.00 ± 0.05 [b]	
$UO_2(N_3)_3^-$		0.0 ± 0.1 [b]	
$(UO_2)_2CO_3(OH)_3^-$		0.00 ± 0.05 [b]	
$Am(SO_4)_2^-$		-0.05 ± 0.05 [c]	
$Am(CO_3)_2^-$		-0.05 ± 0.05 [c]	
SO_3^{2-}		$-0.08 \pm 0.05^{\dagger}$	
SO_4^{2-}	$-0.03 \pm 0.04^{\dagger}$	$-0.12 \pm 0.06^{\dagger}$	-0.06 ± 0.02

(Continued on next page)

Table C.4: (continued)

j $k \rightarrow$ $\downarrow$	Li^+	Na^+	K^+
$S_2O_3^{2-}$		$-0.08 \pm 0.05^{\dagger}$	
HPO_4^{2-}		$-0.15 \pm 0.06^{\dagger}$	$-0.10 \pm 0.06^{\dagger}$
CO_3^{2-}		$-0.08 \pm 0.03^{(d)}$	0.02 ± 0.01
$SiO_2(OH)_2^{2-}$		$-0.10 \pm 0.07^{(a)}$	
$Si_2O_3(OH)_4^{2-}$		$-0.15 \pm 0.06^{(b)}$	
CrO_4^{2-}		$-0.06 \pm 0.04^{\dagger}$	$-0.08 \pm 0.04^{\dagger}$
$UO_2F_4^{2-}$		$-0.08 \pm 0.06^{(b)}$	
$UO_2(SO_4)_2^{2-}$		$-0.12 \pm 0.06^{(b)}$	
$UO_2(N_3)_4^{2-}$		$-0.1 \pm 0.1^{(b)}$	
$UO_2(CO_3)_2^{2-}$		$-0.02 \pm 0.09^{(d)}$	
PO_4^{3-}		$-0.25 \pm 0.03^{\dagger}$	-0.09 ± 0.02
$Si_3O_6(OH)_3^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$Si_3O_5(OH)_5^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$Si_4O_7(OH)_5^{3-}$		$-0.25 \pm 0.03^{(b)}$	
$Am(CO_3)_3^{3-}$		$-0.15 \pm 0.05^{(c)}$	
$P_2O_7^{4-}$		-0.26 ± 0.05	-0.15 ± 0.05
$Fe(CN)_6^{4-}$			-0.17 ± 0.03
$U(CO_3)_4^{4-}$		$-0.09 \pm 0.10^{(b)(d)}$	
$UO_2(CO_3)_3^{4-}$		$-0.01 \pm 0.11^{(d)}$	
$UO_2(CO_3)_3^{5-}$		$-0.62 \pm 0.15^{(d)}$	
$U(CO_3)_5^{6-}$		$-0.30 \pm 0.15^{(d)}$	
$(UO_2)_3(CO_3)_6^{6-}$		$0.37 \pm 0.11^{(d)}$	

[(a)] Evaluated in the NEA-TDB uranium review [92GRE/FUG].

[(b)] Estimated in the NEA-TDB uranium review [92GRE/FUG].

[(c)] Estimated in the NEA-TDB americium review [95SIL/BID].

[(d)] From [80CIA]. These values differ from those reported in the NEA-TDB uranium review [92GRE/FUG]. See the discussion in [95SIL/BID].

Table C.5: Ion interaction coefficients $\varepsilon_{(1,j,k)}$ and $\varepsilon_{(2,j,k)}$ for cations j with k = Cl^-, ClO_4^- and NO_3^- (first part), and for anions j with k = Li^+, Na^+ and K^+ (second part), according to the relationship $\varepsilon = \varepsilon_1 + \varepsilon_2 \log_{10} I_m$. The data are taken from Ciavatta [80CIA, 88CIA]. The uncertainties represent the 95% confidence level.

j $k\rightarrow$ $\downarrow$	Cl^-		ClO_4^-		NO_3^-	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
NH_4^+			-0.088 ± 0.002	0.095 ± 0.012	-0.075 ± 0.001	0.057 ± 0.004
Ag^+					-0.1432 ± 0.0002	0.0971 ± 0.0009
Tl^+			-0.18 ± 0.02	0.09 ± 0.02		
Hg_2^{2+}					-0.2300 ± 0.0004	0.194 ± 0.002
Hg^{2+}					-0.145 ± 0.001	0.194 ± 0.002
Pb^{2+}					-0.329 ± 0.007	0.288 ± 0.018

