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Current Status of the Thermodynamic Data for Technetium and Its Compounds and Aqueous Species

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Abstract

^{99}Tc is a major fission product from nuclear reactors. Because ^{99}Tc has few applications outside of scientific research, most of this technetium will ultimately be disposed of as nuclear waste.

The radioactive decay of ^{99}Tc to ^{99}Ru produces a low energy β^- particle, but because of its fairly long half-life of $t_{1/2} = 2.13 \times 10^5$ years, ^{99}Tc is a major source of radiation in low level waste.

Technetium forms the soluble TcO_4^- anion under oxic conditions and this ion is very mobile in groundwater, but technetium is reduced to less soluble Tc(IV) hydrolyzed species under anoxic conditions. Geochemical modeling of the dissolution of nuclear waste, and of the solubility and speciation of the dissolved radionuclides in groundwaters, is an integral part of the Performance Assessment of the safety of a nuclear waste repository, and this modeling requires a critically-assessed thermodynamic database. Such a database for technetium was published in the book *Chemical Thermodynamics of Technetium*, with literature coverage through 1998. This database is described herein, along with more recent relevant studies. Gaps in the knowledge of the chemical and thermodynamic properties of technetium are pointed out, and recommendations are made for measurements that are needed to eliminate these gaps.

1. Introduction

Technetium is produced in major amounts by the thermal neutron fission of ^{235}U and ^{239}Pu reactor fuels. According to Lieser [1], the burn up of 1 ton of 3 % enriched uranium in a nuclear reactor produces about 1 kg of ^{99}Tc (6.13 % fission yield), which is about 10 mass-% of the fission products. Popova et al. [2] in 2003 cited an estimate that 60 tonnes of ^{99}Tc have been accumulated from spent reactor fuel. El-Weare et al. [3] cited an estimate that 10 % of the ^{99}Tc produced by nuclear reactors has been dissipated into the environment, along with a order of magnitude less of ^{99}Tc as a relic from the atmospheric testing of nuclear weapons. The metastable isotope $^{99\text{m}}\text{Tc}$ (produced by neutron irradiation of ^{98}Mo) is used extensively for diagnostic purposes in nuclear medicine [4]; $^{99\text{m}}\text{Tc}$ undergoes gamma decay to the ground state ^{99}Tc with $t_{1/2} = 6.0$ hours, which is then present in the medical waste. ^{99}Tc is also produced by the spontaneous fission of the ^{238}U present in uranium ores, but the amount formed is so low as to be nearly undetectable (e.g., $\sim 10^{-13}$ mass fraction of ^{99}Tc is present at secular equilibrium in pitchblende containing 50 mass-% uranium [5]).

Unlike $^{99\text{m}}\text{Tc}$, ^{99}Tc and other technetium isotopes have relatively few uses outside of scientific research. Depending on the type of fuel used in the nuclear reactor, the extent of burn up, and other reactor conditions, intermetallic (Mo,Tc,Ru,Rh,Pd) particles may form. These particles are quite difficult to dissolve and usually become part of the highly active waste [1,5]. The remaining waste is generally dissolved in nitric acid as part of the PUREX process or its modifications, and the dissolved ^{99}Tc is co-extracted with uranium and plutonium as mixed anion complexes such as $\text{UO}_2(\text{NO}_3)(\text{TcO}_4)(\text{TBP})_2$ solvated with tributylphosphate (TBP) [1,2,6]. It is possible to destroy ^{99}Tc by transmuting it (via ruthenium isotopes) into stable Rh and Pd isotopes using neutron irradiation [2], but this process is not currently used on a wide scale, and thus much of the surplus ^{99}Tc will eventually need to be disposed of as part of the low level waste.

Under typical oxidizing environmental conditions, technetium forms the pertechnetate ion TcO_4^- , whose salts are soluble and quite mobile in groundwater. The TcO_4^- ion is only slightly absorbed on most rocks and minerals under oxic conditions [3,7], probably by surface ion exchange [7], and it is excluded from some sediments by repulsion with the charged double layer thereby leading to an enhanced geochemical mobility [8]. However, TcO_4^- can be reduced by, and absorbed on, minerals containing Fe(II) or sulfide (e.g. FeS, FeS₂, PbS, Sb₂S₃, FeAs₂) [9,10], and by common bacteria such as *Clostridium sphenoides* [11]. Reduced technetium can bioaccumulate in microorganisms and plants [11–13] and some invertebrates [12].

$\text{TcO}_4^-(\text{aq})$ can be reduced to the sparingly soluble ($\sim 10^{-8} \text{ mol}\cdot\text{kg}^{-1}$) phase $\text{TcO}_2\cdot x\text{H}_2\text{O}(\text{s})$ under strongly reducing conditions [5]. Complex formation with humic acids increases the solubility of the reduced technetium species by one to two orders of magnitude, and depending on the reducing conditions and pH, the technetium can be present as either Tc(III) or Tc(IV) [14,15], possibly as small hydroxy polymers [16]. Chelating agents such as EDTA, NTA, and oxalate are used in some waste separation processes, and some of their complexes with reduced technetium may persist for long times in alkaline tank waste [17].

Understanding the dissolution and potential migration of technetium from a waste repository is critical for Performance Assessment evaluations, and involves the use of geochemical modeling calculations. The reliability of these geochemical modeling calculations clearly depends on the availability of a complete and accurate thermochemical database for the pertinent species, compounds, and complexes. The Thermochemical Database Project (TDB) of the OECD Nuclear Energy Agency (NEA) had published a series of books giving critically assessed thermodynamic data for selected elements pertinent to radioactive waste management. *Chemical Thermodynamics of Technetium* by Rard et al. [5] was published in 1999, with literature coverage through 1998. A subsequent update volume [18] for various radioactive

elements including technetium, with literature coverage through 2002, resulted in no changes in the technetium thermochemical database. In the present report, the database from *Chemical Thermodynamics of Technetium* is summarized, some newer studies elucidating the chemical and thermodynamic properties of technetium are described, and recommendations are made for experimental measurements that are needed to fill existing gaps in the available information.

2. The chemistry and thermodynamics of technetium

Fundamental thermodynamic quantities of substances that are included in thermochemical databases are the standard molar heat capacity at constant pressure $C_{p,m}^{\circ}$, the standard molar entropy S_m° , the standard molar enthalpy of formation $\Delta_f H_m^{\circ}$, the standard molar Gibbs free energy of formation $\Delta_f G_m^{\circ}$, and the equilibrium constant K . Because some of these thermodynamic quantities contain redundant information, not all will appear in a particular database. The standard entropy of a pure element is a very important quantity that is required for the calculation of values of $\Delta_f S_m^{\circ}$ and, in combination with $\Delta_f H_m^{\circ}$, of the values of $\Delta_f G_m^{\circ}$.

2.1 Technetium metal

Tc(cr) occurs as a hcp crystal (P6₃/mmc space group) up to the melting point of (2430 ± 30) K [5]. Heat capacities available at the time of the NEA review were limited to those of Trainor and Brodsky [19] from 3 to 15 K, which yield the Debye temperature and electronic heat capacity, and of Spitsyn et al. [20] from about 950 to 1600 K from thermal diffusion measurements. Unfortunately, the heat capacities of Spitsyn et al. were only presented graphically and not numerically. Fernández Guillermet and Grimvall [21] calculated the heat capacities and entropies of Tc(cr) with a theoretically-based model, using the concept of a temperature-dependent entropy

Debye temperature θ^S , which is based on a logarithmic average of phonon frequencies, and an empirical relation between θ^S for the corresponding 4d and 5d elements. For Tc(cr) and Re,(cr) their empirical relations yield $\theta^S(\text{Tc, cr, } T) = (1.198 \pm 0.016)\theta^S(\text{Re, cr, } T)$, and values of $\theta^S(\text{Tc, cr, } T)$ thus calculated were used to calculate the vibrational contribution to the heat capacity and entropy. The heat capacities and entropies of Tc(cr) recommended for the NEA review [5] from 7.86 K (superconducting transition temperature) to 2430 K (melting temperature) were based on this approach, but were revised using a more recent critical evaluation for Re(cr) to redetermine $\theta^S(\text{Re, cr, } T)$. Heat capacity differences between the source model [19] and the revised model [5] are very small near room temperature, but above about 500 K the differences become significant and increase with temperature, reaching a difference of about 8 % at 1600 K.

