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A THERMODYNAMIC DATA BASE FOR Tc TO CALCULATE EQUILIBRIUM SOLUBILITIES AT TEMPERATURES UP TO 300°C

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ABSTRACT

Thermodynamic data has been selected for solids and aqueous species of technetium. Equilibrium constants have been calculated in the temperature range 0 to 300°C at a pressure of 1 bar for $T < 100°$ C and at the steam saturated pressure at higher temperatures. For aqueous species, the revised Helgeson-Kirkham-Flowers model is used for temperature extrapolations.

The data base contains a large amount of estimated data, and the methods used for these estimations are described in detail. A new equation is presented that allows the estimation of $\Delta_r C°_{pm}$ values for mononuclear hydrolysis reactions. The formation constants for chloro complexes of Tc(V) and Tc(IV), whose existence is well established, have been estimated. The majority of entropy and heat capacity values in the data base have also been estimated, and therefore temperature extrapolations are largely based on estimations. The uncertainties derived from these calculations are described.

Using the data base developed in this work, technetium solubilities have been calculated as a function of temperature for different chemical conditions. The implications for the mobility of Tc under nuclear repository conditions are discussed.

ABSTRACT (Swedish)

Termodynamiska data för fasta faser och specier i vattenlösning av teknetium. Jämviktskonstanter har beräknats i temperaturintervallet 0 till 300°C vid ett tryck av 1 bar för $T < 100°C$ och vid ångmättnadstrycket vid högre temperaturer. Den reviderade Helgeson-Kirkham-Flowers modellen har använts för specier i lösning vid temperatur extrapolationerna.

Databasen innehåller en stor mängd uppskattade data och de metoder som använts för dessa beskrivs i detalj. En ny ekvation presenteras, vilken tillåter uppskattning av $\Delta_r C°_{pm}$ värden för enkärniga hydrolysreaktioner. Bildningskonstanterna för kloridkomplex av Tc(V) och Tc(IV), vilkas existens är väl fastställda har uppskattats. Majoriteten av entropi och värmekapacitetsvärdena i databasen har också uppskattas och därför är temperaturextrapolationerna huvudsakligen baserade på uppskattningar. Osäkerheten i dessa beräkningar diskuteras.

Utgående från den i detta arbete utvecklade databasen har teknetiumlösligheter beräknats som en funktion av temperaturen vid olika kemiska förhållanden. Betydelsen för teknetiums rörlighet under förvarsförhållanden diskuteras.

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1 INTRODUCTION

Calculations of speciation and solubility are a necessary component of the knowledge which is needed to predict the behaviour of radionuclides in natural and artificial environments. Therefore, chemical equilibrium calculations are needed for the safety assessment of nuclear waste repositories, particularly, to define the source term in the near field as a function of temperature and chemical conditions (pH, Eh, *etc*). Calculations of equilibrium speciation are also needed to interpret complementary laboratory experiments.

Technetium can only be obtained from non-natural sources. Relatively large quantities are present in spent nuclear fuel. The chemistry of technetium in aqueous solutions is often simplified to two oxidation states: Tc(VII) (*i.e.*, TcO_4^-) and Tc(IV) (*i.e.*, TcO^{2+}). Nevertheless, the chemical behaviour of this element, due to its redox properties, is far more complex than that, and a larger number of oxidation states exist, sometimes interrelated by reactions which have slow kinetics.

The literature contains several reviews on the aqueous chemistry of technetium (Friedman, 1981; Russell, 1982; Davison and Jones 1982; Jones and Davison 1982; Allard and Torstenfelt 1983; Rard, 1983; Schwochau 1983; Beasley and Lorz 1986; Hughes and Rossotti 1987; Sparkes and Long 1988). Among them, the review of Rard (1983) is perhaps that of greatest interest, as it contains the largest compilation of thermodynamic data for compounds and aqueous complexes of this element. More recently, the Nuclear Energy Agency (NEA) of the Organization for Economic Co-operation and Development (OECD), within the NEA-TDB project (Wanner 1988) has undertaken a critical evaluation of all the experimental literature studies concerning the thermodynamic properties of Tc (Rard *et al.* 1993).

Because of the limited amount of thermodynamic experimental data concerning this element, a complete data base can only be obtained if a considerable amount of the entries are estimated. Therefore, reviews of experimental Tc-studies, such as the NEA-TDB compilation, require additional estimated data for performance assessment studies. The work of Lemire and Garisto (1989) is an example of a such a study where a substantial part of the thermodynamic values for Tc had to be estimated.

The research programme of the Swedish Nuclear Fuel and Waste Management Co. (SKB), has included many efforts to determine experimentally thermodynamic properties of actinide elements. There is also a need within SKB to develop and maintain thermodynamic data bases for nuclear waste safety assessment. The work presented here is part of the SKB data base development program, previously concentrated in uranium and plutonium (Bruno and Puigdomènech 1989, Puigdomènech and Bruno 1988, 1991).

This report presents a thermodynamic data base for Tc, which contains a substantial amount of estimated values. Temperature extrapolations have been performed to generate equilibrium constants in the range 0 to 300°C, and a file in EQ3/6 format has been generated. Aqueous speciations and solubilities (obtained with the data base presented here) are given for a wide range of temperatures and chemical conditions. The implications for the mobility of Tc under repository conditions are discussed.

2 THE DATA BASE

The data base is based in the report of Rard (1983), the report of Lemire and Garisto (1989), and preliminary results of the NEA-TDB review (Rard *et al.*, 1993). The data for auxiliary species (e.g. for $H_2O(l)$, $H_2(g)$, Cl^-, *etc*) are the CODATA key values (Cox *et al.* 1989) and NEA-TDB selected values (Grenthe *et al.* 1992). Standard partial molar heat capacities of auxiliary species at the reference temperature (298.15 K) where taken from the tables in Shock and Helgeson (1988) and Shock *et al.* (1989).

For convenience, the data base description is divided in three topics, *i.e.*,

a) standard Gibbs free energies of formation (and formation equilibrium constants),

b) standard entropies, and

c) standard heat capacities.

The adopted values and their estimated uncertainties are listed in Table 1. The uncertainties listed in that Table depend mainly on the uncertainties for a few key species (TcO_4^-, $TcCl_6^{2-}$, $TcOCl_5^{2-}$, *etc*). However reaction differences in $\Delta_f G^\circ_m$, S°_m or $C^\circ_{p,m}$, that is, equilibrium constants ($\log K^\circ_{eq}$), $\Delta_r S^\circ_m$ or $\Delta_r C^\circ_{p,m}$, usually have less uncertainty, as indicated in the discussion given in the following sections. For this reason, values are reported in Table 1 with more digits than required by their corresponding uncertainty.

2.1 GIBBS FREE ENERGIES

Table 1 lists the selected values of $\Delta_f G^\circ_m$ at the reference temperature (T_o=298.15 K) and 1 bar. The selection of these values is dicussed here. The value for TcO_4^-, which is a key value for the data base, is that of Rard (1983), obtained from the temperature dependence of the solubility of $KTcO_4$(cr), and calorimetric measurements on the dissolution of Tc_2O_7(cr) (Rard 1983, p. 26-27). The $\Delta_f G^\circ_m$ for Tc_2O_7(cr), $HTcO_4$(cr), and $KTcO_4$(cr) are those of Rard (1983, p. 6-7, 15, 13 and 22 respectively). From the protonation constant of TcO_4^- of Nakashima and Lieser (1985):

$$TcO_4^- + H^+ \rightleftarrows HTcO_4(aq) \qquad \log K^\circ_{eq} = +0.1 \pm 0.5$$

the value of $\Delta_f G^\circ_m$ for $HTcO_4$(aq) is obtained. Values of $\Delta_f G^\circ_m$ for aqueous Tc(VI) species are as well those of Rard (1983, p. 31-33), although Rard notes that Tc(VI) is unstable in aqueous solutions.