j $k\rightarrow$ $\downarrow$	Li^+		Na^+		K^+	
	ε_1	ε_2	ε_1	ε_2	ε_1	ε_2
OH^-	-0.039 ± 0.002	0.072 ± 0.006				
NO_2^-	0.02 ± 0.01	0.11 ± 0.01				
NO_3^-			-0.049 ± 0.001	0.044 ± 0.002	-0.131 ± 0.002	0.082 ± 0.006
$B(OH)_4^-$			-0.092 ± 0.002	0.103 ± 0.005		
$H_2PO_4^-$			-0.109 ± 0.001	0.095 ± 0.003	-0.1473 ± 0.0008	0.121 ± 0.004
SO_3^{2-}			-0.125 ± 0.008	0.106 ± 0.009		
SO_4^{2-}	-0.068 ± 0.003	0.093 ± 0.007	-0.184 ± 0.002	0.139 ± 0.006		
$S_2O_3^{2-}$			-0.125 ± 0.008	0.106 ± 0.009		
HPO_4^{2-}			-0.19 ± 0.01	0.11 ± 0.03	-0.152 ± 0.007	0.123 ± 0.016
CrO_4^{2-}			-0.090 ± 0.005	0.07 ± 0.01	-0.123 ± 0.003	0.106 ± 0.007
PO_4^{3-}			-0.29 ± 0.02	0.10 ± 0.01		

Appendix D

Assigned uncertainties[†]

One of the objectives of the NEA Thermochemical Data Base (TDB) project is to provide an idea of the uncertainties associated with the data selected in this review. As a rule, the uncertainties define the range within which the corresponding data can be reproduced with a probability of 95% at any place and by any appropriate method. In many cases, statistical treatment is limited or impossible due to the availability of only one or few data points. A particular problem has to be solved when significant discrepancies occur between different source data. This appendix outlines the statistical procedures which were used for fundamentally different problems and explains the philosophy used in this review when statistics were inapplicable. These rules are followed consistently throughout the series of reviews within the TDB Project. Four fundamentally different cases are considered:

1. One source datum available
2. Two or more independent source data available
3. Several data available at different ionic strengths
4. Data at non-standard conditions: Procedures for data correction and recalculation.

D.1 One source datum

The assignment of an uncertainty to a selected value that is based on only one experimental source is a highly subjective procedure. In some cases, the number of data points the selected value is based on allows the use of the "root mean square" [82TAY] deviation of the data points X_i to describe the standard deviation s_X associated with the average $\overline{X}$:

$$s_X = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}(X_i - \overline{X})^2}\ . \qquad \text{(D.1)}$$

The standard deviation s_X is thus calculated from the dispersion of the equally weighted data points X_i around the average $\overline{X}$, and the probability is 95% that an X_i is within

[†]This Appendix contains essentially the text of the TDB-3 guideline, also printed in the uranium NEA–TDB review as Appendix C [92GRE/FUG]. Because of its importance in the selection of data and to guide the users of the values in Chapters III and IV, the text is reproduced here with minor revisions.

$\overline{X} \pm 1.96\, s_X$, see Taylor [82TAY, *pp.*244-245]. The standard deviation s_X is a measure of the precision of the experiment and does not include any systematic errors.

Many authors report standard deviations s_X calculated with Eq. (D.1) (but often not multiplied by 1.96), but these do not represent the quality of the reported values in absolute terms. It is thus important not to confuse the standard deviation s with the uncertainty σ. The latter reflects the reliability and reproducibility of an experimental value and also includes all kinds of systematic errors s_j that may be involved. The uncertainty σ can be calculated with Eq. (D.2), assuming that the systematic errors are independent.

$$\sigma_{\overline{X}} = \sqrt{s_X^2 + \sum_j (s_j^2)} \tag{D.2}$$

The estimation of the systematic errors s_j (which, of course, have to relate to $\overline{X}$ and be expressed in the same unit) can only be made by a person who is familiar with the experimental method. The uncertainty σ has to correspond to the 95% confidence level preferred in this review. It should be noted that for all the corrections and recalculations made (*e.g.*, temperature or ionic strength corrections) the rules of the propagation of errors have to be followed, as outlined in Section D.4.2.

More often, the determination of s_X is not possible because either only one or two data points are available, or the authors did not report the individual values. The uncertainty σ in the resulting value can still be estimated using Eq. (D.2) assuming that s_X^2 is much smaller than $\sum_j (s_j^2)$, which is usually the case anyway.

D.2 Two or more independent source data

Frequently, two or more experimental data sources are available, reporting experimental determinations of the desired thermodynamic data. In general, the quality of these determinations varies widely, and the data have to be weighted accordingly for the calculation of the mean. Instead of assigning weight factors, the individual source data X_i are provided with an uncertainty σ_i that also includes all systematic errors and represents the 95% confidence level, as described in Section D.1. The weighted mean $\overline{X}$ and its uncertainty $\sigma_{\overline{X}}$ are then calculated according to Eqs. (D.3) and (D.4).

$$\overline{X} \equiv \frac{\sum_{i=1}^{N} \left(\frac{X_i}{\sigma_i^2} \right)}{\sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2} \right)} \tag{D.3}$$

$$\sigma_{\overline{X}} = \sqrt{\frac{1}{\sum_{i=1}^{N} \left(\frac{1}{\sigma_i^2} \right)}} \tag{D.4}$$

Eqs. (D.3) and (D.4) may only be used if all the X_i belong to the same parent distribution. If there are serious discrepancies among the X_i, one proceeds as described below

under Section D.2.1. It can be seen from Eq. (D.4) that $\sigma_{\overline{X}}$ is directly dependent on the absolute magnitude of the σ_i values, and not on the dispersion of the data points around the mean. This is reasonable because there are no discrepancies among the X_i, and because the σ_i values already represent the 95% confidence level. The selected uncertainty $\sigma_{\overline{X}}$ will therefore also represent the 95% confidence level.

