

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

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The technetium isotope ^{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. Geochemical modeling of the dissolution of nuclear waste, and of the solubility and speciation of the dissolved radionuclides in groundwaters, is an important part of the Performance Assessment of the safety of a nuclear waste repository that relies on the availability of a critically-assessed thermodynamic database. Such a database for technetium was published in the book *Chemical Thermodynamics of Technetium*, covering the published literature through 1998. This database is described here, along with a discussion of more recent relevant studies. Gaps in the knowledge of the chemical and thermodynamic properties of technetium are identified here, and recommendations are made for measurements that are required 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 released into the environment, along with an order of magnitude smaller amount of ^{99}Tc as a relic from the atmospheric testing of nuclear weapons. The metastable isotope ^{99m}Tc (produced by neutron irradiation of ^{98}Mo) is used extensively for diagnostic purposes in nuclear medicine;⁴ ^{99m}Tc undergoes gamma decay to the ground state ^{99}Tc , with $t_{1/2} = 6.0$ hours, which then occurs 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 small as to be nearly undetectable.⁵

Unlike ^{99m}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 into stable ruthenium 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. TcO_4^- 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 sorption in some

negatively charged sediments by repulsion within 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 plants¹¹⁻¹³ and in some invertebrates.¹²

$\text{TcO}_4^-(\text{aq})$ can be reduced to the sparingly soluble ($\sim 10^{-8}$ mol·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 hydrolyzed 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 periods 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) published a series of books giving critically assessed thermodynamic data for selected elements pertinent to radioactive waste management. Of these, *Chemical Thermodynamics of Technetium* by Rard et al.⁵ was published in 1999, covering the literature through 1998. A subsequent update volume¹⁸ for various radioactive elements including technetium, with literature coverage through 2002, did not produce 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 data.

2. The Chemistry and Thermodynamics of Technetium

Fundamental thermodynamic quantities of substances that

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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 of them will appear in a particular database. The standard entropy of a pure element is required for the calculation 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. Technetium metal 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 Brodsky¹⁹ from 3 to 15 K, which yield the Debye temperature and electronic heat capacity coefficient, 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 Grimvall²¹ calculated the heat capacities and entropies of Tc(cr) with a theoretically-motivated 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 review⁵ 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 model²¹ and the revised model⁵ 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 Minato²² 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 Reference 5 in this temperature region. Figure 1 compares these $C_{p,m}^\circ$ values 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 Konings²³ are somewhat higher than those of Reference 22, whereas those of Boucharat²⁴ are very low.

The measurements of van der Laan and Konings²³ 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 results²³ with the recommended values⁵ is satisfactory. The minimum and maximum exhibited by the heat capacities of Boucharat²⁴ 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 Boucharat's Tc(cr) sample or a serious calibration error for the differential scanning calorimeter.

The excellent agreement of the experimental heat capacities of Shirasu and Minato²² with those recommended in Reference 5 gives us considerable confidence in the recommended values. However, the calculation of S_m° requires the evaluation of

$$\int_{T=0}^T \{C_{p,m}^\circ/T\}dT, \text{ and there are no experimental } C_{p,m}^\circ \text{ data between}$$

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, resulting

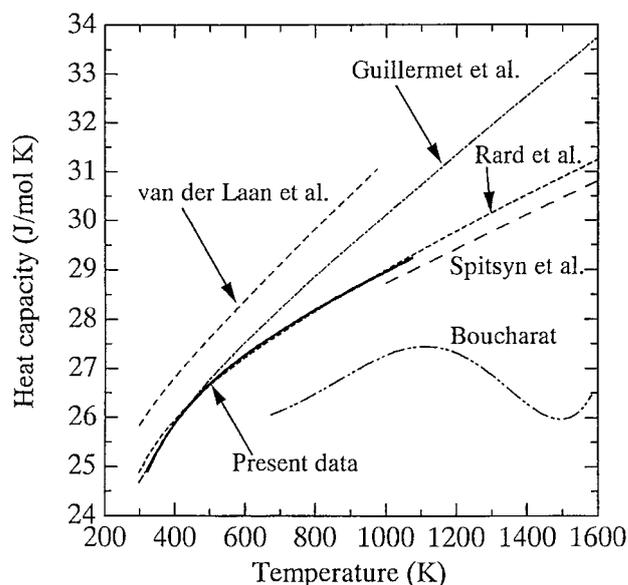


Figure 1. Comparison of experimental heat capacities of technetium metal to those recommended in Reference 5. “Present data” refers to the differential scanning calorimetric measurements of Shirasu and Minato.²² Reprinted from the Journal of Alloys and Compounds, volume 337, Y. Shirasu and K. Minato,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

