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Critical Review of the Chemistry and Thermodynamics of Technetium and Some of its Inorganic Compounds and Aqueous Species

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Abstract

Chemical and thermodynamic data for Technetium (Tc) and some of its inorganic compounds and aqueous species are reviewed here. Major emphasis is given to systems with potential geochemical applications, especially the geochemistry of radioactive waste disposal. Compounds considered include oxides, hydroxides, hydrated oxides, halides, oxyhalides, double halides, and sulfides. The aqueous species considered include those in both noncomplexing media (pertechnetates, technetates, aquo-ions, and hydrolyzed cations) and complexing media (halides, sulfates, and phosphates). Thermodynamic values are recommended for specific compounds and aqueous ions when reliable experimental data are available. Where thermodynamic data are inadequate or unavailable, the chemistry is still discussed to provide information about what needs to be measured, and which chemistry needs to be clarified.

A major application of these thermodynamic data will be for chemical equilibrium modeling and for construction of potential-pH diagrams for aqueous solutions. Unfortunately, the present lack of data precludes such calculations for complexing aqueous media. The situation is much better for noncomplexing aqueous media, but the chemistry and thermodynamics of cationic Tc(V) species and hydrolyzed Tc(III) species are poorly understood.

INTRODUCTION

The existence of element number 43 was predicted by Mendeleev in 1869 and named ekamanganese by him. Various early claims were made for its discovery in natural minerals, and different workers gave it the names ilmenium, davyum, lucium, nipponium, and masurium. All of these claims proved to be in error. All isotopes of element 43 are unstable, and the longest lived isotopes have half-lives of over 10^6 years (^{97}Tc and ^{98}Tc). The amount of primordial material remaining in the earth's crust is extremely small and has not been detected.

The first conclusive experimental evidence for the artifical production of element 43 was given by Perrier and Segré,[1,2] using a sample of Mo bombarded by deuterons in the University of California (Berkeley) cyclotron. They named the element technetium (Tc) from the Greek word τεχνητος meaning artificial. All isotopes of Tc with mass numbers from 90 to 110 have now been prepared, along with several nuclear isomers.

Since then, several isotopes of Tc have been shown to occur in very small amounts in the earth's crust. Its presence in Mo ores and platinum metal group concentrates is generally considered to be of secondary origin, i.e., it is probably formed by the interaction of hard cosmic rays with Mo, Ru, or Nb. Tc also appears in uranium ores from the spontaneous fission of ^{238}U. When present, it is in the amount of about 10^{-10} g Tc/kg of ore. Tc is also known to occur in certain types of cooler stars in relatively large amounts, suggesting continuous production. Several excellent reviews are available regarding its discovery, isotopes, natural occurrence, and applications.[3-8]

Most Tc is now obtained as ^{99}Tc from the thermal neutron fission of ^{235}U with about 6% yield (also from Th or Pu), and it is available in multigram amounts. This is enough to allow many of its chemical and thermodynamic properties to be investigated. ^{99m}Tc and ^{95m}Tc are used extensively in nuclear medicine; one entire issue in 1982 of the International Journal of Applied Radiation and Isotopes was devoted to these applications. Additional applications of Tc in nuclear medicine are given in Clark and Fackler's article.[9] TcO_4^- also has applications to the inhibition corrosion of iron.[10]

An interesting finding about ^{99m}Tc is that its half-life for decay by internal conversion is slightly sensitive to its chemical environment, owing to variations in the electron density of Tc within 0.2 Å of the nucleus.

The 3p and 3d subshell electrons have the greatest influence in this case. Differences in the decay constant of several tenths of a percent are observed.[11,12] Attempts have been made to explain these observations theoretically.[12-14] TcO_4^- has a larger shift than TcX_6^{2-} ($X=Cl^-$, Br^-, or I^-) owing to its more ionic nature.

The best characterized aqueous Tc species is the pertechnetate ion TcO_4^-. It is fairly stable and quite mobile in geological environments. However, when reduced to cationic forms (by Fe^0, Fe^{2+}, etc.), technetium is much more strongly absorbed on minerals.[15-19] Consequently, a complete thermodynamic data base for Tc aqueous species and solids is essential for reliable modeling of Tc migration in the earth's crust. When incomplete thermodynamic data bases are used in geochemical modeling, speciation calculations can be unreliable. One need only examine the published potential-pH diagrams for aqueous Tc to see large differences for the stability regions for various ions.[15,16,18,20,21] Most of these calculations included aqueous TcO_4^- and Tc^{2+} (and Tc^{2+} datum is only an estimated value). Various aqueous species of Tc(III), Tc(IV), Tc(V), and Tc(VI) are also known, but not all of them are stable or even properly characterized.

The present report gives an assessment of the current knowledge of the chemistry and thermodynamics of Tc and some of its inorganic compounds and their aqueous solutions. Values for thermodynamic quantities are recommended when sufficient information is available. Unfortunately, in many cases, the desired data are unavailable.

A number of articles and books provide information about the inorganic chemistry, radiochemistry, thermodynamics, analytical chemistry, and uses of Tc. Several references have been cited already.[3-9,20] Three other books provide additional information.[22-24] Crystal structure data have also been reviewed recently,[25] and a short review of analytical chemistry has appeared.[26]

ANALYSIS OF CHEMICAL AND THERMODYNAMIC DATA

DATA FOR SOLIDS, LIQUIDS, AND GASES

Elemental Technetium

Most available technetium is produced by nuclear reactors (Oak Ridge National Laboratory is a major supplier) and is usually in the form of an aqueous NH_4TcO_4 solution. This is generally converted to the metal or to some other compound.

One of the earliest methods of preparing high purity Tc metal involved forming a black precipitate of Tc_2S_7 upon addition of H_2S to solutions containing TcO_4^-. This was followed by $H_2(g)$ reduction at 1300 to 1400 K.[27] However, very prolonged reduction is required to obtain a sulfur-free product.[28] H_2 reduction of $NH_4TcO_4(c)$ also gives good results in an inert atmosphere,[29] but in the presence of $NH_3(g)$ a nitride is obtained.

Thermal decomposition of hexahalotechnetates $M_2TcX_6(c)$ also yields metallic technetium. Pure Tc is obtained from the ammonium salt,[30-32] but alkali metal salts are a by-product of the thermal decomposition of alkali metal hexahalotechnetates.[32,33] Electrolysis of TcO_4^- ion in H_2SO_4 solutions gives very pure metal,[30,34] but H_2O_2 addition is essential to eliminate $TcO_2 \cdot mH_2O$ formation during the electroreduction. Electroreduction of TcO_4^- at a mercury cathode yields either an amalgam or a fine dispersion.[30]

Three determinations of the melting point of Tc are in reasonably good agreement: 2413 ± 20 K,[35] 2473 ± 50 K,[36] and 2435 ± 40 K.[37] The selected value is the average 2440 ± 30 K. Stull and Sinke's[38] estimated boiling point of 4900 K was accepted here since no experimental values are available.

Published heat capacity data are available for Tc metal only from 3 to 15 K (Tc is superconducting below about 7.8 K).[39] Pulsed heating was used to reduce interference due to radioactive self-heating. These data above 7.86 K yield a Debye constant $\theta_D = 454 \pm 4$ K and an electronic heat capacity coefficient $\gamma = 4.30 \pm 0.05$ mJ/mol-K^2. The θ_D value agrees with the value from low temperature ultrasonic velocity measurements.[40] Values of θ_D depend slightly on temperature[40] as is usual for metals. Since no higher temperature heat capacities exist, Stull and Sinke's estimates[38] of $S^o(298\ K) = 33.5$ J/mol-K and Cp (298 K) = 24.3 J/mol-K were accepted for the solid. This entropy is relative to normal state (nonsuperconducting) low-temperature Tc.

Metallic Tc has a hcp (hexagonal, close-packed) structure, and 7 unit-cell determinations are in fairly good agreement.[29,41-46] The four sets in best agreement[29,42-44] were averaged to obtain "best values" of a = 2.741 ± 0.001 Å and c = 4.399 ± 0.001 Å. Marples and Koch[44] also studied the cell dimensions from 4.2 to 298 K and obtained thermal expansion coefficients (valid from 150 to 298 K) of $\alpha_a = 7.0_4 \times 10^{-6}\ K^{-1}$ and $\alpha_c = 7.0_6 \times 10^{-6}\ K^{-1}$. Electronic bandstructure calculations have been reported for hcp Tc.[47]

Two determinations of the enthalpy of sublimation of Tc(c) are 638.9 ± 9.2 KJ/mol[37] and 661 ± 17 KJ/mol,[48] from third-law analysis of Knudsen mass spectrometry. They are in good agreement and also agree with Stull and Sinke's estimated value of 649 KJ/mol.[38] We accept the experimental average of 650 ± 11 KJ/mol. While the two third-law values agree, the second-law values differ by over 200 KJ/mol and are much less reliable. Only monatomic $Tc^+(g)$ was detected in the vapor phase. Since the vapor pressures also differ by factors of 3 to 6 between these two studies, no free-energy data are recommended. Stull and Sinke[38] have also estimated the enthalpy of vaporization of liquid Tc to be 577 KJ/mol.

Values of the heat capacity and entropy have been calculated by statistical mechanical methods for monatomic Tc vapor.[38,49] Recommended values at 298 K are Cp = 20.8 J/mol-K and $S^o = 181.0$ J/mol-K. Table 1 contains a summary of recommended thermodynamic and structural data for elemental Tc.

Metallic Alloys and Hydrides

These data mainly consist of partial phase diagrams, with very little thermodynamic data. Peacock[7] and Lavrukhina and Pozdynakov[6] cite references for many of the metallic alloys. See especially the paper by Niemiec.[50] Results for the Fe-Tc phase diagram have been reviewed but are fragmentary.[51] Spitsyn et al.[46,52] have investigated the hcp Tc hydride system. There are insufficient data to recommend thermodynamic values for any of these compounds.

TABLE 1. Recommended data for elemental Tc.

Type of property	Value
Melting point, K	2440 ± 30
Boiling point, K	≈ 4900
Debye constant, K	454 ± 3
Electronic heat capacity coefficient, $mJ/mol\text{-}K^2$	4.30 ± 0.05
Entropy (298 K) of solid, J/mol-K	≈ 33.5
Heat capacity (298 K) of solid, J/mol-K	≈ 24.3
Unit cell a-dimension, Å	2.741 ± 0.001
Unit cell c-dimension, Å	4.399 ± 0.001
Thermal expansion a-axis, K^{-1}	7.04×10^{-6}
Thermal expansion c-axis, K^{-1}	7.06×10^{-6}
Enthalpy of sublimation, KJ/mol	650 ± 11
Enthalpy of vaporization, KJ/mol	≈ 577
Entropy of gas (298 K), J/mol-K	181.0
Heat capacity of gas (298 K), J/mol-K	20.8

Colton et al.[53] found that polarographic reduction of TcO_4^- in chloride-containing solutions corresponds to an approximately 8 e^- reduction to a Tc^- species. However, most Tc solution electrochemistry is irreversible so the extent of reduction is not completely certain (their data could also be interpreted as 7, 9, or 10 e^- reductions). Floss and Grosse[54] reduced Tc labeled NH_4ReO_4 with potassium in ethylenediammine and obtained a Re-Tc hydride. They assumed that Tc and Re compounds would be isostructural, and concluded that they had prepared a Tc analogue of $KReH_4 \cdot 2H_2O$. Ginsberg[55] prepared isostructural Tc and Re compounds, and showed that the Tc compound was $K_2TcH_9(c)$ since the structure of the Re analogue was known. A NMR study of Ginsberg's type of material confirms the presence of TcH_9^{2-} ions in basic solution.[56] A molecular orbital description of the TcH_9^{2-} anion has been given.[57]

Small amounts of $K_2TcH_9(c)$ can be dissolved in cold concentrated aqueous base with little decomposition. However, in dilute base, and in acidic solutions, decomposition with H_2 evolution is rapid.[55]

Many potential diagrams for Tc list an estimated electrode potential of -0.5 V for Tc/Tc^-. Since the only hydride species identified so far are TcH_9^{2-} and TcH_4^-, claims for a "Tc^-" species may refer to TcH_4^-. The evidence for K_2TcH_9 is strongest since it is backed up by structural data for both the solid state[55] and for aqueous solution.[56]

Anhydrous Tc_2O_7(c) and Tc_2O_7(g)

The most thoroughly characterized oxide of Tc is the yellow heptoxide Tc_2O_7. It was originally prepared by direct combustion of Tc metal.[58] It's melting point is 392.7 K by direct determination[58] and 391.6 K from the intersection of the liquid and solid vapor pressure curves.[59] Extrapolation of the liquid vapor pressure curve gives an estimated boiling point of 584 K.[59] A "volatile oxide" was described by Fried et al.[28] and was assumed by them to be TcO_3. It was more likely Tc_2O_7. Several properties of Tc_2O_7 have been reported including magnetic susceptibilities[60] of the solid, and Raman spectra of the solid, liquid, and gas.[61]

Aqueous solutions of Tc_2O_7 contain the very strong acid $HTcO_4$, which can be neutralized to form a wide variety of pertechnetate salts. Concentrating aqueous $HTcO_4$ solutions over concentrated H_2SO_4 produced a color change from yellow to dark yellow to red to dark red. Red crystals of $Tc_2O_7 \cdot H_2O$, or anhydrous $HTcO_4$, are ultimately formed.[58]

Two determinations have been reported for the enthalpy of formation of Tc_2O_7(c): (1) Cobble et al.[62] did direct combustion of Tc(c) and obtained ΔH_f^o = -1113 KJ/mol, and (2) Gayer et al.[63] used HgO to oxidize Tc(c) and obtained -1128 KJ/mol. The best value is the average of -1120 ± 8 KJ/mol.

There is no direct determination of the free energy or entropy of formation of Tc_2O_7(c). However, the entropy of $KTcO_4$(c) has been determined calorimetrically by Busey et al.[64] to be 164.8 J/mol-K. Assuming additivity relations apply, and an entropy of 38.5 for K^+ in the crystal,[62] then the entropy of $HTcO_4$(c) is 164.8 - 38.5 = 126.3 J/mol-K. The entropy of Tc_2O_7(c) is related to this by

$$S^o[Tc_2O_7(c)] = 2\ S^o[HTcO_4(c)] - S^o[H_2O(l)] - \Delta S^o_{rxn}\ , \qquad (1)$$

where ΔS^o_{rxn} applies to the reaction

$$Tc_2O_7(c) + H_2O(l) = 2HTcO_4(c) \quad .$$

Smith et al.'s decomposition vapor pressure measurements[59] yield $\Delta S^o_{rxn} = 16.7 \pm 0.8$ J/mol-K. Thus, at 298 K,

$$S^o[Tc_2O_7(c)] = 2(126.3) - 69.93 - 16.7 = 166.0 \pm 13 \text{ J/mol-K} \quad . \qquad (2)$$

The entropy of formation of $Tc_2O_7(c)$ is then

$$\Delta S^o_f[Tc_2O_7(c)] = S^o[Tc_2O_7(c)] - 2S^o[Tc(c)] - 7/2\ S^o[O_2(g)] \qquad (3)$$

$$= -618.6 \pm 13 \text{ J/mol-K} \quad .$$

Combining enthalpy and entropy data give the free energy of formation

$$\Delta G^o_f[Tc_2O_7(c)] = \Delta H^o_f[Tc_2O_7(c)] - T\ \Delta S^o_f[Tc_2O_7(c)] \qquad (4)$$

$$= -1120 - 298.15\ (-618.6)\ (10^{-3})$$

$$= -935.6 \pm 15 \text{ KJ/mol} \quad .$$

Smith et al.[59] studied the vapor pressures of $Tc_2O_7(c)$, which allows one to calculate data for the sublimation of $Tc_2O_7(c)$ to the standard state of unit fugacity:

$$\Delta G^o_{subl} = 48.1 \text{ KJ/mol} \quad ,$$

$$\Delta H^o_{subl} = 132.6 \text{ KJ/mol} \quad , \text{ and}$$

$$\Delta S^o_{subl} = 283.4 \text{ J/mol-K} \quad .$$

Combining the sublimation data with the crystal formation results yields

$$\Delta G_f^o[Tc_2O_7(g)] = -898.5 \pm 16 \text{ KJ/mol}$$

$$\Delta H_f^o[Tc_2O_7(g)] = -987.4 \pm 10 \text{ KJ/mol}$$

$$S^o[Tc_2O_7(g)] = 449.4 \pm 13 \text{ J/mol-K}$$

at 298 K.

Glidewell[65] has calculated an enthalpy of -4603 KJ/mol for the gas-phase reaction

$$Tc_2O_7 + O^{2-} = 2TcO_4^- \quad .$$

Anhydrous TcO_2(c) and TcO_3(c)

Like many transition metals, Tc forms a crystalline dioxide TcO_2(c). It has a distorted rutile structure.[25] Two structural determinations are in fair agreement,[43,66] but the three unit-cell dimensions are known only to a few hundredths of an angstrom. Vinogradov et al.[67] reported interplaner spacings for "TcO_2" that are rather different than for the other two studies. Electron band calculations have been made for $Tc_2O_{10}^{2-}$ clusters in TcO_2(c).[68]

TcO_2(c) is frequently prepared by the thermal decomposition of NH_4TcO_4(c) in an inert atmosphere.[3,43,67] Direct combustion of Tc(c) is unsatisfactory since TcO_2 readily oxidizes to Tc_2O_7.[3]

No experimental thermodynamic data are available for TcO_2(c), although it should be possible to oxidize TcO_2(c) to Tc_2O_7(c) to obtain an enthalpy of formation. Decomposition pressure measurements are frequently used to get free energies of formation. However, TcO_2(s) sublimes unchanged above about 1200 K,[3,43] so this method can not be used here.

There is no convincing experimental evidence for TcO_3(c), although there are unconfirmed reports of red or purple oxide with this composition.[22] However, Cobble et al.[62] have estimated its thermodynamic properties to be $\Delta H_f^o = -540$ KJ/mol, $\Delta G_f^o = -461$ KJ/mol, and $S^o = 72.4$ J/mol-K at 298 K. Fried et al.[28] converted Tc to "the volatile oxide" and suggested this oxide was TcO_3. However, Tc_2O_7 seems more likely. Steffen and Bächmann[69] did a high-temperature chromatographic study of Tc heated in flowing O_2, and concluded that two volatile oxides were present which they thought were TcO_2(g) and

$TcO_3(g)$. The "$TcO_3(g)$" yield decreases with decreasing temperature, and upon condensation decomposes to form TcO_2. That is

$$TcO_3(c) = TcO_2(c) + 1/2\ O_2(g)$$

is thermodynamically favored. This could explain why $TcO_3(c)$ has not been established.