In cases where all the uncertainties are equal $\sigma_i = \sigma$, Eqs. (D.3) and (D.4) reduce to Eqs. (D.5) and (D.6).

$$\overline{X} = \frac{1}{N}\sum_{i=1}^{N} X_i \tag{D.5}$$

$$\sigma_{\overline{X}} = \frac{\sigma}{\sqrt{N}} \tag{D.6}$$

Example D.1:

Five data sources report values for the thermodynamic quantity X. The reviewer has assigned uncertainties that represent the 95% confidence level as described in Section D.1.

i	X_i	σ_i
1	25.3	0.5
2	26.1	0.4
3	26.0	0.5
4	24.85	0.25
5	25.0	0.6

According to Eqs. (D.3) and (D.4), the following result is obtained:

$$\overline{X} = 25.3 \pm 0.2.$$

The calculated uncertainty $\sigma_{\overline{X}} = 0.2$ appears relatively small but is statistically correct, for the values are assumed to follow a Gaussian distribution. As a consequence of Eq. (D.4), $\sigma_{\overline{X}}$ will always come out smaller than the smallest σ_i. Assuming $\sigma_4 = 0.10$ instead of 0.25 would yield $\overline{X} = (25.0 \pm 0.1)$, and $\sigma_4 = 0.60$ would result in $\overline{X} = (25.6 \pm 0.2)$. In fact, the values $(X_i \pm \sigma_i)$ in this example are at the limit of consistency, that is, the range $(X_4 \pm \sigma_4)$ does not overlap with the ranges $(X_2 \pm \sigma_2)$ and $(X_3 \pm \sigma_3)$. There might be a better way to solve this problem. Three possible alternatives seem more reasonable:

i. The uncertainties σ_i are reassigned because they appear too optimistic after further consideration. Some assessments may have to be reconsidered and the uncertainties reassigned. For example, multiplying all the σ_i by 2 would yield $\overline{X} = (25.3 \pm 0.3)$.

ii. If reconsideration of the previous assessments gives no evidence for reassigning the X_i and σ_i (95% confidence level) values listed above, the statistical conclusion will be that all the X_i do not belong to the same parent distribution and cannot therefore be treated in the same group (*cf.* item iii below for a non-statistical explanation). The values for $i = 1, 4$ and 5 might be considered as belonging to Group A and the values for $i = 2$ and 3 to Group B. The weighted average of the values in Group A is $X_A(i = 1, 4, 5) = (24.95 \pm 0.21)$ and of those in Group B $X_B(i = 2, 3) = (26.06 \pm 0.31)$, the second digit after the decimal point being carried over to avoid loss of information. The selected value is now determined as described below under "Discrepancies" (Section D.2.1), Case I. X_A and X_B are averaged (straight average, there is no reason for giving X_A a larger weight than X_B), and $\sigma_{\overline{X}}$ is chosen in such a way that it covers the complete ranges of expectancy of X_A and X_B. The selected value is then $\overline{X} = (25.5 \pm 0.9)$.

iii. Another explanation could be that unidentified systematic errors are associated with some values. If this seems likely to be the case, there is no reason for splitting the values up into two groups. The correct way of proceeding would be to calculate the unweighted average of all the five points and assign an uncertainty that covers the whole range of expectancy of the five values. The resulting value is then $\overline{X} = (25.45 \pm 1.05)$, which is rounded according to the rules in Section D.4.3 to $\overline{X} = (25.4 \pm 1.1)$.

D.2.1 Discrepancies

Two data are called discrepant if they differ significantly, *i.e.*, their uncertainty ranges do not overlap. In this context, two cases of discrepancies are considered. Case I: Two significantly different source data are available. Case II: Several, mostly consistent source data are available, one of them being significantly different, *i.e.*, an "outlier".

Case I. Two discrepant data: This is a particularly difficult case because the number of data points is obviously insufficient to allow the preference of one of the two values. If there is absolutely no way of discarding one of the two values and selecting the other, the only solution is to average the two source data in order to obtain the selected value, because the underlying reason for the discrepancy must be unrecognized systematic errors. There is no point in calculating a weighted average, even if the two source data have been given different uncertainties, because there is obviously too little information to give even only limited preference to one of the values. The uncertainty $\sigma_{\overline{X}}$ assigned to the selected mean $\overline{X}$ has to cover the range of expectation of both source data X_1, X_2, as shown in Eq. (D.7),

$$\sigma_{\overline{X}} \quad = \quad \left|X_i - \overline{X}\right| + \sigma_{\max}, \tag{D.7}$$

where $i = 1, 2$, and $\sigma_{\max}$ is the larger of the two uncertainties σ_i, see Example D.1.ii and Example D.2.