in some uncertainty in the integral at low temperatures, and consequently in 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 TcO₂(cr) which occurs in the monoclinic space group P2₁/c, and Tc₂O₇(cr) which occurs in the orthorhombic space group Pbca. Tc₂O₇(cr) melts at (392.7 ± 0.1) K and extrapolation of the vapor pressures of Tc₂O₇(l) yields an estimated normal boiling temperature of 584 K. Equations for the vapor pressures of Tc₂O₇(cr) and Tc₂O₇(l) as functions of temperature are given in Table 1. Several other

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

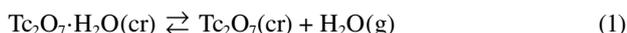
^aThe information in this table was taken from Reference 5, which should be consulted for references and estimated uncertainties. The parameters for Tc(cr) were calculated from an equation for the Gibbs free energy of sublimation given in their Appendix B.2.

solid oxides have been suggested in the literature, in particular $\text{TcO}_3(\text{s})$, but their existence has not been definitely established. $\text{Tc}_2\text{O}_7(\text{cr})$ sublimes congruently to yield $\text{Tc}_2\text{O}_7(\text{g})$. Many other gaseous oxides that have been identified at very high temperature by mass spectrometry are $\text{Tc}_2\text{O}_6(\text{g})$, $\text{Tc}_2\text{O}_5(\text{g})$, $\text{Tc}_2\text{O}_4(\text{g})$, $\text{TcO}_3(\text{g})$, $\text{TcO}_2(\text{g})$, 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 $\text{Ce}(\text{IV})$. Because of experimental difficulties,²⁵ 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 an alternative 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 Figure 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 $\bar{P}1$) is complicated and is not fully established, 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 K⁵ 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.

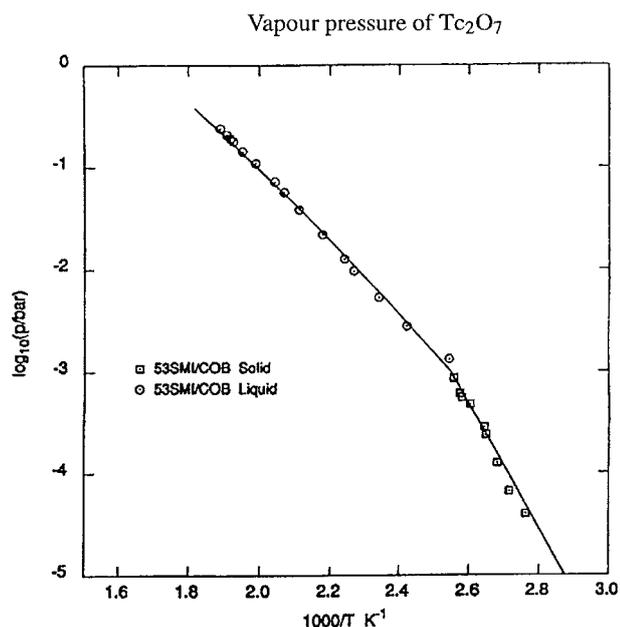


Figure 2. Logarithmic plot of vapor pressures of $\text{Tc}_2\text{O}_7(\text{s}, \text{l})$ against the inverse of temperature. This is Figure V.4, Vapour pressure of Tc_2O_7 , from *Chemical Thermodynamics of Technetium*,⁵ © OECD 1999, with permission from the OECD 2005.

The most commonly encountered hydrous oxide is that of $\text{Tc}(\text{IV})$, 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 setting. There are several reports of a $\text{Tc}(\text{III})$ hydrous oxide being produced during the electrolytic reduction of TcO_4^- , but $\text{Tc}(\text{III})$ is unstable with regard to disproportionation to other valence states at pHs above 3 or 4, and is very sensitive to oxidation by even trace amounts of oxygen.⁵ $\text{Tc}(\text{II})$ and $\text{Tc}(\text{I})$ hydrous oxides have also been claimed to form under very reducing conditions,^{5,26} but they are very likely thermodynamically unstable.

