PSI PAUL SCHERRER INSTITUT

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Titel
The PSI/Nagra Chemical Thermodynamic Database 12/07
(Update of the Nagra/PSI TDB 01/01):
Data Selection for Technetium

Ersetzt

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**Summary:**

This report provides an update of the Nagra/PSI Thermochemical Database 01/01 (HUMMEL et al. 2002) with respect to technetium. All data for technetium in the Nagra/PSI TDB 01/01 were taken from OECD NEA's book "Chemical Thermodynamics of Technetium" by RARD et al. (1999). Newer literature on technetium has been reviewed in "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" by GUILLAUMONT et al. (2003), but these reviews did not result in any changes of the values selected by RARD et al. (1999) and no additional data were recommended.

Therefore, the thermochemical data for technetium selected in the Nagra/PSI Chemical Thermodynamic Database 01/01 have been adopted for our update without any changes, and the present report generally provides only minor textual revisions to Chapter 5.20 (written by W. Hummel) on technetium in HUMMEL et al. (2002). However, a new section has been added concerning ionic strength corrections, where previously missing SIT ion interaction parameters are presented, based on the estimation method by HUMMEL (2009).

The updated database is called PSI/Nagra Chemical Thermodynamic Database 12/07.

This is the 1st of a continuing series of reports concerning the PSI/Nagra Chemical Thermodynamic Database 12/07.

Verteiler

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Informationsliste

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|---|---|---|---|---|---|---|---|---|
| D | 1 | 2 | 3 | 4 | 5 | 8 | 9 | A |

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# 1 Technetium

This report provides an update of the Nagra/PSI Thermochemical Database 01/01 (HUMMEL et al. 2002) with respect to technetium. All data for technetium in the Nagra/PSI TDB 01/01 were taken from OECD NEA's book "Chemical Thermodynamics of Technetium" by RARD et al. (1999). In the "Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium" by GUILLAUMONT et al. (2003), all the literature on technetium was reviewed that was published between 1997 and the end of 2001. The update resulted in no changes in the values selected by RARD et al. (1999) and no new data were selected.

Therefore, the thermochemical data for technetium selected in the Nagra/PSI Chemical Thermodynamic Database 01/01 have been adopted for the PSI/Nagra Chemical Thermodynamic Database 12/07 without any changes, and the present report generally provides only minor textual revisions to Chapter 5.20 (written by W. Hummel) on technetium in HUMMEL et al. (2002).

Note, however, that not all recommended values by RARD et al. (1999) are included in our database since NEA reviews are not restricted to data relevant for radioactive waste management or even environmental modelling in general. Therefore, we tried to exclude from our database all the phases and complexes which most probably will never be relevant in environmental systems. They are all listed in Table 1.1.

The notation of formulae and symbols used in this chapter follows the NEA recommendations and practice.

## 1.1 Elemental technetium

The absolute entropy and heat capacity of Tc(cr) are given in Table 1.2 to quantify the thermochemical properties of elemental technetium. Technetium liquid and gas are not relevant under environmental conditions. Hence, none of these phases is included in the database.

## 1.2 Simple aqueous technetium ions of each oxidation state

Technetium has an extensive redox chemistry, and the most stable oxidation state in contact with air is pertechnetate(VII), $TcO_4^-$, in the entire pH range. $TcO_4^-$ can therefore be used as a reference oxidation state. In aqueous solution, and in the absence of complexing anions other than hydroxide, technetium can assume oxidation numbers from +VII to +III.

### 1.2.1 $TcO_4^-$

Recommended values of thermodynamic properties of $TcO_4^-$ at 298.15 K are

$$\Delta_f G_m^\circ\ (TcO_4^-,\ aq,\ 298.15\ K) = -(637.4 \pm 7.6)\ kJ \cdot mol^{-1}$$

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

$$S_m^\circ\ (TcO_4^-,\ aq,\ 298.15\ K) = (199.6 \pm 1.5)\ J \cdot K^{-1} \cdot mol^{-1}$$

$$C_{p,m}^{\circ}\ (\mathrm{TcO_4^-}, \mathrm{aq}, 298.15\ \mathrm{K}) = -(15 \pm 8)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$