Example D.2:

The following credible source data are given:

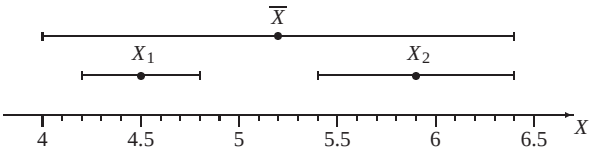
$$X_1 = 4.5 \pm 0.3$$
$$X_2 = 5.9 \pm 0.5.$$

The uncertainties have been assigned by the reviewer. Both experimental methods are satisfactory, and there is no justification to discard one of the data. The selected value is then:

$$\overline{X} = 5.2 \pm 1.2.$$

Case II. Outliers: This problem can often be solved by either discarding the outlying

Figure D.1: Illustration for Example D.2



data point, or by providing it with a large uncertainty to lower its weight. If, however, the outlying value is considered to be of high quality and there is no reason to discard all the other data, this case is treated in a way similar to Case I. Example D.3 illustrates the procedure.

Example D.3:

The following data points are available. The reviewer has assigned the uncertainties and sees no justification for any change.

i	X_i	σ_i
1	4.45	0.35
2	5.9	0.5
3	5.7	0.4
4	6.0	0.6
5	5.2	0.4

There are two sets of data that, statistically, belong to different parent distributions A and B. According to Eqs. (D.3) and (D.4), the following average values are found for the two groups: $X_A(i = 1) = (4.45 \pm 0.35)$ and $X_B(i = 2, 3, 4, 5) = (5.62 \pm 0.23)$. The selected value will be the straight average of X_A and X_B, analogous to Example D.1:

$$\overline{X} = 5.0 \pm 0.9.$$

D.3 Several data at different ionic strengths

The extrapolation procedure used in this review is the specific ion interaction model outlined in Appendix C. The objective of this review is to provide selected data sets at standard conditions, *i.e.*, among others, at infinite dilution for aqueous species. Equilibrium constants determined at different ionic strengths can, according to the specific ion interaction equations, be extrapolated to $I = 0$ with a linear regression model, yielding as the intercept the desired equilibrium constant at $I = 0$, and as the slope the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficient of the target species can usually be extracted from $\Delta\varepsilon$ and is listed in the corresponding table of Appendix C.

The available source data may sometimes be sparse or may not cover a sufficient range of ionic strengths to allow a proper linear regression. In this case, the correction to $I = 0$ should be carried out according to the procedure described in Section D.4.1.

If sufficient data are available at different ionic strengths and in the same inert salt medium, a weighted linear regression will be the appropriate way to obtain both the constant at $I = 0$, $\overline{X}^\circ$, and $\Delta\varepsilon$. The first step is the conversion of the ionic strength from the frequently used molar (mol · dm^{-3}, M) to the molal (mol · kg^{-1}, m) scale, as described in Section II.2. The second step is the assignment of an uncertainty σ_i, to each data point X_i at the molality $m_{k,i}$, according to the rules described in Section D.1. A large number of commercial and public domain computer programs and routines exist for weighted linear regressions. The subroutine published by Bevington [69BEV, *pp.*104-105] has been used for the calculations in the examples of this appendix. Eqs. (D.8) through (D.12) present the equations that are used for the calculation of the intercept $\overline{X}^\circ$ and the slope $-\Delta\varepsilon$:

$$\overline{X}^\circ = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2}\right) \tag{D.8}$$

$$-\Delta\varepsilon = \frac{1}{\Delta}\left(\sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}X_i}{\sigma_i^2} - \sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\sum_{i=1}^{N}\frac{X_i}{\sigma_i^2}\right) \tag{D.9}$$

$$\sigma_{\overline{X}^\circ} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2}} \tag{D.10}$$

$$\sigma_{\Delta\varepsilon} = \sqrt{\frac{1}{\Delta}\sum_{i=1}^{N}\frac{1}{\sigma_i^2}}\,, \tag{D.11}$$

where $$\Delta = \sum_{i=1}^{N}\frac{1}{\sigma_i^2}\sum_{i=1}^{N}\frac{m_{k,i}^2}{\sigma_i^2} - \left(\sum_{i=1}^{N}\frac{m_{k,i}}{\sigma_i^2}\right)^2. \tag{D.12}$$

In this way, the uncertainties σ_i are not only used for the weighting of the data in Eqs. (D.8) and (D.9), but also for the calculation of the uncertainties $\sigma_{\overline{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ in Eqs. (D.10) and (D.11). If the σ_i represent the 95% confidence level, $\sigma_{\overline{X}^\circ}$ and $\sigma_{\Delta\varepsilon}$ will also do so. In other words, the uncertainties of the intercept and the slope do not depend on the dispersion of the data points around the straight line but rather directly on their absolute uncertainties σ_i.