The solid hydrous oxide of $\text{Tc}(\text{IV})$ 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 measured water content and crystallinity may arise from different preparation conditions, i.e. electrolytic or chemical reduction of TcO_4^- versus hydrolysis of $\text{Tc}(\text{IV})$ compounds, or sample age, but determining the water content accurately is difficult owing to the small sample sizes typically used. In Reference 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 for this hydrous oxide.

Recent extended X-ray absorption fine structure (EXAFS) studies now provide definite information about the nature of the $\text{Tc}(\text{IV})$ 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 neighboring technetium atoms (four bridges per technetium). The Tc-Tc distance is $(2.5-2.6) \times 10^{-10} \text{ m}$ and the bridging Tc-O distance is $(2.0-2.1) \times 10^{-10} \text{ m}$. The remaining two coordinated sites of each $\text{Tc}(\text{IV})$ are occupied by trans water molecules.

The recommended value of $\Delta_f G_m^\circ(\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}, \text{am}, 298.15 \text{ K})$ was calculated using the emf data from two concordant studies for the reversible electrochemical cell reaction⁵



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 $\text{Tc}(\text{VII})$, $\text{Tc}(\text{VI})$, $\text{Tc}(\text{V})$, and $\text{Tc}(\text{IV})$ have been synthesized, as have several quaternary oxides containing $\text{Tc}(\text{IV})$. Their compositions and crystal structures are listed in Table V.40 of Reference 5. Some of these $\text{Tc}(\text{IV})$ or $\text{Tc}(\text{VII})$ mixed oxides may form during calcining of low level nuclear waste, but none have been characterized thermodynamically.

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
$\text{NaTcO}_4 \cdot 4\text{H}_2\text{O}^b$	11.30	6.17	
KTcO_4	0.105	5.15×10^{-3}	273.15 K
RbTcO_4			293.15
CsTcO_4	0.017	2.4×10^{-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_4TcO_4	0.59	0.123	
$(\text{CH}_3)_4\text{NTcO}_4$	0.14 (293.15 K)		
$\text{Ph}_4\text{AsTcO}_4$	2.95×10^{-5}		
$\text{Ba}(\text{TcO}_4)_2$	≈ 0.2 (interpolated)		293.15, 308.15 K

^aThe information in this table was taken from Reference 5, which should be consulted for references and estimated uncertainties.

^bThe degree of hydration of this salt is uncertain, but it is probably the tetrahydrate.

Dissolved technetium occurs as TcO_4^- in aqueous solution under oxidizing conditions, and 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). Under normal environmental conditions, these pertechnetate salts are too soluble to become solubility limiting phases.

$\text{KTcO}_4(\text{cr})$ is the most studied pertechnetate salt, 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 eq 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: TcF_6 (cubic and orthorhombic cr, l, g), TcF_5 (cr, l), TcCl_6 (cr), TcCl_4 (s), TcBr_4 (s), and TcBr_3 (s).⁵ TcCl_6 (cr) is unstable with regard to chlorine loss, and TcCl_4 (s) and TcBr_4 (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 remains 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: 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 $\text{TcO}_3\text{Cl}(\text{s}, \text{l}, \text{g})$.⁵ 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 TcF_6 (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 in turn 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 $\text{M}(\text{I})_2\text{TcF}_6(\text{cr})$, $\text{M}(\text{I})_2\text{TcCl}_6(\text{cr})$, $\text{M}(\text{I})_2\text{TcBr}_6(\text{cr})$, $\text{M}(\text{I})_2\text{TcI}_6(\text{cr})$, $\text{M}(\text{II})\text{TcCl}_6(\text{cr})$, and $\text{M}(\text{II})\text{TcBr}_6(\text{cr})$, where M(I) is a monovalent cation and M(II) a divalent cation.⁵ The tendency for the Tc(IV) hexahalo salts to undergo aquation and subsequent hydrolysis in aqueous solutions falls in the order $\text{TcI}_6^{2-} \gg \text{TcBr}_6^{2-} > \text{TcCl}_6^{2-} \gg \text{TcF}_6^{2-}$, with the fluoride salts being quite resistant to hydrolysis whereas the iodide salts are 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 to preclude 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 with average technetium valences of 4 or less.^{5,29} Because most of these polymeric technetium compounds are formed under very reducing conditions, they will not form or survive under normal environmental conditions.