Shirasu and Minato [22] subsequently determined the heat capacities of Tc(cr) from 323 to 1073 K using differential scanning calorimetry. Their results essentially confirm the calculated results reported in *Chemical Thermodynamics of Technetium* in this temperature region [5]. Figure 1 gives a comparison of these heat capacities with those from two other recent determinations [23,24] and the model calculations. The experimental $C_{p,m}^\circ$ values of van der Laan and Konings [23] are somewhat higher, whereas those of Boucharet [24] are very low.

The measurements of van der Laan and Konings [23] were made using a Tc_{0.85}Ru_{0.15} alloy that was obtained by transmutation of part of the ⁹⁹Tc to ¹⁰⁰Ru, and it was non-uniform in composition. Their calculation of $C_{p,m}^\circ$ for Tc(cr) required two approximations: i) that the heat capacities measured for their non-uniform sample are equal to those of a uniform sample having the average composition, and ii) the heat capacity change from forming the alloy is zero. Considering the uncertainty introduced by these approximations, the agreement of their results [23] with the recommended values [5] is satisfactory. The minimum and maximum exhibited by the heat capacities of Boucharet [25] are quite improbable for a metal that has the same crystal

structure over the studied temperature interval, and probably result from significant chemical contamination of Boucharet's Tc(cr).

The excellent agreement of the experimental heat capacities of Shirasu and Minato [22] with those recommended in *Chemical Thermodynamics of Technetium* [5] gives us considerable confidence in the recommended values. However, the calculation of S_m° requires the evaluation of $\int_{T=0}^{T_r} \{C_{p,m}^\circ/T\}dT$, and there are no experimental $C_{p,m}^\circ$ data between 15 and 323 K to compare with the calculated values [5]. The theoretical-based model using the entropy Debye temperature methodology begins to lose its validity below about 100 K, which gives rise to some uncertainty to the integral at low temperatures and thus to the calculated S_m° values. Heat capacity measurements for high purity Tc(cr) in this temperature region are definitely needed.

Assessed thermodynamic values for Tc(g) are available from a combination of statistical thermodynamic calculations combined with enthalpies of sublimation from three independent studies [5]. Although the latter measurements have appreciable uncertainty, the recommended results should be adequate for most applications.

2.2 Technetium oxides and hydrous oxides

Two solid oxides in the technetium-oxygen system have been chemically and structurally characterized [5], $TcO_2(cr)$ which occurs in the monoclinic space group $P2_1/c$, and $Tc_2O_7(cr)$ which occurs in the orthorhombic space group $Pbca$. $Tc_2O_7(cr)$ melts at (392.7 ± 0.1) K and extrapolation of the vapor pressures of $Tc_2O_7(l)$ yields an estimated normal boiling temperature of 584 K. Equations for the vapor pressures of $Tc_2O_7(cr)$ and $Tc_2O_7(l)$ as functions of temperature are given in Table 1. Several other solid oxides have been suggested in the literature, in particular $TcO_3(s)$, but their existence has not been definitely established. $Tc_2O_7(cr)$ sublimates

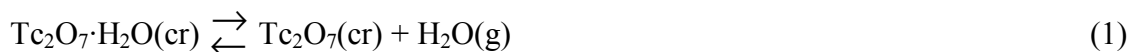
congruently to yield $\text{Tc}_2\text{O}_7(\text{g})$. Many other gaseous oxides have identified at very high temperature by mass spectrometry: $\text{Tc}_2\text{O}_6(\text{g})$, $\text{Tc}_2\text{O}_5(\text{g})$, $\text{Tc}_2\text{O}_4(\text{g})$, $\text{TcO}_3(\text{g})$, $\text{TcO}_2(\text{g})$, and $\text{TcO}(\text{g})$. Out of all of these anhydrous oxides, only $\text{TcO}_2(\text{cr})$, $\text{Tc}_2\text{O}_7(\text{cr})$, $\text{Tc}_2\text{O}_7(\text{l})$, and $\text{Tc}_2\text{O}_7(\text{g})$ are likely to be pertinent to radioactive waste management.

The enthalpy of formation of $\text{Tc}_2\text{O}_7(\text{cr})$ has been determined both by oxygen combustion calorimetry and by solution calorimetry, and that of $\text{TcO}_2(\text{cr})$ by oxidative dissolution using aqueous Ce(IV). Because of experimental difficulties, the value of $\Delta_f H_m^\circ(\text{TcO}_2, \text{cr}, 298.15 \text{ K})$ has a large uncertainty. A redetermination of $\Delta_f H_m^\circ(\text{TcO}_2, \text{cr})$ using some other reaction medium is desirable.

The calculation of $\Delta_f G_m^\circ$ from $\Delta_f H_m^\circ$ also requires the entropies of $\text{TcO}_2(\text{cr})$ and $\text{Tc}_2\text{O}_7(\text{cr})$, but no experimental values are available. The entropy of $\text{TcO}_2(\text{cr})$ at 298.15 K was estimated from known values for other transition metal dioxides, and values for $\text{Tc}_2\text{O}_7(\text{cr})$ as a function of temperature were obtained from statistical thermodynamic calculations for $\text{Tc}_2\text{O}_7(\text{g})$ combined with the entropy of sublimation of $\text{Tc}_2\text{O}_7(\text{cr})$ [5]. Unfortunately, the vapor pressures for $\text{Tc}_2\text{O}_7(\text{cr})$, see Fig. 2, are available only over a narrow temperature range and are of low precision. A more precise determination of the vapor pressures of $\text{Tc}_2\text{O}_7(\text{cr})$ over a wider temperature range, and/or its heat capacities from low to room temperature, are needed to improve the accuracy of the values of $\Delta_f G_m^\circ$ for $\text{Tc}_2\text{O}_7(\text{cr})$ and $\text{Tc}_2\text{O}_7(\text{g})$.

Evaporation of water from $\text{HTcO}_4(\text{aq})$ yields a reddish-black solid having the empirical composition $\text{Tc}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ or $\text{HTcO}_4(\text{cr})$. The crystal structure of this compound (triclinic space group $P\bar{1}$) is complicated and not completely solved, but based on studies by Russian scientists, the compound is probably ionic and polymeric (private communication from K. E. German to J. A. Rard, cited in reference 5). Values of $\Delta_f H_m^\circ$, $\Delta_f G_m^\circ$, and S_m° at 298.15 K [5] were derived

from decomposition vapor pressure measurements, assuming that the empirical formula is $\text{Tc}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$:



$\text{Tc}_2\text{O}_7 \cdot \text{H}_2\text{O}(\text{cr})$ is extremely hygroscopic and deliquesces when exposed to atmospheric air.