Example D.4:

Ten independent determinations of the equilibrium constant $\log_{10}^{*}\beta$ for the reaction

$$UO_2^{2+} + HF(aq) \quad \rightleftharpoons \quad UO_2F^{+} + H^{+} \tag{D.13}$$

are available in $HClO_4/NaClO_4$ media at different ionic strengths. Uncertainties that represent the 95% confidence level have been assigned by the reviewer. A weighted linear regression, $(\log_{10}^{*}\beta + 2D)$ *vs.* m_k, according to the formula $\log_{10}^{*}\beta$(D.13)$+2D = \log_{10}^{*}\beta^\circ$(D.13)$ - \Delta\varepsilon\, m_k$, will yield the correct values for the intercept $\log_{10}^{*}\beta^\circ$(D.13) and the slope $\Delta\varepsilon$. In this case, m_k corresponds to the molality of ClO_4^-. D is the Debye-Hückel term, *cf.* Appendix C.

i	$m_{ClO_4^-,i}$	$\log_{10}^{*}\beta_i + 2D$	σ_i
1	0.05	1.88	0.10
2	0.25	1.86	0.10
3	0.51	1.73	0.10
4	1.05	1.84	0.10
5	2.21	1.88	0.10
6	0.52	1.89	0.11
7	1.09	1.93	0.11
8	2.32	1.78	0.11
9	2.21	2.03	0.10
10	4.95	2.00	0.32

The results of the linear regression are:

$$\begin{aligned} \text{intercept} &= 1.837 \pm 0.054 = \log_{10}^{*}\beta^\circ(\text{D.13}) \\ \text{slope} &= 0.029 \pm 0.036 = -\Delta\varepsilon. \end{aligned}$$

Calculation of the ion interaction coefficient $\varepsilon_{(UO_2F^+,ClO_4^-)} = \Delta\varepsilon + \varepsilon_{(UO_2^{2+},ClO_4^-)} - \varepsilon_{(H^+,ClO_4^-)}$: From $\varepsilon_{(UO_2^{2+},ClO_4^-)} = (0.46 \pm 0.03)\,\text{kg}\cdot\text{mol}^{-1}$, $\varepsilon_{(H^+,ClO_4^-)} = (0.14 \pm 0.02)\,\text{kg}\cdot\text{mol}^{-1}$ (see Appendix C) and the slope of the linear regression, $\Delta\varepsilon = -(0.03 \pm 0.04)\,\text{kg}\cdot\text{mol}^{-1}$, it follows that $\varepsilon_{(UO_2F^+,ClO_4^-)} = (0.29 \pm 0.05)\,\text{kg}\cdot\text{mol}^{-1}$. Note that the uncertainty $(\pm 0.05)\,\text{kg}\cdot\text{mol}^{-1}$ is obtained based on the rules of error propagation as described in Section D.4.2:

$$\sigma = \sqrt{(0.04)^2 + (0.03)^2 + (0.02)^2}\,.$$

The resulting selected values are thus

$$\begin{aligned} \log_{10}{}^{*}\beta^{\circ}\,(\text{D.13}) &= 1.84 \pm 0.05 \\ \varepsilon_{(UO_2F^+,ClO_4^-)} &= (0.29 \pm 0.05)\ \text{kg} \cdot \text{mol}^{-1}. \end{aligned}$$

D.3.1 Discrepancies or insufficient number of data points

Discrepancies are principally treated as described in Section D.2. Again, two cases can be defined. Case I: Only two data are available. Case II: An "outlier" cannot be discarded. If only one data point is available, the procedure for correction to zero ionic strength outlined in Section D.4 should be followed.

Case I. Too few molalities: If only two source data are available, there will be no straightforward way to decide whether or not these two data points belong to the same parent distribution unless either the slope of the straight line is known or the two data refer to the same ionic strength. Drawing a straight line right through the two data points is an inappropriate procedure because all the errors associated with the two source data would accumulate and may lead to highly erroneous values of $\log_{10} K^{\circ}$ and $\Delta\varepsilon$. In this case, an ion interaction coefficient for the key species in the reaction in question may be selected by analogy (charge is the most important parameter), and a straight line with the slope $\Delta\varepsilon$ as calculated may then be drawn through each data point. If there is no reason to discard one of the two data points based on the quality of the underlying experiment, the selected value will be the unweighted average of the two standard state data obtained by this procedure, and its uncertainty must cover the entire range of expectancy of the two values, analogous to Case I in Section D.2. It should be mentioned that the ranges of expectancy of the corrected values at $I = 0$ are given by their uncertainties which are based on the uncertainties of the source data at $I \neq 0$ and the uncertainty in the slope of the straight line. The latter uncertainty is not an estimate but is calculated from the uncertainties in the ion interaction coefficients involved, according to the rules of error propagation outlined in Section D.4.2. The ion interaction coefficients estimated by analogy are listed in the table of selected ion interaction coefficients (Appendix C), but they are flagged as estimates.

Case II. Outliers and inconsistent data sets: This case includes situations where it is difficult to decide whether or not a large number of points belong to the same parent distribution. There is no general rule on how to solve this problem, and decisions are left to the judgement of the reviewer. For example, if eight data points follow a straight line reasonably well and two lie way out, it may be justified to discard the "outliers". If, however, the eight points are scattered considerably and two points are just a bit further out, one can probably not consider them as "outliers". It depends on the particular case and on the judgement of the reviewer whether it is reasonable to increase the uncertainties of the data to reach consistency, or whether the slope $\Delta\varepsilon$ of the straight line should be estimated by analogy.