The standard partial molar Gibbs free energy for the Tc(V) master species: TcO_4^{3-}, is also that of Rard (1983, p.33-37), and is derived from $E^\circ = -0.600 \pm 0.026$ V ($\log K^\circ_{eq} = -20.3 \pm 0.9$) for

$$TcO_4^- + 2\,e^- \rightleftarrows TcO_4^{3-}.$$

The value of $\Delta_f G^\circ_m$ for $TcOCl_5^{2-}$ is estimated as described later. The values for $TcOCl_4^-$ and $TcO_2Cl_4^{3-}$ are then obtained from the values of $\log K_{eq}$ determined for the following two reactions (Koltunov and Gomonova 1984, Thomas *et al.* 1985) approximately extrapolated to zero ionic strength:

$$TcOCl_5^{2-} \rightleftarrows TcOCl_4^- + Cl^- \qquad \log K^\circ_{eq} = +5.3 \pm 1.5$$

$$TcOCl_5^{2-} + H_2O(l) \rightleftarrows TcO_2Cl_4^{3-} + Cl^- + 2\,H^+ \qquad \log K^\circ_{eq} = -2.9 \pm 0.2$$

For Tc(IV), the hydrous oxide formed by electrodeposition or hydrazine reduction is assumed to be $TcO_2 \cdot 1.63H_2O$(s), which is the water contents measured by Meyer *et al.* (1991). The $\Delta_f G^\circ_m$ for this solid is obtained from the standard redox potential, E°= +0.747±0.004 ($\log K^\circ_{eq}$= +37.9±0.2) for

$$TcO_4^- + 4\,H^+ + 3\,e^- \rightleftarrows TcO_2 \cdot xH_2O(s) + (2-x)\,H_2O(l) \qquad (2.1)$$

determined by Meyer and Arnold (1991). Then, solubility constant of Eriksen *et al* (1992):

$$TcO_2{\cdot}xH_2O(s) \rightleftarrows TcO(OH)_2(aq) + (x-1)\ H_2O(l) \qquad \log K^\circ_{eq} = -8.17 \pm 0.05$$

is used to obtain $\Delta_f G^\circ_m$ for $TcO(OH)_2(aq)$.

The hydrolysis equilibrium constants of Gorski and Koch (1969) for TcO^{2+}, and $TcO(OH)^+$, extrapolated to zero ionic strength, and the solubility constant of Eriksen *et al.* (1992) for $TcO(OH)_3^-$,

$$TcO^{2+} + 2\ H_2O(l) \rightleftarrows TcO(OH)_2(aq) + 2\ H^+ \qquad \log K^\circ_{eq} = -3.56 \pm 0.08$$

$$TcO(OH)^+ + H_2O(l) \rightleftarrows TcO(OH)_2(aq) + H^+ \qquad \log K^\circ_{eq} = -2.43 \pm 0.07$$

$$TcO_2{\cdot}xH_2O(s) \rightleftarrows TcO(OH)_3^- + H^+ + (x-2)\ H_2O(l) \qquad \log K^\circ_{eq} = -19.2 \pm 0.30$$

are used to obtain $\Delta_f G^\circ_m$ values for these species. For $[TcO(OH)_2]_2(aq)$, the equilibrium constant of Sundrehagen (1979), is used:

$$2\ TcO(OH)_2(aq) \rightleftarrows [TcO(OH)_2]_2(aq) \qquad \log K^\circ_{eq} = +6.5 \pm 0.04$$

although there are two reasons to question the existence of this species: there are large experimental difficulties in performing spectrophotometric measurements at the wave lengths used by Sundrehagen (*cf.* Meyer *et al.* 1991) and secondly, the magnitude of the dimerisation constant is such that the species is never predominant in aqueous solutions. Therefore the uncertainty assigned to the equilibrium constant given above is increased to ± 1 logarithmic units.

The solubility constants of Eriksen *et al.* (1992):

$$TcO_2{\cdot}xH_2O(s) + CO_2(g) \rightleftarrows TcOCO_3(aq) + x\ H_2O(l) \qquad \log K^\circ_{eq} = -7.09 \pm 0.08$$

$$TcO_2{\cdot}xH_2O(s) + CO_2(g) \rightleftarrows TcOCO_3OH^- + H^+ + (x-1)\ H_2O(l) \qquad \log K^\circ_{eq} = -15.35 \pm 0.07 \qquad (2.2)$$

are used to obtain the $\Delta_f G^\circ_m$ of $TcOCO_3(aq)$ and $TcOCO_3OH^-$.

For $TcOSO_4(aq)$, the value of $\Delta_f G^\circ_m$ used here is the one estimated and given by Rard (1983).

The value of $\Delta_f G^\circ_m$ for $TcCl_6^{2-}$ is estimated as described later. The value for $TcCl_5^-$ is then obtained from the equilibrium constant for the following reaction:

$$TcCl_6^{2-} \rightleftarrows TcCl_5^- + Cl^- \qquad \log K^\circ_{eq} = 0\pm1$$

reported by Kawashima *et al.* (1976) (see Rard 1983, p.64-65).

For Tc^{3+}, the experimental source for its $\Delta_f G^\circ_m$ value is $E^\circ = 0.319\pm0.04$ V for:

$$TcO^{2+} + 2H^+ + e^- \rightleftarrows Tc^{3+} + H_2O(l)$$

measured by Grassi *et al.* (1979), see p.55 in Rard (1983). For $TcCl_3OH^-$ we use the redox potential (Huber *et al.* 1987) for the equilibrium reaction:

$$TcCl_6^{2-} + H_2O(l) + e^- \rightleftarrows TcCl_3OH^- + 3\,Cl^- + H^+$$

$E = +0.318\pm0.004$ V ($\log K_{eq} = +5.38\pm0.07$) in $[Cl^-]=5$ M. Our approximate extrapolation to $I = 0$ (using tabulated values of activity coefficients for NaCl(aq) and HCl(aq)) is $\log K^\circ_{eq} = +6.8\pm0.5$, from which the value of $\Delta_f G^\circ_m$ for $TcCl_3OH^-$ can be calculated.

The measured equilibrium redox potential between Tc(IV) and Tc(III) in carbonate media (Paquette *et al.* 1985), is assumed to correspond to the following reaction

$$TcOCO_3OH^- + 2\,H_2O(l) + e^- \rightleftarrows TcCO_3(OH)_4^{3-} + H^+$$

where the stoichiometry of the carbonate complex of Tc(IV) has been established by Eriksen *et al.* (1992). The value of $E = -0.887$ V (at $I = 1$), is again approximately extrapolated to $I = 0$ to give $\log K^\circ_{eq} = -16.9\pm0.6$ for the above reaction, which is used to calculate $\Delta_f G^\circ_m$ for the hydroxo-carbonato complex of Tc(III).

For Tc^{2+}, the estimated value (Rard 1983, p. 56) is used here. Rard did not include this species in his selection because it had a substantial predominance, over Tc(IV), on an Eh/pH diagram. However, in chloride solutions the species $TcCl_3OH^-$ considered here (and not included by Rard 1983) makes the predominance of Tc^{2+} negligible in our calculated Eh/pH diagrams, and therefore, Tc^{2+} is included in our model.

We have not been able to find any experimental work in the literature describing the possible stability of Tc(I) compounds or aqueous ions and complexes.

An important part of the work presented in this report is that $\Delta_f G_m^\circ$ values have been estimated for species which have well established stability, namely, the chloride (and oxy-chloride or hydroxy-chloride) complexes of Tc(V) and Tc(IV). The standard partial molar Gibbs free energy of formation for $TcCl_6^{2-}$ and $TcOCl_5^{2-}$ have been estimated as described shortly, while the $\Delta_f G_m^\circ$ for the rest of the oxy-chloride complexes of Tc(V), (IV) and (III) are then derived from the key values for $TcCl_6^{2-}$ and $TcOCl_5^{2-}$ and equilibrium constants determined experimentally.

For the oxychloride complex of Tc(V), $TcOCl_5^{2-}$, two experimental facts are used for the estimation of $\Delta_f G_m^\circ$: **1**) it is known that TcO_4^- solutions are reduced by concentrated HCl to Tc(V) and Tc(IV), and **2**) the solubility of $TcO_2{\cdot}xH_2O(s)$ in 1 M HCl has been measured by Meyer *et al.* (1991), and therefore the calculated concentration of Tc(V) oxychloride complexes in these solutions cannot be higher than the measured solubility. This two factors constrain the value of the equilibrium constant for the following reaction:

$$TcO_2{\cdot}xH_2O(s) + 5\,Cl^- + 3\,H^+ \rightleftarrows TcOCl_5^{2-} + \tfrac{1}{2}\,H_2(g) + (1{+}x)\,H_2O(l)$$

to $\log K^\circ_{eq} = -16.8 \pm 2$, from which $\Delta_f G_m^\circ$ for $TcOCl_5^{2-}$ is obtained.

These two experimental facts are also used to set a limit in the stability of Tc(IV) chloride complexes. The equilibrium constant is constrained to $\log K^\circ_{eq} = -3.6 \pm 2$ for the reaction

$$TcO_2{\cdot}xH_2O(s) + 6\,Cl^- + 4\,H^+ \rightleftarrows TcCl_6^{2-} + (2{+}x)\,H_2O(l)$$

from which $\Delta_f G_m^\circ$ of $TcCl_6^{2-}$ can be calculated.