Anhydrous Solid Ternary Oxides

Valence states of metals that are unstable for the pure binary oxides are sometimes stablized in ternary oxides. They are of some interest because they indicate what valence states could occur in other solid compounds (e.g. oxyhalides), and in aqueous solutions. Only a few typical compounds will be given from the many that have been reported.[43,70-72] Pertechnetate salts are a very important class and will be discussed in more detail in another section.

Examples of Tc(VII) compounds include Li_5TcO_6, Na_3TcO_5, $Ba(TcO_4)_2$, $Ba_3(TcO_5)_2$, and $Ba_5(TcO_6)_2$. Examples of Tc(VI) compounds are Li_4TcO_5, Li_6TcO_6, and $Ba_3Tc_2O_9$. Tc(IV) double oxides are represented by Li_2TcO_3, Na_4TcO_4, Ba_2TcO_4, $SrTcO_3$, and $Sm_2Tc_2O_7$. $NaTcO_2$ has been prepared for Tc(III), and $NaTcO_3$ and Li_3TcO_4 for Tc(V). Valences of IV, VI, and VII predominate.

Hydrated TcO_2(am)

A black amorphous hydrated dioxide of Tc is one of the most thoroughly studied compounds. It can be prepared by reduction of aqueous pertechnetates with metallic zinc,[3] electrolytically,[3,45,73] with Sn^{2+} perchlorate,[74] or with certain other reducing agents. It is sparingly soluble in acidic solutions[73] and usually has a composition close to the dihydrate $TcO_2 \cdot 2H_2O$. It can be reoxidized chemically, electrolytically, or with γ-rays to form TcO_4^- ions (see below).

$TcO_2 \cdot 2H_2O$ is generally considered to be a hydrated dioxide but, since it is amorphous, x-ray diffraction provides little information. Its IR spectrum has few features to help identify its nature.[45] Some authors consider it to be the tetrahydroxide $Tc(OH)_4$ instead. Below pH = $\approx$1.3 in aqueous solution, Tc(IV) exists as TcO^{2+} [or $Tc(OH)_2^{2+}$].[74] Slightly above pH = ≈1.3 it hydrolyzes[74-76] to form $TcO(OH)^+$ [or $Tc(OH)_3^+$, etc], $TcO(OH)_2^o$, and $[TcO(OH)_2]_2^o$. Colloidal suspensions are also known. $TcO_2 \cdot 2H_2O$ untimately precipitates from these solutions. Only the solid will be considered in this section.

Cobble et al.[62] measured electrode potentials for the aqueous reactions

$$TcO_2 \cdot 2H_2O = TcO_4^- + 4H^+ + 3e^-$$

in acidic solution, and

$$TcO_2 \cdot 2H_2O + 4OH^- = TcO_4^- + 4H_2O + 3e^-$$

in basic solution. To calculate free energies of formation of $TcO_2 \cdot 2H_2O$ requires free energy of formation data for $OH^-(aq)$, $H_2O(1)$, and $TcO_4^-(aq)$. CODATA values of ΔG_f^o were used for OH^- and H_2O. The ΔG_f^o of $TcO_4^-(aq)$, -621.1 KJ/mol, will be derived in the aqueous solution section of this report. Cobble et al.'s data thus yield $\Delta G_f^o[TcO_2 \cdot 2H_2O(am)]$ = -850.2 ± 10.5 KJ/mol.

Cartledge and Smith[77] reinvestigated the aqueous cell involving $TcO_2 \cdot 2H_2O/TcO_4^-$ in acidic solution. They found the reaction was sluggish at 298 K, and was affected by the presence of O_2. Since Cobble et al.[62] did not exclude air, Cartledge and Smith[77] concluded that the earlier results were slightly in error. Their new potential measurement gave $\Delta G_f^o[TcO_2 \cdot 2H_2O]$ = -837.2 ± 10.0 KJ/mol. Cartledge[78] also measured corrosion potentials, which yield -835.3 ± 2.5 KJ/mol for a surface film of $TcO_2 \cdot 2H_2O$. The last two values were averaged to produce the recommended value $\Delta G_f^o[TcO_2 \cdot 2H_2O(am)]$ = -836.3 ± 7.0 KJ/mol at 298 K.

Other Hydrated Oxides and Hydroxides: TcOH, $Tc(OH)_2$, $Tc(OH)_3$, Tc_3O_4, Tc_4O_7, and $Tc_4O_5 \cdot mH_2O$

Cartledge[78] measured a number of stationary "corrosion" potentials for Tc in aqueous H_2SO_4 at 297 K. Several of these were also obtained in another of his studies.[79] Cartledge attributed them to lower oxides or hydroxides of Tc. His assignment of the chemical formulas will be accepted [except for $TcO_2 \cdot 2H_2O$ instead of $Tc(OH)_4$] for want of any unambigious criteria for distinguishing hydroxides from hydrated oxides. However, the identification of Tc_4O_7 as one of these compounds is not completely certain.

Using our results for $\Delta G_f^o([TcO_2 \cdot 2H_2O]$ and the CODATA value for $H_2O(1)$ allows us to calculate the following values:

$$\Delta G_f^o[TcOH] = -234.7 \pm 3.8 \text{ KJ/mol}$$

$$\Delta G_f^o[Tc(OH)_2] = -461.2 \pm 3.8 \text{ KJ/mol}$$

$$\Delta G_f^o[Tc(OH)_3] = -658.5 \pm 3.8 \text{ KJ/mol}$$

$$\Delta G_f^o[Tc_3O_4] = -863.8 \pm 3.8 \text{ KJ/mol}$$

and

$$\Delta G_f^o[Tc_4O_7] = -1324 \pm 21 \text{ KJ/mol.}$$

These are actually for surface films. However, for $TcO_2 \cdot 2H_2O$ the difference from bulk phase was fairly small, so they can also be applied to bulk phases.

Spitsyn et al.[80] reported the formation of $Tc_4O_5 \cdot mH_2O$ from the hydrolysis of $Tc_2Cl_8^{3-}$. They deduced this formula since they saw little evidence for oxidation. Additional evidence for this compound would be desirable.

Table 2 contains a summary of thermodynamic data for anhydrous oxides, hydrated oxides, and hydroxides.

Solid Pertechnetates

The most thoroughly studied aqueous ion of technetium is the pertechnetate ion TcO_4^- which is stable in environments not strongly reducing. It can be

TABLE 2. Recommended data for oxides and hydroxides at 298 K.

Compound	Phase	ΔG_f^o in KJ/mol	ΔH_f^o in KJ/mol	S^o in J/mol-K
Tc_2O_7	Crystal	-935.6 ± 15	-1120 ± 8	166.0 ± 13
Tc_2O_7	Gas	-888.5 ± 16	-987.4 ± 10	449.4 ± 13
TcO_3	Crystal	≈ -461	≈ -540	≈72.4
$TcO_2 \cdot 2H_2O$	Solid (am)	-836.3 ± 7.0	--	--
TcOH	Solid (am?)	-234.7 ± 3.8	--	--
$Tc(OH)_2$	Solid (am?)	-461.2 ± 3.8	--	--
$Tc(OH)_3$	Solid (am?)	-658.5 ± 3.8	--	--
Tc_3O_4	Solid (am?)	-863.8 ± 3.8	--	--
Tc_4O_7	Solid (am?)	-1324 ± 21	--	--

prepared by oxidation of almost any lower valence aqueous species or suspended solid in aqueous solution. Dissolution of Tc_2O_7 in H_2O gives a solution of $HTcO_4$ which can be neutralized to provide a wide variety of salts. Many of these have been isolated as solid compounds.

A number of solid pertechnetates have been prepared and partially characterized by x-ray diffraction powder pattern data and, in some cases, by elemental analysis.[81-91] A partial listing includes:
NaX, KX, RbX, CsX, NH_4X, AgX, TlX, $MgX_2 \cdot 4H_2O$, $MgX_2 \cdot 2H_2O$, MgX_2, $PbX_2 \cdot 2H_2O$, PbX_2, $CdX_2 \cdot 2H_2O$, CdX_2, $ZnX_2 \cdot 4H_2O$, $ZnX_2 \cdot 2H_2O$, ZnX_2, $ScX_3 \cdot 3H_2O$, $ScX_3 \cdot H_2O$, ScX_3, $PrX_3 \cdot 4H_2O$, $PrX_3 \cdot H_2O$, PrX_3, $NdX_3 \cdot 4H_2O$, $NdX_3 \cdot H_2O$, and NdX_3.[67,81-91]

The pertechnetate ion has been denoted by X here for brevity. It is clear that almost any cation can form a salt with this anion. The scheelite structure is common for most anhydrous monovalent cation salts. Thermal decomposition of pertechnetate salts usually gives TcO_2(c) or a double oxide of Tc.

Aqueous solubility data have been reported as a function of temperature for $KTcO_4$,[63] $CsTcO_4$, $AgTcO_4$, and $TlTcO_4$.[83] The solubility of $RbTcO_4$ at 293 K and $NaTcO_4$ at 298 K have also been determined.[83,92]

The temperature dependences of solubilities yield enthalpies of solution. Values obtained by this method are 33.6 KJ/mol for $TlTcO_4$, 28.0 KJ/mol for $CsTcO_4$, and 40.3 KJ/mol for $AgTcO_4$.[83] Direct measurement of the enthalpy of solution of $KTcO_4$ gave 53.41 KJ/mol.[64] Busey et al.'s[64] equation for the enthalpy of solution as a function of temperature is correct for T = °C and not K as stated by them. Busey et al. also estimated the activity coefficient of saturated $KTcO_4$ (0.1057 mol/kg) at 298 K to be $\gamma \pm = 0.676 \pm 0.010$. This yields a free energy of solution of $\Delta G^o_{sol} = -RT \ln (m\ \gamma\pm)^2_{sat} = 13.06 \pm 0.13$ KJ/mol, and an entropy of solution $\Delta S^o_{sol} = 135.3 \pm 1.3$ J/mol-K.

Busey et al.[64] also measured the heat capacity of $KTcO_4(c)$ from 9.00 to 308.56 K. Their data yield a heat capacity of 123.3 J/mol-K and absolute entropy $S^o = 164.78$ J/mol-K. An earlier unpublished study in their laboratory for $KTcO_4$ was rejected by them because the sample was not completely anhydrous.

The above data can be used to obtain the ΔG, ΔH, and ΔS of formation of $KTcO_4(c)$, by using solution data. Also required are $\Delta H^o_f[TcO_4^-(aq)] = -716.3 \pm 4.5$ KJ/mol, and $\Delta G^o_f[TcO_4^-(aq)] = -623.8 \pm 10.0$ KJ/mol. These values will be derived in the aqueous solution section of this paper. Thus,

$$\Delta G^o_f[KTcO_4(c)] = \Delta G^o_f[KTcO_4(aq)] - \Delta G^o_{sol} \tag{5}$$

$$= \Delta G^o_f[K^+(aq)] + \Delta G^o_f[TcO_4^-(aq)] - \Delta G^o_{sol}$$

$$= -919.2 \pm 10.0 \text{ KJ/mol}$$

Also,

$$\Delta H^o_f[KTcO_4(c)] = \Delta H^o_f[KTcO_4(aq)] - \Delta H^o_{sol} \tag{6}$$

$$= \Delta H^o_f[K^+(aq)] + \Delta H^o_f[TcO_4^-(aq)] - \Delta H^o_{sol}$$

$$= -1022.2 \pm 5.5 \text{ KJ/mol}$$

Boyd[92] reported isopiestic measurements for $NaTcO_4$ solutions at 298 K from 0.108 to 9.464 mol/kg. He also measured the solubility to be 11.299 mol/kg. A modest extrapolation of his isopiestic data yields $\gamma \pm = 0.52 \pm 0.03$ for the saturated solution.

Thus,

$$\Delta G^{o}_{sol} = -RT\ \ln(m\gamma\pm)^{2}_{sat} = 8.78 \pm 0.28\ \text{KJ/mol} \tag{7}$$

and

$$\Delta G^{o}_{f}[NaTcO_4(c)] = \Delta G^{o}_{f}[Na^{+}(aq)] + \Delta G^{o}_{f}[TcO_4^{-}(aq)] - \Delta G^{o}_{sol} \tag{8}$$

$$= -877.0 \pm 10.1\ \text{KJ/mol}$$

For these calculations the CODATA values were used for ΔG^{0}_{f} of aqueous K^{+} and Na^{+}.

Smith et al.[59] reported decomposition pressure data for $HTcO_4(c)$ which can be combined with vaporization data for H_2O to yield

$$2HTcO_4(c) = H_2O(1) + Tc_2O_7(c)$$

and it is not known whether the solid is actually $HTcO_4(c)$ or $Tc_2O_7 \cdot H_2O(c)$. Their pressure measurements yield (at 298 K) $\Delta H^{o}_{rxn} = 1.80 \pm 0.21$ KJ/mol, $\Delta G^{o}_{rxn} = 6.83 \pm 0.08$ KJ/mol, and $\Delta S^{o}_{rxn} = -16.7 \pm 0.8$ J/mol-K. For the decomposition reaction,

$$\Delta H^{o}_{rxn} = \Delta H^{o}_{f}[Tc_2O_7(c)] + \Delta H^{o}_{f}[H_2O(1)] - 2\ \Delta H^{o}_{f}\ [HTcO_4(c)] \tag{9}$$

Thus

$$\Delta H^{o}_{f}[HTcO_4(c)] = 1/2(\Delta H^{o}_{f}[Tc_2O_7(c)] + \Delta H^{o}_{f}[H_2O(1)] - \Delta H^{o}_{rxn}) \tag{10}$$

$$= -703.8 \pm 9.6\ \text{KJ/mol}\quad ,$$

using the CODATA value for $H_2O(1)$ and $\Delta H^{o}_{f}[Tc_2O_7(c)]$ obtained earlier. A similar equation could be given for $\Delta S^{o}_{f}[HTcO_4(c)]$. Unfortunately, there is no available entropy data for either $Tc_2O_7(c)$ or

$HTcO_4(c)$. Consequently, $S^o[HTcO_4(c)]$ was obtained (as earlier) from $S^o[KTcO_4(c)]$ assuming additivity relations apply. The estimated value is 126.3 J/mol-K. The entropy of formation of $HTcO_4(c)$ is then

$$\Delta S^o_f[HTcO_4(c)] = S^o[HTcO_4(c)] - S^o[Tc(c)] - 2S^o[O_2(g)] - 1/2\ S^o[H_2(g)] \qquad (11)$$

$$= -382.5 \pm 3 \text{ J/mol-K} \ .$$

Combining results gives

$$\Delta G^o_f[HTcO_4(c)] = \Delta H^o_f[HTcO_4(c)] - T\ \Delta S^o_f[HTcO_4(c)] \qquad (12)$$

$$= -589.8 \pm 10.5 \text{ KJ/mol} \ .$$

Solid Tetraoxotechnetates (TcO_4^{2-})

Electrolytic reduction of aqueous TcO_4^- in noncomplexing media under different conditions can involve 1, 2, 3, or more electrons. A one electron reduction is sometimes observed in basic media, but the Tc(VI) species produced is very unstable and rapidly disproportionates to TcO_4^- and a Tc(IV) species. Some studies indicate the reduction potential for Tc(VII)/Tc(VI) is not pH dependent, so no oxygens should be lost from the TcO_4^- ion. That is, the initial reduction product is the unstable TcO_4^{2-} ion.

Support for this deduction comes from the studies of Schwochau and co-workers.[93-95] In certain nonaqueous media (mainly acetonitrile), reduction of TcO_4^{2-} salts yield violet TcO_4^{2-} salts. Astheimer et al.[94] studied the solid tetramethyl ammonium salt $[(CH_3)_4N]_2TcO_4$ using IR, magnetic susceptibilities, optical spectra, and electron transfer spectra. Structural information was provided by powder pattern data.[94] Under carefully controlled conditions, up to 90% of the TcO_4^- initially present could be converted to TcO_4^{2-}.[95]

Salts of TcO_4^{2-} decompose in the presence of moisture[94] and are not present in significant amounts for aqueous solutions at eqilibrium. However, their presence in the solid state supports the evidence for their existence as intermediates in the reduction of TcO_4^- salts. No thermodynamic data have been reported for solid TcO_4^{2-} salts.

Anhydrous Technetium Halides

Early attempts to prepare Tc chlorides by direct reaction of $Cl_2(g)$ with Tc metal under static conditions were unsuccessful.[3] However, it was later found that when a stream of Cl_2 was used, reaction does occur. The initial reaction produces a mixture of dark green $TcCl_6(c)$ and "dark" or "blood" red $TcCl_4(c)$. $TcCl_6$ is very unstable, even in the presence of $Cl_2(g)$, and decomposes to form $TcCl_4$ and Cl_2.[96,97] $TcCl_6$ hydrolyzes and disproportionates in aqueous solution according to the reaction[96]

$$3Tc(VI) = 2Tc(VII) + Tc(IV)$$

$TcCl_4(c)$ also hydrolyzes in water,[97] but in concentrated HCl solution produces the $TcCl_6^{2-}$ ion. $TcCl_4(c)$ can be sublimed in a $Cl_2(g)$ stream.[97]

$TcCl_4$ has also been prepared by the reaction of Tc_2O_7 with CCl_4.[98] Crystal structure data have been reported,[97,99] but no thermodynamic data are available for $TcCl_4$. Thermodynamic data have been estimated for $TcCl_3$ by Brewer et al.,[100] but there is no experimental evidence for its existence.[101] A large number of monomeric, dimeric, and trimeric Tc chloride cluster ions have been detected in the vapor phase by mass spectrometry.[102] A gas chromatographic study[103] of $Tc(c)-Cl_2(g)$ at high temperatures indicated two volatile $TcCl_x$ species, which the authors thought were $TcCl_4$ and $TcCl_5$. More direct evidence for $TcCl_5$ would be desirable, since most pentavalent Tc compounds are thermodynamically unstable.