Example D.5:

Six reliable determinations of the equilibrium constant $\log_{10}\beta$ of the reaction

$$UO_2^{2+} + SCN^- \quad \rightleftharpoons \quad UO_2SCN^+ \qquad \text{(D.14)}$$

are available in different electrolyte media:

I_c = 0.1 M (KNO_3): $\log_{10}\beta$(D.14) = 1.19 ± 0.03
I_c = 0.33 M (KNO_3): $\log_{10}\beta$(D.14) = 0.90 ± 0.10
I_c = 1.0 M ($NaClO_4$): $\log_{10}\beta$(D.14) = 0.75 ± 0.03
I_c = 1.0 M ($NaClO_4$): $\log_{10}\beta$(D.14) = 0.76 ± 0.03
I_c = 1.0 M ($NaClO_4$): $\log_{10}\beta$(D.14) = 0.93 ± 0.03
I_c = 2.5 M ($NaNO_3$): $\log_{10}\beta$(D.14) = 0.72 ± 0.03

The uncertainties are assumed to represent the 95% confidence level. From the values at $I_c = 1$ M, it can be seen that there is a lack of consistency in the data, and that a linear regression like in Example D.4 would not be appropriate. Instead, the use of $\Delta\varepsilon$ values from reactions of the same charge type is encouraged. Analogies with $\Delta\varepsilon$ are more reliable than analogies with single ε values due to cancelling effects. For the same reason, the dependency of $\Delta\varepsilon$ on the type of electrolyte is often smaller than for single ε values.

A reaction of the same charge type as Reaction D.14, and for which $\Delta\varepsilon$ is well known, is

$$UO_2^{2+} + Cl^- \quad \rightleftharpoons \quad UO_2Cl^+ \tag{D.15}$$

The value of $\Delta\varepsilon$(D.15) $= -(0.25 \pm 0.02)$ was obtained from a linear regression using 16 experimental data between $I_c = 0.1$ M and $I_c = 3$ M Na(Cl,ClO_4) [92GRE/FUG]. It is thus assumed that

$$\Delta\varepsilon(\text{D.14}) \quad = \quad \Delta\varepsilon(\text{D.15}) \quad = \quad -0.25 \pm 0.02$$

The correction of $\log_{10}\beta$(D.14) to $I_c = 0$ is done using the specific ion interaction equation, *cf.* TDB-2, which uses molal units:

$$\log_{10}\beta + 4D \quad = \quad \log_{10}\beta^\circ - \Delta\varepsilon I_m \tag{D.16}$$

D is the Debye-Hückel term in molal units and I_m the ionic strength converted to molal units by using the conversion factors listed in [76BAE/MES, *p.*439]. The following list gives the details of this calculation. The resulting uncertainties in $\log_{10}\beta$ are obtained based on the rules of error propagation as described in Section D.4.2.

I_m	electrolyte	$\log_{10}\beta$	$4D$	$\Delta\varepsilon I_m$	$\log_{10}\beta^\circ$
0.101	KNO_3	1.19 ± 0.03	0.438	−0.025	1.68±0.03[(a)]
0.335	KNO_3	0.90 ± 0.10	0.617	−0.084	1.65±0.10[(a)]
1.050	$NaClO_4$	0.75 ± 0.03	0.822	−0.263	1.31±0.04
1.050	$NaClO_4$	0.76 ± 0.03	0.822	−0.263	1.32±0.04
1.050	$NaClO_4$	0.93 ± 0.03	0.822	−0.263	1.49±0.04
2.714	$NaNO_3$	0.72 ± 0.03	0.968	−0.679	1.82±0.13[(a)]

[(a)] These values were corrected for the formation of the nitrate complex $UO_2NO_3^+$ by using $\log_{10} K(UO_2NO_3^+) = (0.30 \pm 0.15)$ [92GRE/FUG].

As was expected, the resulting values $\log_{10}\beta^\circ$ are inconsistent and have therefore to be treated as described in Case I of Section D.2. That is, the selected value will be the unweighted average of $\log_{10}\beta^\circ$, and its uncertainty will cover the entire range of expectancy of the six values. A weighted average would only be justified if the six values of $\log_{10}\beta^\circ$ were consistent. The result is

$$\log_{10}\beta^\circ \quad = \quad 1.56 \pm 0.39$$

D.4 Procedures for data handling

D.4.1 Correction to zero ionic strength

The correction of experimental data to zero ionic strength is necessary in all cases where a linear regression is impossible or appears inappropriate. The method used throughout the review is the specific ion interaction equations described in detail in Appendix C. Two variables are needed for this correction, and both have to be provided with an uncertainty at the 95% confidence level: the experimental source value, $\log_{10} K$ or $\log_{10}\beta$, and the stoichiometric sum of the ion interaction coefficients, $\Delta\varepsilon$. The ion interaction coefficients (see Tables C.3, C.4 and C.5 of Appendix C) required to calculate $\Delta\varepsilon$ may not all be known. Missing values therefore need to be estimated. It is recalled that the electric charge has the most significant influence on the magnitude of the ion interaction coefficients, and that it is in general more reliable to estimate $\Delta\varepsilon$ from known reactions of the same charge type, rather than to estimate single ε values. The uncertainty of the corrected value at $I = 0$ is calculated by taking into account the propagation of errors, as described below. It should be noted that the ionic strength is frequently given in moles per dm^3 of solution (molar, M) and has to be converted to moles per kg H_2O (molal, m), as the model requires. Conversion factors for the most common inert salts are given in Table II.5.