### 1.2.2 $TcO_4^{2-}$

Because of the instability of $TcO_4^{2-}$, it is not meaningful to include a Tc(VII)/Tc(VI) reduction potential or the derived $\log_{10}K^{\circ}$ value in a thermodynamic database, without including the rate constant for the disproportionation of $TcO_4^{2-}$ at the same time. In practice, Tc(VI) is only of potential relevance in the area of chemical syntheses, and in elucidating the stepwise redox behaviour of technetium. It will never be a stable oxidation state in aqueous equilibrium systems and is therefore not included in our database.

### 1.2.3 Tc(V)

Tc(V) is not a stable species as it decomposes further, and its consideration in chemical equilibrium calculations is thus not necessary.

### 1.2.4 Tc(IV)

In contrast to Tc(VI) and Tc(V), Tc(IV) is a stable oxidation state. Tc(IV) is the most important oxidation state of technetium under reducing conditions. From the pH independence of the solubility of $TcO_2{\cdot}xH_2O(s)$, it is evident that an uncharged Tc(IV) species dominates in non-complexing solutions in the pH range $3 < \mathrm{pH} < 10$. Possible chemical formulae of this uncharged Tc(IV) species are $Tc(OH)_4(aq)$, $TcO(OH)_2(aq)$ and $TcO_2(aq)$. It is fairly well established today that a maximum of two protons can be forced upon the uncharged Tc(IV) complex in the pH range of aqueous solutions. This leaves $TcO^{2+}$ (and not the free $Tc^{4+}$) as an undissociable unit, and it is thus reasonable to follow the current practice and to use $TcO(OH)_2(aq)$ as the reference formula of the uncharged Tc(IV) complex.

The redox potential of the redox pair Tc(VII)/Tc(IV), derived from potentiometric redox measurements in the presence of $TcO_2{\cdot}xH_2O(s)$, is given as a half cell involving aqueous species only:

$$\mathrm{TcO_4^-} + 4\,\mathrm{H^+} + 3\,\mathrm{e^-} \Leftrightarrow \mathrm{TcO(OH)_2(aq)} + \mathrm{H_2O(l)}$$

$$E^{\circ}\ (298.15\ \mathrm{K}) = (0.579 \pm 0.016)\ \mathrm{V}$$

$$\log_{10}K^{\circ}\ (298.15\ \mathrm{K}) = 29.4 \pm 0.8$$

### 1.2.5 $Tc^{3+}$

There is a total absence of thermodynamic data for the Tc(III) species. A value of $\Delta_f G_m^{\circ}$ for $Tc^{3+}$ is discussed by RARD et al. (1999) but it is not recommended. Thus, the state-of-the-art concerning Tc(III) is such that no data can be recommended for these systems, neither for any Tc(III) species, nor for any of the redox reactions connected with Tc(III).

### 1.2.6 $Tc^{2+}$

There is no experimental evidence for the existence of $Tc^{2+}$ as a viable chemical species in aqueous solution.

## 1.3 Oxide and hydrogen compounds and complexes

### 1.3.1 Aqueous species formed by hydrolysis and protonation reactions

#### 1.3.1.1 The acid/base chemistry of Tc(IV)

The existence of a species such as $TcO^{2+}$ is not certain. Only a few solubility data are available between pH = 0 and pH = 3 for an estimate of the first two protonation constants of $TcO(OH)_2(aq)$. RARD et al. (1999) therefore preferred to select a limiting value for the equilibrium constant including the species $TcO^{2+}$ and to use $TcO(OH)_2(aq)$ as the main Tc(IV) species.

Solubility measurements for $TcO_2{\cdot}xH_2O(s)$ in aqueous 0.05 to 2.6 M NaCl solutions at pH = 6.9 to 9.3 revealed no significant variation of the solubility with chloride concentration. Since $TcO(OH)_2(aq)$ is the predominant aqueous species at low ionic strengths and at $3 < pH < 10$, the observed independence of solubility on chloride concentration implies that this species persists even in concentrated chloride solutions. Thus, chloride and mixed hydroxide-chloride complexes of Tc(IV) probably do not form in significant amounts in solutions with pH > 3.