It is of some interest to compare the $\Delta_f G_m^\circ$ values estimated by us with those for complexes of ruthenium and rhenium, which are close to technetium in the periodic table of the elements. Data from the NBS tables (Wagman *et al.* 1982) and from Rard (1985) are used. The following reaction can be compared between Tc and Re (the entropy estimation for $TcCl_6^{2-}$ is described later):

$$TcO_4^- + 5\,H^+ + 1.5\,H_2(g) + 6\,Cl^- \rightleftarrows TcCl_6^{2-} + 4\,H_2O(l)$$

$$\log K^\circ_{eq} = +34.3; \qquad \Delta_r S_m^\circ = -236\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

$$ReO_4^- + 5\,H^+ + 1.5\,H_2(g) + 6\,Cl^- \rightleftarrows ReCl_6^{2-} + 4\,H_2O(l)$$
$$\log K^\circ_{eq} = +9.9; \qquad \Delta_r S^\circ_m = -202\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

The next two equilibrium reactions for Tc and Ru are not completely equivalent,

$$TcO^{2+} + 2\,H^+ + 5\,Cl^- \rightleftarrows TcCl_5^- + H_2O(l) \qquad \log K^\circ_{eq} = +1$$

$$Ru(OH)_2^{2+} + 4\,Cl^- \rightleftarrows RuCl_4(OH)_2^{2-} \qquad \log K^\circ_{eq} = +2.8$$

however, the protonation of chloride complexes of Tc(IV) and Ru(IV) only takes place at pH ≤ 0, *i.e.*, the equilibrium constant for the protonation must be close to one ($\log K^\circ_{eq}=0$). Therefore, both $\log K^\circ_{eq}$ for the previous two reactions are comparable.

The reported stoichiometry of chloride complexes formed by Tc(III) and Ru(III) are not completely equivalent either, but their comparison is nevertheless useful. The following two constant are given by Rard (1985):

$$Ru^{3+} + 4\,Cl^- \rightleftarrows RuCl_4^- \qquad \log K^\circ_{eq} = +4.2$$

$$Ru^{3+} + H_2O(l) \rightleftarrows Ru(OH)^{2+} + H^+ \qquad \log K^\circ_{eq} = -2.2$$

while for Tc(III) we obtain from the estimated values:

$$Tc^{3+} + H_2O(l) + 3\,Cl^- \rightleftarrows TcCl_3OH^- + H^+ \qquad \log K^\circ_{eq} = +2.4$$

From the comparisons given above between experimental data for Re and Ru, and our estimated values for Tc, it can be concluded that the estimated data is within the range of values expected for this type of complexes. Because Cl^- is a common ligand in nature, and HCl is often used in laboratory experiments, the data estimated here for $TcCl_6^{2-}$ and $TcOCl_5^{2-}$, are very relevant to model the aqueous chemistry of Tc, specially at low pH values.

Due to its instability, the solid TcO_3(cr) (Migge 1989) is not included in this data base. For the reasons discused by Meyer *et al.* (1986), we disregard the E° values reported by Cartledge (1971) involving amorphous "thin films" of hydroxides of Tc in oxidation state lower than IV. Meyer *et al.* (1986) point out that the assignment of the stoichiometries for these redox reactions was questionable, and that the experimental evidence was insufficient.

However, it must be kept in mind that the probable stability of hydroxides or oxides of Tc(III) and Tc(II) might affect the structure of the calculated Eh/pH diagrams.

2.2 ENTROPIES

Entropies (at the reference temperature, T_0=298.15 K, and at 1 bar) are reported in Table 1 and they had to be estimated, with the exception of the few values which have been determined experimentally: *i.e.*, for the element and for $KTcO_4$(cr). S°_m values reported by Rard (1983), and Knacke *et al.* (1991) are used here for Tc(cr), Tc_2O_7(cr) and $KTcO_4$(cr).

For $TcO_2 \cdot 1.63H_2O$(s), the estimation method of Latimer (1952) is used here, with the entropy contributions tabulated by Naumov *et al.* (1971) which are also listed in the uranium NEA-TDB book (Grenthe *et al.* 1992). The contribution for each water of hydration is set to 44.7 $J \cdot K^{-1} \cdot mol^{-1}$ (Grenthe *et al.* 1992, Appendix D). The contribution of Tc to the entropy of a solid, is estimated to be 51.88 $J \cdot K^{-1} \cdot mol^{-1}$, *i.e.*, 12.4 $cal \cdot K^{-1} \cdot mol^{-1}$, which is the average from the values for Mo and Ru (Naumov *et al.* 1971, Table I-2, p.42).

For TcO_4^-, the selected value is that calculated by Rard, S°_m= +199 $J \cdot K^{-1} \cdot mol^{-1}$, from experimental data on the dissolution of $KTcO_4$(cr) as a function of temperature (see Rard 1983, p. 26-27). This agrees well with S°_m= +197 $J \cdot K^{-1} \cdot mol^{-1}$ estimated with the molar volume (Neck and Kanellakopulos 1987, Lemire *et al.* 1992) and Eq.(92) in Shock and Helgeson (1988). A value of S°_m= +214 $J \cdot K^{-1} \cdot mol^{-1}$ is estimated with Eq.(2) of Cobble (1953a) using r= 2.00 Å .

For aqueous Tc^{2+}, Tc^{3+} and Tc^{4+}, the standard partial molar entropy was estimated with Eq.(58) in Shock and Helgeson (1988) using ionic radii of r= 0.78, 0.69 and 0.645 Å respectively (Shannon, 1976). The entropy of the non-existent Tc^{4+} is needed to estimate the S°_m value of $[TcO(OH)_2]_2$(aq), as described later.

For TcO^{2+}, S°_m may be estimated as −131±65 $J \cdot K^{-1} \cdot mol^{-1}$ with the method of Lemire and Garisto (1989): using Eq.(7) of Cobble (1953b) with r= 2.04 Å , and assuming that the molecular composition for this ion is $Tc(OH)_2^{2+}$. However, we prefer the estimate S°_m= −120±15 $J \cdot K^{-1} \cdot mol^{-1}$ as determined from a plot, for oxy-cations, of $S^\circ_m - 1.5 \cdot R \cdot \ln(M_w) - S_e$ *versus* Z^2/r_{eff} (*cf.* Figure 1), where M_w is the molecular weight of the oxy-cation, Z the ionic charge, r_{eff} is the ionic radius, and S_e the internal electronic entropy. This value gives $\Delta_f H^\circ_m(TcO^{2+})$= −137 $kJ \cdot mol^{-1}$ which fits nicely in a plot of $\Delta_f G^\circ_m$ *versus* $\Delta_f H^\circ_m$ for the same oxy-cations, *cf.* Figure 2. Plots similar to that in Figure 2 are used by Phillips *et al.* (1988) to estimate thermodynamic properties. However, the graph in Figure 1 gives S°_m estimates with a uncertainty which is less than 1/4 of the uncertainty in the S°_m estimates that could be obtained in Figure 2.

For the anions TcO_4^{3-}, and TcO_4^{2-}, S°_m was estimated with r_{12}= 2.04 and 2.02 Å respectively, and Eq.(2) of Cobble (1953a).

The entropy change for the protonation steps of the anions TcO_4^{2-} and TcO_4^- are assumed to be equal to the $\Delta_r S^\circ_m$ values for the protonation of SO_4^{2-}, HSO_3^- and NO_3^-, *i.e.*: +113, +68 and +32 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ respectively, all calculated from the S°_m values listed by Shock and Helgeson (1988), and Shock *et al.* (1989).

For the chloride complexes of Tc, the entropy change of each Cl^- coordination may be assumed to be 42 $J{\cdot}K^{-1}{\cdot}mol^{-1}$, *i.e.*, 10 $cal{\cdot}K^{-1}{\cdot}mol^{-1}$. This is a "reasonable" value for chloride complexation, see for example Ruaya (1988). However, in this work we use the method of Cobble, (1953b, Eqs. (7) and (8)), as described by Lemire and Garisto (1989), which may be used for complexes of hydroxide, chloride and carbonate.

The method of Lemire and Garisto (1989) consists in the assumption that in order to use Eqs. (7) and (8) in Cobble (1953b), the species are assumed to contain hydroxo ligands instead of oxo groups (Lemire and Garisto, 1989, pp. 91-92). Therefore, $S^\circ_m(TcOX) = [S^\circ_m(Tc(OH)_2X) - S^\circ_m(H_2O(l))]$, where X is any ligand, and charges are left out for clarity.

This procedure is used in this work for the hydroxo-chloride and hydroxo-carbonate complexes of Tc(III), as well as for the oxy-chloride complexes of Tc(V) and the chloride complexes of Tc(IV), *i.e.*: $TcOCl_5^{2-}$, $TcOCl_4^-$, $TcO_2Cl_4^{3-}$, $TcCl_6^{2-}$, $TcCl_3OH^-$ and $TcCO_3(OH)_4^{3-}$.