Technetium bromides have been studied even less. Direct reaction of Br_2 with Tc does not seem to be favorable, but oxidation of Tc with H_2O_2 followed by evaporation with HBr produced solid $TcBr_4$.[101] This compound is brown-red, and hydrolyzes in moist air. Tsalas and Bächmann[104] found evidence for it in their high-temperature gas chromatographic study. No descriptions of TcI_x compounds were found. Brewer et al.[100] estimated thermodynamic data for $TcBr_3$, TcI_3, $TcBr_5$, and TcI_5, none of which have been isolated.

Both TcF_5 and TcF_6 are known, but only TcF_6 has been studied in any detail.[24] TcF_6 exists in two crystalline modifications, and unit cell dimensions have been reported for both forms.[105] Raman spectra are available for TcF_6 vapor.[106]

Detailed thermodynamic data are also available for TcF_6. Selig and Malm[107] measured vapor pressures of the two solid crystalline modifications and of the liquid. The solid-solid phase transition occurs at 268.34 K, and the melting point is 311.14 ± 0.05 K.[108] Intersection of the vapor pressure curves gave 310.6 K,[107] which is in reasonable agreement with the directly measured melting point.

Osborne et al.[108] have performed a careful and detailed study of the heat capacities of solid and liquid TcF_6. Combined with Selig and Malm's vapor pressures[107] they yield data for gaseous TcF_6 also. Results at 298 K for the high-temperature solid are 157.85 J/mol-K for the heat capacity and 253.52 ± 0.25 J/mol-K for entropy. Their third law results for the vapor phase are 120.92 J/mol-K for heat capacity and 371.28 ± 0.75 J/mol-K for entropy. They calculated an entropy of 367.52 J/mol-K using spectroscopic data and statistical calculations, and the agreement is fairly good.[108] Another statistical calculation[109] gave much lower results.

Hexahalotechnetate (IV) Salts

Tc(IV) in aqueous solution exists in a variety of hydrolyzed forms. At very high concentrations of halogen ions, complexes of the type TcX_6^{2-} form. Direct evidence for this comes from solid compounds containing this anion. Even the free acid $H_2[TcCl_6]\cdot 9H_2O(c)$ has been prepared and its crystal structure investigated.[110,111] Most K^+, Rb^+, Cs^+, and NH_4^+ salts of TcF_6^{2-}, $TcCl_6^{2-}$, $TcBr_6^{2-}$, and TcI_6^{2-} have been reported.[8,25,31,33,112-118] Some of these salts have been studied by x-ray diffraction, IR, Raman, and in some cases, magnetic susceptibilities. Thermal decomposition of them generally gives metallic Tc. Transition metal hexahalometallates undergo solid-state structural transitions, and the transition temperature for each fixed alkali metal cation increases with the atomic number of the anion.[117] The hydrazine salt $N_2H_6TcF_6$ forms in anhydrous HF but it is fairly unstable.[119] Chloride salts of the protonated forms of pyridine, dipyridine, and quinoline have also been reported.[120,121]

Vinogradov et al.[122] have reported solubilities for the NH_4^+, K^+, Rb^+, and Cs^+ salts of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ in solutions of their corresponding hydrohalic acids. Solubilities depended little on the acid concentrations, and were fairly small (10^{-2} to 10^{-4} mol/kg). Boyd[3] cited 333 ± 4 J/mol-K as the entropy of K_2TcCl_6(c) but gave no details.

Other Halotechnetate Salts

Edwards et al.[123] and Hulgill and Peacock[124] have reported alkali metal compounds $MTcF_6$(c), which contain pentavalent technetium. Likewise the hydrazine compound $N_2H_6(TcF_6)_2$, containing Tc(V), can be formed in anhydrous HF.[119] However, it decomposes at room temperature and it is moisture sensitive. Vinogradov et al. reported that thermal decomposition of K_2TcI_6 produced K_2TcI_3.[32] This material disproportionates in aqueous base. None of these compounds are stable in aqueous solution.

Solid Octahaloditechnetate Salts

In 1963 Eakins et al.[125] reported preparing salts of the $Tc_2Cl_8^{3-}$ anion. They can be prepared by the reduction of $TcCl_6^{2-}$ salts in concentrated aqueous HCl using reducing agents such as H_2 or Zn. These mixed valence technetium salts have been studied by a number of workers.

Salts of this type that have been reported are $(NH_4)_3[Tc_2Cl_8]\cdot 2H_2O$,[125-127] $K_3[Tc_2Cl_8]\cdot 2H_2O$,[125,128] $Cs_3[Tc_2Cl_8]\cdot 2H_2O$,[121] $Y[Tc_2Cl_8]\cdot 9H_2O$,[125,129] $(PyH)_3[Tc_2Cl_8]\cdot 2H_2O$,[130] $(QuinH)_3[Tc_2Cl_8]\cdot 2H_2O$,[131] and $(TBA)_3[Tc_2Cl_8]$.[132] Here Py represents pyridine, Quin represents quinoline, and TBA represents tetrabutyl ammonium groups. Molecular orbital calculations have been reported for the $Tc_2Cl_8^{3-}$ ion.[133-135] Koz'min and Novitskaya[136] claim to have prepared the compound $K_8[Tc_2Cl_8]_3\cdot(H_3O)\cdot 3H_2O$ and report its crystal structure, but evidence for it is not very strong.

Spitsyn et al.[80] claimed that $Tc_2Cl_8^{3-}$ hydrolyzes without oxidation or reduction to form the mixed valence oxide $Tc_4O_5\cdot mH_2O$. Oblova et al.[137] studied the thermal decomposition of $K_3[Tc_2Cl_8]\cdot 2H_2O$ in argon. Anhydrous $K_3[Tc_2Cl_8]$ was formed initially, followed by decomposition to K_2TcCl_6, KCl, and metallic Tc.

Schwochau et al.[138] reported that reduction of TcO_4^- in aqueous HCl using H_3PO_2 gave the TBA salt of $Tc_2Cl_8^{2-}$ with both Tc atoms in the +3 state. Preetz and Peters[132] reduced $TcCl_6^{2-}$ with Zn in concentrated HCl and obtained a mixture of $(TBA)_2[Tc_2Cl_8]$ and $(TBA)_3[Tc_2Cl_8]$ which were extracted with ether. The red bromo analogue $(TBA)_2[Tc_2Br_8]$ was also reported. They characterized their salts by elemental analyses, IR, Raman, and absorption spectra.

Recently, Kryuchkov et al.[139] prepared a number of Tc(II) salts of NH_4^+ and K^+ by 30 atm H_2 reduction of Tc salts in concentrated hydrohalic acid solutions. Salts reported are $M_2Tc_2Cl_6 \cdot 2H_2O$, $M_2Tc_2Br_6 \cdot 2H_2O$, $(TcBr_2 \cdot 0.5H_2O)_n$, and $(TcI_2 \cdot 0.5H_2O)_n$. Koz'min et al.[140] have provided evidence for the complex salt $[Tc_8Br_{12}]Br[(H_2O)_2H]$.

Anhydrous Oxyhalides

Canterford and Colton[24] list the known oxychlorides of Tc as TcO_3Cl, $TcOCl_4$, and $TcOCl_3$. The latter two compounds are the products of direct chlorination of $TcO_2(c)$, with the trichloride being the major product.[141] Identification of $TcOCl_4$ was tentative. They readily hydrolyze in H_2O. Rudolph and Bächmann[103] found evidence for $TcOCl_3$ and $TcOCl_4$ from their high-temperature gas-chromatographic study. Their presence was inferred by analogy to other metals, but no direct evidence was obtained. Spectroscopic data have been reported for $TcOCl_3$, but $TcOCl_4$ was too unstable to permit IR measurements.[142]

TcO_3Cl can be prepared by the reaction of O_2 with $TcCl_4$. Spectroscopic data have been reported for TcO_3Cl in the gaseous, liquid, and solid states.[143-145] These allow the calculation of thermodynamic functions for TcO_3Cl vapor from statistical thermodynamic methods. Baran[146] has performed these calculations and obtained 80.46 J/mol-K for the heat capacity and 317.6 J/mol-K for the entropy. It is also claimed that TcO_3Cl forms when Tc_2O_7 dissolves in concentrated H_2SO_4 in the presence of chloride ions.[147] TcO_3Cl hydrolyzes in basic solution to form TcO_4^-.

Direct bromination of $TcO_2(c)$ yields the oxybromide $TcOBr_3$,[141,142] as does the reaction of Br_2 with pertechnetate salts.[141] IR spectra have been reported.[142] This compound has been studied very little.

A number of technetium oxyfluorides have been reported, mainly by reduction of TcO_4^- by anhydrous HF. Compounds reported are: TcO_3F,[7,24] $TcOF_4$,[7,24] $Tc_2O_5F_4$,[56] and TcO_2F_3.[56] identification of the last two oxyfluorides is tentative. $TcOF_4$ exists in at least two crystal modifications: a metastable, green trimeric form and a stable blue monomer.[148] TcO_3F can also be prepared by direct fluorination of TcO_2.[149]

TcO_3F is the most thoroughly studied oxyfluoride. Its spectroscopic properties have been reported for vapor and liquid.[149,150] Vapor pressure measurements have also been reported for solid and liquid TcO_3F.[151] These data yield a melting point of 291.5 K, an approximate boiling point of 373 K, an enthalpy of sublimation of 62.0 KJ/mol, an enthalpy of fusion of 22.5 KJ/mol, and an enthalpy of vaporization of 39.5 KJ/mol.

Peacock[7] has cited unpublished vapor pressure measurements of A. J. Edwards for both $TcOF_4$ solid modifications and for the liquid. These data yield the solid-solid transition point at 357.7 K, a melting point of 406 K, and a boiling point of 438 K. The enthalpy change for sublimation of the low temperature solid is 106.3 KJ/mol, for sublimation of the high-temperature solid 76.6 KJ/mol, for fusion of the high-temperature solid 28.0 KJ/mol, and 48.5 KJ/mol for vaporization. Unfortunately, no enthalpy or free energy of formation data have been published for the compound.

Solid Tc(V) Oxyhalide Salts

It is known that pertechnetate salts added to concentrated hydrochloric or hydrobromic acid react fairly rapidly to produce Tc(V) complex ions, but if the reaction is allowed to continue or the solution warmed, TcX_6^{2-} ions are produced. Since salts of the Tc(V) complex ions can be isolated, they provide evidence for this species being present in solution.

Reaction of pertechnetate salts with 11 to 12 molar HCl produces Tc(V) ions, but at lower HCl concentrations addition of H_3PO_2 may be required for the reaction to occur at a reasonable rate. Busey reported this reaction but did not isolate any salts.[152,153]

Jeżowska-Trzebiatowska and co-workers[154-156] prepared solid salts of the general type $M_2[TcOCl_5]$ by direct reduction of TcO_4^- ions with concentrated HCl. The K^+, Cs^+, and NH_4^+ salts have been characterized by various spectroscopic methods and by elemental analyses.[154-158]

Other workers have prepared slightly different salts of the type $M[TcOCl_4]$.[153,159] Like $M_2[TcOCl_5]$ salts, they can be considered double salts of the oxychloride $TcOCl_3$. Salts of the type $M[TcOCl_4]$ form where the cation is TBA^+, $(n\text{-}C_4H_9)_4N^+$, or $(Ph_3P)_2N^+$, where TBA^+ represents the tetrabutyl ammonium cation and Ph represents the phenyl group. Since these two types of salts are produced under nearly identical conditions, cation size may determine which type forms. That is, small cations favor $M_2[TcOCl_5]$ whereas large cations produce $M[TcOCl_4]$. Derivatives of Tc(V) oxychlorides with organic ligands are also known.[160]

Analogous bromide salts $Cs_2[TcOBr_5]$ and $TBA[TcOBr_4]$ are produced by the same method.[157,159,161] Ligand exchange of $M[TcOCl_4]$ salts with I^- salts is the favored method to produce $M[TcOI_4]$.[161,162] Although direct reaction of HI with TcO_4^- also works, reduction to TcI_6^{2-} is usually much too rapid to allow $TcOI_4^-$ salts to be isolated. No thermodynamic data have been reported for any of these Tc(V) oxyhalide salts. However, they are all thermodynamically unstable with regard to hydrolysis and disproportionation to form $TcO_2 \cdot 2H_2O$ and TcO_4^- (aq) in H_2O,[161] and to form TcX_6^{2-} in concentrated hydrohalic acid solutions.[154]

These oxyhalides can be isolated as solid compounds owing to their slow reduction kinetics to Tc(IV) in aqueous solution. Partial hydrolysis of K_2TcOCl_5(c) was reported to form $K_2TcO(OH)Cl_4$, but it was difficult to achieve exact stoichiometry.[158]

Solid Tc(IV) and Tc(VI) Oxyhalide Salts

Ziolkowski et al. showed that tracer amounts of Tc(IV) could be incorporated into $K_4[Re_2OCl_{10}]$.[163] Since many quadrivalent transition metals (Ru, W, etc.) form similar compounds, it is reasonable to assume Tc(IV) can also. However, one compound with the correct empirical formula was proved to be $K_2Tc(OH)Cl_5$ by crystal structure determination[112] [i.e. it is not 1/2 $K_4(Tc_2OCl_{10} \cdot H_2O)$], and it is isostructural with K_2TcCl_6. Being isostructural indicates that OH^- randomly replaces Cl^- within the salt.[112] Fergusson et al.[157] recently described the preparation of $M_2Tc(OH)Cl_5$ ($M=K^+$, Rb^+, or Cs^+) and $Cs_2(OH)Br_5$, from I^- reduction of TcO_4^- in HCl and HBr solutions.

Colton and Tomkins[141] reacted thionyl chloride (an extremely strong Lewis acid) with NH_4TcO_4 to prepare the thionyl chloride adduct $(NH_4)_2[TcO_2Cl_4] \cdot SO_2Cl_2$ which contains Tc(VI). Several technetium oxychloride complexes with organic ligands are also known.[25]

Technetium Sulfides, Nitrides, Borides, and Carbides

Rulfs and Meinke[164] found that H_2S reduces TcO_4^- to Tc_2S_7 in HCl solution. Heating this Tc_2S_7 with excess sulfur, followed by sublimation yields TcS_2.[3] Neither of these compounds have published data for ΔG_f^o or ΔH_f^o. However, McDonald and Cobble[165] have estimated ΔH_f^o = -224 KJ/mol for TcS_2, -276 KJ/mol for TcS_3, and -615 KJ/mol for Tc_2S_7. Their estimated ΔG_f^o values are -216 KJ/mol for TcS_2, - 263 KJ/mol for TcS_3, and -581 KJ/mol for Tc_2S_7. Their estimated entropies are 71 J/mol-K for TcS_2, 84 J/mol-K for TcS_3, and 176 J/mol-K for Tc_2S_7. However, there is no experimental evidence for TcS_3.

Table 3 contains recommended thermodynamic data for the various pure technetium compounds discussed earlier.

TABLE 3. Recommended data for anhydrous pertechnetates, halides, oxyhalides, and sulfides at 298 K.

Compound	Phase	ΔG_f^o in KJ/mol	ΔH_f^o in KJ/mol	S^o in J/mol-K
$KTcO_4$	Crystal	-919.2 ± 10.0	-1022.2 ± 5.5	164.78
$NaTcO_4$	Crystal	-877.0 ± 10.1	-	-
$HTcO_4$	Crystal	≈ -589.8 ± 10.5	-703.8 ± 9.6	≈126.3
TcF_6	High-T crystal	-	-	253.52 ± 0.25
TcF_6	Gas	-	-	371.28 ± 0.75
K_2TcCl_6	Crystal	-	-	333±4
TcO_3Cl	Gas	-	-	317.6
TcS_2	Crystal	≈ -216	≈ -224	≈71
TcS_3	Crystal	≈ -263	≈ -276	≈84
Tc_2S_7	Crystal	≈ -581	≈ -615	≈176

Thermal decomposition of NH_4TcO_4, in the presence of argon, or of $(NH_4)_2TcX_6$ ($X=Cl^-$ or Br^-)[166] yield material with the approximate composition $TcN_{0.75}$ or $TcN_{0.76}$.[29,67] Heating NH_4TcO_4 in NH_3 or argon-ammonia mixtures yields a nitride approaching stoichiometric TcN.[67] Several borides of Tc have also been reported: Tc_3B, Tc_7B_3, TcB, Tc_3B_4, and TcB_2.[29] None of these compounds have published ΔG_f^o or ΔH_f^o data. A bond dissociation energy of 561 ± 29 KJ/mol has been reported for TcC(g).[167]

Comments on Thermodynamic Stability and the Effects of Radiation

Thermodynamic data can be used to calculate the distribution of various compounds and ions of an element at thermodynamic equilibrium. However, in the presence of a significant radiation flux, Tc can undergo reactions not anticipated from thermodynamic considerations.

For example, Cobble et al.[168] noted that Tc metal is difficult to maintain in the zerovalent (metallic) state in moist air, and Cartledge's[78] study indicates that radiation probably participates in some of the reactions involving hydrous oxides/hydroxides on a metallic Tc surface. Tc atoms can be ionized by radiation and, in that state, are more prone to oxidation.

Under certain conditions radiation fluxes will increase the likelihood of oxidation. For example, Ferradini et al.[169] found that β decay of ^{99}Mo in H_2O produces mainly $^{99}TcO_4^-$ both in the presence and absence of air (even when the parent ^{99}Mo was originally in the +4 state). Lefort[73] found that γ -radiolysis caused aqueous $TcO_2 \cdot mH_2O$ to be oxidized predominantly to TcO_4^-. Cifka and Vesely[170] found Tc(IV) was unstable in neutral solutions, and was oxidized to TcO_4^- by γ -radiolysis. They also found that once O_2 is depleted, then radiolysis caused Tc to be reduced rather than oxidized.