Example D.6:

For the equilibrium constant of the reaction

$$M^{3+} + 2H_2O(l) \quad \rightleftharpoons \quad M(OH)_2^+ + 2\,H^+ \qquad \text{(D.17)}$$

only one credible determination in 3 M $NaClO_4$ solution is known, $\log_{10}^{*}\beta$(D.17) = -6.31, to which an uncertainty of ± 0.12 has been assigned. The ion interaction coefficients are as follows:

$$\begin{aligned} \varepsilon_{(M^{3+},ClO_4^-)} &= (0.56 \pm 0.03)\,\text{kg·mol}^{-1} \\ \varepsilon_{(M(OH)_2^+,ClO_4^-)} &= (0.26 \pm 0.11)\,\text{kg·mol}^{-1} \\ \varepsilon_{(H^+,ClO_4^-)} &= (0.14 \pm 0.02)\,\text{kg·mol}^{-1}. \end{aligned}$$

The values of $\Delta\varepsilon$ and $\sigma_{\Delta\varepsilon}$ can be obtained readily (*cf.* Eq. D.19):

$$\Delta\varepsilon = \varepsilon_{(M(OH)_2^+,ClO_4^-)} + 2\varepsilon_{(H^+,ClO_4^-)} - \varepsilon_{(M^{3+},ClO_4^-)} = -0.02\,\text{kg·mol}^{-1}$$
$$\sigma_{\Delta\varepsilon} = \sqrt{(0.11)^2 + (2\times 0.02)^2 + (0.03)^2} = 0.12\text{kg·mol}^{-1}.$$

The two variables are thus:

$$\log_{10}{}^{*}\beta(\text{D.17}) = -6.31 \pm 0.12$$
$$\Delta\varepsilon = -(0.02 \pm 0.13)\text{kg·mol}^{-1}$$

According to the specific ion interaction model the following equation is used to correct for ionic strength for the reaction considered here:

$$\log_{10}{}^{*}\beta(\text{D.17}) + 6D = \log_{10}{}^{*}\beta^{\circ}(\text{D.17}) - \Delta\varepsilon\, m_{ClO_4^-}$$

D is the Debye-Hückel term: $D = 0.509\sqrt{I_m}/(1+1.5\sqrt{I_m})$. The ionic strength I_m and the molality $m_{ClO_4^-}$ ($I_m \approx m_{ClO_4^-}$) have to be expressed in molal units, 3 M $NaClO_4$ corresponding to 3.5 m $NaClO_4$ (see Section II.2), giving $D = 0.25$. This results in

$$\log_{10}{}^{*}\beta^{\circ}(\text{D.17}) = -4.88.$$

The uncertainty in $\log_{10}{}^{*}\beta^{\circ}$ is calculated from the uncertainties in $\log_{10}{}^{*}\beta$ and $\Delta\varepsilon$ (*cf.* Eq. D.19):

$$\sigma_{\log_{10}{}^{*}\beta^{\circ}} = \sqrt{\sigma^2_{\log_{10}{}^{*}\beta} + \left(m_{ClO_4^-}\,\sigma_{\Delta\varepsilon}\right)^2} = \sqrt{(0.12)^2 + (3.5\times 0.12)^2} = 0.44.$$

The selected, rounded value is

$$\log_{10}{}^{*}\beta^{\circ}(\text{D.17}) = -4.9 \pm 0.4.$$

D.4.2 Propagation of errors

Whenever data are converted or recalculated, or other algebraic manipulations are performed that involve uncertainties, the propagation of these uncertainties has to be taken into account in a correct way. A clear outline of the propagation of errors is given by Bevington [69BEV]. A simplified form of the general formula for error propagation is given by Eq. (D.18), supposing that X is a function of $Y_1, Y_2, \ldots, Y_N$.

$$\sigma_X^2 = \sum_{i=1}^{N}\left(\frac{\partial X}{\partial Y_i}\sigma_{Y_i}\right)^2 \qquad \text{(D.18)}$$

Eq. (D.18) can be used only if the variables $Y_1, Y_2, \ldots, Y_N$ are independent or if their uncertainties are small, that is the covariances can be disregarded. One of these two assumptions can almost always be made in chemical thermodynamics, and Eq. (D.18) can thus almost universally be used in this review. Eqs. (D.19) through (D.23) present

explicit formulas for a number of frequently encountered algebraic expressions, where c, c_1, c_2 are constants.