The solubility of $TcO_2{\cdot}xH_2O(s)$ increases at pH > 10. The few reported high pH data suggest a slope of 0.5 rather than 1 in a plot of Tc solubility versus pH (see Figure V.3 in RARD et al. 1999). However, the scarce data are insufficient to propose a more complex mechanism than the formation of $TcO(OH)_3^-$. The reactions are thus written as follows:

$$TcO(OH)_2(aq) + H^+ \Leftrightarrow TcO(OH)^+ + H_2O(l)$$

$$\log_{10}{}^*K^\circ\ (298.15\ \mathrm{K}) = 2.5 \pm 0.3$$

$$TcO(OH)_2(aq) + 2\ H^+ \Leftrightarrow TcO^{2+} + 2\ H_2O(l)$$

$$\log_{10}{}^*K^\circ\ (298.15\ \mathrm{K}) < 4$$

$$TcO(OH)_2(aq) + H_2O(l) \Leftrightarrow TcO(OH)_3^- + H^+$$

$$\log_{10}{}^*K^\circ\ (298.15\ \mathrm{K}) = -10.9 \pm 0.4$$

#### 1.3.1.2 The acid/base chemistry of other Tc oxidation states

RARD et al. (1999) do not consider any of the reported values for the protonation of $TcO_4^-$ to be reliable. Aqueous solutions of $HTcO_4$ are thus considered to be fully dissociated by RARD et al. (1999).

Protonation constants of $TcO_4^{2-}$ have been estimated based on pulse radiolysis at various pH values and variable ionic strength. However, the species $HTcO_4^-$ and $H_2TcO_4$(aq) are of no relevance in equilibrium systems due to the instability of Tc(VI) (see 1.2.2).

### 1.3.2 Solid technetium oxides and their hydrates

**$Tc_2O_7$(cr)**: Tc(VII) oxide is hygroscopic and thus of no relevance for environmental systems and is therefore not included in our database.

**$Tc_2O_7 \cdot xH_2O$(s)**: This compound is compatible with the formulation of either $Tc_2O_7 \cdot xH_2O$(s) or $HTcO_4$(s). It is a very hygroscopic compound and thus of no relevance for environmental systems and is not included in our database.

**$TcO_3$(s)**: Because the existence of $TcO_3$(s) has not been established with certainty, RARD et al. (1999) do not recommend any estimated thermodynamic values for it.

**$TcO_2$(cr)**: There are several studies in which attempts were made to measure solubilities that could be used to calculate $\Delta_f G_m^\circ$ of $TcO_2$(cr). Some of these studies found the solubility of $TcO_2$(cr) to be lower than that of $TcO_2 \cdot xH_2O$(s) whereas others found it to be higher. Generally, amorphous or poorly crystalline hydrous oxides are more soluble than their corresponding anhydrous oxides. In addition, there is no way to be sure whether the surface layer of the $TcO_2$(cr) remained unhydrated during the solubility experiments, and thus it is possible that the observed solubilities actually refer to a partially hydrated dioxide. Because of these uncertainties, RARD et al. (1999) based their evaluation of the thermodynamic properties of $TcO_2$(cr) on calorimetric measurements. These data are not included in our database (see discussion below).

**$TcO_2 \cdot xH_2O$(s):** There is considerable information about the hydrous oxides of Tc(IV). Since the exact value of $x$ in $TcO_2 \cdot xH_2O$(s) is of no importance in aqueous chemistry, a notation such as $TcO_2$(s,hyd) for this compound would be a reasonable simplification. However, in order to visibly indicate in the chemical formula that the solid phase in question is hydrated, RARD et al. (1999) prefer to use the formula $TcO_2 \cdot 1.6H_2O$(s) as 1.6 seems to be a reasonable average hydration number in spite of possible larger variations. From two reliable solubility studies of $TcO_2 \cdot 1.6H_2O$(s) a recommended solubility constant has been derived:

$$TcO_2 \cdot 1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6\ H_2O(l)$$

$$\log_{10} K^\circ\ (298.15\ K) = -8.4 \pm 0.5$$

From this solubility constant and the Gibbs energy of formation of the solid, derived from measurements with the $TcO_4^-/TcO_2 \cdot 1.6H_2O$(s) electrode,