Ianovici et al.[171-173] have done several studies with ^{95m}Tc. The internal conversion $^{95m}Tc \rightarrow {}^{95g}Tc$ for TcO_4^- in solution had chemical effects that depended on pH. At pH = 0.1 or 8, about 86% of the Tc remained as TcO_4^- whereas the rest was reduced. However, the amount of TcO_4^- remaining decreased to 35% at pH = 3.[173]

Internal conversion of ^{95m}Tc in the compounds $(NH_4)_2TcCl_6(c)$ or $K_2TcCl_6(c)$ produced little oxidation and only a few percent of TcO_4^- was found upon dissolution.[171,172] Self-radiolysis of these compounds in solution gave more extensive oxidation.[172]

If the radiation flux is reduced, then these systems should gradually return to thermodynamic equilibrium. However, thermodynamic calculations should be done with caution when this is not the case (e.g. concentrated nuclear reactor wastes).

DATA FOR AQUEOUS SOLUTIONS

General Comments

A large number of studies of the aqueous electrochemistry of Tc have been reported. These include acidic, basic, and neutral solutions, and in both noncomplexing and complexing media. Such varied techniques as polarography, radiopolarography, cyclic voltammetry, coulometry, and chronoamperometry have been applied. However, our understanding of these systems is far from complete. Several recent reviews summarize these data and illustrate the numerous conflicting claims in the literature.[20,147,174-177]

There are a number of reasons why the interpretation of this electrochemistry is so difficult. Nearly all of the electrochemical redox couples of Tc in noncomplexing and chloride containing solutions are thermodynamically irreversible, which makes it very difficult to extract meaningful thermodynamic data. Also, while some redox reactions are reversible in complexing media, the nature of the oxidized and reduced species involved usually are not known. Catalytic discharge of hydrogen sometimes interferes with the measurements, for example, when

$$Tc^{3+}(aq) + 3e^- = Tc^o(c)$$

is being studied in acidic solutions. In addition Hg(l), which is used as an electrode for most polarographic measurements, reduces TcO_4^- to lower valence species in acidic media. Because of these and other problems, electrochemical data must be used with caution. These problems will be discussed in more detail later.

Aqueous Pertechnetates and $HTcO_4$

The one case where unambiguous and accurate data exist in aqueous solution is for TcO_4^- salts. This is because data are available both for $Tc_2O_7(c)$ and $KTcO_4(c)$, and for the thermodynamics of their dissolution in H_2O.

$Tc_2O_7(c)$ dissolves in water according to the reaction

$$Tc_2O_7 + H_2O = 2TcO_4^-\ (aq) + 2H^+$$

to form pertechnetic acid. Its ionization constant is about 10^9, so it is as strong an acid as HBr.[147] Isopiestic activity measurements have been made for $HTcO_4$ solutions from 0.106 to 5.440 mol/kg.[178]

$Tc_2O_7(c)$ is yellow and dilute solutions of $HTcO_4(aq)$ are colorless. However, by about 5 mol/kg, $HTcO_4$ solutions are pink and the color darkens to red at higher concentrations. This red color is usually assumed to be due to $HTcO_4$, but Rulfs et al.[147] provided evidence that the color could be due to small amounts of TcO_4^{2-} or TcO_4^{3-}, which are produced by the reduction of TcO_4^- by H_2O or by dust particles in very acid solutions.

The aqueous TcO_4^- ion is tetrahedral with small perturbations due to close association with water molecules.[179] Rulfs et al.[147] found no evidence that TcO_4^- aggregates to form dimers or higher order clusters in 1 mol/l acid or base. Properties of crystalline TcO_4^- salts were discussed above.

Schwochau and Astheimer[180] measured the electrical conductivity of aqueous $KTcO_4$ at 298 K and obtained a limiting ionic conductance for $TcO_4^-(aq)$ of 55.5 ± 0.5 cm^2/ohm-equiv. This yields a tracer diffusion coefficient of $(1.48 \pm 0.01) \times 10^{-5}$ cm^2/s at 298 K. A more approximate ionic conductance of 47.2 ± 3.0 cm^2/ohm-equiv. at 291 K was obtained using electrophoresis.[181] These data are important since diffusion coefficients sometimes help in interpreting polarographic measurements.

Shvedov and Kotegov[181] used their electrophoresis measurements to calculate dissociation constants for pertechnetate ion pairs in aqueous solution

$$MTcO_4(aq) = M^+(aq) + TcO_4^-(aq)$$

They obtained $K_{diss} = 0.122 \pm 0.004$ mol/l for $KTcO_4$ and $K_{diss} = 0.23 \pm 0.03$ mol/l for $CsTcO_4$. Estimated activity coefficients were used so these are "thermodynamic constants." It is difficult to judge the accuracy of such calculated values, but the method did work fairly well (5%) for acetic acid. They claim agreement with a "theoretical value" from Cobble et al. for $KTcO_4$,[62] but Cobble et al. actually gave a solubility product and not K_{diss} so the agreement in numerical values was fortuitous.

As was mentioned above, Busey et al.'s[64] heat capacity data for $KTcO_4(c)$ yield $S^o[KTcO_4(c)] = 164.78$ J/mol-K. They also give the entropy of solution of $KTcO_4(c)$ as $\Delta S^o_{sol} = 135.3 \pm 1.3$ J/mol-K based on solubilities as a function of temperature. The "absolute" entropy of aqueous $KTcO_4$ is then

$$S^o[KTcO_4(aq)] = S^o[KTcO_4(c)] + \Delta S_{sol} = 300.1 \pm 1.3 \text{ J/mol-K} \qquad (13)$$

at 298 K. Subtracting the ionic entropy of K^+ (CODATA) gives $S^o[TcO_4^-(aq)] = 199.0 \pm 1.3$ KJ/mol.

Cobble et al.[62] determined the enthalpy of formation of $Tc_2O_7(c)$ to be -1113.4 ± 10.9 KJ/mol. Their enthalpy of solution for

$$Tc_2O_7(c) + H_2O(l) = 2HTcO_4(aq)$$

is -48.49 ± 0.33 KJ/mol. The enthalpy of formation of aqueous $HTcO_4$ can be obtained from the reaction

$$2Tc(c) + 7/2\ O_2(g) + H_2O(l) = 2HTcO_4(aq) \quad ,$$

so

$$\Delta H^o_{rxn} = 2\Delta H^o_f[HTcO_4(aq)] - 2\Delta H^o_f[Tc(c)] - 7/2\ \Delta H^o_f[O_2(g)] - \Delta H^o_f[H_2O(l)], \quad (14)$$

where $\Delta H^o_{rxn}[Tc(c)] = \Delta H^o_f[O_2(g)] = 0$ by definition. Thus,

$$\Delta H^o_{rxn} = 2\Delta H^o_f[HTcO_4(aq)] - \Delta H^o_f[H_2O(1)] \quad (15)$$

and $\Delta H^o_f[H_2O(1)] = -264.91$ KJ/mol from CODATA. However, it is also true that

$$\Delta H^o_{rxn} = \Delta H^o_f[Tc_2O_7(c)] + \Delta H^o_{sol} \;, \quad (16)$$

so $\Delta H^o_{rxn} = -1161.9 \pm 11.2$ KJ/mol, and

$$\Delta H^o_f[HTcO_4(aq)] = 1/2 \left\{ \Delta H^o_{rxn} + \Delta H^o_f[H_2O(1)] \right\} = -713.4 \pm 5.6 \text{ KJ/mol} \;. \quad (17)$$

Independent data by Gayer et al.[63] gives $\Delta H^o_{sol} = -45.6 \pm 1.3$ KJ/mol and $\Delta H^o_f[Tc_2O_7(c)] = -1127.6 \pm 7.9$ KJ/mol. For these data, $\Delta H^o_{rxn} = -1173.2 \pm 8.0$ KJ/mol and $\Delta H^o_f[HTcO_4(aq)] = -719.1 \pm 4.0$ KJ/mol.

For a standard-state thermodynamic-value additivity applies. That is,

$$\Delta H^o_f[HTcO_4(aq)] = \Delta H^o_f[H^+(aq)] + \Delta H^o_f[TcO_4^-(aq)] = \Delta H^o_f[TcO_4^-(aq)] \quad (18)$$

since $\Delta H^o_f[H^+(aq)] = 0$ by convention. The average of $\Delta H^o_f\ [TcO_4^-(aq)] = -716.3 \pm 4.5$ KJ/mol is accepted as the best value.

To calculate $\Delta G^o_f[TcO_4^-(aq)]$ requires ΔH^o_f and ΔS^o_f values. The ΔS^o_f for $TcO_4^-(aq)$ can be calculated from

$$S^o[TcO_4^-(aq)] = \Delta S^o_f[TcO_4^-(aq)] + S^o[Tc(c)] + 2S^o[O_2(g)] + S^o(e^-) \;, \quad (19)$$

where $S^o(e^-) = 65.29$ J/mol-K is the hydrogen value and is required to maintain consistency with the hydrogen-ion convention. Thus, $\Delta S^o_f[TcO_4^-(aq)] = -309.7 \pm 2.5$ J/mol-K and

$$\Delta G^o_f[TcO_4^-(aq)] = \Delta H^o_f[TcO_4^-(aq)] - T\Delta S^o_f[TcO_4^-\ (aq)] = -621.1 \pm 10.0 \text{ KJ/mol.} \quad (20)$$

Aqueous TcO_4^{2-}, $HTcO_4^-$, and H_2TcO_4

Most studies of the reduction of TcO_4^- in aqueous solutions indicate a $2e^-$ or $3e^-$ reduction to form a Tc(V) or Tc(IV) species. Under some conditions a $1e^-$ reduction occurs to form Tc(VI), which is unstable and rapidly disproportionates. The mode of reduction and decomposition usually suggested for alkaline solutions[182] is

$$TcO_4^- + e^- = TcO_4^{2-}$$

$$2TcO_4^{2-} = TcO_4^- + TcO_4^{3-}$$

and TcO_4^{3-} is also unstable. However, other variants for the alkaline solution disproportionation of TcO_4^{2-} include[183]

$$3TcO_4^{2-} + H_2O = 2TcO_4^- + TcO_3^{2-} + 2OH^-$$

Somewhat different reactions have been proposed for acidic solutions. One claim is that reduction in acidic solutions follows the mechanism[184]

$$TcO_4^- + 2H^+ + e^- = TcO_3 + H_2O$$

$$TcO_3 + e^- = TcO_3^-$$

$$TcO_3^- + 3H^+ + 2e^- = TcO(OH) + H_2O \quad .$$

An alternate claim for acidic solutions is the disproportionation mechanism[185]

$$2Tc(VI) = Tc(VII) + Tc(V)$$

$$2Tc(V) = Tc(VI) + Tc(IV) \quad .$$

Here Tc(VI) could be TcO_4^{2-}, $HTcO_4^-$, or H_2TcO_4, Tc(VII) is TcO_4^-, and the nature of Tc(IV) is uncertain. If TcO_4^{2-} were unprotonated, then the first reaction would be identical to the alkaline solution case. There is no concensus for the reduction mechanisms, and they are probably slightly different in acidic and basic media.

The isolation of a crystalline TcO_4^{2-} salt by Astheimer et al.[94] suggests that the Tc(VI) aqueous species could be TcO_4^{2-}. Their observation that this salt decomposed in moist air is concordant with the instability of TcO_4^{2-} in aqueous solution. Decomposition of this TcO_4^{2-} salt in neutral deaerated H_2O gave equal amounts of Tc(VII) and Tc(V) when the product was analyzed immediately after mixing.[95] This agrees completely with the above mechanisms for disproportionation of Tc(VI) in solution.

Evidence for this same structure for aqueous Tc(VI) is also available from the electrochemical reduction of TcO_4^- in alkaline solution. Kissel and Feldberg[182] found that the variation of the rate of disproportionation of Tc(VI) with ionic strength confirmed that the Tc(VI) species was doubly charged. Also, in basic solution, reduction of TcO_4^- with a pulsed electron beam had first order kinetics for both TcO_4^- and e^-,[186,187] which implies a $1e^-$ reduction is occurring. In addition, the species produced by electron beam reduction in alkaline solution had an absorption spectra[186,187] very similar to the crystalline TcO_4^{2-} salt.[94] Together, these studies provide convincing evidence that in aqueous alkaline solutions the Tc(VI) species is present as TcO_4^{2-}.

Hurst[186] and Deutsch et al.[187] noted that the absorption spectra of TcO_4^{2-} in alkaline media, produced by pulsed radiolysis with an electron beam, looked very different from Pikaev et al.'s[188] results by the same method in neutral solutions. Pikaev et al.[188] attributed spectral details to the successive protonation of TcO_4^{2-} to form $HTcO_4^-$ and H_2TcO_4. Their later,[185] more detailed study confirmed this and provides values for the dissociation constants of this acid.

Pihlar[184] found that the rate determining step for TcO_4^- reduction in acidic media was second order in hydrogen ion and suggested that the rate determining step involved

$$TcO_4^- + 2H^+ + e^- = TcO_3 + H_2O \quad .$$

However, it is known that TcO_4^{2-} protonates to form $HTcO_4^-$ and H_2TcO_4.[185,188] These species could be responsible for the observed rate law, rather than the deoxygenation reaction suggested by Pihlar.[184] We will assume that TcO_3 does not form in the following discussion, but this is a provisional assumption for very acid solutions. The only case where this distinction is important is in obtaining acid dissociation constants[185] of H_2TcO_4, since TcO_3 has no associated protons.

Further support for disproportionation of Tc(VI) to form Tc(V) and Tc(VII) comes from Crouthamel's[189] spectrophotometric study of the chemical reduction of TcO_4^- in H_2SO_4 solution. However, Crouthamel suggested that Tc(VI) also rapidly reacts with Tc(IV) to produce Tc(V):

$$\mathrm{Tc(VI)} + \mathrm{Tc(IV)} = 2\mathrm{Tc(V)}$$

with the slower subsequent reaction

$$3\mathrm{Tc(V)} = \mathrm{Tc(VII)} + 2\mathrm{Tc(IV)} \quad .$$

This indicates that the decomposition of Tc(VI) in acidic solution may be even more complex than assumed by other workers.

Rulfs et al.[147] and Majumdar et al.[190] suggested that the red color of concentrated $HTcO_4$ solutions may be due to formation of some H_2TcO_4 by reduction of $HTcO_4$ by H_2O or dust. A similar color was obtained as an intermediate stage of TcO_4^- reduction by hydrazine. They originally thought this was due to Tc(VI),[147] but later decided that Tc(V) was more likely.[190]

The TcO_4^{2-} ion is very short lived in aqueous solution under normal conditions. Hurst[186] and Deutsch et al.[187] found that in alkaline solutions it had a lifetime of at least 10 ms, but that noticeable reactions occur within 50 ms. Kissel and Feldberg[182] studied the decomposition kinetics of TcO_4^- in 0.001 to 0.10 mol/l NaOH and found the disproportionation to be slower at higher NaOH concentrations. Kruchkov et al.[185] studied this decomposition kinetics from about pH = −1 to +12, and they found the disproportionation rate had a maximum around pH = 8 to 9. The rate decrease above pH = 9 agrees with Kissel and Feldberg.[182] The rate of disappearance of TcO_4^{2-} was second order in TcO_4^{2-},[185] so disproportionation to Tc(V) and Tc(VII) is likely.

The disproportionation of TcO_4^{2-} is fairly rapid, so most standard electrochemical techniques do not observe the 1e$^-$ reduction of TcO_4^- to TcO_4^{2-}. Instead a 2e$^-$ or 3e$^-$ reduction of TcO_4^- is observed. However, Kissel and Feldberg[182] found that addition of small amounts of gelatin (≈0.005 weight %) to alkaline TcO_4^- kinetically blocks the decomposition of TcO_4^{2-} to TcO_4^{3-}, so the species TcO_4^{2-} lasts sufficiently long to be characterized electrochemically. By studying the number of electrons involved in the electrochemical reduction of TcO_4^- as a function of NaOH and of gelatin concentrations, they were able to demonstrate a switch from a 2e$^-$ to a 1e$^-$ reduction mechanism in neutral and basic solutions.

Several studies give values for the reduction potential for

$$TcO_4^- + e^- = TcO_4^{2-}$$

in aqueous basic solution. Most reduction potentials are reported vs. the saturated calomel electrode. In this and subsequent sections, all potentials cited were converted (if necessary) to reduction potentials vs. the normal hydrogen electrode (NHE), by using 0.242 V as the potential of the saturated calomel electrode vs. NHE.

Kissel and Feldberg[182] studied alkaline TcO_4^- using chronoamperometric methods. Without gelatin, reduction from TcO_4^- to TcO_4^{3-} occurs directly. When 0.005% or more gelatin was added, the mechanism shifts to a 1e$^-$ reduction. Their "apparent n" vs. step potential curves allow the

$$TcO_4^- + e^- = TcO_4^{2-}$$

quasi-reversible aqueous reduction potential in basic media to be estimated as being ≈ −0.63 ± 0.05 V at an ionic strength of $I = 1.0$.

A polarographic value of ≈ −0.52 V was obtained for this reduction potential in a NaOH-Na_2SO_4 solution at $I = 3.0$ (but they may have misidentified the reduction wave),[191] and ≈ −0.56 V for reduction in buffered alkaline media.[177] Spitsyn et al.[192] reported ≈ −0.60 V.

All of the above potential values are known only to one significant figure but do cluster around −0.6 V. A more detailed study of this potential was made by Hurst[186] and Deutsch et al.[187] using fast-scan cyclic voltammetry on a hanging-drop mercury electrode. Reduction curves are always present, but under normal conditions no reoxidation curve is seen since decomposition of TcO_4^{2-} is too rapid. In 1 mol/l NH_4OH no reoxidation was observed at any scan rate.

In NaOH solutions at low scan rates no reoxidation of TcO_4^{2-} is found, but at 100 V/s reoxidation is nearly complete in 0.12 mol/l aqueous NaOH.[186,187] In 1 mol/l NaOH[186] similar results are obtained, but results are less clearcut since the TcO_4^{2-} decomposition rate also seems to be enhanced. These same authors found that analysis of the cyclic voltammetry curves shows a $2e^-$ reduction at 1 V/s but a $1e^-$ process at 100 V/s. Thus, the fast scan potential is for the TcO_4^-/TcO_4^{2-} redox couple. They recommend a standard potential $E^o = -0.61$ V in 0.12 mol/l NaOH. Since their 1.0 mol/l curve seems to give the same value, this was assumed equal to the $I = 0$ value.