For the sulphate complexation of TcO^{2+}, we adopt the estimation of Rard (1983), *i.e.*, the same reaction properties as those for the formation of $RuOSO_4(aq)$.

For CO_3^{2-} complexation of TcO^{2+}, we have used the value recommended in the NEA uranium review (Grenthe *et al*, 1992) for the entropy of the reaction:

$$UO_2^{2+} + CO_3^{2-} \rightleftarrows UO_2CO_3(aq) \qquad \Delta_r S^\circ_m = +202 \pm 7\ J{\cdot}K^{-1}{\cdot}mol^{-1}$$

which results in S°_m = +32 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ for $TcOCO_3(aq)$, and we assign an estimated uncertainty of ±50 $J{\cdot}K^{-1}{\cdot}mol^{-1}$ to this value. This value agrees with the estimation according to the method of Lemire and Garisto (1989) described above, namely $S^{\circ}_{\mathrm{m}} = +36\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

For the hydrolysis reactions of $\mathrm{TcO^{2+}}$, we use Eqs. (11), (20) and (23) in Baes and Mesmer (1981) as follows.

For $\mathrm{[TcO(OH)_2]_2(aq)}$, the method described by Lemire and Garisto (1989, p. 92) was used here: S°_{m} was estimated for the following reaction:

$$2\ \mathrm{Tc^{4+}} + 8\ \mathrm{H_2O(l)} \rightleftarrows \mathrm{[Tc(OH)_4]_2(aq)} + 8\ \mathrm{H^+}$$

using $r = 2.04$ Å, with Eq.(20) in Baes and Mesmer (1981):

$$S^{\circ}_{\mathrm{m},xy} = 4.184{\cdot}8{\cdot}(-17.5 + 16.2{\cdot}(4\,/\,2.04) + (1+8-2)/8){\cdot}\mathrm{R}{\cdot}\ln(55.51) = +711\ \ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

where R is the gas constant R=1.9872 $\mathrm{cal{\cdot}K^{-1}{\cdot}mol^{-1}}$. Then,

$$S^{\circ}_{\mathrm{m}}(\mathrm{[Tc(OH)_4]_2(aq)}) = +711 + 2{\cdot}S^{\circ}_{\mathrm{m}}(\mathrm{Tc^{4+}}) + 8{\cdot}S^{\circ}_{\mathrm{m}}(\mathrm{H_2O(l)}) = +335\ \ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$$

$$S^{\circ}_{\mathrm{m}}(\mathrm{[TcO(OH)_2]_2(aq)}) = S^{\circ}_{\mathrm{m}}(\mathrm{[Tc(OH)_4]_2(aq)}) - 2{\cdot}S^{\circ}_{\mathrm{m}}(\mathrm{H_2O(l)}) = +195\ \ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}.$$

For $\mathrm{TcO(OH)^+}$, S°_{m} was estimated by using Eq.(11) in Baes and Mesmer (1981) for:

$$\mathrm{TcO^{2+}} + \mathrm{H_2O(l)} \rightleftarrows \mathrm{TcO(OH)^+} + \mathrm{H^+}$$

with $\log K^{\circ}_{\mathrm{eq}} = -1.13$ (Gorski and Koch 1969, see discussion above for Gibbs free energies) which results in $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}} = +70 \pm 40\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, and $S^{\circ}_{\mathrm{m}}(\mathrm{TcO(OH)^+}) = +20 \pm 43\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$. Note however, that this does not agree well with the results obtained from Eq.(7) in Cobble (1953b) which, assuming a composition of $\mathrm{Tc(OH)_3^+}$ and $r = 2.04$ Å, gives $S^{\circ}_{\mathrm{m}}(\mathrm{TcO(OH)^+}) = +140 \pm 60\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

From Eq.(23), reaction (22) and Figure 5 in Baes and Mesmer (1981), $\Delta_{\mathrm{r}}S^{\circ}_{\mathrm{m}} = -23 \pm 60\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$ was obtained for reaction:

$$\mathrm{TcO(OH)^+} + \mathrm{H_2O(l)} \rightleftarrows \mathrm{TcO(OH)_2(aq)} + \mathrm{H^+}.$$

This gives $S^{\circ}_{\mathrm{m}}(\mathrm{TcO(OH)_2(aq)}) = +67 \pm 74\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$, and agrees (within the uncertainty) with the results obtained from Eq.(8) in Cobble (1953b), which assuming a composition of $\mathrm{Tc(OH)_4(aq)}$ and $r = 2.04$ Å, gives $S^{\circ}_{\mathrm{m}}(\mathrm{TcO(OH)_2}) = +36 \pm 60\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$.

Finally, for $TcO(OH)_3^-$, S°_m was also estimated with Eq.(23) in Baes and Mesmer (1981) which gives $\Delta_r S^\circ_m = -75 \pm 60$ J·K⁻¹·mol⁻¹ for reaction:

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

from which $S^\circ_m(TcO(OH)_3^-) = +62 \pm 95$ J·K⁻¹·mol⁻¹. This does not agree well with the value obtained using Eq.(7) in Cobble (1953b), *i.e.* $S^\circ_m(TcO(OH)_3^-) = +282 \pm 60$ J·K⁻¹·mol⁻¹, using the procedure proposed by Lemire and Garisto (1989).

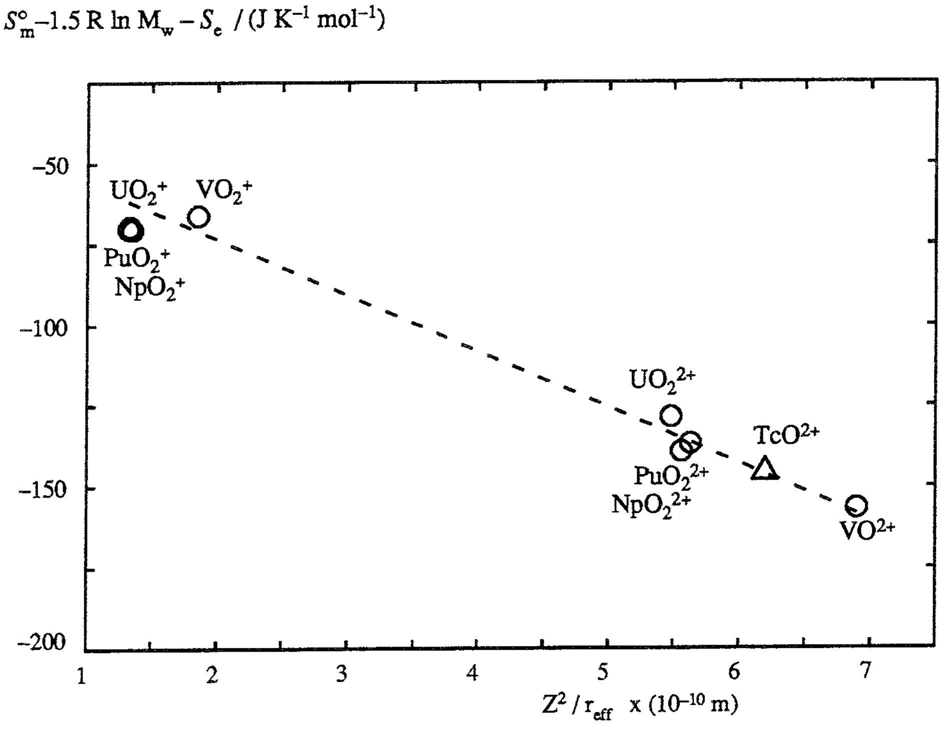

Figure1: Correlation, for oxy-cations, between Z^2/r_{eff} and the standard partial molar entropies (corrected for molecular weight and internal electronic effects).

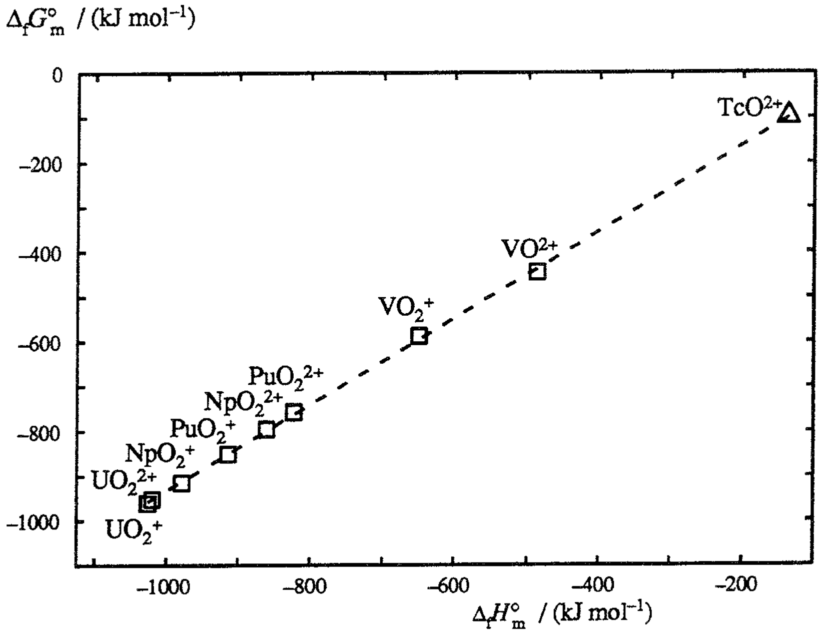

Figure 2: Plot of $\Delta_f G^\circ_m$ *versus* $\Delta_f H^\circ_m$ for oxy-cations.