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

RARD et al. (1999) derived the recommended Gibbs energy of formation for the uncharged Tc(IV) hydrolysis species:

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

Because of their large relative uncertainties, values of the assessed thermodynamic properties of $TcO_2$(cr) and $TcO_2 \cdot 1.6H_2O$(s) should not be used simultaneously in the thermodynamic calculations. The thermodynamic data for $TcO_2 \cdot 1.6H_2O$(s) and the aqueous species are thermodynamically consistent, and thus it is the appropriate substance to be considered in aqueous solubility calculations. Hence, we decide to include $TcO_2 \cdot 1.6H_2O$(s) in our database and to discard $TcO_2$(cr).

**Lower valence hydrous Tc oxides and mixed valence Tc oxides:** The preparation of several lower valence and mixed valence hydrous oxides has been claimed, e.g. $Tc_4O_7$(s), $Tc_3O_4$(s), "$Tc(OH)_4$(s)", $Tc(OH)_3$(s), $Tc(OH)_2$(s), TcOH(s) (CARTLEDGE 1971) and "$Tc_4O_5 \cdot xH_2O$(s)". The existence of these compounds is not proven. Further compounds such as "$Tc_2O_3$(s)" were postulated without characterisation. However, both Tc(III) solutions and the hydrous oxide of Tc(III) are quite unstable and tend to disproportionate at pH above 3 or 4. There are several published thermodynamic databases for technetium and several potential/pH diagrams which include $\Delta_f G_m^\circ$ values calculated from the E° values of CARTLEDGE (1971). These potential/pH diagrams predict that $Tc_3O_4$(s) can be a solubility limiting phase for the Tc-$O_2$-$H_2O$ system under certain reducing conditions. However, in view of all of the available evidence, RARD et al. (1999) consider $Tc_3O_4$(s) to be a questionable compound. It is more likely that $TcO_2 \cdot xH_2O$(s), and probably Tc(cr) are the actual solubility limiting phases under various reducing conditions.

### 1.3.3 Gaseous technetium oxides

Gaseous technetium oxides are not relevant under environmental conditions and are therefore not included in our database.

### 1.3.4 Technetium hydrides

Binary and ternary technetium hydrides decompose under normal environmental conditions. No thermodynamic data are available for these compounds.

## 1.4 Halogen compounds and complexes

### 1.4.1 Fluorine compounds and complexes

There are few studies in the literature on technetium complexation with fluoride anions. Only the $Tc(IV)F_6^{2-}$ complex has been identified, but no thermodynamic data are available.

RARD et al. (1999) recommended an equilibrium constant for the reaction $TcF_6$(cr, cubic) ⇔ $TcF_6$(g). Since $\Delta_f G_m^\circ$ is not known for both phases, they cannot be related to any other technetium species or phases. In addition, this reaction is hardly relevant under environmental conditions. These fluoride phases are therefore not included in our database.

The same is true for $TcO_3F(g)$ which is also not included in our database, all the more so as RARD et al. (1999) only recommended values for $S_m°$ and $C_{p,m}°$.

### 1.4.2 Chlorine, bromine and iodine compounds and complexes

$TcO_3Cl(g)$ is not included in our database, since RARD et al. (1999) only recommended values for $S_m°$ and $C_{p,m}°$ and gaseous technetium compounds are irrelevant under environmental conditions.

#### 1.4.2.1 Aqueous Tc(IV) halides

Whereas $TcF_6^{2-}$ is stable even in water and dilute solutions of alkali hydroxide, $TcCl_6^{2-}$ could only be stabilised in concentrated $Cl^-$ solutions and $TcBr_6^{2-}$ needs concentrated HBr solutions to remain stable. As discussed in 1.3.1.1, the formation of chloride and mixed hydroxide-chloride complexes of Tc(IV) in saline solutions with pH > 3 is unlikely. In addition, no equilibrium constant is recommended by RARD et al. (1999) relating $TcCl_6^{2-}$ to $TcO(OH)_2(aq)$ and consequently, no value for the Gibbs energy of formation has been selected. Hence, $TcCl_6^{2-}$ is not included in our database.