This potential of -0.61 V yields

$\Delta G^o_{rxn} = 58.9 \pm 1.7$ KJ/mol for the reaction

$$TcO_4^-(aq) + e^-(aq) = TcO_4^{2-}(aq) \quad .$$

However, this value is also equal to

$$\Delta G^o_{rxn} = \Delta G^o_f[TcO_4^{2-}(aq)] - \Delta G^o_f[TcO_4^-(aq)] \ . \qquad (21)$$

Therefore,

$$\Delta G^o_f[TcO_4^{2-}(aq)] = -562.2 \pm 10.0 \text{ kJ/mol}$$

using our recommended value for TcO_4^-, and assuming the redox potential was uncertain by 0.02 V.

Krychkov et al.[185] studied the absorption spectra of TcO_4^{2-}, produced by electron-beam pulsed radiolysis, at various pH values. Dissociation constants for H_2TcO_4 were obtained for these data. For aqueous

$$HTcO_4^- = TcO_4^{2-} + H^+$$

they found $pK_2 = 8.7 \pm 0.5$. Then,

$$\Delta G_f^0[\mathrm{HTcO_4^-(aq)}] = \Delta G_f^o[\mathrm{TcO_4^{2-}(aq)}] + RT \ln K_2 = -611.9 \pm 10.5 \text{ KJ/mol} , \qquad (22)$$

where $\Delta G_f^o[\mathrm{H^+(aq)}] = 0$ by convention.

A similar calculation can be done for the first acid dissociation of H_2TcO_4:

$$\mathrm{H_2TcO_4 = H^+ + HTcO_4^-}$$

for which they[185] roughly estimated $pK_1 = 0.3 \pm 0.8$. This gives

$$\Delta G_f^0[\mathrm{H_2TcO_4(aq)}] = \Delta G_f^o[\mathrm{HTcO_4^-(aq)}] + RT \ln K_1 = -613.6 \pm 12.1 \text{ KJ/mol} , \qquad (23)$$

which is well within the experimental uncertainty of $\Delta G_f^o[\mathrm{HTcO_4^-(aq)}] + \Delta G_f^o[\mathrm{H^+(aq)}]$. Thus, (as for H_2SO_4) the first acid dissociation can be treated as nearly complete.

Aqueous TcO_4^{3-} and Other Aqueous Tc(V) Species

It was noted in the section on solid Tc(V) oxyhalide salts that the $TcOCl_4^-$ and $TcOCl_5^{2-}$ anions can be isolated from the products of reduction of TcO_4^- by concentrated HCl. This suggests that aqueous solutions of Tc(V) in noncomplexing media could contain TcO^{3+} and its various hydrolysis products: $TcO(OH)^{2+}$, $TcO(OH)_2^+$(or TcO_2^+), $TcO(OH)_3^o$ [or $TcO_2(OH)^o$], and possibly dimeric or polymeric species. Several of these species were previously suggested by Bratu et al.,[183] but no thermodynamic data are available for any of them. "Strong hydrolysis" of $TcOCl_5^{2-}$ was reported for H^+ concentrations below 3.15 mol/l.[193]

All of these Tc(V) cationic and neutral aqueous species seem to be unstable with regard to formation of Tc(VII) and Tc(IV). In the section on solid ternary oxides it was noted that while Tc(VII), Tc(VI), and Tc(IV) predominate, formation of Tc(V) double oxides can sometimes occur in the solid state. A number of ligand substituted oxytechnetium (V) complexes have been prepared which are possibly related to the hydrolyzed Tc(V) species in aqueous solutions.

These complexes contain cores of either TcO^{3+} (or its dimer $Tc_2O_2^{6+}$), trans-TcO_2^+, or $Tc_2O_3^{4+}$.[160,194]

For electrolytic reduction of TcO_4^- in acidic media, a $3e^-$ or $4e^-$ reduction is usually observed which produces a Tc(IV) or Tc(III) species. In neutral or basic solution, the reduction involves $2e^-$ or $3e^-$ depending on conditions. This case will concern us in this section since we are interested in Tc(V).

Miller et al.[195] obtained the same value for the

$$Tc(VII) + 2e^- = Tc(V)$$

reduction potential in 0.1 mol/l NaOH, alkaline KCl, and NH_4Cl. Similarly, Astheimer and Schwochau[196] studied this reduction potential in 0.1, 0.5, and 1.0 mol/l NaOH, and also LiCl solutions at these same concentrations. While the reduction potentials depended on ionic strength, they were essentially equal in the NaOH and LiCl solutions at the same ionic strength. Likewise, Bratu et al.[183] obtained identical reduction potentials for 0.1 mol/l KOH, NaOH, or KCl, and also for 1 mol/l $NaClO_4$. Russell and Cash[177] likewise found that this reduction potential was pH independent. These studies indicate that no hydrogen ions participate in the $2e^-$ reduction of TcO_4^- in nonacidic solutions. Thus, the reaction is

$$TcO_4^- + 2e^- = TcO_4^{3-}$$

Zhdanov et al.[191] studied the polarographic reduction of TcO_4^- in acidic, neutral, and basic Na_2SO_4 solutions. The number of electrons involved in the reduction changed from three in neutral and acidic solutions to two "one-electron" waves in alkaline solutions (they seem to have misidentified the first alkaline solution wave). They suggested that Tc(V) combines with fewer oxygen atoms to produce this effect. However, for NaOH concentrations of 6×10^{-3} mol/l and above, no shift in the reduction potential of the first wave occurred with increasing NaOH concentration (i.e. it is pH independent). This agrees with the 4 studies cited in the previous paragraph, and supports TcO_4^{3-} as the Tc(V) species present. Solid Li_3TcO_4 [70] has been prepared, but it is not known whether this TcO_4^{3-} has the same structure as the aqueous species.

TcO_4^{3-} in aqueous nonacidic solutions disproportionates by

$$2TcO_4^{3-} = TcO_4^{2-} + Tc(IV) \quad .$$

As noted earlier, TcO_4^{2-} is also unstable and disproportionates to form TcO_4^{3-} and TcO_4^-. Thus, ultimately TcO_4^{3-} is converted to TcO_4^- and Tc(IV). Because of these complicated reactions, the TcO_4^-/TcO_4^{3-} redox couple is found to be irreversible when investigated by standard electrochemical methods. The overall disproportionation reaction seems to be[183]

$$3TcO_4^{3-} = TcO_4^- + 2Tc(IV) \quad .$$

The $1e^-$ reduction of TcO_4^- to TcO_4^{2-} was also found to be irreversible by standard electrochemical methods, but it became reversible when fast-scan cyclic voltammetry was used.[186,187] The same procedure does not work for TcO_4^-/TcO_4^{3-}, since under fast-scan conditions the $2e^-$ irreversible reduction switches to a $1e^-$ reversible reduction. However, since the chemical nature of TcO_4^{3-} is very similar to TcO_4^-, except for charge, the $2e^-$ reduction potential may possibly give valid thermodynamic data.

There are numerous determinations of the TcO_4^-/TcO_4^{3-} reduction potential,[21,53,95,177,182,183,186,195-198] and they are summarized in Table 4. All of these reduction potentials (except for Kuzina et al.'s[197] which is too high) were fitted to the least-squares equation

$$E(I) = E^o(I = 0) + A\sqrt{I} \quad . \tag{24}$$

Best values are E(I = 0) = −0.600 V, A = 0.0639, with a standard deviation of 0.026 V. Magee et al.[199] obtained a slightly more negative reduction potential in 2 mol/l NaOH, but they thought it was for a $3e^-$ reduction. Salaria et al.'s point[200] of −0.57 V at pH = 13 agrees with the results of Table 4, but they likewise attributed it to a $3e^-$ reduction.

TABLE 4. Two electron reduction potentials of TcO_4^- to TcO_4^{3-}.

Potential, V vs NHE	Ionic strength	Media	Reference
-0.61	0.10	KOH	Colton et al.[53]
≃ -0.56	0.1	NaOH, NH_4Cl, or alkaline KCl	Miller et al.[195]
-0.55	?	pH = 10 borate buffer	Miller et al.[195]
-0.63	1.0	$NaClO_4$ + KOH	Kuzina et al.[197]
-0.571	0.1	NaOH	Astheimer and Schwochau[196]
-0.534	0.5	NaOH	Astheimer and Schwochau[196]
-0.518	1.0	NaOH	Astheimer and Schwochau[196]
-0.575	0.1	LiCl	Astheimer and Schwochau[196]
-0.541	0.5	LiCl	Astheimer and Schwochau[196]
-0.535	1.0	LiCl	Astheimer and Schwochau[196]
-0.568	0.6	0.5 $NaClO_4$ +0.1 NaOH	Münze[198]
≃ -0.55	1.0	NaOH	Kissel and Feldberg[182]
-0.56	0.1	NaOH, KOH, KCl, or $LiClO_4$	Bratu et al.[183]
-0.60	0.05	$(C_2H_5)_4NClO_4$	Astheimer and Schwochau[95]
-0.56	≃0.1	pH = 13 KOH	Russell and Cash[177]
≃ -0.58	0.5	KCl-NaOH	Grassi et al.[21]
≃ -0.56	0.12	KOH	Hurst[186]

This least-squares potential at I = 0 yields ΔG^o_{rxn} = 115.8 ± 5.0 KJ/mol for

$$TcO_4^- + 2e^- = TcO_4^{3-}$$

and

$$\Delta G^o_f[TcO_4^{3-}(aq)] = \Delta G^o_f[TcO_4^-(aq)] + \Delta G^o_{rxn} = -505.3 \pm 11.2 \text{ KJ/mol} \quad . \qquad (25)$$

TcO_4^{3-} is the fully dissociated form of the possibly hypothetical acid H_3TcO_4, but no dissociation constant data are available for it.

In the discussion of TcO_4^{2-}, it was noted that the disproportionation reaction

$$2TcO_4^{2-} = TcO_4^- + TcO_4^{3-}$$

appears to occur rapidly and extensively. For this reaction,

$$\Delta G^o_{rxn} = \Delta G^o_f[TcO_4^-(aq)] + \Delta G^o_f[TcO_4^{3-}(aq)] - 2\Delta G^o_f[TcO_4^{2-}(aq)] \qquad (26)$$

$$= -2.0 \pm 12 \text{ KJ/mol}$$

and

$$K = \frac{[TcO_4^-][TcO_4^{3-}]}{[TcO_4^{2-}]^2} = 2.2 \quad . \qquad (27)$$

This K value is uncertain by about 2 orders of magnitude. Since TcO_4^{3-} also decomposes, this value may be reasonable.

It has been suggested that in acidic solutions, TcO_4^{3-} decomposes by the reaction[198]

$$TcO_4^{3-} + 2H^+ = TcO_3^- + H_2O \quad .$$

No thermodynamic data are available for TcO_3^- to check this assumption.

The emf data for reduction of TcO_4^- in alkaline media indicate the 1e$^-$ and 2e$^-$ processes have nearly identical redox potentials. That the 2e$^-$ process is usually observed owes more to kinetics than thermodynamics.

In addition, a catalytic H_2O_2 polarographic wave can occur in the same[201] potential region.

Polarography, Coulometry, and the Identification of Tc Aqueous Species

Polarography and controlled-potential coulometry provide methods for determining the number of electrons involved in an electrolytic reduction or oxidation. Together with the observed dependence (or lack of a dependence) of this process on pH, the chemistry of the species involved can be deduced. For example, a pH independent $2e^-$ reduction of TcO_4^- in aqueous alkaline media clearly would correspond to the formation TcO_4^{3-}. Unfortunately, unambigious results are rarely available for aqueous Tc species.

Some of the difficulties have already been described. For examples, virtually all of the aqueous redox processes involving Tc are irreversible, product disproportionation or reaction with water frequently occurs, catalytic discharge of H_2 sometimes occurs close to Tc reduction waves, and conflicting claims are sometimes made about the number of electrons involved in a particular redox process. Attempts to determine the number of electrons involved in a reduction process by polarography and controlled potential reduction sometimes give different values at the same reduction potential.

Differences between the two methods have been attributed either to absorption phenomena[21] on the electrode surface, or to polarography and coulometry sometimes seeing different reactions due to different time scales.[202,203] For example, aqueous TcO_4^- can be reduced by $2e^-$ to form TcO_4^{3-} in basic solutions as indicated by polarography. In contrast, if controlled potential coulometry is used, then a $3e^-$ reduction is observed at the same potential. However, TcO_4^{3-} is unstable with regard to disproportionation to TcO_4^- and Tc(IV) as noted earlier. Under controlled potential conditions this "new" TcO_4^- would then be reduced to TcO_4^{3-}, etc., with all of the TcO_4^- eventually ending up as Tc(IV). Thus, the different methods have different time scales and so observe different reactions.

These differences agree with Crouthamel's potentiometric reduction of TcO_4^- in 12 mol/l H_2SO_4 with Ti(III).[189] Rapid titration gave potential breaks corresponding to formation of both Tc(V) and Tc(IV). However, if the titration was interrupted before the second end point, the potential would then increase for about one hour. By doing this at several points during the titration process (equivalent to a very slow titration), a titration curve was obtained with a single break at Tc(IV). These are clearly the potentiometric titration equivalents of polarography and controlled potential coulometry.

Controlled potential coulometry indicates a $4e^-$ reduction of TcO_4^- in neutral and acidic solution. In basic solutions $3e^-$ or $4e^-$ can occur, with $3e^-$ usually obtained for potentials of −0.5 to −0.6 V, and $4e^-$ for more negative potentials. These coulometric data have been tabulated by Russell and Cash.[177] They also tabulate conflicting polarographic results as to whether the reduction in base at −0.6 V involves $2e^-$ or $3e^-$, and whether the −0.8 to −0.9 V peak involves $3e^-$ or $4e^-$.

It is well known that in acid solution TcO_4^- can be reduced by metallic Hg to form lower valence Tc species, with the reduction ultimately proceeding to Tc metal at longer contact times.[21,191,197,203,204] Similar results have been reported in HCl, $HClO_4$, and H_2SO_4 solutions, and the reaction rate seems to increase with increased acidity. Prolonged contact with Hg(l) can yield solutions that show only Hg^{2+} polarographic waves. Polarographic waves are usually measured with dropping mercury electrodes. Thus, in acidic solutions, some prereduction of Tc by Hg can occur, which further complicates the interpretation of results.

Aqueous TcO^{2+}, $TcO(OH)^+$, $TcO(OH)_2^o$, $[TcO(OH)_2^o]_2$, Colloidal TcO_2, and Other Tc(IV) Species

Important information about the valence of Tc in aqueous solutions can sometimes be obtained by examining compounds that precipitate when their solubility limits have been exceeded. Salaria et al.[200,203] found that a $3e^-$ reduction of TcO_4^- in acidic solution produced "TcO_2" for initial pH values of −0.3 to 2.0. Mazzocchin et al.[205] produced $TcO_2 \cdot 2H_2O$ by coulometric reduction of TcO_4^- above pH = 3. These compounds are probably identical and equivalent to Carteledge's[78] $Tc(OH)_4$ (diffraction data cannot tell any difference since they are amorphous). This same substance was also obtained by adding base to electrolytically reduced TcO_4^-.[147]

$TcO_2 \cdot 2H_2O$ can also be produced by raising the pH of very acidic solutions of Tc(IV). Spitsyn et al.[45] found that the Tc(IV) spectra changed above pH = 4 and $TcO_2 \cdot 2H_2O$ precipitated. Likewise, Paquette et al.[206]

reported that reduction of TcO_4^- above pH = 4 also produced $TcO_2 \cdot 2H_2O$, as did Owunwanne et al.[74] by hydrolysis of Tc(IV). There is little doubt that Tc(IV) is produced by reduction of TcO_4^- in acidic solution, and that $TcO_2 \cdot 2H_2O$ precipitates above pH = 3 or 4.

As discussed earlier, salts of the type TcX_6^{2-} ($X = Cl^-$, Br^-, I^-, or F^-) are well known in the solid state and in aqueous solution. Koyama et al.[207] and Kanchiku[208] have studied the aquation (replacement of Cl^- by H_2O) of $TcCl_6^{2-}$ salts in aqueous HCl solutions. $TcCl_6^{2-}$ salts are kinetically inert in the dark but undergo aquation when exposed to visible or UV light. The extent of aquation depends on HCl concentration. Species separated by ion-exchange are $TcCl_6^{2-}$, $Tc(H_2O)Cl_5^-$, $Tc(H_2O)_2Cl_4^o$, and $Tc(H_2O)_3Cl_3^+$. The first two ions were characterized both in terms of charge and Tc/Cl ratio. The neutral species and the cation were characterized in terms of charge, but they could not be removed from the ion-exchange resin without decomposition. That is, the experiments could not tell $Tc(H_2O)_2Cl_4^o$ from $Tc(H_2O)_2(OH)Cl_3^o$, etc. These aquo-type complexes seem to exist only in complexing media. In weakly complexing or noncomplexing media, hydrolysis is quite extensive. In fact, Koyama et al.[207] suggested that

$$Tc(H_2O)Cl_5^- = Tc(OH)Cl_5^{2-} + H^+$$

could occur subsequent to the aquation of $TcCl_6^{2-}$.

At pH values of about 1 to 3, there is strong evidence for the nature of hydrolyzed Tc(IV) in aqueous solution. Gorski and Koch[75] studied the electrophoretic mobility of Tc(IV) in KNO_3 solutions and found sharp decreases around pH = 1.3 and 2.15. The mobility decreased to zero about pH = 2.2. This decrease to zero probably corresponds to formation of a neutral species, and the two previous breaks to stepwise hydrolysis. That is,

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+$$

and

$$TcO(OH)^+ + H_2O = TcO(OH)_2^o + H^+$$

are the probable reactions. As noted above, TcO^{2+} and $Tc(OH)_2^{2+}$ cannot be distinguished by these methods.

Owunwanne et al.[74] studied the charge on Tc(IV) prepared by Sn^{2+} reduction of TcO_4^- in perchlorate solutions using ion-exchange techniques. For $2.0 > pH > 1.1$ they verified that the overall charge on Tc(IV) was 2+. By pH = 2.2, however, the slope of the distribution curve changed owing to further hydrolysis. Spitsyn et al.[45] studied the brown solution formed from the dissolution of $TcO_2 \cdot 2H_2O$ in H_2SO_4 solutions. The solution species was not colloidal and had a charge of 2-. Its probable formula was $Tc(OH)_2(SO_4)_2^{2-}$. The ionized form of this would contain the $Tc(OH)_2^{2+}$ or TcO^{2+} ion. Sundrehagen[76] saw no evidence for TcO^{2+} in his optical density study of Tc(IV) for pH $\geq$ 1.3, but this is the region where further hydrolysis of TcO^{2+} is starting to occur.