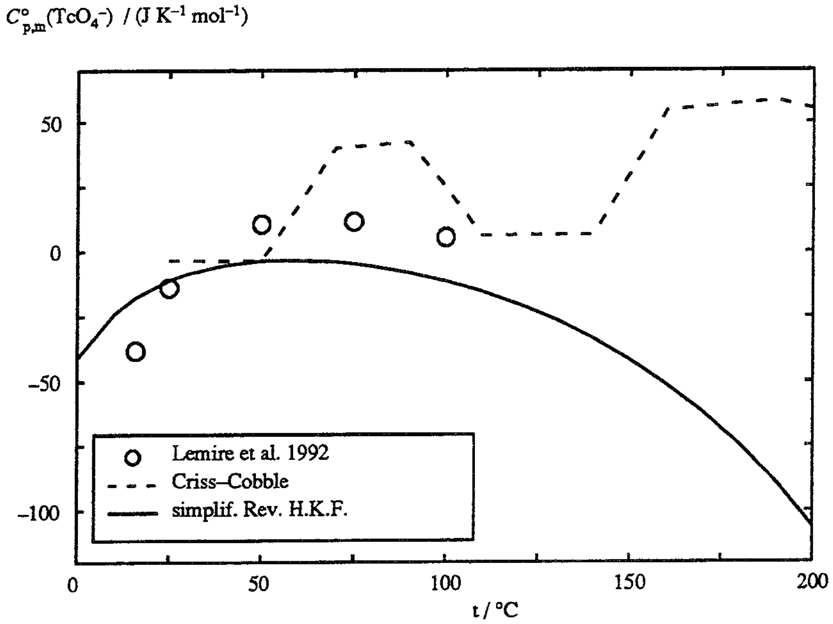

Figure 3: The experimental standard partial molar heat capacity of TcO_4^- as a function of temperature (circles, Lemire *et al.* 1992). The figure also shows $C^\circ_{p,m}(T)$ functions calculated for the correspondence principle of Criss and Cobble, and for the simplified revised Helgeson-Kirkham-Flowers model. This last model, has been used to make the temperature extrapolations described in the text (*cf.* Section 3).

2.3 HEAT CAPACITIES

Selected values for $C^{\circ}_{p,m}$ at T_o=298.15 K and 1 bar are listed in Table 1. Heat capacity values were taken from the literature for the following solids: Tc(cr) (Knacke *et al.* 1991), $KTcO_4$(cr) (Rard 1983), and Tc_2O_7(cr) (Knacke *et al.* 1991). All other heat capacities for solid phases have been estimated with the method of Kubaschewski and Alcock (1979). The heat capacity contribution of cationic Tc in a solid is estimated to be 24.3±0.4 $J \cdot K^{-1} \cdot mol^{-1}$, *i.e.*, 5.8 $cal \cdot K^{-1} \cdot mol^{-1}$, which is the average of the values for Nb and Ag (Kubaschewski and Alcock 1979, Table X, p.182). The hydrogen contribution to $C^{\circ}_{p,m}$ in $HTcO_4$(cr), is taken to be the value listed by Sturtevant (1959), *i.e.*, 9.62 $J \cdot K^{-1} \cdot mol^{-1}$. For each water of hydration in $TcO_2 \cdot 1.63H_2O$(s), the heat capacity of ice is added, which at 25°C, is estimated by extrapolation from the tables of CODATA as $C^{\circ}_{p,m}$(ice, 298.15 K)= +40.8±0.2 $J \cdot K^{-1} \cdot mol^{-1}$.

With one exception, all standard partial molar heat capacities of aqueous species had to be estimated.

Lemire *et al.* (1992) have experimentally determined values of $C^{\circ}_{p,m}$ for aqueous solutions of $NaTcO_4$ as a function of temperature (16 to 100° C) and at 6 bar. Using the standard partial molar heat capacities of aqueous solutions of NaCl and HCl (Pitzer *et al.* 1984; Saluja *et al.* 1986), $C^{\circ}_{p,m}(TcO_4^-)$ at 1 bar can be obtained as function of temperature, and is plotted in Figure 3. This Figure also shows the temperature dependence of $C^{\circ}_{p,m}(TcO_4^-)$ calculated with both the correspondence principle of Criss and Cobble (1964a) and with the simplified revised Helgeson-Kirkham-Flowers, HKF, model (Shock and Helgeson, 1988).

The method of Criss-Cobble uses the value of $S^{\circ}_{m}(T_o)$ (where T_o= 298.15 K) to calculate ionic entropies at higher temperatures. It is therefore a one-parameter model, *cf.* Eqs. (3.6) and (3.7).

The revised HKF model can be simplified (*cf.* Section 3) to use the values of $S^{\circ}_{m}(T_o)$ and $C^{\circ}_{p,m}(T_o)$ to estimate the temperature dependence of $C^{\circ}_{p,m}(T)$. It is therefore a two-parameter model.

Figure 3 shows that the method of Criss and Cobble gives a discontinuous $C^{\circ}_{p,m}(T)$ curve. This is because according to Eq.(7) in Criss and Cobble (1964a):

$$S^{\circ}_{m}(T) = a(T) + b(T)\cdot(S^{\circ}_{m}(T_o) - 20.9\cdot Z_i) - S^{\circ}_{m}(H^+,T)$$

which can be rearranged to:

$$S^\circ_m(\mathrm{T}) = A(\mathrm{T}) + B(\mathrm{T})\cdot S^\circ_m(\mathrm{T_o}) \tag{2.3}$$

where $a(\mathrm{T})$, $b(\mathrm{T})$, $S^\circ_m(\mathrm{H^+,T})$ are parameters which are assumed to vary linearly between the tabulated values at given temperatures, and therefore $A(\mathrm{T})$ and $B(\mathrm{T})$ have also a linear dependence with temperature. Because

$$\frac{C^\circ_{p,m}(\mathrm{T})}{\mathrm{T}} = \left(\frac{\partial\, S^\circ_m(\mathrm{T})}{\partial\, \mathrm{T}}\right)_P$$

$C^\circ_{p,m}(\mathrm{T})$ can be calculated by numerical differentiation, *cf.* Eq.(3.6) in Section 3. The resulting stepping curve for $C^\circ_{p,m}(\mathrm{T})$ is the result of the discontinuous temperature variation of parameters $A(\mathrm{T})$ and $B(\mathrm{T})$ in Eq.(2.3), which are calculated from the tabulated values of $a(\mathrm{T})$, $b(\mathrm{T})$ and $S^\circ_m(\mathrm{H^+,T})$ in Criss and Cobble (1964 a), at the temperatures of 25, 60, 100 and 150°C.

The maximum deviation between experimental $C^\circ_{p,m}(\mathrm{TcO_4^-})$ values and the simplified revised HKF model in Figure 3 is about 20 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, but if the full revised HKF model is used, a good fit to the experimental data can be achieved by adjusting the 3 model parameters: c_1, c_2 and ω. However, this was considered unnecessary for this work.

In the range T = 0 – 150°C the temperature dependence of the equilibrium constants gives similar results if calculated by the Criss and Cobble method or the revised HKF model, even if the Criss and Cobble $C^\circ_{p,m}(\mathrm{T})$ function shows clear discontinuities. Keeping $C^\circ_{p,m}$ constant in this range of temperatures gives also similar results. This is due to the fact that $\log K^\circ_{eq}(\mathrm{T})$ values are not very sensitive to $C^\circ_{p,m}(\mathrm{T})$ changes for $\mathrm{T} \leq 150$°C.

For T>150°C, the $C^\circ_{p,m}(\mathrm{T})$ values calculated by the Criss and Cobble method are too positive, which overestimates the corresponding ionic entropies and underestimates the ionic Gibbs free energies. For some equilibrium reactions these over and under estimates will cancel each other, giving some reasonable agreement between the calculated $\log K^\circ_{eq}(\mathrm{T})$ values and the experimentally determined $\log K^\circ_{eq}(\mathrm{T})$ values even at T>150°C.