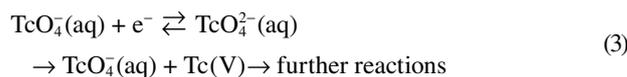
Reduction of TcO_4^- with concentrated aqueous HCl in the presence of the iodide ion, or by HI in the presence of chloride or bromide ions, yields salts containing the $\text{TcCl}_5(\text{OH})^{2-}$ or $\text{TcBr}_5(\text{OH})^{2-}$ anions.⁵ There is a lack of thermodynamic data for these salts, but they are probably unstable with respect to hydrolysis by water.

Reduction of TcO_4^- by aqueous HCl or HBr yields salts containing the TcOCl_5^{2-} , TcOBr_5^{2-} , TcOCl_4^- , and TcOBr_4^- ions 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 respect to hydrolysis and disproportionation to 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. Reaction 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, under reducing conditions $\text{Tc}_2\text{S}_7(\text{s})$ has the potential for being the solubility-limiting phase for technetium in groundwater. However, two attempts to determine the solubility product of $\text{Tc}_2\text{S}_7(\text{s})$ have been unsuccessful,^{3,30} because Tc_2S_7 readily forms colloids in aqueous solutions^{30,31} and the smaller colloids could not be removed by filtration.³⁰ Kunze et al.³⁰ studied the precipitation of $\text{Tc}_2\text{S}_7(\text{s})$ from Na_2S solutions at 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 equilibration, 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 solutions varies between +7 in TcO_4^- to +3. A stability field for Tc(II) appears in many potential-pH diagrams, even though this species has not been experimentally observed. As discussed in Reference 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 a series of complicated and irreversible processes, involving multiple (mostly irreversible) steps 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 reversible reduction of $\text{TcO}_4^-(\text{aq})$ involving one electron 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 Tc(V), and the unstable Tc(V) further disproportionates to Tc(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 Tc(V) which similarly disproportionates. In acidic solutions, $\text{TcO}_4^-(\text{aq})$ can be reduced to Tc(III) or Tc(IV) depending on the pH, which involves converting some of the oxygen atoms into water molecules. These other redox reactions are irreversible and do not yield thermodynamic data. The Tc(VI) and Tc(V) species are thermodynamically unstable with regard to disproportionation.

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

2.8. Aqueous Tc(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 $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{am})$, the hydrolysis constants relating $\text{TcO}^{2+}(\text{aq})$, $\text{TcO}(\text{OH})^+(\text{aq})$, $\text{TcO}(\text{OH})_2(\text{aq})$, and $\text{TcO}(\text{OH})_3(\text{aq})$, and, in carbonate solutions, the stability con-

stants 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 Figure 3. Nguyen Trung et al.³⁵ measured solubilities that are probably consistent, but the underlying experimental data have not yet been 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 Reference 5, but adjusting in addition the hydrolysis constant for the reaction:



As can be seen by comparing the left- and right-hand plots in Figure 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 aging effects of unknown origin were present in their saturated solutions when $\text{pH} < 4$. Table 3 gives a summary of the reac-

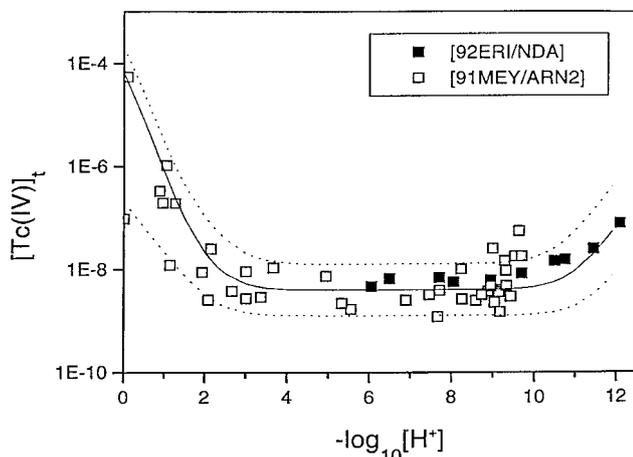


Figure 3. Plot of solubility of $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ against the negative logarithm of the hydrogen ion concentration. This is Figure V.3, Solubility measurements of hydrous Tc(IV) oxide at 25 °C, from *Chemical Thermodynamics of Technetium*,⁵ ©OECD 1999, with permission from the OECD 2005.