Three studies provide both qualitative and quantitative information about the additional hydrolysis of TcO^{2+}. These are the electrophoresis study of Gorski and Koch,[75] the solvent extraction study of Guénnec and Guillaumont,[209] and Sundrehagen's[76] absorption spectra study. They lead to the stepwise hydrolysis mechanism

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2^o + H^+$$

$$2TcO(OH)_2^o = [TcO(OH)_2^o]_2 \quad .$$

Sundrehagen[76] found no evidence for trimer formation.

Lefort[73] reported that the solubility of $TcO_2 \cdot 2H_2O$ was approximately 5×10^{-4} mol/l in 0.05 and 0.5 mol/l H_2SO_4. We earlier concluded that $TcO_2 \cdot 2H_2O$ precipitates by pH = 3 or 4. Below pH = 3 or 4, concentrations exceeding the solubility can exist as colloidal material. Noll et al.[210] found that 10^{-2} mol/l Tc(IV) exists predominately as a colloid above pH = 0.5 (this is much above Lefort's[73] solubility).

Thus the following picture has emerged for the hydrolysis of Tc(IV). For pH about 1.5 and less, Tc(IV) exists predominately as TcO^{2+}. Between pH = 1.5 and 2.2, TcO^{2+} hydrolyzes further to form $TcO(OH)^+$ and $TcO(OH)_2^o$. By pH = 2.7 most of the Tc(IV) exists as $TcO(OH)_2^o$ or $[TcO(OH)_2^o]_2$, and above pH = 3 or 4 $TcO_2 \cdot 2H_2O$ precipitates. Below pH = 3 to 4, Tc(IV) exists as a colloid if the solubility limit is exceeded. It is possible (but not established) that a Tc^{4+} aquo ion could exist if $[H^+]$ is several mol/l.

It was previously noted that a $2e^-$ reduction of TcO_4^- to TcO_4^{3-} occurs in aqueous alkaline solution at about -0.6 V. There are a few claims that a $3e^-$ polarographic reduction can also occur in neutral and alkaline media at nearly this same potential.[20,174,177] Some of these same authors also observed the $2e^-$ reduction at this potential under very similar conditions. However, in alkaline solutions controlled potential coulometry gives $3e^-$, whereas it gives $4e^-$ for neutral and acidic solutions. At this potential[177] our analysis of polarographic data indicates a $2e^-$ reduction of TcO_4^- to TcO_4^{3-}, with the $3e^-$ reduction being rendered unlikely under these conditions on kinetic grounds (although it can occur in coulometry).

In neutral and basic solutions (and occasionally even in acidic solutions) a second polarographic reduction wave is usually observed between -0.7 and -0.9 V, with the potential depending more on ionic strength than pH. Unfortunately, this wave is very ill-defined compared to most polarographic waves and consequently harder to characterize. Its potential can rarely be estimated to better than 0.1 V. The first reduction wave of TcO_4^- will be discussed later.

There is some controversy as to the polarographic reduction processes involved with the -0.7 to -0.9 V TcO_4^- reduction wave in alkaline media. Some workers claim that a $3e^-$ reduction occurs to form Tc(IV).[21,176,196,202] In contrast, other workers claim this reduction involves $4e^-$ to form Tc(III).[200,203] However, the workers who thought that the reduction was to Tc(III) also claimed the first reduction wave at ≈ -0.6 V was to Tc(IV), and not to Tc(V) as concluded here. Magee et al.[199] also thought the first wave was a $3e^-$ reduction, but could not identify the second wave. Controlled potential coulometry indicates a $4e^-$ reduction at -0.7 to -0.9 V in alkaline media, but the time scale is much longer than for polarography. We tentatively conclude that the -0.7 to -0.9 V polarographic wave involves reduction of TcO_4^- to Tc(IV) aqueous species. For acidic media, there are also claims of a $7e^-$ reduction of TcO_4^- directly to the metal at ≈ -0.7 V.[177]

There are other conflicting claims that this polarographic alkaline solution wave actually corresponds to a 1e$^-$ reduction of Tc(V), which had formed by the 2e$^-$ reduction of TcO_4^- at ≈ −0.6 V.[53] Alternately, Russell and Cash[177] found the second wave could correspond to 3 to 5e$^-$ reductions of TcO_4^- depending on system characteristics.

We have noted that for a pH of 3 or 4 and above, $TcO_2 \cdot 2H_2O$ precipitates from solutions of Tc(IV). For the polarographic wave at −0.7 to −0.9 V, a 3e$^-$ reduction of TcO_4^- in alakline solution would give $TcO_2 \cdot 2H_2O$ directly as the thermodynamically stable product. However, Cartledge and Smith[77] found the $TcO_4^-/TcO_2 \cdot 2H_2O$ cell to be very slow to reach equilibrium in acidic solution, and a similar situation might be true in basic solution. That is, because of slow kinetics it is not clear what form of Tc(IV) this 3e$^-$ reduction corresponds to.

Several obvious possible reduction schemes for the second wave include direct reduction[21,191]

$$TcO_4^- + 3e^- + 2H_2O = TcO_2\downarrow + 4OH^-$$

Alternately, reduction could occur by

$$TcO_4^- + 3e^- = TcO_4^{4-} \quad ,$$

to be followed later by

$$TcO_4^{4-} + H_2O = TcO_3^{2-} + 2OH^- \quad ,$$

and then

$$TcO_3^{2-} + H_2O = TcO_2\downarrow + 2OH^- \quad .$$

Another possibility is that this second wave represents[198]

$$TcO_4^{3-} + e^- + H_2O = TcO_3^{2-} + 2OH^- \quad ,$$

where the TcO_4^{3-} would be formed during the first reduction wave. Since the reduction mechanism is uncertain, and the second reduction wave poorly defined, no attempt will be made to extract thermodynamic data from it.

For want of better data, Lefort's approximate solubilities[73] of $TcO_2 \cdot 2H_2O$ will be analyzed to yield the solubility product. Since the least hydrolyzed form of Tc(IV) was found to be TcO^{2+}, we will express the solubility of $TcO_2 \cdot 2H_2O$ in terms of it by the equation

$$TcO_2 \cdot 2H_2O(am) = TcO^{2+} + 2OH^- + H_2O(1) \quad .$$

The solubility product is then given by

$$K_s = \frac{[TcO^{2+}][H_2O][OH^-]^2}{[TcO_2 \cdot 2H_2O]} = [TcO^{2+}][H_2O][OH^-]^2 \quad . \tag{28}$$

Lefort measured the total solubility of Tc(IV) in 0.05 and 0.5 mol/l H_2SO_4 solutions to be approximately 5×10^{-4} mol/l.[73] This is a total solubility, S, and is due to a number of species present:

$$S = [TcO^{2+}] + [TcO(OH)^+] + [TcO(OH)_2^o] + [(TcO(OH)_2)_2^o] \tag{29}$$
$$+ [\text{colloidal material}] + [\text{sulfate complexes}] \quad .$$

Colloidal material is known to be present in acidic solutions of Tc(IV) above its solubility limit, but is it not known whether any was present in Lefort's solutions. Its presence must be neglected for want of better information.

Gorski and Koch[75] studied the hydrolysis of TcO^{+2} at an ionic strength of 0.1 mol/l using electrophoresis. The first hydrolysis step

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+$$

had a hydrolysis constant of

$$K_{h1} = \frac{[TcO(OH)^+][H^+]}{[TcO^{2+}][H_2O]} = (4.3 \pm 0.4) \times 10^{-2} \quad . \tag{30}$$

For the second hydrolysis step,

$$TcO(OH)^+ + H_2O = TcO(OH)_2^o + H^+$$

and the hydrolysis constant is given by

$$K_{h2} = \frac{[TcO(OH)_2^o][H^+]}{[TcO(OH)^+][H_2O]} \quad . \tag{31}$$

Three determinations of K_{h2} have been made, Guénnec and Guillaumont[209] obtained ≈0.1 by liquid extraction. Gorski and Koch[75] obtained $K_{h2} = (3.7 \pm 0.4) \times 10^{-3}$ in 0.1 KNO_3 mol/l solution. A similar value of $K_{h2} = (9.3 \pm 2.0) \times 10^{-3}$ in 0.2 mol/l $HClO_4$ + $NaClO_4$ was reported by Sundrehagen.[76] These latter two values[75,76] appear to be the more reliable and were accepted for subsequent calculations. Extrapolations to infinite dilution, or to any other ionic strength, were made with Helgeson's B-dot approach,[211] which is a modification of the Åkerlöf-Thomas rule.[212] A constant ion-size of 3.65 Å was assumed for all Tc ions since no experimental values are available.

The dimerization reaction

$$2TcO(OH)_2^o = [TcO(OH)_2^o]_2$$

was also studied by Sundrehagen[76] who obtained

$$K_d = \frac{[(TcO(OH)_2)_2^o]}{[TcO(OH)_2^o]^2} = (3.14 \pm 0.28) \times 10^6 \quad .$$

This value will be assumed to be independent of ionic strength since both species involved are neutral.

Sulfate complexes are known to form for TcO^{2+},[45] but unfortunately no quantitative data are available. The stability constants of simple divalent metal sulfates MSO_4 have very similar values. A similar situation may occur for $MOSO_4$ salts also. Consequently, data for $RuOSO_4$ were used to estimate the stability constant K_{ip} for $TcOSO_4$ in H_2SO_4 solutions.[213]

The solubility calculation requires values of $[OH^-]$ and $[SO_4^{2-}]$ for the two H_2SO_4 solutions. They were taken from Wirth[214] who reported free sulfate concentration in H_2SO_4 solutions (graphically), and also free H^+ concentrations.

The total solubility in these H_2SO_4 solutions is then given by the complicated expression

$$S = \frac{K_s}{[H_2O][OH^-]^2} + \frac{[SO_4^{2-}]}{[H_2O][OH^-]^2} K_{ip}K_s + \frac{K_sK_{h1}}{K_w[H_2O][OH^-]} + \frac{K_sK_{h1}K_{h2}}{K_w^2[H_2O]} + \frac{K_s^2K_{h1}^2K_{h2}^2K_d}{K_w^4[H_2O]^4} \quad , \tag{33}$$

where $K_w = 10^{-14}$ is the ionization constant for H_2O. Lefort's data[73] then yield $K_s = 2.6 \times 10^{-31}$ (3.2×10^{-30} if sulfate complexes are neglected) for 0.05 mol/l H_2SO_4. In 0.5 mol/l H_2SO_4, $K_s = 7.5 \times 10^{-33}$ (1.3×10^{-31} neglecting sulfate complexes). Extrapolation to infinite dilution and averaging gives

$$\mathrm{Log}_{10}K_s^o = -33.45 \pm 1.0 \quad .$$

Allard et al.[15] used Pourbaix's correlation of solubilities with hydrolysis constants to estimate

$$\log_{10}K_s^o \approx -31 \quad .$$

The agreement of experimental and estimated values is fairly reasonable, so their average of -32.2 ± 1.3 will be accepted as the best current estimate.

For the solution reaction,

$$TcO_2 \cdot 2H_2O = TcO^{2+} + H_2O + 2OH^-$$

the free energy change is given by

$$\Delta G^o_{sol} = \Delta G^o_f[TcO^{2+}(aq)] + \Delta G^o_f[H_2O(1)] + 2\Delta G^o_f[OH^-(aq)]$$

$$- \Delta G^o_f[TcO_2 \cdot 2H_2O(am)] = \Delta G^o_f[TcO^{2+}(aq)] + 284.4 \quad , \qquad (34)$$

where CODATA values were used for H_2O and OH^-, and $TcO_2 \cdot 2H_2O(am)$ was obtained earlier. However, we also know

$$\Delta G^o_{sol} = -RT \ln K_s$$

$$= 183.8 \pm 7.4 \text{ KJ/mol}$$

from the above solubility data. Thus,

$$\Delta G^o_f[TcO^{2+}(aq)] = -100.6 \pm 10.5 \text{ KJ/mol} \quad .$$

Using hydrolysis constant data extrapolated to infinite dilution and dimerization constant data allows free energies of formation to be calculated for other Tc(IV) species. Results are $\Delta G^o_f[TcO(OH)^+(aq)] = -331.3 \pm 10.5$ KJ/mol, $\Delta G^o_f[TcO(OH)^o_2(aq)] = -556.0 \pm 10.5$ KJ/mol, and $\Delta G^o_f[(TcO(OH)^o_2)_2(aq)] = -1149.2 \pm 21.3$ KJ/mol.

A more detailed study of the solubility of $TcO_2 \cdot 2H_2O$ would be very desirable since it would provide more accurate data for all of the Tc(IV)aqueous species. This study should be made in noncomplexing media to avoid corrections for sulfate complexes.

Aqueous Tc^{3+}, TcO^+, Tc^{2+}, and other Lower Valence Tc Species

As noted above, polarographic reduction of TcO_4^- in aqueous acidic solutions is generally reported to involve an initial $3e^-$ or $4e^-$ reduction. This polarographic reduction wave is pH-dependent and irreversible. A second irreversible reduction is usually observed that is pH-independent, and it is generally considered to correspond to formation of metallic Tc. A very large catalytic wave occurs almost immediately after the second wave.

Controlled potential coulometry of TcO_4^- in neutral and acidic solutions indicates a $4e^-$ reduction process at the potential of the first polarographic wave, whereas a $3e^-$ reduction is usually observed in base.[177] However, when phosphates or polyphosphates are present, reduction to Tc(II) species can occur owing to complex formation.[215] Mixed valence polymers of Tc(3.5) form by $SnCl_2$ reduction of TcO_4^- in DTPA.[216]

In noncomplexing media very little is known about aqueous Tc(II) except that it is unstable. Armstrong and Taube[217] reported formation of a pink transient (several seconds) species formed by reduction of TcO_4^- by Eu^{2+} in very acidic media. They attributed this color to unstable, and possibly polymeric, Tc(II). Solid state compounds of Tc(I), Tc(II), and Tc(III) are well known.[9,194,218] However, these valence states are stabilized only when electron donating groups such as phosphine, nitrosyl, or thiocyanate are present. K_2TcI_3 was mentioned earlier, but it decomposes in aqueous solution.

Earlier, salts containing $Tc_2Cl_8^{3-}$, $Tc_2Br_8^{3-}$, $Tc_2Cl_8^{2-}$, $Tc_2Br_8^{2-}$, $Tc_2Cl_6^{2-}$, $Tc_2Br_6^{2-}$, $TcBr_2$, and TcI_2 were mentioned. They contain Tc with average formal valencies of +2.5, +3, or +2. These salts can exist in concentrated aqueous hydrohalic acid solutions only under very reducing conditions. Of these lower valence states, only Tc(III), appears to be a significant species for aqueous noncomplexing solutions. Russell[176] has suggested that unstable Tc(I) and Tc(II) species could be involved in catalytic hydrogen evolution. Thus Tc(I) and Tc(II), if they form, either rapidly reduce water or rapidly disproportionate.

Salaria et al.[200] found that $4e^-$ coulometric reduction of TcO_4^- occurred in 1 mol/l H_2SO_4 (pH = -0.3) and produced a black precipitate. However, in HCl-KCl mixtures at pH = 1 to 2, a $4e^-$ coulometric reduction at -0.5 or -0.3 V formed a green solution. Elsewhere, these authors reported[203] that suspended "TcO_2" could not be further reduced by varying the potential. However, if the initial reduction was done at more negative potentials then a brown-black suspension of "Tc_2O_3" was obtained. Rulfs et al.[147] reduced TcO_4^- in 1 mol/l H_2SO_4 coulometrically below the +4 state. But, when base was added, $TcO_2 \cdot 2H_2O$ precipitated and not Tc_2O_3.

Pihlar[184] noted that solid, hydrolyzed Tc(III) could be TcO(OH), $Tc(OH)_3$, or Tc_2O_3. To these possibilities can be added hydrates such as $Tc_2O_3 \cdot H_2O$, $TcO(OH) \cdot H_2O$, etc. No matter what the chemical sate of the solid Tc(III) compound, it should be equivalent to Cartledge's[78] $Tc(OH)_3$ which is reported in Table 2.

If TcO_4^- is reduced in HCl solutions by controlled potential reduction, at potentials that correspond to the first polarographic reduction wave, the final product is a green or yellow-green solution for $pH \leq 3$.[200,205,206] On the basis of coulometry, these authors variously described the formal valence of reduced Tc as being either below 4, intermediate between 3 and 4, or equal to +3.

In $NaHSO_4$-Na_2SO_4 mixtures, a pale yellow, reduced Tc species forms that probably contains Tc^{3+}.[21] Thus, the green color of Tc(III) in HCl solutions may be due to technetium chloride complexes rather than aquo ions.

Armstrong and Taube[217] reported that potentiometric reduction of TcO_4^- for initial $[H^+] < 1$ mol/l gave "TcO_2", but "more extensive" reduction occurred when $[H^+] = 4$ mol/l. Mazzocchin et al.[205] likewise obtained a yellow-green solution by reduction of TcO_4^- at $pH < 3$, but $TcO_2 \cdot 2H_2O$ precipitated when $pH \geq 3$. They suggested, from their cyclic voltammetry study, that Tc_2O_3/TcO_2 mixtures form for $pH < 4$, but only TcO_2 forms when $pH > 4$.

Grassi et al.[21] reported that reducing TcO_4^- in $NaHSO_4$-H_2SO_4 mixtures precipitated black material, presumably "TcO_2", when the pH was increased above 4.5. They interpreted this as due to disproportionation of Tc(III) to form "TcO_2" (and Tc^0?). Further support for this possibility comes from Paquette et al.'s study in CF_3SO_3H,[206] in which disproportionation of Tc(III) occurred above $pH = 4$. In this same pH region, $TcO_2 \cdot 2H_2O$ precipitates from Tc(IV) solutions. Disproportionation could explain why Rulfs et al.[147] obtained $TcO_2 \cdot 2H_2O$ when trying to precipitate Tc(III) with base.