Although some compounds with stoichiometry $M_2TcX_6(cr)$ (with M = $NH_4$, K, Rb, Cs and X = Cl and Br) exhibit low solubility products, these compounds are not included in our database. Because of the instability of $TcCl_6^{2-}$ and $TcBr_6^{2-}$ under environmental conditions, these compounds are not relevant under environmental conditions.

#### 1.4.2.2 Aqueous Tc(V) halides

The Tc(V) oxychloride $TcOCl_5^{2-}$ has been shown to exist in aqueous solution by spectroscopic methods. RARD et al. (1999) discussed kinetic studies of the hydrolysis of $TcOCl_5^{2-}$, which were interpreted by use of the following reaction

$$TcOCl_5^{2-} + H_2O(l) \Leftrightarrow TcO_2Cl_4^{3-} + 2H^+ + Cl^-$$

RARD et al. (1999) raised doubts about the validity of this reaction and stated that "Further clarifiction of the equilibrium reaction is necessary before the value of $\log_{10}K°$ ... can be recommended". Consequently, the Tc(V) oxychlorides are not included in our database. Note, however, that a $\log_{10}K°$ for the reaction is erroneously listed by RARD et al. (1999) in Table 7-2 of selected thermodynamic data for reactions involving technetium compounds and complexes.

### 1.5 Chalcogen compounds and complexes

### 1.5.1 Technetium sulphides

From measured combustion enthalpies for several rhenium sulphides, thermochemical data for $Tc_2S_7(s)$, $TcS_3(s)$ and $TcS_2(s)$ have been estimated. No direct thermochemical data are available for these technetium sulphides. In addition, there are no reports of the preparation of $TcS_3$(s). There are no reliable solubilities for $Tc_2S_7$(s). No thermodynamic data are recommended by RARD et al. (1999).

RARD et al. (1999) recommend thermodynamic data for TcS(g). However, gaseous technetium sulphide is not relevant under environmental conditions and is not included in our database.

### 1.5.2 Technetium sulphates

No thermodynamic data are available for technetium sulphates. However, the results of several polarographic studies imply that $SO_4^{2-}$ complexes of Tc(IV) and Tc(III) are weak or non-existent at pH > 4 owing to competition from hydrolysis.

## 1.6 Group 15 compounds and complexes

### 1.6.1 Nitrogen compounds and complexes

There are no experimental studies on the thermodynamic properties of technetium nitrogen compounds. A polarographic study of the reduction of $NH_4TcO_4$ in $HNO_3$ solutions provided no evidence for technetium nitrate complexes.

### 1.6.2 Phosphorous compounds and complexes

No thermodynamic data are available for technetium phosphate compounds or complexes. There are some indications on the formation of Tc(III) and Tc(IV) phosphate complexes but no single species has been identified.

## 1.7 Group 14 compounds and complexes

### 1.7.1 Carbon compounds and complexes

#### 1.7.1.1 Technetium carbides

RARD et al. (1999) recommend thermodynamic data for TcC(g). However, gaseous monocarbide is not relevant under environmental conditions and is not included in our database.

#### 1.7.1.2 Technetium carbonates

A solubility study for $TcO_2 \cdot xH_2O$(s) as a function of pH in the absence and presence of carbonate revealed an increase of the solubility of $TcO_2 \cdot xH_2O$(s) in the presence of $CO_2$(g) at a partial pressure up to 1 bar in the pH range 6.3 to 8.6. These findings have been interpreted in terms of the formation of two hydroxide-carbonate complexes, a neutral and an anionic one:

$$TcO(OH)_2(aq) \ + \ CO_2(g) \ \Leftrightarrow \ TcCO_3(OH)_2(aq)$$

$$\log_{10}K^\circ \ (298.15 \text{ K}) \ = \ 1.1 \ \pm \ 0.3$$

$$TcO(OH)_2(aq) + CO_2(g) + H_2O(l) \Leftrightarrow TcCO_3(OH)_3^- + H^+$$

$$\log_{10}K° \text{ (298.15 K)} = -7.2 \pm 0.6$$

Using the selected carbonate equilibrium constants relating $CO_2(g)$ with $CO_3^{2-}$