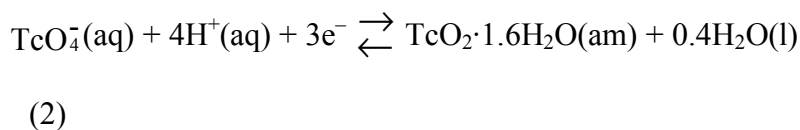
The hydrous oxide of Tc(IV) is the most commonly encountered one, and it is the most important one under reducing conditions. $\text{Tc}_4\text{O}_5 \cdot x\text{H}_2\text{O}(\text{s})$ and $\text{Tc}_2\text{O}_5 \cdot x\text{H}_2\text{O}(\text{s})$ have been reported [2,5], but such mixed valence hydrated oxides are not likely to be found outside of a laboratory situation. There are several reports of a Tc(III) hydrous oxide being produced during the electrolytic reduction of TcO_4^- , but it is unstable with regard to disproportionation at pHs above 3 or 4, and it is very sensitive to oxidation by even a trace of oxygen. Tc(II) and Tc(I) hydrous oxides have also been claimed to form under very reducing conditions [5,26], but they are undoubtedly thermodynamically unstable.

The solid hydrous oxide of Tc(IV) has variously been described as being amorphous or poorly crystalline. It has been formulated variously as $\text{Tc}(\text{OH})_4$, $\text{TcO}(\text{OH})_2$, TcO_2 , and $\text{TcO}_2 \cdot x\text{H}_2\text{O}$, where $x = 0.44$ to 4.22 [5]. Some of this variation in the water content and crystallinity may reflect different preparation conditions, i.e., electrolytic or chemical reduction of TcO_4^- versus hydrolysis of Tc(IV) compounds, or sample age, but determining the water content accurately is difficult owing to the typically small sample sizes used. In *Chemical Thermodynamics of Technetium* [5], the formulation $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{am})$ was accepted as a reasonable average of reported compositions.

Recent extended X-ray absorption fine structure (EXAFS) studies now provide definite information about the nature of the Tc(IV) hydrous oxides [16, 27, 28]. $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ has a one-dimensional chain structure with two μ -oxo bridges between each neighboring technetium atoms (four per technetium). The Tc-Tc distance is $(2.5\text{--}2.6) \times 10^{-10}$ m and the bridging Tc-O distance

is $(1.8\text{--}2.1) \times 10^{-10}$ m. The remaining two coordinate sites of each Tc(IV) are occupied by water molecules.

The recommended value of $\Delta_f G_m^\circ(\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}, \text{am}, 298.15 \text{ K})$ [5] was calculated using the emf data from two concordant studies for the reversible electrochemical cell reaction



The available emfs are restricted to 298.15 K, and additional measurements at other temperatures are needed to determine $\Delta_f G_m^\circ$ of this important solid phase as a function of temperature.

2.3 Mixed oxides of technetium and pertechnetate salts

Numerous ternary oxides containing Tc(VII), Tc(VI), Tc(V), and Tc(IV) have been synthesized, as have several quaternary oxides containing Tc(IV). Their compositions and crystal structures are listed in Table V.40 of *Chemical Thermodynamics of Technetium* [5]. Some of these Tc(IV) or Tc(VII) mixed oxides could conceivably form during calcining of low level nuclear waste, but none have been characterized thermodynamically.

Dissolved technetium occurs as TcO_4^- in aqueous solution under oxic conditions, and very many pertechnetate salts have been prepared [5]. Table 2 summarizes the solubilities of these pertechnetate salts at 298.15 K along with their solubility products (activity products). These pertechnetate salts are too soluble to become solubility limiting phases under normal environmental conditions.

$\text{KTcO}_4(\text{cr})$ is the most thoroughly studied solid pertechnetate, with heat capacities (and thus entropies) being available from 9.00 to 308.56 K, enthalpies of solution at 298.15 K, and accurate solubilities at 273.15 and 298.15 K [5]. These data were used to calculate the entropy of

formation of TcO_4^- , and when combined with the enthalpy of formation of this ion obtained from $\text{Tc}_2\text{O}_7(\text{cr})$ data, yielded $\Delta_f G_m^\circ(\text{TcO}_4^-, \text{aq}, 298.15 \text{ K})$. $\Delta_f G_m^\circ(\text{TcO}_4^-, \text{aq}, 298.15 \text{ K})$ was then used for the calculation of $\Delta_f G_m^\circ(\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}, \text{s}, 298.15 \text{ K})$ using equation (2), and of $\Delta_f G_m^\circ$ for the various Tc(IV) hydrolyzed aqueous species [5].

2.4 Binary technetium halides and oxyhalides

The following binary halides have been reported [5]: TcF_6 (cubic and orthorhombic cr, l, g), $\text{TcF}_5(\text{cr}, \text{l})$, $\text{TcCl}_6(\text{cr})$, $\text{TcCl}_4(\text{s})$, $\text{TcBr}_4(\text{s})$, and $\text{TcBr}_3(\text{s})$. $\text{TcCl}_6(\text{cr})$ is unstable with regard to chlorine loss, and $\text{TcCl}_4(\text{s})$ and $\text{TcBr}_4(\text{s})$ are hydrolytically unstable in the presence of water vapor or liquid water. The most important of these compounds is TcF_6 . Technetium is co-extracted with uranium and plutonium during the reprocessing of spent nuclear fuel by the PUREX process, and any technetium not subsequently removed ends up with the uranium or plutonium. Conversion of this uranium to UF_6 for isotopic enrichment by vapor diffusion of $\text{UF}_6(\text{g})$ yields volatile TcF_6 as a byproduct, and $\text{TcF}_6(\text{g})$ has been a source of technetium loss from reprocessing plants.

The following technetium oxyhalides have been reported [5]: TcOF_4 (two crystalline forms, l, g), $(\text{TcOF}_4)_3(\text{cr})$, $\text{TcO}_2\text{F}_3(\text{cr})$, $\text{TcO}_3\text{F}(\text{s}, \text{l}, \text{g})$, $\text{Tc}_2\text{O}_5\text{F}_4(\text{s})$, $\text{TcOCl}_3(\text{s}, \text{g})$, $\text{TcOBr}_3(\text{s}, \text{g})$, $\text{TcOCl}_4(\text{s})$, and $\text{TcO}_3\text{Cl}(\text{s}, \text{l}, \text{g})$. Most, if not all, of these compounds are hydrolytically unstable. Equations for the vapor pressures of TcF_6 , TcO_3F , and TcOF_4 are given in Table 1. Experimental heat capacities (and thus entropies) are available from 5.809 to 347.937 K for TcF_6 (both solid forms and liquid), and for $\text{TcF}_6(\text{g})$ from statistical thermodynamic calculations. A determination of the standard enthalpy of formation for $\text{TcF}_6(\text{cubic})$ or $\text{TcF}_6(\text{g})$ is needed to complete the

calculation of $\Delta_f G_m^\circ$ of one of these phases, which can be combined with the vapor pressure data to yield $\Delta_f G_m^\circ$ of the other phase.

2.5 Ternary technetium halides, hydroxyhalides, and oxyhalides

A very large number of ternary of Tc(IV) halides have been prepared with formulae of $M(I)_2TcF_6(cr)$, $M(I)_2TcCl_6(cr)$, $M(I)_2TcBr_6(cr)$, $M(I)_2TcI_6(cr)$, $M(II)TcCl_6(cr)$, and $M(II)TcBr_6(cr)$, where M(I) is a monovalent cation and M(II) a divalent cation [5]. The tendency for these salts to undergo aquation and subsequent hydrolysis in aqueous solutions falls in the order $TcI_6^{2-} \gg TcBr_6^{2-} > TcCl_6^{2-} \gg TcF_6^{2-}$, with the fluoride salts being quite resistant to hydrolysis and the iodide salts being readily hydrolyzed. The $TcBr_6^{2-}$ and $TcCl_6^{2-}$ ions are stabilized by very high concentrations of the corresponding halide ions and high levels of acidity, and are resistant to hydrolysis when stored in the dark (otherwise they undergo photochemical aquation). Solubilities of several of these chloride and bromide salts are available at 298.15 K in their corresponding concentrated hydrohalic acids [5].

Numerous dinuclear and polynuclear technetium halides have been prepared, where the average technetium valence is 4 or less [5, 29]. Because most of these polymeric technetium compounds are formed under very reducing conditions, they will neither form nor survive under normal environmental conditions.