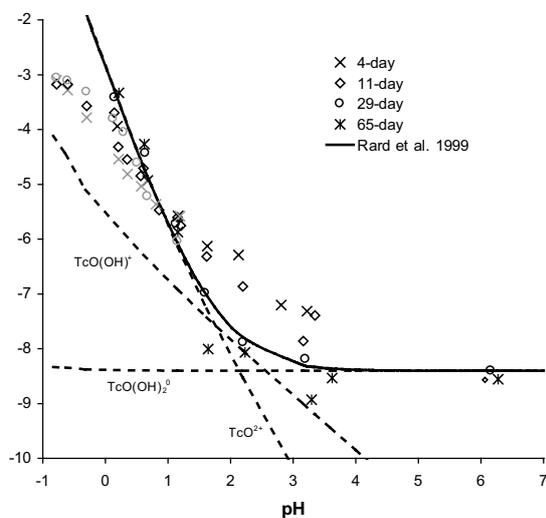


TABLE 3: Solubility Product for $\text{TcO}_2 \cdot 1.6\text{H}_2\text{O}(\text{s})$ and Equilibrium Constants for the Hydrolysis of Tc(IV) and Formation of Complexes with Inorganic Ions at $\approx 298 \text{ K}$

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

^aThe source solubility data used for the evaluation in Reference 5 were from the studies of Meyer et al.³³ and Eriksen et al.³⁴ ^bThis value should only be used in combination with the adjusted hydrolysis constant (reported above) from that study.

tions 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 $\text{Tc}(\text{OH})_n^{2-n}(\text{aq})$ rather than as $\text{Tc}(\text{OH})_m^{4-m}(\text{aq})$ 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} indicate that $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{s})$ contains μ -oxo rather than hydroxo bridges, suggesting that formulating the monomeric core solution species as $\text{TcO}^{2+}(\text{aq})$ was a reasonable choice.⁵ 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 review⁵ because of the probable presence of significant concentrations of $\text{TcO}_4^-(\text{aq})$, and possible colloid formation from the apparently oversaturated solutions. The chemical reduction of $\text{TcO}_4^-(\text{aq})$ to form oversaturated solutions of Tc(IV) initially yields small hydrolyzed polymers²⁸ and very fine colloids that could be removed by ultrafiltration but

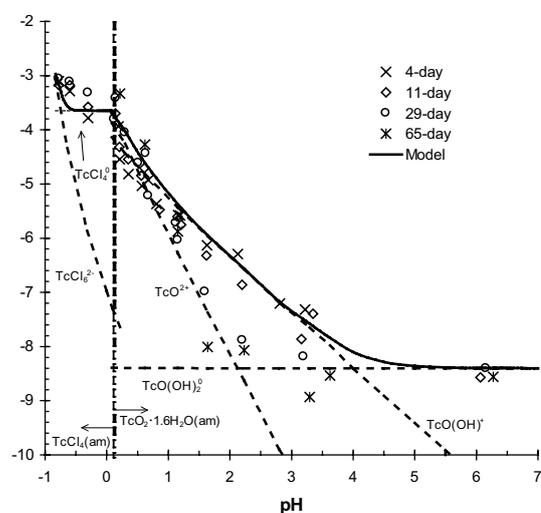
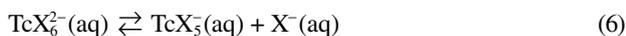


Figure 4. Plots of $\log_{10}(C_{\text{Tc(IV)}}/\text{mol} \cdot \text{kg}^{-1})$ against the pH from the study of Hess et al.³⁶ where $C_{\text{Tc(IV)}}$ is the total concentration of dissolved Tc(IV) and $0.02 \text{ mol} \cdot \text{L}^{-1}$ hydrazine was present to maintain reducing conditions. Solid curves: comparison of these experimental measurements against model predictions made using the assessed $\Delta_r G_m^\circ$ values from (left plot) Reference 5, and from (right plot) the parameterized model of Hess et al. with inclusion of chloride complexes. This is Figure 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 Tc(IV)– Na^+ – Cl^- – H^+ – OH^- – H_2O System, ©2004 Plenum Publishing Corporation, with kind permission from Springer Science and Business Media.