$$HCO_3^- + H^+ \Leftrightarrow CO_2(g) + H_2O(l)$$

$$\log_{10}K° \text{ (298.15 K)} = 7.82$$

$$HCO_3^- \Leftrightarrow CO_3^{2-} + H^+$$

$$\log_{10}K° \text{ (298.15 K)} = -10.329$$

the above values have been converted to

$$TcO(OH)_2(aq) + CO_3^{2-} + 2\,H^+ \Leftrightarrow TcCO_3(OH)_2(aq) + H_2O(l)$$

$$\log_{10}{}^*K° \text{ (298.15 K)} = 19.3 \pm 0.3$$

$$TcO(OH)_2(aq) + CO_3^{2-} + H^+ \Leftrightarrow TcCO_3(OH)_3^-$$

$$\log_{10}{}^*K° \text{ (298.15 K)} = 11.0 \pm 0.6$$

These values are included in the database due to the relevance for environmental systems.

#### 1.7.1.3 Technetium cyanides and oxycyanides

No thermodynamic data are available for these compounds and complexes.

### 1.7.2 Silicon compounds and complexes

There is no published study of the Tc-Si-O phase system. No information about silicon complexes of technetium could be located by RARD et al. (1999).

## 1.8 Pertechnetates and mixed oxides

The pertechnetate anion $TcO_4^-$ has little tendency to form complexes with cations in aqueous solutions. However, a large number of pertechnetate salts has been prepared. The solubilities of these salts in general are very high (see Table V.36 in RARD et al. 1999): The dissolution of $NaTcO_4{\cdot}4H_2O(cr)$ gives 11.3 M pertechnetate solutions, $KTcO_4(cr)$ 0.1 M and $NH_4TcO_4(cr)$ 0.6 M solutions. A few salts with small solubility products are known, i.e. $AgTcO_4(cr)$ and $TlTcO_4(cr)$. However, under groundwater conditions the concentration of Ag or Tl is extremely low and consequently the pertechnetate concentration has to reach molar concentrations to precipitate these solids. None of these pertechnetate salts is relevant under environmental conditions and thus, none of these phases is included in the database. $CsTcO_4(cr)$ has a solubility product similar to that of $AgTcO_4(cr)$. The precipitation of $CsTcO_4(cr)$ would require at least a concentration of $2 \times 10^{-2}$ mol $kg^{-1}$ for either $Cs^+$ or $TcO_4^-$, which is unrealistically high under environmental conditions, even in the near-field of a radioactive waste repository. Therefore, $CsTcO_4(cr)$ is also not included in the database.

## 1.9 Ionic strength corrections

Neither RARD et al. (1999) nor GUILLAUMONT et al. (2003) selected any SIT ion interaction coefficients. Based on a statistical analysis of published SIT ion interaction coefficients, HUMMEL (2009) provided a method to estimate missing ion interaction coefficients for cations with $Cl^-$ and $ClO_4^-$, and for anions with $Na^+$ from the charge of the considered species. This method was used to estimate the ion interaction coefficients of our selected technetium species (see Table 1.3).

**Table 1.1:** Technetium data selected by NEA (RARD et al. 1999 and GUILLAUMONT et al. 2003) but not included in TDB Version 12/07. For explanations see text.