Reduction of TcO_4^- with concentrated aqueous HCl in the presence of the iodide ion, or by HI in the presence of chloride or bromide ions, yields salts containing the $TcCl_5(OH)^{2-}$ or $TcBr_5(OH)^{2-}$ anions [5]. There is a lack of thermodynamic data for these salts, but they are probably unstable with regard to hydrolysis by water.

Reduction of the TcO_4^- by aqueous HCl or HBr yielded salts containing the TcOCl_5^{2-} , TcOBr_5^{2-} , TcOCl_4^- , and TcOBr_4^- with technetium in the unstable Tc(V) valence state [5]. Lower reaction temperatures of 265 to 273 K favor the formation of these Tc(V) salts, whereas Tc(IV) salts are produced at higher reaction temperatures. These Tc(V) oxyhalide salts should be unstable with regard to hydrolysis and disproportionation to form TcO_4^- and Tc(IV). A mixed valence oxychloride has been reported and formulated as $\text{K}_3\text{Tc}_2\text{O}_2\text{Cl}_8(\text{s})$, but its characterization is incomplete and thus its stoichiometry is uncertain.

2.6 Binary technetium sulfides

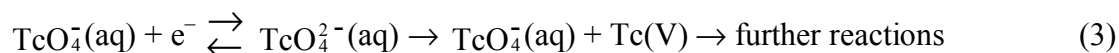
Reduction of $\text{TcO}_4^-(\text{aq})$ with H_2S yields $\text{Tc}_2\text{S}_7(\text{s})$, and heating $\text{Tc}_2\text{S}_7(\text{s})$ in the absence of oxygen produces $\text{TcS}_2(\text{s})$ [5]. Because of its very low solubility in water, $\text{Tc}_2\text{S}_7(\text{s})$ has the potential for being the solubility limiting phase for technetium in groundwater under reducing conditions. However, two attempts to determine the solubility product of $\text{Tc}_2\text{S}_7(\text{s})$ have been unsuccessful [3,30]. Tc_2S_7 readily forming colloids in aqueous solutions [30,31] and the finer colloids could not be removed by filtration [30]. Kunze et al. [30] also studied the dissolution of $\text{Tc}_2\text{S}_7(\text{s})$ from pH = 8 to 10 in simulated brines and in the presence of iron or zircalloy. The observed dissolved technetium concentrations were $< 10^{-8} \text{ mol}\cdot\text{L}^{-1}$ after 150 days of equilibrium, which is consistent with $\text{TcO}_2\cdot x\text{H}_2\text{O}(\text{s})$ having replaced $\text{Tc}_2\text{S}_7(\text{s})$ as the solubility limiting phase.

2.7 Technetium redox chemistry in aqueous solutions in the absence of a complexing ligand

The valence state of dissolved technetium in aqueous solution varies between +7 for TcO_4^- to +3 under reducing conditions. A stability field for Tc(II) appears in many potential-pH diagrams, even though this species has not been observed. As discussed in *Chemical Thermodynamics of*

Technetium [5], this results from the uncritical use of a $\text{Tc}^{2+}(\text{aq})/\text{Tc}(\text{s})$ redox potential of unknown origin given by Latimer [32].

The electrolytic reduction of $\text{TcO}_4^-(\text{aq})$ occurs through complicated and irreversible processes, involving multiple steps (mostly irreversible) and alternate pathways that depend on the pH of the solution and kinetic factors. However, by using very rapid scanning techniques such as pulse polarography or fast cyclic voltammetry, a one electron reversible reduction of $\text{TcO}_4^-(\text{aq})$ was observed in alkaline solutions [5]:

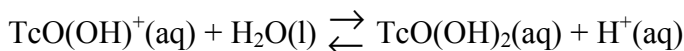


The $\text{TcO}_4^{2-}(\text{aq})$ ion is very unstable and rapidly disproportionates irreversibly to form $\text{TcO}_4^-(\text{aq})$ and $\text{Tc}(\text{V})$, and the unstable $\text{Tc}(\text{V})$ further disproportionates to $\text{Tc}(\text{IV})$ and a higher valence state of technetium. Using conventional (slower) electrochemical techniques, $\text{TcO}_4^-(\text{aq})$ is reduced by a two electron process to $\text{Tc}(\text{V})$ which similarly disproportionates. In acidic solutions, $\text{TcO}_4^-(\text{aq})$ can be reduced to $\text{Tc}(\text{III})$ and $\text{Tc}(\text{IV})$, which involves converting some of the oxygens to water molecules. These other redox reactions are irreversible and do not yield thermodynamic data. The $\text{Tc}(\text{VI})$ and $\text{Tc}(\text{V})$ species are thermodynamically unstable with regard to disproportionation.

A quasi-reversible potential for a $\text{Tc}(\text{IV})/\text{Tc}(\text{III})$ redox couple has been reported, but does not yield unambiguous results because of uncertainties about the hydrolysis state of $\text{Tc}(\text{III})$, and that for $\text{Tc}(\text{III})/\text{Tc}(\text{s})$ in acidic solutions is irreversible [5]. However, the $\text{Tc}(\text{IV})/\text{Tc}(\text{III})$ redox boundary is probably very close to the boundary for reduction of H_2O , and $\text{Tc}(\text{III})$ will not be a significant aqueous species under normal environmental conditions.

2.8 Aqueous $\text{Tc}(\text{IV})$ species and carbonate complexes

The variation of the solubility of $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{am})$ with pH was analyzed to yield the solubility product of $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{am})$, and the hydrolysis constants relating $\text{TcO}^{2+}(\text{aq})$, $\text{TcO}(\text{OH})^+(\text{aq})$, $\text{TcO}(\text{OH})_2(\text{aq})$, and $\text{TcO}(\text{OH})^-(\text{aq})$, and the stability constants for $\text{Tc}(\text{CO}_3)(\text{OH})_2(\text{aq})$ and $\text{Tc}(\text{CO}_3)(\text{OH})_3^-(\text{aq})$ [5]. The recommended equilibrium constants were derived from the solubility studies of Meyer et al. [33] and Eriksen et al. [34], whose results are compared in Fig. 3. Nguyen Trung et al. [35] measured solubilities that are probably consistent, but the experimental data have yet to be published. Hess et al. [36] recently reported very extensive solubility experiments for $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{am})$ in the presence of hydrazine (to maintain reducing conditions) with different concentrations of added NaCl. They were able to represent their solubilities with the solubility product and hydrolysis constants from *Chemical Thermodynamics of Technetium* [5], except for adjusting the hydrolysis constant for the following reaction:



(4)

As can be seen by comparing the left- and right-hand plots of Fig. 4, using the adjusted value of $\log_{10}K$ for reaction (4) gives a better representation of the solubility data of Hess et al. [36] for 4 and 11 day equilibrations, whereas the results of their 29 and 65 day equilibrations are better represented by the hydrolysis constant recommended in reference [5]. These plots indicate that there were aging effects of unknown origin occurring in their saturated solutions when $\text{pH} < 4$. Table 3 gives a summary of the reactions involving Tc(IV) and the recommended $\log_{10}K$ values.

It is very difficult to distinguish between oxy and hydroxy coordination in sparingly soluble Tc(IV) species. The formulation of the hydrolyzed Tc(IV) species as $\text{TcO}(\text{OH})_n^{2-n}(\text{aq})$ rather than as $\text{Tc}(\text{OH})_m^{2-m}(\text{aq})$ was mainly due to the recognition that the charge of the Tc(IV) species never increased above +2 even at $\text{pH} = 0$. The recent extended EXAFS studies [16, 27, 28] that indicate $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ contains μ -oxo rather than hydroxo bridges suggest that formulating the

monomeric core solution species as $\text{TcO}^{2+}(\text{aq})$ was a reasonable choice. Because of the strong tendency of Tc(IV) to form hexacoordinated complexes, any unassigned coordination sites on the Tc(IV) species are presumed to be occupied by water molecules.