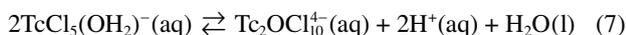
not by sedimentation.³⁷ At higher degrees of Tc(IV) oversaturation, colloid growth was observed, and the addition of increasing amounts of NaCl caused coagulation and then precipitation.³⁷

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 Equilibrium is reached very slowly in the Tc(IV) halide systems in the absence of chemical or photochemical catalysis. Equilibrium constants are available for the equilibria



where X = Cl or Br, but the reported equilibrium constants are limited to concentrated acidic chloride and bromide solutions.^{5,38}

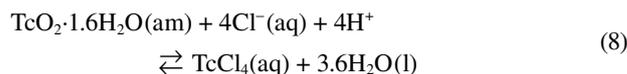
A recent study by Ben Said et al.³⁹ indicates that aged solutions of Tc(IV) in 1 mol·L⁻¹ HCl contain $\text{TcCl}_5(\text{aq})$ and $\text{TcCl}_4(\text{aq})$. However, a recent thesis³⁸ reports strong evidence for formation of the Tc(IV) complex $\text{Tc}_2\text{OCl}_{10}^{4-}$ at pH = 0 and 1 in aqueous solutions containing 3 mol·L⁻¹ Cl⁻, by the dimerization reaction:



Evidence was also obtained for the partially dissociated form of this ion, $\text{Tc}_2\text{OCl}_8^{2-}(\text{aq})$, and possibly for the μ -oxo bridged $\text{Tc}_2\text{O}_2\text{Cl}_{10-x}(\text{aq})$ 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 Figure 5. Based on the change in slope at pH ≈ 0.5, they concluded that although the solid phase was $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ at higher pHs, a new phase, possibly $\text{TcCl}_4(\text{am})$, 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 actually assumed, their data at low pHs may

require reinterpretation in the future. However, they were able to evaluate the Gibbs free energy change for the reaction



An equilibrium constant, calculated from information given in their paper, is reported in Table 3.

2.10. Thermodynamic modeling at finite ionic strengths. Tables 4 and 5 summarize the $\Delta_f G_m^\circ$, $\Delta_f H_m^\circ$, S_m° , and $C_{p,m}^\circ$ values that are available for technetium compounds and aqueous ions. The many gaps in these tables indicate areas where additional 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 the available SIT parameter values.^{5,18} At high ionic strengths, Pitzer's ion interaction model⁴⁰ 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 review⁴⁰ and other reports by Pitzer should be consulted for the significance of these parameters.

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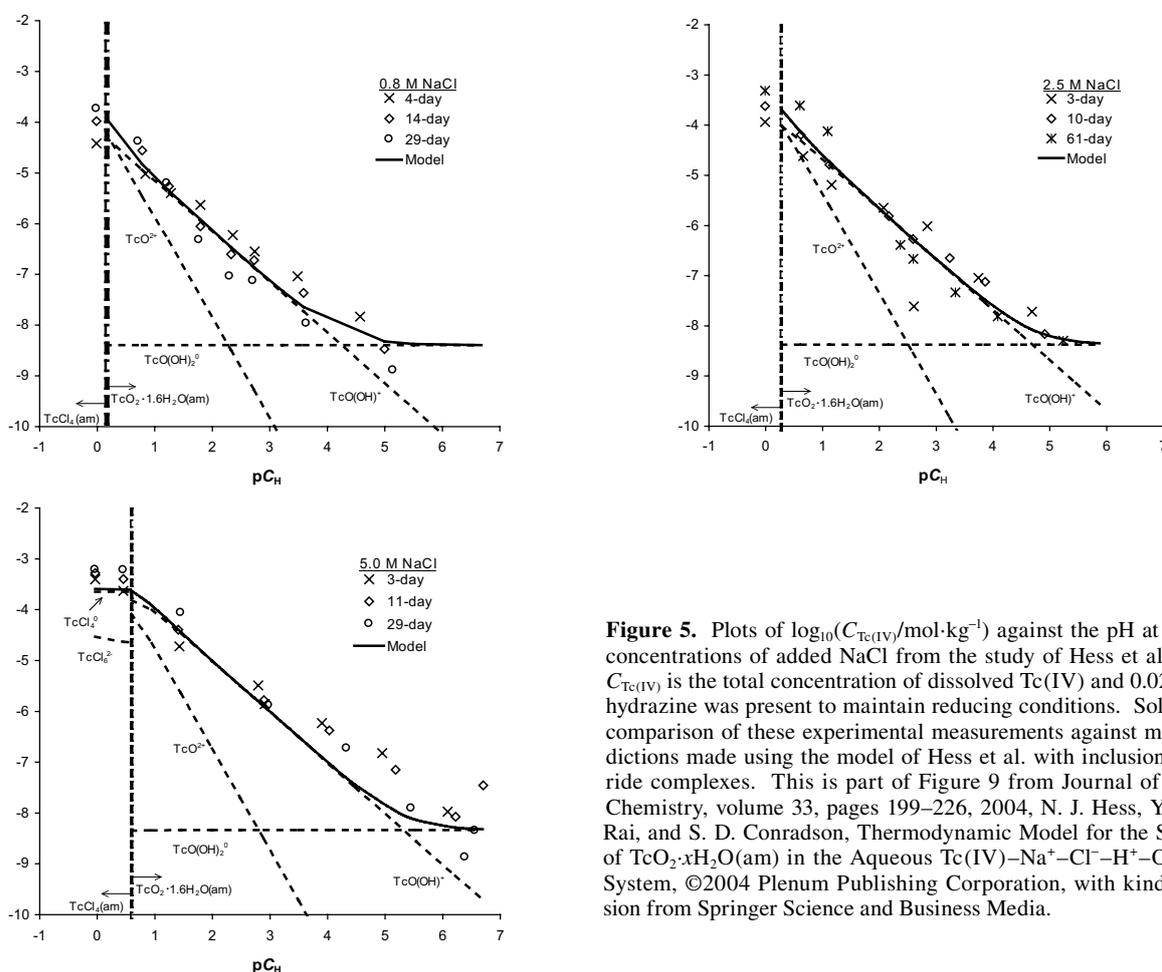