$$X = c_1Y_1 \pm c_2Y_2: \quad \sigma_X^2 = (c_1\sigma_{Y_1})^2 + (c_2\sigma_{Y_2})^2 \tag{D.19}$$

$$X = \pm cY_1Y_2 \text{ and } X = \pm\frac{cY_1}{Y_2}: \quad \left(\frac{\sigma_X}{X}\right)^2 = \left(\frac{\sigma_{Y_1}}{Y_1}\right)^2 + \left(\frac{\sigma_{Y_2}}{Y_2}\right)^2 \tag{D.20}$$

$$X = c_1Y^{\pm c_2}: \quad \frac{\sigma_X}{X} = c_2\frac{\sigma_Y}{Y} \tag{D.21}$$

$$X = c_1\, e^{\pm c_2 Y}: \quad \frac{\sigma_X}{X} = c_2\sigma_Y \tag{D.22}$$

$$X = c_1\, \ln(\pm c_2 Y): \quad \sigma_X = c_1\frac{\sigma_Y}{Y} \tag{D.23}$$

Example D.7:

A few simple calculations illustrate how these formulas are used. The values have not been rounded.

Eq. (D.19): $\Delta_r G_m = 2[-(277.4 \pm 4.9)]\,\mathrm{kJ\cdot mol^{-1}} - [-(467.3 \pm 6.2)]\,\mathrm{kJ\cdot mol^{-1}}$
$= -(87.5 \pm 11.6)\,\mathrm{kJ\cdot mol^{-1}}$

Eq. (D.20): $K = \frac{(0.038\pm0.002)}{(0.0047\pm0.0005)} = (8.09 \pm 0.92)$

Eq. (D.21): $K = 4(3.75 \pm 0.12)^3 = (210.9 \pm 20.3)$

Eq. (D.22): $K^\circ = e^{\frac{-\Delta_r G_m^\circ}{RT}}$;

$$\begin{aligned} \Delta_r G_m^\circ &= -(2.7 \pm 0.3)\ \mathrm{kJ\cdot mol^{-1}} \\ R &= 8.3145\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}} \\ T &= 298.15\,\mathrm{K} \end{aligned}$$

$K^\circ = 2.97 \pm 0.36$

Note that powers of 10 have to be reduced to powers of e, *i.e.*, the variable has to be multiplied by $\ln(10)$, *e.g.*,

$$\log_{10} K = (2.45 \pm 0.10); \quad K = 10^{\log_{10} K} = e^{(\ln(10)\ \log_{10} K)} = (282 \pm 65).$$

Eq. (D.23): $\Delta_r G_m^\circ = -RT \ln K^\circ$;

$$\begin{aligned} K^\circ &= (8.2 \pm 1.2) \times 10^6 \\ R &= 8.3145\,\mathrm{J\cdot K^{-1}\cdot mol^{-1}} \\ T &= 298.15\,\mathrm{K} \end{aligned}$$

$$\begin{aligned} \Delta_r G_m^\circ &= -(39.46 \pm 0.36)\,\mathrm{kJ\cdot mol^{-1}} \\ \ln K^\circ &= 15.92 \pm 0.15 \\ \log_{10} K^\circ &= \ln K^\circ / \ln(10) = 6.91 \pm 0.06 \end{aligned}$$

Again, it can be seen that the uncertainty in $\log_{10} K^\circ$ cannot be the same as in $\ln K^\circ$. The constant conversion factor of $\ln(10) = 2.303$ is also to be applied to the uncertainty.

D.4.3 Rounding

The standard rules to be used for rounding are:

1. When the digit following the last digit to be retained is less than 5, the last digit retained is kept unchanged.
2. When the digit following the last digit to be retained is greater than 5, the last digit retained is increased by 1.
3. When the digit following the last digit to be retained is 5 and
   (a) there are no digits (or only zeroes) beyond the 5, an odd digit in the last place to be retained is increased by 1 while an even digit is kept unchanged.
   (b) other non-zero digits follow, the last digit to be retained is increased by 1, whether odd or even.

This procedure avoids introducing a systematic error from always dropping or not dropping a 5 after the last digit retained.

When adding or subtracting, the result is rounded to the number of decimal places (not significant digits) in the term with the least number of places. In multiplication and division, the results are rounded to the number of significant digits in the term with the least number of significant digits.

In general, all operations are carried out in full, and only the final results are rounded, in order to avoid the loss of information from repeated rounding. For this reason, several additional digits are carried in all calculations until the final selected set of data is developed, and only then are data rounded.

D.4.4 Significant digits

The uncertainty of a value basically defines the number of significant digits a value should be given.

$$\begin{array}{lll} \text{Example:} & 3.478 & \pm 0.008 \\ & 3.48 & \pm 0.01 \\ & 2.8 & \pm 0.4 \end{array}$$

In the case of auxiliary data or values that are used for later calculations, it is often not convenient to round to the last significant digit. In the value (4.85 ± 0.26), for example, the "5" is close to being significant and should be carried along a recalculation path in order to avoid loss of information. In particular cases, where the rounding to significant digits could lead to slight internal inconsistencies, digits with no significant meaning in absolute terms are nevertheless retained. The uncertainty of a selected value always contains the same number of digits after the decimal point as the value itself.

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