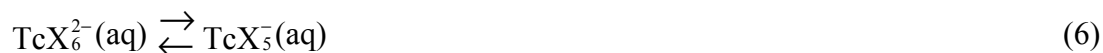
A reported dimerization constant for the reaction



was not accepted in the NEA review [5] because of the probable presence of significant concentrations of $\text{TcO}_4^-(\text{aq})$ and possibly colloid formation from the apparently oversaturated solutions. Recent studies of the chemical reduction of $\text{TcO}_4^-(\text{aq})$ to form oversaturated solutions of Tc(IV) initially yields small hydroxy polymers [28] and very fine colloids that could be removed by ultrafiltration but not by sedimentation [37]. At higher degrees of Tc(IV) oversaturation, colloid growth was observed, and addition of increasing amounts of NaCl caused coagulation and then precipitation.

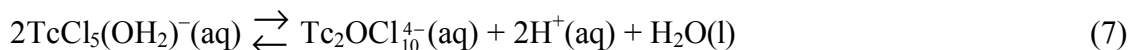
2.9 Aqueous Tc(IV) and Tc(III) chloride and bromide complexes

The following Tc(IV) halide complexes have been proposed in the literature $\text{TcF}_6^{2-}(\text{aq})$, $\text{TcCl}_6^{2-}(\text{aq})$, $\text{TcCl}_5^-(\text{aq})$, $\text{TcCl}_4(\text{aq})$, $\text{TcCl}_3^+(\text{aq})$, $\text{TcBr}_6^{2-}(\text{aq})$, $\text{TcBr}_5^-(\text{aq})$, and $\text{TcBr}_4(\text{aq})$, as have several Tc(III) and Tc(IV) monohydroxy chloride and bromide complexes [5]. Equilibration is reached very slowly in the Tc(IV) halide systems in the absence of chemical or photochemical catalysis. Equilibrium constants are available for the following equilibria



where $X = \text{Cl}$ or Br , but the reported equilibration constants are limited to concentrated acidic chloride solutions [5,38].

A recent study by Ben Said et al. [39] indicates that aged solutions of Tc(IV) in 1 mol·L⁻¹ HCl contain TcCl₅(aq) and TcCl₄(aq). However, a very recent thesis [38] reports strong evidence for the formation the of the Tc(IV) complex Tc₂OCl₁₀⁴⁻ at pH = 0 and 1 in aqueous solutions containing 3 mol·L⁻¹ Cl⁻, by the dimerization reaction:



Evidence was also obtained for the partially dissociated form of this ion, Tc₂OCl₈²⁻(aq), and possible also for the μ -oxo bridged Tc₂O₂Cl_{10-x}^{-4+x}(aq) complexes.

The results from Tc(IV) solubility measurements by Hess et al. [36] in 0.8, 2.5, and 5.0 mol·L⁻¹ NaCl are shown in Fig. 5. Based on the change in slope at pH \approx 0.5, they concluded that although the solid phase was TcO₂·xH₂O(am) at higher pHs, a new phase, possibly TcCl₄(am), occurred at lower pHs and high chloride concentrations. Because the identification of this second phase is speculative, and more solution species may have been present than assumed, their data at lower pHs may require reinterpretation in the future. However, they were able to evaluate the Gibbs free energy change for the reaction



An equilibrium constant for this reaction was calculated from information given in their paper, and its value is reported in Table 3.

2.10 Thermodynamic modeling at finite ionic strengths

Tables 4 and 5 summarize which $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, S_m° , and $C_{p,m}^\circ$ values are available for technetium compounds and aqueous ions. There are many blanks in these tables that indicate where thermodynamic measurements are needed. These standard state values are for pure phases and ideal aqueous solutions. At finite solution concentrations, the NEA recommends the use of

the Specific Ion Interaction Theory (SIT), and they have reported available SIT parameter values [5,18]. At high ionic strengths, Pitzer's ion interaction model [40] is widely used and has been incorporated in many geochemical modeling codes. Ion-interaction parameters are available for several single aqueous pertechnetates and some mixtures at 298.15 K [41–44], and these values are given in Tables 6 and 7. Pitzer's review [40] and other reports by Pitzer should be consulted for the significance of these parameters.

Acknowledgments

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Table 1. Parameters for the vapor pressure equation $\ln(p/\text{bar}) = a + b(K/T) + c\ln(T/K)$ for Tc(cr) and various inorganic technetium compounds. ^a

Phase	<i>a</i>	<i>b</i>	<i>c</i>	Temperature Range / K
Tc(cr)	17.342	-80978		≈1900–2350
Tc ₂ O ₇ (s)	35.469	-16590		362.2–391.2
Tc ₂ O ₇ (l)	14.101	-8222.5		393.3–529.4
TcF ₆ (cr, ortho.)	88.0741	-8208.3	-10.787	256.83–267.68
TcF ₆ (cr, cubic)	28.6883	-5015.0	-2.295	268.32–310.03
TcF ₆ (l)	50.5040	-5537.5	-5.8036	311.11–324.82
TcO ₃ F(s)	22.042	-7459.0		264.37–291.43
TcO ₃ F(l)	12.761	-4753.9		291.43–324.97
TcOF ₄ (solid I)	31.718	-12793		298.15–357.7
TcOF ₄ (solid II)	21.702	-9210		357.7–406
TcOF ₄ (l)	16.682	-5844		406–423

^a The information in this table was taken from *Chemical Thermodynamics of Technetium* [5], which should be consulted for references and estimated uncertainties. The parameters for Tc(cr) were calculated from an equation for the Gibbs free energy of sublimation given in their Appendix B.2.

Table 2. Solubilities of pertechnetate salts in water. ^a

Solid Phase	Solubility at 298.15 K / mol·kg ⁻¹	Solubility Product at 298.15 K, K_S	Other Temperatures Studied
NaTcO ₄ ·4H ₂ O ^b	11.30	6.17	
KTcO ₄	0.105	5.15×10 ⁻³	273.15 K
RbTcO ₄			293.15
CsTcO ₄	0.017	2.5×10 ⁻⁴	288.15–313.15 K
AgTcO ₄	0.027	5.4×10 ⁻⁴	288.15–313.15 K
TlTcO ₄	0.0025	4.8×10 ⁻⁶	293.15–313.15 K
NH ₄ TcO ₄	0.59	0.123	
(CH ₃) ₄ NTcO ₄	0.14 (293.15 K)		
Ph ₄ AsTcO ₄	2.95×10 ⁻⁵		
Ba(TcO ₄) ₂	≈0.2 (interpolated)		293.15, 308.15 K

^a The information in this table was taken from *Chemical Thermodynamics of Technetium* [5], which should be consulted for references and estimated uncertainties. ^b The degree of hydration of this salt is uncertain, but it is probably the tetrahydrate.

Table 3. Solubility product for $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s})$ and equilibrium constants for the hydrolysis of Tc(IV) and formation of complexes with inorganic ions at $\approx 298 \text{ K}$.