Figure 5. Plots of $\log_{10}(C_{\text{Tc(IV)}}/\text{mol}\cdot\text{kg}^{-1})$ against the pH at different concentrations of added NaCl from the study of Hess et al.³⁶ where $C_{\text{Tc(IV)}}$ is the total concentration of dissolved Tc(IV) and 0.02 mol·L⁻¹ hydrazine was present to maintain reducing 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 Figure 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.

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

^aThe information in this table was taken from Reference 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. ^bThe simplest empirical formula of this substance is Tc₂O₇·H₂O(s), but it is probably polymeric. ^cThe 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			

^aMost of the information in this table was taken from Reference 5, which should be consulted for references and numerical values. An alternative value of $\Delta_f G_m^\circ$ for TcO(OH)⁺ 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. ^bOnly 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	$\beta^{(0)}/\text{mol}^{-1}\cdot\text{kg}$	$\beta^{(1)}/\text{mol}^{-1}\cdot\text{kg}$	$C^\phi/\text{mol}^{-2}\cdot\text{kg}^2$	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. ^{43,44}
CsTcO ₄ (aq) ^c	-0.1884	-0.1588	0	Könnecke et al. ⁴²
Mg(TcO ₄) ₂ (aq) ^a	0.3138	1.840	0.0114	Neck et al. ^{43,44}
Ca(TcO ₄) ₂ (aq) ^c	0.2964	1.661	0	Neck et al. ⁴⁴

^aBased on isopiestic experiments. ^bAlso see Rard and Miller.⁴¹ ^cBased 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	$\theta_{\text{Cl,TcO}_4}/\text{mol}^{-1}\cdot\text{kg}$	$\theta_{\text{SO}_4,\text{TcO}_4}/\text{mol}^{-1}\cdot\text{kg}$	$\psi_{\text{M,Cl,TcO}_4}/\text{mol}^{-2}\cdot\text{kg}^2$	$\psi_{\text{M,SO}_4,\text{TcO}_4}/\text{mol}^{-2}\cdot\text{kg}^2$	Reference
TcO ₄ ⁻	0.067	0.179			Könnecke et al. ⁴² Neck et al. ⁴³
Na ⁺ , TcO ₄ ⁻			-0.0085	-0.003	Könnecke et al., ⁴² Neck et al. ⁴³
K ⁺ , TcO ₄ ⁻			-0.011	0.002	Neck et al. ⁴³
Cs ⁺ , TcO ₄ ⁻			-0.0011	0.024	Könnecke et al., ⁴² Neck et al. ⁴³
Mg ²⁺ , TcO ₄ ⁻			-0.0115	-0.030	Neck et al. ⁴³
Ca ²⁺ , TcO ₄ ⁻			-0.033		Neck et al. ⁴⁴

^aThe value $\psi_{\text{Na,Mg,TcO}_4} = -0.020 \text{ mol}^{-2}\cdot\text{kg}^2$ is also given in Reference 43.

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