| | |
|---|---|
| Gases | $Tc(g)^{ad}$, $TcO(g)^{a}$, $Tc_2O_7(g)^{ad}$, $TcF_6(g)^{bc}$, $TcO_3F(g)^{b}$, $TcO_3Cl(g)^{b}$, $TcS(g)^{a}$, $TcC(g)^{a}$ |
| Solids | $TcO_2(cr)^{a}$, $Tc_2O_7(cr)^{ad}$, $Tc_2O_7{\cdot}H_2O(s)^{ad}$, $TcF_6(cr, cubic)^{bc}$, $NH_4TcO_4(cr)^{ac}$, $(NH_4)_2TcCl_6(cr)^{c}$, $(NH_4)_2TcBr_6(cr)^{c}$, $TlTcO_4(cr)^{ac}$, $AgTcO_4(cr)^{ac}$, $NaTcO_4{\cdot}4H_2O(s)^{ac}$, $KTcO_4(cr)^{ac}$, $K_2TcCl_6(cr)^{c}$, $K_2TcBr_6(cr)^{c}$, $Rb_2TcCl_6(cr)^{c}$, $Rb_2TcBr_6(cr)^{c}$, $CsTcO_4(cr)^{ac}$, $Cs_2TcCl_6(cr)^{c}$, $Cs_2TcBr_6(cr)^{c}$ |
| Aqueous species | $TcO_4^{2-\,ac}$, $TcO_2Cl_4^{3-\,c}$, $TcOCl_5^{2-\,c}$, $TcCl_6^{2-\,c}$, $TcBr_6^{2-\,c}$ |

[a] Single species data including $\Delta_f G_m°$
[b] Single species data excluding $\Delta_f G_m°$
[c] Reaction data including $\log_{10}K°$
[d] Reaction data excluding $\log_{10}K°$

**Table 1.2:** Selected technetium data. All data included in TDB Version 12/07 are taken from Rard et al. (1999), which are identical with the data by Guillaumont et al. (2003). TDB Version 01/01 refers to Hummel et al. (2002).

| | | **TDB Version 01/01** | | | | **TDB Version 12/07** | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Name** | **Redox** | $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | $S_{\mathrm{m}}^{\circ}$ $[\mathrm{J \cdot K^{-1} \cdot mol^{-1}}]$ | $C_{p,\mathrm{m}}^{\circ}$ $[\mathrm{J \cdot K^{-1} \cdot mol^{-1}}]$ | $\Delta_{\mathrm{f}}G_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | $S_{\mathrm{m}}^{\circ}$ $[\mathrm{J \cdot K^{-1} \cdot mol^{-1}}]$ | $C_{p,\mathrm{m}}^{\circ}$ $[\mathrm{J \cdot K^{-1} \cdot mol^{-1}}]$ | **Species** |
| Tc(cr) | 0 | 0 | 0 | 32.5 ± 0.7 | 24.9 ± 1.0 | 0 | 0 | 32.5 ± 0.7 | 24.9 ± 1.0 | Tc(cr) |
| TcO(OH)2 | IV | -568.2 ± 8.8 | - | - | - | -568.2 ± 8.8 | - | - | - | $\mathrm{TcO(OH)_2(aq)}$ |
| TcO4- | VII | -637.4 ± 7.6 | -729.4 ± 7.6 | 199.6 ± 1.5 | -15 ± 8 | -637.4 ± 7.6 | -729.4 ± 7.6 | 199.6 ± 1.5 | -15 ± 8 | $\mathrm{TcO_4^-}$ |

| | | **TDB Version 01/01** | | **TDB Version 12/07** | | |
|---|---|---|---|---|---|---|
| **Name** | **Redox** | $\log_{10}\beta^{\circ}$ | $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | $\log_{10}\beta^{\circ}$ | $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | **Reaction** |
| TcO+2 | IV | < 4 | - | < 4 | - | $\mathrm{TcO(OH)_2(aq) + 2\,H^+ \Leftrightarrow TcO^{2+} + 2\,H_2O(l)}$ |
| TcO(OH)+ | IV | 2.5 ± 0.3 | - | 2.5 ± 0.3 | - | $\mathrm{TcO(OH)_2(aq) + H^+ \Leftrightarrow TcO(OH)^+ + H_2O(l)}$ |
| TcO(OH)3- | IV | -10.9 ± 0.4 | - | -10.9 ± 0.4 | - | $\mathrm{TcO(OH)_2(aq) + H_2O(l) \Leftrightarrow TcO(OH)_3^- + H^+}$ |
| TcCO3(OH)2 | IV | 19.3 ± 0.3 | - | 19.3 ± 0.3 | - | $\mathrm{TcO(OH)_2(aq) + CO_3^{2-} + 2H^+ \Leftrightarrow TcCO_3(OH)_2(aq) + H_2O(l)}$ |
| TcCO3(OH)3- | IV | 11.0 ± 0.6 | - | 11.0 ± 0.6 | - | $\mathrm{TcO(OH)_2(aq) + CO_3^{2-} + H^+ \Leftrightarrow TcCO_3(OH)_3^-}$ |
| TcO4- | VII | -29.4 ± 0.8 | - | -29.4 ± 0.8 | - | $\mathrm{TcO(OH)_2(aq) + H_2O(l) \Leftrightarrow TcO_4^- + 4\,H^+ + 3\,e^-}$ |