Reaction	$\log_{10}K$	Reference ^a
$\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s}) \xrightleftharpoons{\quad} \text{TcO}(\text{OH})_2(\text{aq}) + 0.6\text{H}_2\text{O}(\text{l})$	-8.4 ± 0.5	Rard et al. [5]
$\text{TcO}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l}) \xrightleftharpoons{\quad} \text{TcO}(\text{OH})_2(\text{aq}) + 2\text{H}^+(\text{aq})$	> -4.0	Rard et al. [5]
$\text{TcO}(\text{OH})^+(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{\quad} \text{TcO}(\text{OH})_2(\text{aq}) + \text{H}^+(\text{aq})$	-2.5 ± 0.3	Rard et al. [5]
	-4.0 ± 0.4	Hess et al. [36]
$\text{TcO}(\text{OH})_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{\quad} \text{TcO}(\text{OH})_3^-(\text{aq}) + \text{H}^+(\text{aq})$	-10.9 ± 0.4	Rard et al. [5]
$\text{TcO}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) \xrightleftharpoons{\quad} \text{Tc}(\text{CO}_3)(\text{OH})_2(\text{aq})$	1.1 ± 0.3	Rard et al. [5]
$\text{TcO}(\text{OH})_2(\text{aq}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{l}) \xrightleftharpoons{\quad} \text{Tc}(\text{CO}_3)(\text{OH})_3^-(\text{aq}) + \text{H}^+(\text{aq})$	-7.2 ± 0.6	Rard et al. [5]
$\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{am}) + 4\text{Cl}^-(\text{aq}) + 4\text{H}^+ \xrightleftharpoons{\quad} \text{TcCl}_4(\text{aq}) + 3.6\text{H}_2\text{O}(\text{l})$	$-2.8 \pm 0.2^{\text{b}}$	Hess et al. [36]

^a The source solubility data used for the evaluation in *Chemical Thermodynamics of Technetium* [5] were from the studies of Meyer et al. [33] and Eriksen et al. [34].

^b This value should only be used in combination with the adjusted hydrolysis constant (reported above) from that study.

Table 4. Solid and gaseous technetium compounds and pertechnetate salts with assessed standard thermodynamic quantities at 298.15 K and 0.1 MPa (1 bar).^a

Substance	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	S_m°	$C_{p,m}^\circ$
Tc(cr)	X	X	X	X
Tc(g)	X	X	X	X
TcO(g)	X	X	X	X
TcO ₂ (cr)	X	X	X	
Tc ₂ O ₇ (s)	X	X	X	X
Tc ₂ O ₇ (g)	X	X	X	X
Tc ₂ O ₇ ·H ₂ O(s) ^b	X	X	X	
TcO ₂ ·1.6H ₂ O(am)	X			
NaTcO ₄ ·4H ₂ O(s) ^c	X			
KTcO ₄ (cr)	X	X	X	X
CsTcO ₄ (cr)	X			
TlTcO ₄ (cr)	X			
AgTcO ₄ (cr)	X			
NH ₄ TcO ₄ (cr)	X			
TcF ₆ (cr, cubic)			X	X
TcF ₆ (g)			X	X
TcO ₃ F(g)			X	X
TcO ₃ Cl(g)			X	X
TcC(g)	X	X	X	
TcS(g)	X	X	X	X

^a The information in this table was taken from *Chemical Thermodynamics of Technetium* [5], which should be consulted for references and numerical values. An X denotes that an evaluated value is available, whereas a blank denotes that no reliable value is available. ^b The simplest empirical formula of this substance is Tc₂O₇·H₂O(s), but it is probably polymeric. ^c The degree of hydration of this solid phase is uncertain, but it is probably the tetrahydrate.

Table 5. Aqueous technetium species with assessed standard thermodynamic quantities at 298.15 K and 0.1 MPa (1 bar). ^a

Species	$\Delta_f G_m^\circ$	$\Delta_f H_m^\circ$	S_m°	$C_{p,m}^\circ$
TcO ₄ ⁻	X	X	X	X
TcO ₄ ²⁻	X			
TcO ²⁺	X ^b			
TcO(OH) ⁺	X			
TcO(OH) ₂	X			
TcO(OH) ₃ ⁻	X			
Tc(CO ₃)(OH) ₂	X			
Tc(CO ₃)(OH) ₃ ⁻	X			
TcCl ₄	X			

^a Most of the information in this table was taken from *Chemical Thermodynamics of Technetium* [5], which should be consulted for references and numerical values. An alternative value of $\Delta_f G_m^\circ$ is given by Hess et al. [36] who also reported the value for TcCl₄(aq). An X denotes that an evaluated value is available, whereas a blank denotes that no reliable value is available. ^b Only a lower bound is available for $\Delta_f G_m^\circ$ of this ion.

Table 6. Experimentally based ion-interaction model (Pitzer’s model) parameters for aqueous pertechnetate electrolytes at 298.15 K.

Solute	$\beta^{(0)}/$ $\text{mol}\cdot\text{kg}^{-1}$	$\beta^{(1)}/$ $\text{mol}\cdot\text{kg}^{-1}$	$C^\phi/$ $\text{mol}^2\cdot\text{kg}^{-2}$	Reference
HTcO ₄ (aq) ^a	0.07854	0.25685	0.01839	Rard and Miller [41]
NaTcO ₄ (aq) ^{a,b}	0.01111	0.15954	0.00236	Könnecke et al. [42]
KTcO ₄ (aq) ^c	-0.0578	0.006	0	Neck et al. [44]
CsTcO ₄ (aq) ^c	-0.1884	-0.1588	0	Könnecke et al. [42]
Mg(TcO ₄) ₂ (aq)	0.3138	1.840	0.0114	Neck et al. [43,44]
a				
Ca(TcO ₄) ₂ (aq) ^c	0.2964	1.661	0	Neck et al. [44]

^a Based on isopiestic experiments. ^b Also see Rard and Miller [41]. ^c Based on solubility measurements.

Table 7. Experimentally based ion-interaction model (Pitzer’s model) parameters for aqueous mixtures containing the pertechnetate ion at 298.15 K. ^a

ions	$\theta_{\text{Cl},\text{TcO}_4^-}/$ $\text{mol}\cdot\text{kg}^{-1}$	$\theta_{\text{SO}_4,\text{TcO}_4^-}/$ $\text{mol}\cdot\text{kg}^{-1}$	$\psi_{\text{M},\text{Cl},\text{TcO}_4^-}/$ $\text{mol}^2\cdot\text{kg}^{-2}$	$\psi_{\text{M},\text{SO}_4,\text{TcO}_4^-}/$ $\text{mol}^2\cdot\text{kg}^{-2}$	Reference
TcO_4^-	0.067	0.179			Könnecke et al. [42], Neck et al. [43]
$\text{Na}^+, \text{TcO}_4^-$			-0.0085	-0.003	Könnecke et al. [42], Neck et al. [43]
$\text{K}^+, \text{TcO}_4^-$			-0.011	0.002	Neck et al. [43]
$\text{Cs}^+, \text{TcO}_4^-$			-0.0011	0.024	Könnecke et al. [42], Neck et al. [43]
$\text{Mg}^{2+}, \text{TcO}_4^-$			-0.0115	-0.030	Neck et al. [43]
$\text{Ca}^{2+}, \text{TcO}_4^-$			-0.003		Neck et al. [44]

^a The value $\psi_{\text{Na},\text{Mg},\text{TcO}_4^-} = -0.020 \text{ mol}^{-2}\cdot\text{kg}^2$ is also given in reference [43].