Eq.(91) in Shock and Helgeson (1988) is used to estimate the standard partial molar heat capacity (from $S^\circ_m(\mathrm{T_o})$ values) for the following aqueous ions: $\mathrm{TcO_4^{2-}}$, $\mathrm{Tc^{3+}}$ and $\mathrm{Tc^{2+}}$. For $\mathrm{TcO_4^{3-}}$ the same equation is used, because even though the equation is valid only for divalent oxy-anions, it also fits the $C^\circ_{p,m}(PO_4^{3-})$ within ±10 $J\cdot K^{-1}\cdot mol^{-1}$.

The value of $C^\circ_{p,m}$ for Tc^{4+} is needed to estimate the heat capacity of $TcCl_5^-$ and $TcCl_6^{2-}$, as described below. For this "non-existing" ion, there are no estimation methods. $C^\circ_{p,m}(Tc^{4+})$ may be assumed to be equal to the heat capacity of an ion of the same charge: Th^{4+} (= −1±11 $J\cdot K^{-1}\cdot mol^{-1}$, Morss and McCue 1976). However, this value seems unusually positive, as $C^\circ_{p,m}$ values tend to be increasingly negative with charge, and for metallic ions with a charge of +3, $C^\circ_{p,m}$ values are in the −165±80 $J\cdot K^{-1}\cdot mol^{-1}$ range, *cf.* Figure 15 in Shock and Helgeson (1988). Therefore, a value of $C^\circ_{p,m}(Tc^{4+})= -180\pm100$ $J\cdot K^{-1}\cdot mol^{-1}$ is adopted. In the NEA uranium review, Grenthe *et al.* (1992) adopted the Criss-Cobble average heat capacity between 25° and 200° C ($C^\circ_{p,m}(U^{4+})= -48\pm15$ $J\cdot K^{-1}\cdot mol^{-1}$). However, in view of the uncertainties in the $C^\circ_{p,m}$ values obtained using the Criss-Cobble correspondence principle (*cf.* Figure 3), we feel that a more negative value should be used for aqueous metal ions with charge +4.

For TcO^{2+}, the estimated entropy, and a plot of $C^\circ_{p,m}$ *versus* S°_m (with the few available data) are used to estimate $C^\circ_{p,m}(TcO^{2+})= -5\pm25$ $J\cdot K^{-1}\cdot mol^{-1}$, *cf.* Figure 4.

For coordination reactions, the "isocoulombic" approach is used (see for example Phillips and Silvester 1983, Jackson and Helgeson 1985, Ruaya 1988): heat capacity changes are assumed to be equal for reactions involving ions with the same ionic charges. Thus, $\Delta_r C^\circ_{p,m}$ for the protonation steps of the anions TcO_4^{2-} and TcO_4^- are assumed to be equal to those for the protonation of the anions SO_4^{2-}, and NO_3^-, which are calculated from the tabulated $C^\circ_{p,m}$ values in Shock and Helgeson (1988) and Shock *et al.* (1989). This gives $\Delta_r C^\circ_{p,m}$ values which agree well with the average $\Delta_r C^\circ_{p,m}$ for oxy-acid dissociations given by Smith *et al.* (1986). The $C^\circ_{p,m}(H_2TcO_4(aq))$ is estimated with the average value for the protonation reaction given by Smith *et al.* (1986).

For carbonate complexation, *i.e.*, for the complexes $TcCO_3(OH)_4^{3-}$, $TcOCO_3OH^-$ and $TcOCO_3(aq)$, $\Delta_r C^\circ_{p,m}$ for the coordination of a CO_3^{2-} ion is assumed to be equal to +600±300 $J\cdot K^{-1}\cdot mol^{-1}$, based on our interpretation of the T-dependence of the equilibrium constant of formation of $CaCO_3(aq)$ studied by Plummer and Busenberg (1982). Note however that Phutela and Pitzer (1986) report $\Delta_r C^\circ_{p,m} = +170$ $J\cdot K^{-1}\cdot mol^{-1}$ for the formation of $MgSO_4(aq)$, and according to the isocoulombic approximation, both values should be equal. The $\Delta_r C^\circ_{p,m}$ for the formation of $TcOSO_4(aq)$ is assumed to be equal to that of the formation of $MgSO_4(aq)$.

The change in heat capacity for hydroxide complexation at 25°C, is assumed to be:

$$M(OH)_n^{Z+} + OH^- \rightleftarrows M(OH)_{n+1}^{(Z-1)+} \qquad (2.4)$$

$$\Delta_r C^\circ_{p,m} = +130 + (40 \cdot Z) \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

This equation has been derived to give results close to the reported $\Delta_r C^\circ_{p,m}$ values for Al^{3+} hydrolysis. The aluminium (III) system was chosen because the $C^\circ_{p,m}(T_o)$ value of $Al(OH)_4^-$ seems to be the only well known value for a hydroxide complex (*i.e.*, several research groups give results in agreement, see Tremaine 1990, Hovey *et al.* 1988, Apps and Neil 1990). The uncertainty in using Eq.(2.4) to estimate $C^\circ_{p,m}$ for an aqueous species is expected to be ±30 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$. Use of Eq.(2.4) implies the "isocoulombic" approximation mentioned above.

Eq.(2.4) is used to estimate $C^\circ_{p,m}$ values for $TcO(OH)^+$, $TcO(OH)_2(aq)$, $TcO(OH)_3^-$ and $TcCO_3(OH)_4^{3-}$. The same values are used for chloride complexation, as required by the isocoulombic approximation. Eq.(2.4) is therefore also used in this work for the oxychlorides of Tc(V), the chlorides and hydroxy complexes of Tc(IV) and Tc(III):$TcOCl_5^{2-}$, $TcOCl_4^-$, $TcO_2Cl_4^{3-}$, $TcCl_6^{2-}$, $TcCl_5^-$ and $TcCl_3OH^-$. For example, for $TcCl_6^{2-}$:

$$Tc^{4+} + 6\,Cl^- \rightleftarrows TcCl_6^{2-}$$

$$\Delta_r C^\circ_{p,m} = +290 +250 +210 +170 +130 +90 = +1140 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$$
$$C^\circ_{p,m}(TcCl_6^{2-}) = +1140 + 6 \cdot C^\circ_{p,m}(Cl^-) + C^\circ_{p,m}(Tc^{4+}) = +221 \pm 120 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}.$$

In order to confirm this estimation procedure, for TcO^{2+}, the value obtained above from Figure 4, $C^\circ_{p,m}(TcO^{2+}) = -5 \pm 25 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, should also agree with the $C^\circ_{p,m}$ value estimated from the procedure used for $TcCl_6^{2-}$ in the preceding reaction, *i.e.*:

$$Tc^{4+} + 2\,OH^- \rightleftarrows Tc(OH)_2^{2+} \rightleftarrows TcO^{2+} + H_2O(l)$$

according to Eq.(2.4),

$$\begin{aligned} C^\circ_{p,m}(Tc(OH)_2^{2+}) &= +290 +250 + C^\circ_{p,m}(Tc^{4+}) + 2 \cdot C^\circ_{p,m}(OH^-) \\ &= +540 + (-180) + 2 \cdot (-137.2) = +85.6 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \\ C^\circ_{p,m}(TcO^{2+}) &= C^\circ_{p,m}(Tc(OH)_2^{2+}) - C^\circ_{p,m}(H_2O(l)) \\ &= +85.6 - (75.35) = +10 \pm 120 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}} \end{aligned}$$

where the large uncertainty originates from $C^\circ_{p,m}(Tc^{4+})$. Both values of $C^\circ_{p,m}(TcO^{2+})$ (that from Figure 4, $C^\circ_{p,m} = -5\pm25$ J·K^{-1}·mol^{-1}, and that from Eq.(2.4)) agree within the given uncertainties.