Tc(III) solutions are also very prone to oxidation to Tc(IV) both electrochemically and by atmospheric oxygen.[20,21,206] In fact, reoxidation of Tc(III) or Tc(IV) to TcO_4^- can be done under rather gentle conditions. However, no clearly defined polarographic oxidation wave usually occurs for Tc(III)/Tc(IV) since it is masked by the Hg oxidation wave in acidic solutions. There is also the possibility that Tc(III) and TcO_4^- may react to form hydrated TcO_2.[176]

It has been known for many years that aqueous Tc salts can be electrolyzed to the metal. Voltz and Holt[34] did a detailed study of plating of metallic Tc from sulfuric acid solutions, and found that Tc^0 could be obtained in high yield for a variety of conditions and pH values. However, addition of H_2O_2 was required to eliminate partial formation of $TcO_2 \cdot 2H_2O$. Love and Greendale[219] suggested that a surface amalgam of Tc formed by polarographic reduction of Tc(III) at about 1.2 V in alkaline citrate solutions.

Salaria et al.[200,203] studied the reduction of TcO_4^- in aqueous acidic chloride and sulfate solutions. A pH-independent second-reduction wave occurred at -0.69 V for pH values of 3.5 to well below pH = 0. The number of electrons involved could not be determined due to the proximity of a catalytic hydrogen wave. The dropping mercury electrode had a film which could be chemically extracted to yield Tc. They suggested this may be a thin film of technetium metal.

Rulfs et al.[204] investigated this "amalgam" in greater detail. They found that Tc powder digested in mercury at 300 K did not dissolve. Since Tc is a high melting solid and is probably coated with oxide, this insolubility is not very surprising. Reduction of TcO_4^- in acidic solutions by liquid Hg produced a Tc surface film, with small amounts of Tc inside the Hg drop.

Centrifuging this mercury resulted in a 4-fold separation of the Tc. This is consistent with solid particles having radii between 10^{-6} and 10^{-5} cm dispersed in the Hg. These particles could either be metallic Tc or a Tc amalgam insoluble in Hg.

Grassi et al.[21,220] have reinvestigated the reduction of TcO_4^- in acidic solutions. Their results using classical polarography agreed with other workers. They suggested that the metallic film on the Hg drop may reduce the hydrogen over-voltage on Hg, thus allowing the catalytic hydrogen wave to appear once the reduction to Tc^o occurs (note that it was also suggested that transient Tc(I) or Tc(II) produces this effect[176]).

Grassi et al.'s radiopolarographic study[220] provided the first quantitative evidence that Tc(III) reduction in acidic solutions is a $3e^-$ reduction to Tc^o (i.e. there is no hydride formation as in basic solutions). The ratio of the diffusion currents of the first two polarographic diffusion controlled reduction waves was 4/3. Since the first wave is a $4e^-$ reduction of TcO_4^- to Tc(III), the second reduction wave should be a $3e^-$ reduction to Tc^o (assuming similar diffusion coefficients). This measurement was made at pH = 2.83 where the catalytic hydrogen current is low enough to allow the diffusion current and half-wave potential to be measured for the second wave. These authors considered the fact they even got radiopolarograms to indicate Tc^o formation. Their data cannot distinguish metallic Tc formation from amalgam formation.

It thus appears that Tc(III) is reduced to Tc^o at ≈ -0.6 to -0.7 V in acidic noncomplexing media for pH values of 3.5 or lower. The lack of a pH-dependence below pH = 3.5 implies that unhydrolyzed Tc(III) is involved. That is, the reaction is

$$Tc^{3+} + 3e^- = Tc^o(\text{in Hg}) \quad .$$

Unfortunately, it is not known whether this Tc is present as small metallic particles in the Hg or as an insoluble Tc amalgam.

Rulfs et al.[204] studied the polarographic reduction of TcO_4^- in deaerated solutions of $HClO_4$-$NaClO_4$. The second polarographic reduction occurred at -0.34 to -0.49 V with the potential becoming more negative with increasing pH. They suggested that this pH dependence may be due to variations in the amount of prereduction of TcO_4^- by mercury. This prereduction by Hg may have effected Colton et al.'s[53] results also. It is also possible that the $HClO_4$ may have partially reoxidized Tc(III) in Rulfs et al.'s study,[204] since Grassi et al.[21] found that it can occur.

Salaria et al.[203] did the same type of polarographic reduction in 0.4-0.5 mol/l HCl-KCl and 0.25-0.4 mol/l H_2SO_4-K_2SO_4 mixtures. For pH values of ≈ -1 to +3.5, the second reduction wave occurred at a half-wave potential of -0.69 V. This wave was irreversible but diffusion limited. Since the same potential was obtained in sulfate and in chloride containing media, and at different ionic strengths, neither complex formation or ionic strength has a significant effect on it.

Russell and Cash[177] also found the second polarographic reduction wave to be pH-independent from pH = 1 to 4.8 ($HClO_4$, sulfate, phosphate, citrate, DTPA, ascorbate, and acetate were used to vary pH). They thought that the reduction was probably a $7e^-$ reduction to the metal. However, since the reduction potential was -0.70 ± 0.04 V and independent of pH, it more likely corresponds to the $3e^-$ reduction of Tc^{3+} to the metal.

Grassi et al.[220] studied the second reduction wave of TcO_4^- by both classical and radiopolarography. The half-wave potential was hard to determine by classical polarography owing to the near proximity of the calalytic hydrogen discharge wave. However, at pH = 2.83 in 0.5 mol/l KCl +

HCl, the catalytic current was low enough to allow the half-wave potential to be estimated as -0.66 V. Radiopolarography gave -0.62 V in the same media and it was independent of pH from 1 to 3. Much lower concentrations of Tc are used in the radiopolarography measurements than in classical polarography.

The "best-value" for the reduction potential of

$$Tc^{3+} + 3e^- = Tc^o \text{ (in Hg)}$$

is the average of -0.668 ± 0.036 V. No attempt was made to extrapolate this potential to infinite dilution since the precision of its determination is not great enough to warrant it. This corresponds to a free energy of reaction of $\Delta G^o_{rxn} = 193.4 \pm 10.4$ KJ/mol. This can be related the free energy of formation of Tc^{3+} by

$$\Delta G^o_{rxn} = \Delta G^o_f[Tc^o \text{ in Hg}] - \Delta G^o_f[Tc^{3+}(aq)] \tag{35}$$

If the Tc^o exists as pure metal suspended in Hg, then $\Delta G^o_f[Tc^o \text{ in Hg}] \approx 0$

and

$$\Delta G^o_f[Tc^{3+}(aq)] = -\Delta G^o_{rxn} = -193.4 \pm 10.4 \text{ KJ/mol} \quad . \tag{36}$$

If, instead, the Tc^o is present as an amalgam, its free energy can be estimated assuming an ideal solution forms. The composition of this possibly hypothetical amalgam is unknown, but the maximum free energy of mixing expected is -3.4 kJ/mol. Since we do not know whether an amalgam actually forms, we will just increase our uncertainty limit by half of that amount: $\Delta G^o_f[Tc^{3+}(aq)] = -193.4 \pm 12.1$ KJ/mol.

Potential-pH diagram calculations were made by Dana Isherwood at this laboratory, using the data base obtained in this review. Using $\Delta G^o_f[Tc^{3+}(aq)] = -193.4 \pm 12.1$ KJ/mol leads to the incorrect prediction that Tc^{3+} is much more stable than the Tc(IV) species.

This implies either that the second reduction wave for TcO_4^- in acidic media has been misidentified, or that it does not yield valid thermodynamic results. In contrast (fortunately), the oxidation potentials for Tc(III) to Tc(IV) gives much more reasonable results.[21] Consequently, the reduction wave data were rejected, and oxidation wave results accepted instead.

Grassi et al.[21] studied the oxidation of Tc(III) to Tc(IV) in aqueous sulfate solutions between pH = 1.6 and 3.0. This oxidation was quasi-reversible, and involved $1e^-$ and $2H^+$ ions. They noted that the following three reactions are consistent with this observation:

$$Tc^{3+} + H_2O = TcO^{2+} + 2H^+ + e^- \quad ,$$

$$Tc(OH)^{2+} + H_2O = TcO(OH)^+ + 2H^+ + e^- \quad ,$$

and

$$TcO^+ + H_2O = TcO_2 + 2H^+ + e^- \quad ;$$

where "TcO_2" is equivalent to our $TcO(OH)_2^o$ discussed earlier. They concluded, as here, that neutral soluble TcO_2 [or $TcO(OH)_2$] is the dominant stable species of Tc(IV) in this pH region. Since the polarographic oxidation potential varied linearly with pH, only one Tc(III) and one Tc(IV) species should be present. Since "TcO_2" should be the Tc(IV) species present at equilibrium, they concluded the Tc(III) was present as TcO^+ ions. In contrast, in this same pH region, reduction of Tc(III) to Tc^o led to the conflicting conclusion that Tc^{3+} was present as the dominant aqueous species.

We earlier concluded that reduction of TcO_4^- may involve slow kinetics and that some reactions may not be seen on the polarographic time scale. The same situation may also occur for the oxidation of Tc(III). Both the oxidation and reduction behavior of Tc(III) in very acid solutions can be explained if Tc(III) is present as Tc^{3+}. The polarographic oxidation then corresponds to

$$Tc^{3+} + H_2O = TcO^{2+} + 2H^+ + e^-$$

and subsequent hydrolysis of TcO^{2+} to form $TcO(OH)^+$ and $TcO(OH)_2^o$

(or "TcO_2") would be too slow to be observed by polarography. Grassi et al.'s[21] half-wave reduction potential is 0.319 V under standard conditions. For reduction, $\Delta G^o_{rxn} = -30.8$ KJ/mol. Using the CODATA value for $H_2O(1)$ and our evaluation for TcO^{2+}, we obtain $\Delta G^o_f[Tc^{3+}(aq)] =$ 105.8 ± 10.5 kJ/mol. Potential-pH diagram calculations by Dana Isherwood indicate that this value gives quite reasonable results, and it correctly predicts disproportionation of Tc^{3+} to Tc(IV) species for pH ≥ 3.

The first reduction wave for TcO_4^- in acidic solutions is strongly pH dependent and irreversible. For very acid solutions, a $4e^-$ reduction to Tc(III) can be observed (which becomes $3e^-$ at higher but still acidic pH value). Various reactions have been proposed for this wave. Rulfs et al.[204] considered it to be due to

$$TcO_4^- + 8H^+ + 4e^- = Tc^{3+} + 4H_2O$$

in perchlorate solutions. Alternate reduction schemes include Pihlar's[184]

$$TcO_4^- + 5H^+ + 4e^- = TcO(OH) + 2H_2O$$

with a rate determining step

$$TcO_4^- + 2H^+ + e^- = TcO_3 + H_2O$$

The large variation of the first reduction wave with pH is clearly seen in Russell and Cash's study.[177] Their half-wave potential varied as $E = 0.24 - 0.10$ pH for $0 < pH < 7$. They suggested that the rate-determining step was

$$HTcO_4 + e^- = HTcO_4^-$$

Thus there is disagreement about both the rate determining-step and the reduction mechanism.

Reduction of TcO_4^- to Tc^{3+} involves stripping four oxygens from the TcO_4^- ion, and probably involves slow kinetics for several intermediate steps. Consequently, no attempt will be made to obtain thermodynamic data from the first reduction wave of TcO_4^- in acidic media.

These two polarographic reduction waves are seen in acidic solutions (below pH = 4 for the second wave). However, it should be noted in very concentrated strong acids (eg. 2 to 10 mol/l H_2SO_4, 4 mol/l $HClO_4$, etc.) no well defined polarographic waves occur.[175] Also, mercury oxidation becomes more of a problem at these very low pH values.

There is no experimental value for the

$$Tc^{2+} + 2e^- = Tc^o$$

reduction potential owing to the thermodynamic instability of Tc^{2+}. We use the estimated value of 0.40 V cited by Magee and Cardwell,[20] which is originally due to Latimer. This gives $\Delta G_f^o[Tc^{2+}(aq)] = 77.2$ KJ/mol. The reaction

$$3Tc^{2+} = 2Tc^{3+} + Tc^o$$

will then have a free energy change of 20 KJ/mol and an equilibrium constant of

$$K_{eq} = \frac{[Tc^{3+}]^2[Tc^o]}{[Tc^{2+}]^3} = \frac{[Tc^{3+}]^2}{[Tc^{2+}]^3} = 3 \times 10^3 \qquad (37)$$

This indicates that the disproportionation of Tc^{2+} is favorable, and it is consistent with the lack of experimental evidence for this species.

Unfortunately, potential-pH diagram calculations with this value also predict that Tc^{2+} is more stable than Tc(IV) over a wide range of potential values. This conflicts with experimental results. Consequently, $\Delta G_f^o(Tc^{2+})$ is not included with the recommended results, and Latimer's estimated potential is probably somewhat in error.

Table 5 contains a summary of thermodynamic data for aqueous Tc species. Table 6 contains standard reduction potentials for a variety of aqueous redox couples calculated from these data. The third figure past the decimal point is not significant in most cases.

TABLE 5. Thermodynamic data for aqueous Tc species at 298 K.

Species	ΔG_f^o in KJ/mol	ΔH_f^o in KJ/mol	S^o in J/mol-K
TcO_4^-	-621.1 ± 10.0	-716.3 ± 4.5	199.0 ± 1.3
TcO_4^{2-}	-562.2 ± 10.0	--	--
$HTcO_4^-$	-611.9 ± 10.5	--	--
$H_2TcO_4^o$	-613.6 ± 12.1	--	--
TcO_4^{3-}	-505.3 ± 11.2	--	--
TcO^{2+}	-100.6 ± 10.5	--	--
$TcO(OH)^+$	-331.3 ± 10.5	--	--
$TcO(OH)_2^o$	-556.0 ± 10.5	--	--
$[TcO(OH)_2^o]_2$	-1149.2 ± 21.3	--	--
Tc^{3+}	+105.8 ± 10.5	--	--

Reduction of TcO_4^- by Aqueous Hydrohalic Acids, and the Hydrolysis of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ Ions

In an earlier section, various oxyhalide salts were discussed that have

TABLE 6. Standard aqueous reduction potentials for Tc.

Reaction	E° in V
$TcO_4^- + e^- = TcO_4^{2-}$	-0.610
$TcO_4^- + 2e^- = TcO_4^{3-}$	-0.600
$TcO_4^- + H^+ + e^- = HTcO_4^-$	-0.095
$TcO_4^- + 2H^+ + e^- = H_2TcO_4^o$	-0.078
$TcO_4^- + 8H^+ + 7e^- = Tc(c) + 4H_2O$	+0.485
$TcO_4^- + 6H^+ + 3e^- = TcO^{2+} + 3H_2O$	+0.660
$TcO_4^- + 5H^+ + 3e^- = TcO(OH)^+ + 2H_2O$	+0.638
$TcO_4^- + 4H^+ + 3e^- = TcO(OH)_2^o + H_2O$	+0.595
$TcO_4^- + 3H_2O + 3e^- = TcO^{2+} + 6OH^-$	-0.995
$TcO_4^- + 3H_2O + 3e^- = TcO(OH)^+ + 5OH^-$	-0.742
$TcO_4^- + 3H_2O + 3e^- = TcO(OH)_2^o + 4OH^-$	-0.509
$TcO_4^- + 4H_2O + 4e^- = Tc^{3+} + 8OH^-$	-1.080
$TcO_4^{3-} + 3H_2O + e^- = TcO^{2+} + 6OH^-$	-1.785
$TcO_4^{3-} + 6H^+ + e^- = TcO^{2+} + 3H_2O$	+3.181
$TcO^{2+} + 2H^+ + e^- = Tc^{3+} + H_2O$	+0.319
$Tc^{3+} + 3e^- = Tc(c)$	+0.366
$TcO(OH)^+ + 3H^+ + e^- = Tc^{3+} + 2H_2O$	+0.387
$TcO(OH)_2^o + 4H^+ + e^- = Tc^{3+} + 3H_2O$	+0.516
$TcO_4^- + 4H^+ + 3e^- = 1/2[TcO(OH)_2^o]_2 + H_2O$	+0.659
$TcCl_6^{2-} + H_2O + e^- = Tc(OH)Cl_5^{3-} + Cl^- + H^+$	-0.233
$TcBr_6^{2-} + H_2O + e^- = Tc(OH)Br_5^{3-} + Br^- + H^+$	-0.304

been isolated and characterized in crystalline forms. These salts contain the anions $TcOCl_4^-$, $TcOCl_5^{2-}$, $TcOBr_4^-$, $TcOBr_5^{2-}$, or $TcOI_4^-$. All contain Tc in the unstable pentavalent form. The chloride and bromide salts are usually formed by direct reduction of TcO_4^- by HCl or HBr, whereas the iodide salt is usually obtained by ligand exchange with chloride salts. This section is concerned with the reduction of TcO_4^- by hydrohalic acids, and the ultimate "thermodynamic fate" of Tc in these solutions.

Reduction of TcO_4^- by aqueous HCl seems to occur at all HCl concentrations, with the reduction being very slow at low HCl concentrations and very fast at high HCl concentrations. At HCl concentrations of about 5 mol/l and above, reduction is extensive and rapid. Below about 5 mol/l, the reaction rate drops rapidly with decreasing HCl concentration. Increasing the temperature increases the rate at which TcO_4^- is reduced. The effects of concentration and temperature are discussed by a number of workers.[221-229] It is worth noting that ^{99m}Tc is reduced more rapidly than ^{99}Tc by aqueous HCl.[227]

Most of these studies of reduction of TcO_4^- by HCl and HBr involved the separation and identification of various Tc valence states by chromatography. It is generally accepted that TcO_4^- is initially reduced to Tc(V) oxyhalides, followed by a much slower reduction to Tc(IV) in the form of TcX_6^{2-}. For example, reduction of TcO_4^- by concentrated HCl to Tc(V) is nearly instantaneous at room temperature, but aging for 2 years was required to obtain "chromatographically pure" $TcCl_6^{2-}$. However, at 373 K, Cifka[228] reported that 11.4 mol/l HCl reduced TcO_4^- to $TcCl_6^{2-}$ in 10 minutes. In contrast, Ossicini et al.[221] found some Tc(V) remained after 4 hours heating at this temperature (but no TcO_4^- was left).