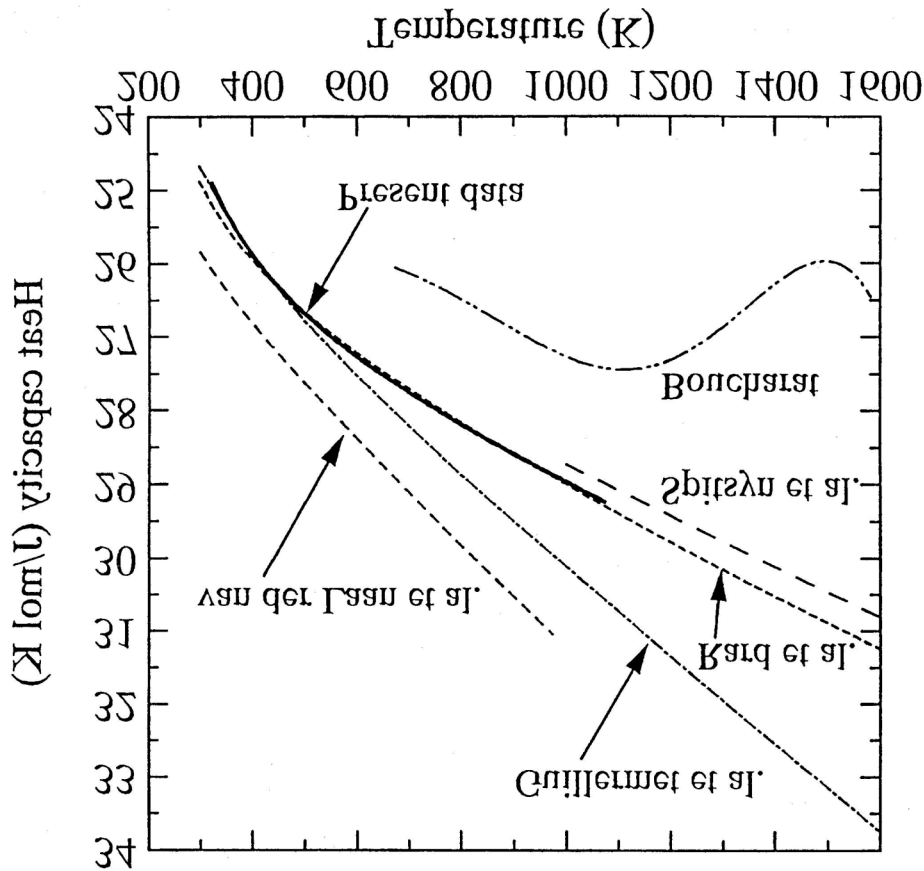


Fig. 1. Comparison of experimental heat capacities of technetium metal to those recommended in *Chemical Thermodynamics of Technetium* [5]. “Present data” refers to the differential scanning calorimetric measurements of Shirasu and Minato [22]. Reprinted from the Journal of Alloys and Compounds, volume 337, Y. Shirasu and K. Minato, Heat Capacities of Technetium Metal and Technetium-Ruthenium Alloy, pages 243–247, copyright 2002, with permission from Elsevier.

Vapour pressure of Tc_2O_7

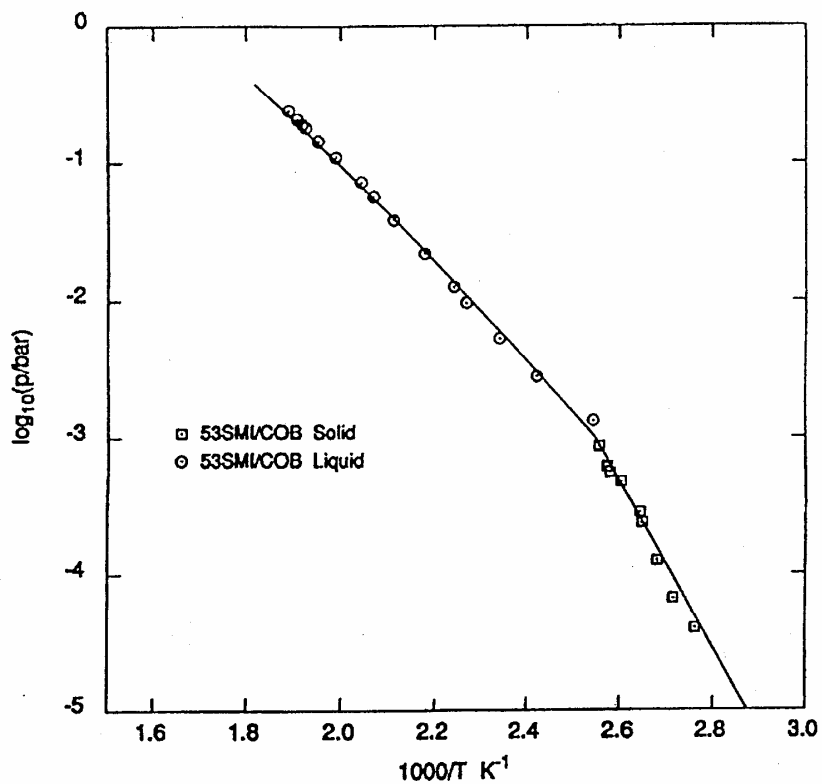


Fig 2. Logarithmic plot of vapor pressures of $Tc_2O_7(s, l)$ against the inverse of temperature. This is Figure V.4, Vapour pressure of Tc_2O_7 , from *Chemical Thermodynamics of Technetium* [5], © OECD 1999, with permission from the OECD 2005.

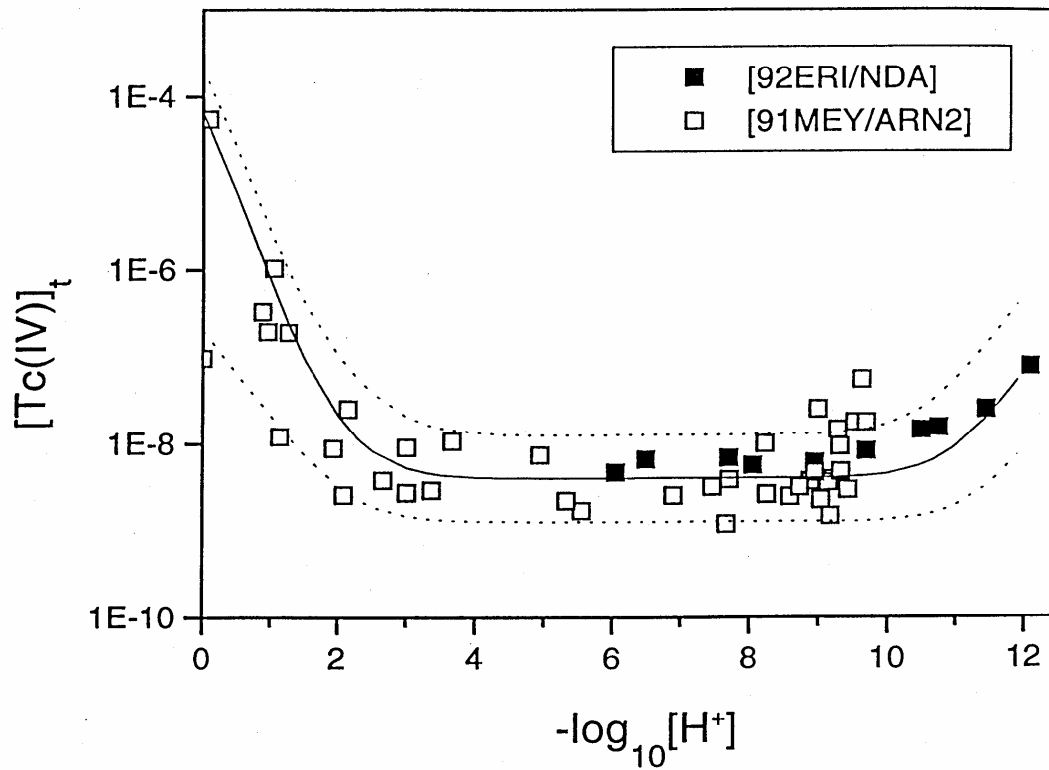


Fig 3. Plot of solubility of $TcO_2 \cdot xH_2O(s)$ against the negative logarithm of the hydrogen ion concentration. This is Figure V.3, Solubility measurements of hydrous Tc(IV) oxide at 25 °C, from *Chemical Thermodynamics of Technetium* [5], © OECD 1999, with permission from the OECD 2005.