For $TcOCl_5^{2-}$, it is first assumed that TcO_4^{3-} may be written as $TcO(OH)_6^{3-}$, and that $\Delta_r C^\circ_{p,m}=0$ for the isocoulombic reaction:

$$TcO(OH)_6^{3-} + 5\ Cl^- \rightleftarrows TcOCl_5OH^{3-} + 5\ OH^-$$

and that $\Delta_r C^\circ_{p,m} = +50$ J·K^{-1}·mol^{-1}, *cf.* Eq.(2.4), for:

$$TcOCl_5^{2-} + OH^- \rightleftarrows TcOCl_5OH^{3-}$$

and therefore,

$$C^\circ_{p,m}(TcOCl_5^{2-}) = -50 - 6\cdot C^\circ_{p,m}(OH^-) + 5\cdot C^\circ_{p,m}(Cl^-) + C^\circ_{p,m}(TcO_4^{3-}) + 3\cdot C^\circ_{p,m}(H_2O(l)).$$

Similarly, for $TcO_2Cl_4^{3-}$, we assume that it may be written as $TcO(OH)_2Cl_4^{3-}$, and that $\Delta_r C^\circ_{p,m}=0$ for the following isocoulombic reaction:

$$TcO(OH)_6^{3-} + 4\ Cl^- \rightleftarrows TcO(OH)_2Cl_4^{3-} + 4\ OH^-$$

and therefore,

$$C^\circ_{p,m}(TcO_2Cl_4^{3-}) = 0 - 4\cdot C^\circ_{p,m}(OH^-) + 4\cdot C^\circ_{p,m}(Cl^-) + C^\circ_{p,m}(TcO_4^{3-}) + 3\cdot C^\circ_{p,m}(H_2O(l)).$$

For $[TcO(OH)_2]_2(aq)$, it is assumed that $\Delta_r C^\circ_{p,m}=0$ for the following reaction (which involves only neutral species):

$$2\ TcO(OH)_2(aq) \rightleftarrows [TcO(OH)_2]_2(aq).$$

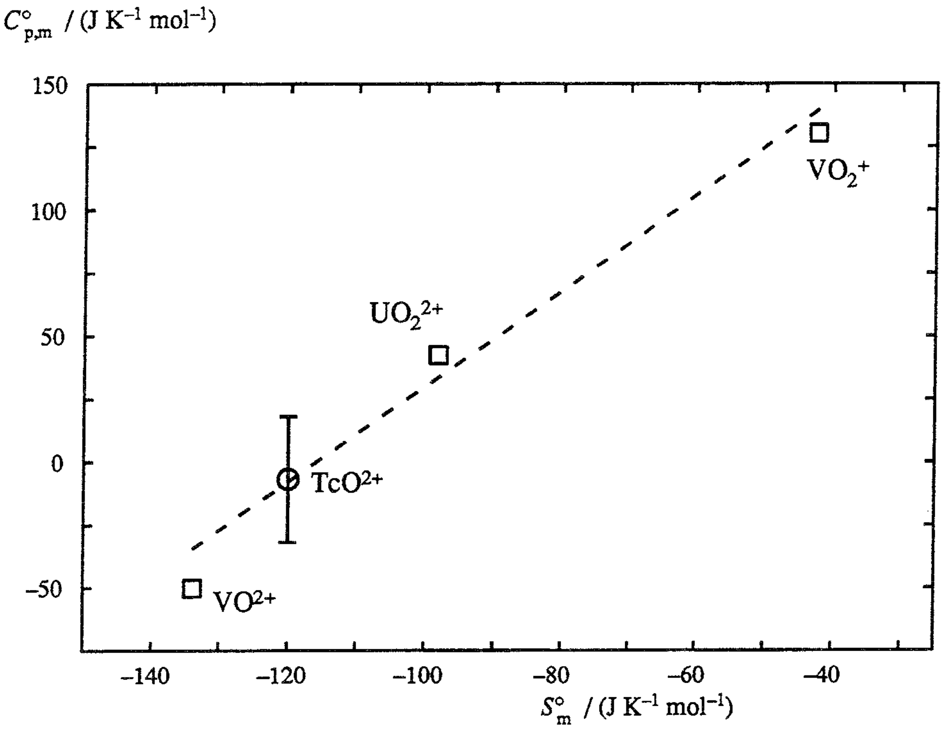

Figure 4: Correlation for oxy-cations between standard partial molar heat capacities and entropies, showing the estimated value of $C^\circ_{p,m}(TcO^{2+})$.

Table 1 Thermodynamic values at 298.15 K and 1 bar, and their estimated uncertainties, for technetium, and some of its inorganic compounds and aqueous species. The sources and criteria for the selection of the values are given in the text.

species	$\Delta_f G^\circ_m$ kJ·mol^{-1}	S°_m J·K^{-1}·mol^{-1}	$C^\circ_{p,m}$ J·K^{-1}·mol^{-1}
Tc(cr)	0	33.5 ± 1	25.3^a± 1
Tc(VII):			
Tc_2O_7(cr)	−935.6 ±15	184.1 ± 2	211^b ± 4
$HTcO_4$(cr)	−589.8 ±11	126.3 ± 5	108^c ± 4
$KTcO_4$(cr)	−919.2 ±10	164.8 ± 0.3	123^c ± 2
TcO_4^-	−621.1 ± 5	199.0 ± 1.3	−11 ± 8
$HTcO_4$(aq)	−621.7 ± 6	231 ± 20	146 ± 30
Tc(VI):			
TcO_4^{2-}	−562.2 ±10	91 ± 15	−222 ± 15
$HTcO_4^-$	−611.9 ±11	204 ± 20	71 ± 30
H_2TcO_4(aq)	−613.6 ±12	272 ± 20	205 ± 20
Tc(V):			
TcO_4^{3-}	−505.3 ± 7	−74 ± 15	−354 ± 20
$TcOCl_5^{2-}$	−686 ±12	220 ±100	13 ± 50
$TcOCl_4^-$	−585.1 ±15	352 ±100	46 ± 50
$TcO_2Cl_4^{3-}$	−775.3 ±12	86 ±100	−72 ± 50

[a] $C^\circ_{p,m}(T) / (J \cdot K^{-1} \cdot mol^{-1}) = 23.748 + 5.406 \cdot 10^{-3}\, T - 8 \cdot 10^{3}\, T^{-2}$

[b] $C^\circ_{p,m}(T) / (J \cdot K^{-1} \cdot mol^{-1}) = 104.6 + 0.35564\, T$

[c] $C^\circ_{p,m}$ was kept constant in the temperature extrapolations.

Table 1 (Continued)

species	$\Delta_f G^\circ_m$ kJ·mol^{-1}	S°_m J·K^{-1}·mol^{-1}	$C^\circ_{p,m}$ J·K^{-1}·mol^{-1}
Tc(IV):			
$TcO_2 \cdot 1.63H_2O(s)$	−749.56 ± 5	127.3 ± 5	127.6[c] ± 4
$TcCl_6^{2-}$	−655.4 ±12	219 ±100	221 ±120
$TcCl_5^-$	−524.2 ±13	350 ±100	254 ±120
TcO^{2+}	−99.55 ± 5	−120 ± 15	−5 ± 25
$TcO(OH)^+$	−330.25 ± 5	20 ± 43	68 ± 30
$TcO(OH)_2(aq)$	−553.54 ± 5	67 ± 74	101 ± 30
$[TcO(OH)_2]_2$	−1144.1 ± 6	195 ±100	202 ± 45
$TcO(OH)_3^-$	−728.02 ± 5	62 ± 95	93 ± 40
$TcOCO_3(aq)$	−717.0 ± 5	32 ± 50	304 ±300
$TcOCO_3OH^-$	−907.0 ± 5	220 ± 75	377 ±300
$TcOSO_4(aq)$	−856.33 ± 6	−169 ± 20	−104 ± 30
Tc(III):			
Tc^{3+}	+106.82 ± 6	−293 ± 15	−138 ± 20
$TcCl_3OH^-$	−537.75 ±13	280 ±100	−15 ± 30
$TcCO_3(OH)_4^{3-}$	−1284.8 ± 6	230 ±100	382 ±300
Tc(II):			
Tc^{2+}	+77.2 ±20	−100 ± 15	−30 ± 20

[c] $C^\circ_{p,m}$ was kept constant in the temperature extrapolations.

3 TEMPERATURE EXTRAPOLATIONS

Equilibrium constants can be calculated as a function of temperature using the thermodynamic parameters in Table 1 for technetium species, and those for auxiliary species listed by CODATA (Cox *et al.* 1989) and the standard partial molar heat capacities for aqueous ions and molecules at 298.15 K tabulated by Shock ad Helgeson (1988) and Shock *et al.* (1989).

In general a heat capacity integration is performed to calculate, at each temperature of interest, the apparent standard molar Gibbs free energy of formation (or, for aqueous species, the apparent standard partial molar Gibbs free energy of formation), $\Delta_a G^\circ_m(i,T)$, where "i" stands for each one of the reactants and products in the equilibrium reaction:

$$\Delta_a G^\circ_m(i,T) = \Delta_f G^\circ_m(i,T_o) + (G^\circ_m(i,T) - G^\circ_m(i,T_o)) \tag{3.1}$$

$$\begin{aligned}\Delta_a G^\circ_m(i,T) = \Delta_f G^\circ_m(i,T_o) - S^\circ_m(i,T_o)\cdot(T-T_o) + \int_{T_o}^{T} C^\circ_{p,m}(i,T)\,dT \\ - T\int_{T_o}^{T}\frac{C^\circ_{p,m}(i,T)}{T}dT\end{aligned} \tag{3.2}$$

where T_o is the reference temperature $T_o = 298.15$ K, and $C^\circ_{p,m}(i,T)$ is a temperature function describing the standard heat capacity.