Reduction of TcO_4^- by HBr is more rapid than by HCl. Ossicini et al.[221] found that concentrated HBr rapidly reduced TcO_4^- to Tc(V) at room temperature, and that all TcO_4^- was converted to Tc(IV) within one day. At lower concentrations the reduction is considerably slower. However, at 373 K, less than 30 minutes of heating converts all TcO_4^- to $TcBr_6^{2-}$ in concentrated HBr.

Shukla[224] studied the reduction of TcO_4^- in 7 mol/l HCl. Reduction to Tc(V) was complete after 2 hours, but less than 17% Tc(IV) was present even after 50 days. However, when small amounts of Br^- were added to these solutions, reduction to Tc(V) was complete within 45 minutes and was followed by reduction to pure Tc(IV) within 3 days. This increased reduction rate by Br^- is in agreement with relative reduction rates in pure HCl and HBr solutions.[221] Shukla[224] also found that adding I^- to the 7 mol/l HCl caused instantaneous reduction to Tc(IV). However, this Tc(IV) could be $Tc(OH)Cl_5^{2-}$ rather than $TcCl_6^{2-}$ when I^- reduction is used.[157]

These observations explain why thermodynamically unstable Tc(V) oxyhalides can be prepared by the direct reduction of TcO_4^- by HCl or HBr.[152-159] Conditions can be chosen to give high yields of Tc(V) since the further reduction to Tc(IV) is usually much slower. It is also clear that the ultimate "thermodynamic fate" of Tc(V) oxyhalides left in hydrohalic acid solutions is to be converted into TcX_6^{2-} ($X = Cl^-$ or Br^-) since the yield of Tc(IV) generally increases with time. However, HI reduces TcO_4^- directly to TcI_6^{2-} under most conditions. Consequently, ligand exchange of I^- with $TcOCl_4^-$ or $TcOBr_4^-$ in neutral nonaqueous solution is the favored synthesis route for $TcOI_4^-$.

The formation of Tc oxyhalides in HCl or HBr occurs by the net reactions

$$TcO_4^- + 6HX = TcOX_4^- + 3H_2O + X_2$$

or

$$TcO_4^- + 7HX = TcOX_5^{2-} + 3H_2O + X_2 + H^+ \quad .$$

Thus, increased reaction rates in more concentrated HX solutions are expected since both halide and hydrogen ions participate in the reaction.

Shukla[223] studied the reduction of TcO_4^- by HCl-LiCl mixtures at a total chloride concentration of 12 mol/l. If $[H^+] = 12$, then reduction of TcO_4^- to Tc(V) is instantaneous. For $[H^+] = 7$ and $[Li^+] = 5$, two hours were required. The reduction time increased to 7 hours for $[H^+] = 6$ and $[Li^+] = 6$. For $[H^+] = 2$ and $[Li^+] = 10$, reduction to Tc(V) was not complete even after 50 days. This indicates that stripping of one or more oxygen atoms from TcO_4^- must occur before X^- will produce reduction, and that reduction is quite slow except at very high acidities.

Rajec et al.[193] reported that $TcOCl_n^{-n+3}$ is strongly hydrolyzed if $[H^+] < 3.15$ mol/l. They also reported that if $[Cl^-] < 5$, then the oxyhalide solution was more sensitive to oxidation. Liquid extraction experiments showed that $TcOCl_5^{2-}$ dominated when $[Cl^-] = 6$ and $3.15 < [H^+] < 6$. However, when $5 < [Cl^-] < 6$ several different $TcOCl_n^{-n+3}$ species were present.

Rajec and Macasek[230] studied the electrochemical reduction of $TcOCl_5^{2-}$ in 4 mol/1 HCl. They postulated the mechanism

$$TcOCl_5^{2-} + 2H^+ + e^- = Tc(H_2O)Cl_5^-$$

followed by

$$Tc(H_2O)Cl_5^- + Cl^- = TcCl_6^{2-} + H_2O \quad .$$

However, some direct reaction

$$TcOCl_5^{2-} + 2H^+ + Cl^- + e^- = TcCl_6^{2-} + H_2O$$

could also have occurred. Thus, electrolytic reduction of Tc(V) oxyhalides produces TcX_6^{2-} as does reduction of TcO_4^- by HX. However, the electrode catalyzed reduction of Tc(V) is more rapid.

There is one claim that Tc(V) is not formed as an intermediate species,[229] but that hydrolyzed $TcCl_6^{2-}$ species occur instead. The above discussion, and the isolation of salts of the type $TcOX_n^{-3+n}$, leave little doubt that this speculation is incorrect.

Noll and Münze[226] studied the reduction of TcO_4^- by HCl and suggested that a "lower" oxidation state of Tc forms initally, which then reacts with TcO_4^- to produce the Tc(V) oxyhalides. They also claimed that Tc(IV) species and TcO_4^- then form by disproportionation of Tc(V). If so, this is the same type of disproportionation that occurs in noncomplexing (halide free) solutions.

Since chemical reduction is involved in these reactions, other chemical species can effect the kinetics. Cifka[228] found that ferric chloride and ascorbic acid increased the TcO_4^- reduction rate. $SnCl_2$, which is a reducing agent, reduces TcO_4^- in HCl directly to Tc(IV).[216] Shukla[223] studied the HCl reduction of TcO_4^- at constant $[H^+]$. Adding LiCl to the solution increased the reduction rate, but NaCl slowed it down.

TcX_6^{2-} is more resistant to oxidation than most Tc(IV) oxy-species, but it can be reoxidized to TcO_4^-. Shukla[231] found that excess H_2O_2 oxidizes $TcCl_6^{2-}$ directly to TcO_4^-, whereas Cl_2 oxidation produces Tc(V) first and TcO_4^- later. Atmospheric O_2, even in the presence of sunlight, caused no oxidation. However, Cifka[228] found that $TcCl_6^{2-}$ was less stable with regard to oxidation above pH = 4. Most strong oxiding agents such as HNO_3, MnO_4^-, and Ce^{4+} oxidize TcX_6^{2-} to TcO_4^-. [4]

While TcX_6^{2-} species are stable in concentrated hydrohalic acid solutions, hydrolysis can occur as the pH is increased. Ossicini et al.[221] studied the hydrolysis of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ in the corresponding hydrohalic acids at ≈ 1 mol/l acid. They concluded that $TcCl_6^{2-}$ was much more stable with regard to hydrolysis than $TcBr_6^{2-}$. In agreement with this, Schwochau[232] found the step wise formation constant for

$$Tc(H_2O)X_5^- + X^- = TcX_6^{2-} + H_2O$$

was about a factor of 10 larger for $X = Cl^-$ than for $X = Br^-$. The TcF_6^{2-} ion is even less prone to hydrolysis.[221] If I^- follows the same trend, then stability to hydrolysis follows the order $TcF_6^{2-} > TcCl_6^{2-} > TcBr_6^{2-} > TcI_6^{2-}$. Hydrolysis of $TcCl_6^{2-}$ will be discussed in more detail since several studies of it have been published.

$TcCl_6^{2-}$ solutions are reported to be very stable with regard to hydrolysis when stored in the dark.[207,208] This is true no matter what HCl concentration they are dissolved in,[233] or whether the $TcCl_6^{2-}$ is in $HClO_4$.[208] This is true for $TcCl_6^{2-}$ up to pH = 7, [227] but in basic solution hydrolysis is claimed to be rapid.[175] Friedman's article[175] provides useful background information.

Koyama et al.,[207] Kanchiku,[208] Fujinaga et al.,[233] and Kawashima et al.[234] have studied hydrolysis of $TcCl_6^{2-}$ (and to a lesser extent $TcBr_6^{2-}$) in some detail. Spectra of solutions in HCl, stored in the dark, showed no change with time. When irradiated with UV or visible light, however, the spectra changed with time but gradually approached equilibrium. Ion-exchange separation yielded anionic, neutral, and cationic peaks whose amounts depended on irradiation time and HCl concentration during the irradiation. One peak corresponded to a Cl^-/Tc^{4+} ratio of 6:1 and had a charge of ≈ -2; this was obviously unhydrolyzed $TcCl_6^{2-}$.[207,208] Another peak had Cl^-/Tc^{4+} ratio of 5:1 and a charge of ≈ -1; this was clearly $Tc(H_2O)Cl_5^-$.[207,208] Two other peaks were found with charges of zero and $\approx +1$.[206] These could have been $Tc(H_2O)Cl_4^0$ and $Tc(H_2O)_2Cl_3^+$. However, they were not stable enough to remove from the ion-exchange column for Cl^- analysis, so the Cl^-/Tc^{4+} ratios are unknown. If these experiments were repeated with radioactive Cl^- ions, then both Cl^- and Tc^{4+} could be determined simultaneously for them.

Kawashima et al.[234] likewise separated ions with Br^-/Tc^{4+} ratios of 6:1 and 5:1, presumably $TcBr_6^{2-}$ and $Tc(H_2O)Br_5^-$, from hydrolyzed $TcBr_6^{2-}$. They also studyed the hydrolysis kinetics of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ and found aquation rates to be first order both in X^- and H^+.

Identification of the neutral and cationic species was tentative since the Cl^-/Tc^{4+} ratios could not be measured for them. Other species could fit the same description, eg. $Tc(H_2O)(OH)Cl_3^0$ and $Tc(H_2O)_2(OH)Cl_2^+$. This possibility was noted by Koyama et al.[207] Both $TcCl_6^{2-}$ and $Tc(H_2O)Cl_5^-$ are yellow. However, if pH > 1, then the $Tc(H_2O)Cl_5^-$ solution became brown. They thought this could be due to the reaction

$$Tc(H_2O)Cl_5^- = Tc(OH)Cl_5^{2-} + H^+ \quad .$$

Likewise the green neutral complex, presumably $Tc(H_2O)_2Cl_4^0$, hydrolyzed to form a brown basic solution that eventually precipitated $TcO_2 \cdot 2H_2O$. A similar brown color was reported for the uncharged hydrolysis product of $TcCl_6^{2-}$ in aqueous H_2SO_4.[235] Ianovici et al.[235] did comparative hydrolysis studies of $TcCl_6^{2-}$ in aqueous HCl, $HClO_4$, and H_2SO_4.

Whereas $TcCl_6^{2-}$ is resistant to oxidation, $Tc(H_2O)Cl_5^-$ and $Tc(H_2O)Cl_4^0$ can be slowly oxidized by air to form TcO_4^-.[207] Ianovici et al.[235] found that this oxidation was faster in $HClO_4$ solutions than in HCl, but it was much slower in H_2SO_4. Reduction of TcX_6^{2-} can occur electrolytically, and the TcX_6^{3-} formed readily undergoes ligand substitution[9] (however, most reduction studies obtain $Tc(OH)X_5^{3-}$, see below).

The spectral characteristics of $TcCl_6^{2-}$ in $HClO_4$ and H_2SO_4 solutions do not depend on length of irradiation with light (but peak intensities do).[235] Changes continue to occur in HCl solutions, suggesting that more than one cationic species may be present. Further evidence for this comes from the color of these solutions: hydrolyzed cationic Tc(IV) chloride is green in HCl, brown in $HClO_4$, and pink in H_2SO_4.

We earlier discussed haloditechnetate ions which can be isolated as crystalline salts: $Tc_2Cl_8^{3-}$, $Tc_2Cl_8^{2-}$, and $Tc_2Br_8^{2-}$.[125-138] They exist only in reducing conditions and in fairly concentrated HCl or HBr. Hydrolysis of $Tc_2Cl_8^{3-}$ was claimed to give $Tc_4O_5 \cdot mH_2O$.[80] By analogy, hydrolysis of $Tc_2Cl_8^{2-}$ and $Tc_2Br_8^{2-}$ might yield $Tc(OH)_3$ (or Tc_2O_3).

Cotton and Pedersen[236] found the reduction

$$[Tc_2Cl_8]^{2-} + e^- = [Tc_2Cl_8]^{3-}$$

to be quasi-reversible in HCl-ethanol mixtures.

Thermodynamic Data for Aqueous Technetium Halide and Hydroxy-Halide Complexes

The stepwise association constant for

$$Tc(H_2O)X_5^- + X^- = TcX_6^{2-} + H_2O$$

with X = Cl^- or Br^-, has been determined by several workers. The association constant is given by

$$K_{56} = \frac{[TcX_6^{2-}]}{[Tc(H_2O)X_5^-]\ [X^-]} \quad . \tag{38}$$

Since $[H_2O]$ varies little, it is absorbed into K_{56}. Kawashima et al.[234] studied this equilibrium for $X = Cl^-$ and Br^- by measuring optical densities. The chloride salt was studied from 348 to 363 K; the bromide salt from 313 to 328 K. Rajac and Macášek[230] obtained $K_{56} = 0.80 \pm 0.04$ for the chloride at 298 K using nearly identical technique. They extrapolated Kawashima et al.'s data to 298 K to obtain = 1.24. Both studies were in 4 mol/l HCl. The agreement is fair, and the "best value" is the average of 1.0 ± 0.2 for chloride salts. Rajac and Macášek noted that their results could be "steady state ratios" rather than K_{56}. Unfortunately, Schwochau's potentiometric study in 3 mol/l $HClO_4$ at 288 K yields K_{56} values for both chloride and bromide that differ by several orders of magnitude from the other two studies.[232]

Another type of equilibria has been studied polarographically by various workers. It corresponds to

$$TcX_6^{2-} + H_2O(l) + e^- = Tc(OH)X_5^{3-} + X^- + H^+ \quad ,$$

where $X = Cl^-$ or Br^-.[186,202,237,238] This $1e^-$ reduction is reversible.[186,202,238] Münze reported a reduction potential of about −0.213 V for the chloride[202,238] whereas Hurst[186] obtained a value of −0.252 V for the chloride and −0.304 V for the bromide. These values are also listed in Table 6, and refer to I=1 to 4 for the chloride salt and I=6 for the bromide salt. No attempt will be made to extract free energies of formation from this data, or from values of K_{56} reported above, since they give only relative values.

Trop et al.[239] have studied the oxidation

$$TcX_6^{2-} = TcX_6^- + e^- \quad ,$$

where $X = Cl^-$, Br^-, or NCS^-. These oxidized species contain Tc(V) which is quite unstable in aqueous solution owing to its disproportionation to Tc(IV) and TcO_4^-. Consequently, these workers did their electrochemical measurements in anhydrous acetonitrile.

Aqueous Sulfate, Carbonate, Phosphate, Pyrophosphate, and Tripolyphosphate Complexes

Spitsyn et al.[45] studied Tc(IV) in H_2SO_4 solutions and separated a brown, noncolloidal, anionic complex by electrophoresis. Variation of its spectra with pH suggested $Tc(OH)_2(SO_4)_2^{2-}$, which we shall write as $TcO(SO_4)_2^{2-}$ to maintain consistency with our other notation. This same complex was invoked by Grassi et al.[21] to explain some features of the reduction of TcO_4^- in Na_2SO_4 – $NaHSO_4$ solutions. If $TcO(SO_4)_2^{2-}$ can form at high sulfate concentrations, then $TcOSO_4^o$ is possible at lower concentrations. No published thermodynamic data are available for either of these complexes.

Paquette et al.[16,206] have briefly discussed carbonate complexes of Tc(III) and Tc(IV). If $[CO_3^{2-}]/[Tc^{n+}] > 30$, then hydrolysis is suppressed and precipitation of $TcO_2 \cdot 2H_2O$ eliminated. Also, Tc(III) is stabilized by these complexes, and does not disproportionate even up to $pH = 12$ (it disproportionates above $pH \approx 3$ to 4 in noncomplexing media). Spectroscopic evidence also exists for these complexes, but neither their stoichiometry or thermodynamics have been measured.

Reduction of TcO_4^- in aqueous PO_4^{3-}, $P_2O_7^{4-}$, and $P_3O_{10}^{5-}$ gives evidence for a number of lower valence complexes.[195,215,240] In phosphate solutions green Tc(III) and pink Tc(IV) form. A mixed valence Tc(III) – Tc(IV) complex, probably also containing Sn(II), is formed by the $SnCl_2$ reduction of TcO_4^- in phosphate solutions. Pyrophosphate solutions can contain light blue Tc(III), pink Tc(IV), and possibly yellowish Tc(II). In tripolyphosphate solutions, pink Tc(IV), orange Tc(IV) + Tc(III), and yellow Tc(III) complexes have been reported. For phosphate-buffered tripolyphosphate solutions, there are pink Tc(IV), gray Tc(IV) + Tc(III), and green Tc(III).

Several of these systems have reversible redox couples. Unfortunately, the nature and stoichiometry of the PO_4^{3-}, $P_2O_7^{4-}$, and $P_3O_{10}^{5-}$ complexes with Tc(III) and Tc(IV) are unknown. Consequently, they cannot be used to calculate thermodynamic data. Friedman's[175] literature survey contains more references and details.

Brief Summary and Recommendations for Future Studies

Thermodynamic and chemical data for Tc and many of its inorganic compounds and their aqueous solutions have been critically reviewed. Values for thermodynamic properties have been recommended when good measurements are available and the chemistry adequately understood.

A few general comments are in order. In noncomplexing aqueous solutions, and for simple inorganic compounds, certain valence states predominate. Under oxidizing conditions Tc(VII) is stable (e.g. Tc_2O_7, $HTcO_4$, Tc_2S_7, TcO_4^- salts). Under moderately reducing conditions Tc(III) compounds can form, but they are generally sensitive to oxidation. Tc(IV) is the most stable state under moderately reducing conditions. Tc(V) and Tc(VI) generally disporportionate to the other valence states.

Thermodynamic data are unavailable for a number of significant species and should be measured. Examples includfe $TcCl_4$(c), $TcCl_6$(c), $TcBr_4$(c), TcO_2(c), various Tc oxyhalides (c, l, g), Tc_2S_7(c), TcS_2(c), TcO_4^{2-} solid salts, and aqueous Tc(III) and Tc(IV) halide, sulfate, and carbonate complexes. Quality solubility data for $TcO_2 \cdot 2H_2O$(am) are required for many applications. Experimental heat capacities for Tc(c) above 15 K are also needed. Qualitative information is needed about the nature of the Tc(III) and Tc(IV) phosphate and polyphosphate complexes. Hydrolysis of cationic Tc(V) is also not well understood. Until these data are reported, thermodynamic chemical equilibrium modeling calculations for some systems cannot be completely trusted.

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