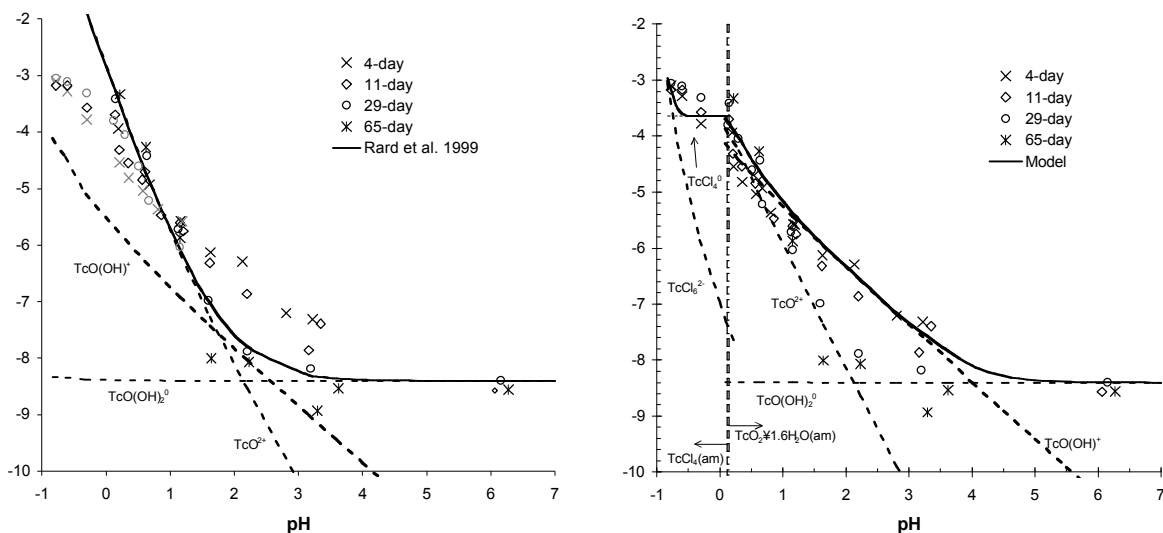


Fig. 4. Plots of $\log_{10}(C_{\text{Tc(IV)}}/\text{mol}\cdot\text{kg}^{-1})$ against the pH from the study of Hess et al. [36], where $C_{\text{Tc(IV)}}$ is the total concentration of dissolved Tc(IV) and $0.02 \text{ mol}\cdot\text{L}^{-1}$ hydrazine was present to maintain reducing conditions. Solid curves: comparison of these experimental measurements against model predictions made using the assessed $\Delta_f G_m^\circ$ values from (left plot) *Chemical Thermodynamics of Technetium* [5], and from (right plot) the parameterized model of Hess et al. with inclusion of chloride complexes. This is Fig. 8 from *Journal of Solution Chemistry*, volume 33, pages 199–226, 2004, N. J. Hess, Y. Xia, D. Rai, and S. D. Conradson, Thermodynamic Model for the Solubility of $\text{TcO}_2\cdot x\text{H}_2\text{O}(\text{am})$ in the Aqueous $\text{Tc(IV)}-\text{Na}^+-\text{Cl}^--\text{H}^+-\text{OH}^--\text{H}_2\text{O}$ System, ©2004 Plenum Publishing Corporation, with kind permission from Springer Science and Business Media.

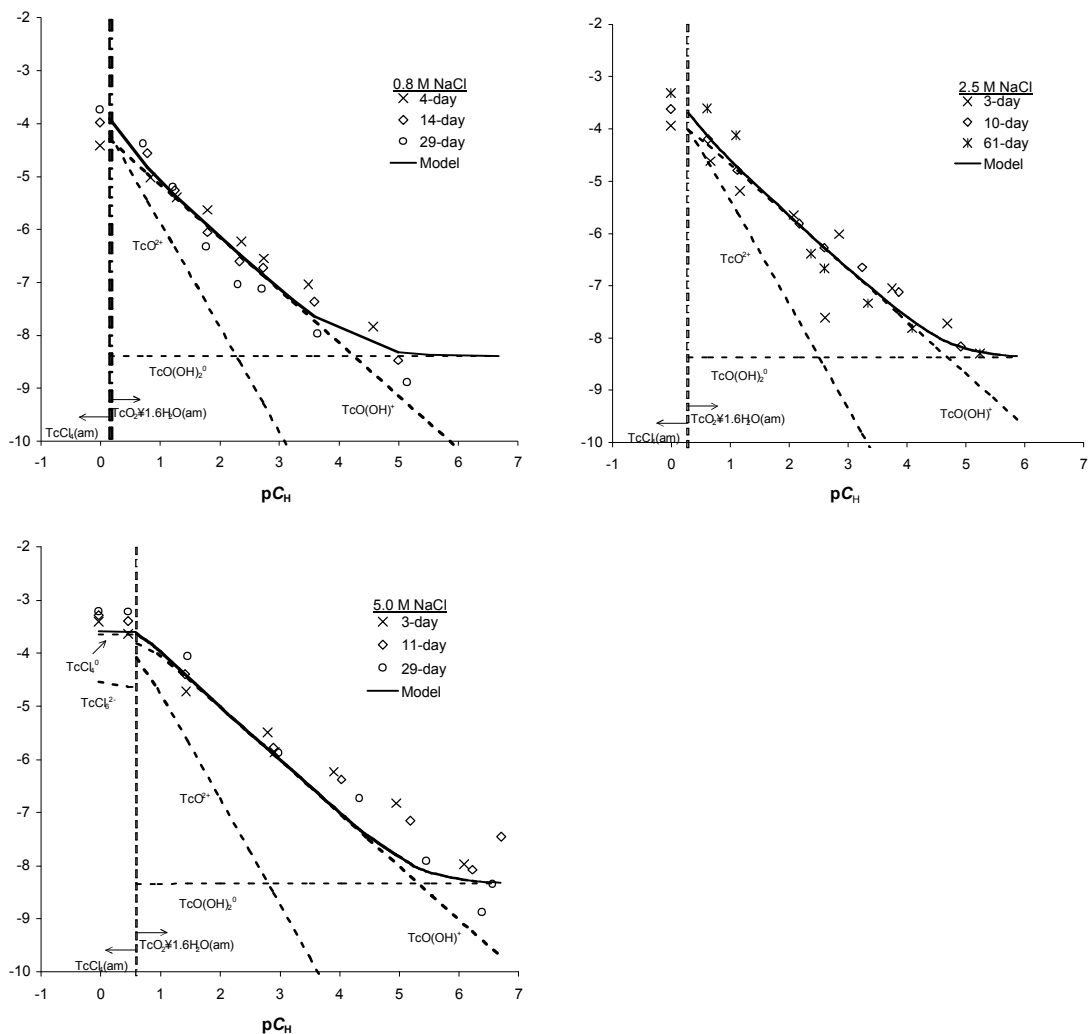


Fig. 5. Plots of $\log_{10}(C_{\text{Tc(IV)}}/\text{mol}\cdot\text{kg}^{-1})$ against the pH at different concentrations of added NaCl from the study of Hess et al. [36], where $C_{\text{Tc(IV)}}$ is the total concentration of dissolved Tc(IV) and $0.02 \text{ mol}\cdot\text{L}^{-1}$ hydrazine was present to maintain reducing conditions. Solid curve: comparison of these experimental measurements against model predictions made using the model of Hess et al. with inclusion of chloride complexes. This is part of Fig. 9 from Journal of Solution Chemistry, volume 33, pages 199–226, 2004, N. J. Hess, Y. Xia, D. Rai, and S. D. Conradson, Thermodynamic Model for the Solubility of $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ in the Aqueous $\text{Tc(IV)}-\text{Na}^+-\text{Cl}^- - \text{H}^+-\text{OH}^- - \text{H}_2\text{O}$ System, ©2004 Plenum Publishing Corporation, with kind permission from Springer Science and Business Media.