| | | **TDB Version 01/01** | | **TDB Version 12/07** | | |
|---|---|---|---|---|---|---|
| **Name** | **Redox** | $\log_{10}K_{s,0}^{\circ}$ | $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | $\log_{10}K_{s,0}^{\circ}$ | $\Delta_{\mathrm{r}}H_{\mathrm{m}}^{\circ}$ $[\mathrm{kJ \cdot mol^{-1}}]$ | **Reaction** |
| TcO2:1.6H2O | IV | -8.4 ± 0.5 | - | -8.4 ± 0.5 | - | $\mathrm{TcO_2{\cdot}1.6H_2O(s) \Leftrightarrow TcO(OH)_2(aq) + 0.6\,H_2O(l)}$ |

**Table 1.3:** Selected SIT ion interaction coefficients $\varepsilon_{j,k}$ [kg · mol$^{-1}$] for technetium species. Neither RARD et al. (1999) nor GUILLAUMONT et al. (2003) selected any ion interaction coefficients. Data estimated according to HUMMEL (2009) are shaded.

| *j* *k*→ ↓ | $Cl^-$ $\varepsilon_{j,k}$ | $ClO_4^-$ $\varepsilon_{j,k}$ | $NO_3^-$ $\varepsilon_{j,k}$ | $Li^+$ $\varepsilon_{j,k}$ | $Na^+$ $\varepsilon_{j,k}$ | $K^+$ $\varepsilon_{j,k}$ |
|---|---|---|---|---|---|---|
| TcO+2 | 0.15 ± 0.1 | 0.4 ± 0.1 | - | 0 | 0 | 0 |
| TcO(OH)+ | 0.05 ± 0.1 | 0.2 ± 0.1 | - | 0 | 0 | 0 |
| TcO(OH)2 | 0 | 0 | 0 | 0 | 0 | 0 |
| TcO(OH)3- | 0 | 0 | 0 | - | -0.05 ± 0.1 | - |
| TcCO3(OH)2 | 0 | 0 | 0 | 0 | 0 | 0 |
| TcCO3(OH)3- | 0 | 0 | 0 | - | -0.05 ± 0.1 | - |
| TcO4- | 0 | 0 | 0 | - | -0.05 ± 0.1 | - |

## 1.10 References

CARTLEDGE, G.H. (1971): Free energies of formation of hydrous oxides of technetium in its lower valencies. J. Electrochem. Soc., 118, 231-236.

GUILLAUMONT, R., FANGHÄNEL, T., FUGER, J., GRENTHE, I., NECK, V., PALMER, D.A., RAND, M.A. (2003): Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium. Elsevier, Amsterdam, 763p.

HUMMEL, W., BERNER, U., CURTI, E., PEARSON, F.J., THOENEN, T. (2002): Nagra/PSI Chemical Thermodynamic Data Base 01/01. Nagra NTB 02-16, Nagra, Wettingen, Switzerland. Also published by Universal Publishers/upublish.com, Parkland, USA.

HUMMEL, W. (2009): Ionic strength corrections and estimation of SIT ion interaction coefficients. PSI Internal Report, TM-44-09-01, Paul Scherrer Institut, Villigen, Switzerland, 15 p.

RARD, J.A., RAND, M.H., ANDEREGG, G., WANNER, H. (1999): Chemical Thermodynamics of Technetium. Elsevier, Amsterdam, 544p.