Once the apparent standard molar Gibbs free energies of each species is known at a given T, the $\Delta_r G^\circ_m(T)$ for the reaction can be calculated:

$$\Delta_r G^\circ_m(T) = \sum_i^n \nu(i)\ \Delta_a G^\circ_m(i,T) \tag{3.3}$$

where "$\nu(i)$" are the stoichiometric coefficients of the "n" reactants in the reaction. The equilibrium constant can be calculated from:

$$\log K^\circ_{eq}(T) = -\Delta_r G^\circ_m(T) / (R\cdot T\cdot \ln(10)) \tag{3.4}$$

where the gas constant is $R = 8.31451\ J\cdot K^{-1}\cdot mol^{-1}$.

For equilibrium reactions including water as a reactant or product, the values of $\Delta_a G^\circ_m(H_2O(l),T)$ used here are a combination of the CODATA values, and the equation of state of Saul and Wagner (1989). For the dielectric constant of water, the temperature and pressure function of Archer and Wang (1990) is used to calculate the Born functions in the revised HKF model.

For solid compounds, an equation of the type:

$$C^\circ_{p,m}(T) = a + b \cdot T + c \cdot T^2 \tag{3.5}$$

is normally used, where a, b and c are T-independent parameters, and an analytical integration of the $C^\circ_{p,m}(T)$ equation is then performed to obtain values of $\Delta_a G^\circ_m(i,T)$ with Eq.(3.2).

For aqueous species, $\Delta_a G^\circ_m(i,T)$ is also calculated from analytical integration of a heat capacity function, but in this case, the equation $C^\circ_{p,m}(i,T)$ is usually not a simple polynomial function of T.

In this work, the heat capacity T-function for aqueous species containing technetium is that of the simplified version of the revised Helgeson, Kirkham and Flowers (HKF) model, described in Tanger and Helgeson (1988), Shock and Helgeson (1988), and Shock *et al.* (1989). For this simplified version, only the value of $C^\circ_{p,m}(i,T_o)$ is needed. This value and $S^\circ_m(i,T_o)$ are used to estimate the revised HKF parameters: c_1, c_2 and ω, *cf.* Eqs. (29), (31), (35), (45), (56), (57) and (89) in Shock and Helgeson (1988), and Eqs. (21), (23), (26), (44) and (45) in Shock *et al.* (1989).

For auxiliary aqueous species (*i.e.*, those not containing technetium), the complete Revised-HKF model mentioned above is used. The parameters needed are: c_1, c_2 and ω, and these were taken from the tables of Shock and Helgeson (1988) and Shock *et al.* (1989).

An alternative heat capacity function for aqueous ions is Eq.(7) in Criss and Cobble (1964a). If the method of Criss-Cobble is used, the value of $C^\circ_{p,m}$ at any temperature can be approximately calculated by numerical differentiation (*cf.* Eq.(4) in Criss and Cobble 1964b), for example:

$$C^\circ_{p,m}(T) = \frac{1}{2}\left[\frac{S^\circ_m(T+2) - S^\circ_m(T)}{\ln((T+2)/T)} - \frac{S^\circ_m(T-2) - S^\circ_m(T)}{\ln((T-2)/T)}\right] \tag{3.6}$$

where $S^\circ_m(T)$ is calculated with Eq.(7) in Criss and Cobble (1964a):

$$S^\circ_m(T) = a(T) + b(T)\cdot(S^\circ_m(T_0) - 20.9\cdot Z_i) - S^\circ_m(H^+,T) \qquad (3.7)$$

using linear interpolation among the values for $S^\circ_m(H^+,T)$ and the "a(T)" and "b(T)" parameters in Table III of Criss and Cobble (1964a).

A computer program, written in FORTRAN, has been developed to perform the calculations for reactions of interest, as well as to write output in a format adequate for geochemical computer programs (EQ3/6 and PHREEQE). The program (called "TePeX") has been run on IBM-PC and VAX computers.

Equilibrium constants suited for the computer programs EQ3/6 are listed in the Appendix.

3.1 UNCERTAINTIES

The uncertainties in extrapolated $\log K^\circ_{eq}$ values at high temperatures, are of special interest, because some of them affect directly the uncertainty in the calculated equilibrium solubilities at high temperatures.

According to Eqs. (3.2) and (3.4), errors of ±10 $kJ\cdot mol^{-1}$ in $\Delta_f G^\circ_m(i,T_o)$ correspond to ±1.9 and ±0.9 units in $\log K^\circ_{eq}$ at 0 and 300° C respectively. Similarly, errors of ±10 $J\cdot K^{-1}\cdot mol^{-1}$ in $S^\circ_m(i,T_o)$ contribute to a maximum uncertainty at 300° C of ±0.25 logarithmic units in the equilibrium constant, and an error of ±10 $J\cdot K^{-1}\cdot mol^{-1}$ in $C^\circ_{p,m}(i,T_o)$ corresponds to a maximum error of ±0.09 in $\log K^\circ_{eq}$ at 300° C. However, the uncertainty contribution from the heat capacity will depend on the type of T-function used for this quantity.

The reaction

$$TcO_2\cdot xH_2O(s) + HCO_3^- \rightleftarrows TcOCO_3OH^- + (x+1)\,H_2O(l) \qquad (3.8)$$

may be used as an example. This reaction is chosen because it is of interest in estimating Tc solubilities, and it includes some of the species with highest uncertainties in entropy and heat capacity (*cf.* Table 1).

The uncertainties in $\Delta_a G^\circ_m(i,T)$ in reaction (3.8), range from zero for H^+ (by definition), to an undetermined quantity for $TcO_2\cdot xH_2O(s)$ due to the fact that the temperature dependence of $C^\circ_{p,m}$ is not known for this solid (*i.e.*, only parameter "a" is known in Eq.(3.5)). Therefore, for the hydrous oxide of Tc(IV), only a minimum uncertainty may be given.

The maximum uncertainty in $\Delta_a G^\circ_m$ for water in the temperature range 25-300° C is given in the CODATA tables (Cox *et al.* 1989) as ±0.02 kJ·mol^{-1}. For HCO_3^-, the uncertainties at 25°C are ±0.25 kJ·mol^{-1}, for $\Delta_f G^\circ_m$, ±0.5 J·K^{-1}·mol^{-1} for S°_m, and about ±5 J·K^{-1}·mol^{-1} for $C^\circ_{p,m}$ (Cox *et al.* 1989). From an inspection of the uncertainties listed in Table 1, it can be concluded that the contributions from water and the bicarbonate ion are negligible for the estimation of errors in the temperature extrapolation of $\log K^\circ_{eq}(3.8)$.

Figure 5 shows the maximum and minimum values for $\log K^\circ_{eq}(3.8)$ calculated by systematic sensitivity analysis using the simplified revised HKF model. The temperature extrapolation using the Criss-Cobble principle is also shown in Figure 5 for comparison. For the Criss-Cobble calculations, both HCO_3^- and $TcOCO_3OH^-$ were considered to be "acid oxy anions".

At low temperatures (<100°C), the uncertainty shown in Figure 5 is overestimated. This is due to the fact that the uncertainty in $\Delta_r G^\circ_m(3.8)$ obtained from the values in Table 1, is manly due to the uncertainty in $\Delta_f G^\circ_m(TcO_4^-, T_o)$, *cf.* reaction (2.1). However, reaction (2.2) indicates that $\Delta_r G^\circ_m(3.8)$ has in fact a much lower uncertainty at 25°C.

At higher temperatures, the uncertainty shown in Figure 5 is due to the large uncertainties in the estimated values of $S^\circ_m(T_o)$ and $C^\circ_{p,m}(T_o)$ for $TcOCO_3OH^-$ (*cf.* Table 1).

Figure 5 also shows that the Criss-Cobble method produces values of $\log K^\circ_{eq}$ which differ substantially at T>200°C from the values calculated with the revised HKF model. The inadequacy of the Criss-Cobblle method at temperatures >150°C has already been commented when the values of $C^\circ_{p,m}(TcO_4^-, T)$ in Figure 3 were discussed.

Substancial differences might also be obtained if the heat capacity of $TcO_2{\cdot}xH_2O(s)$ is not assumed to be T-independent. This shows that systematic errors introduced in the method of temperature extrapolation might in some cases introduce uncertainties larger than those arising from uncertainties in the values of $S^\circ_m(i, T_o)$ or $C^\circ_{p,m}(i, T_o)$.

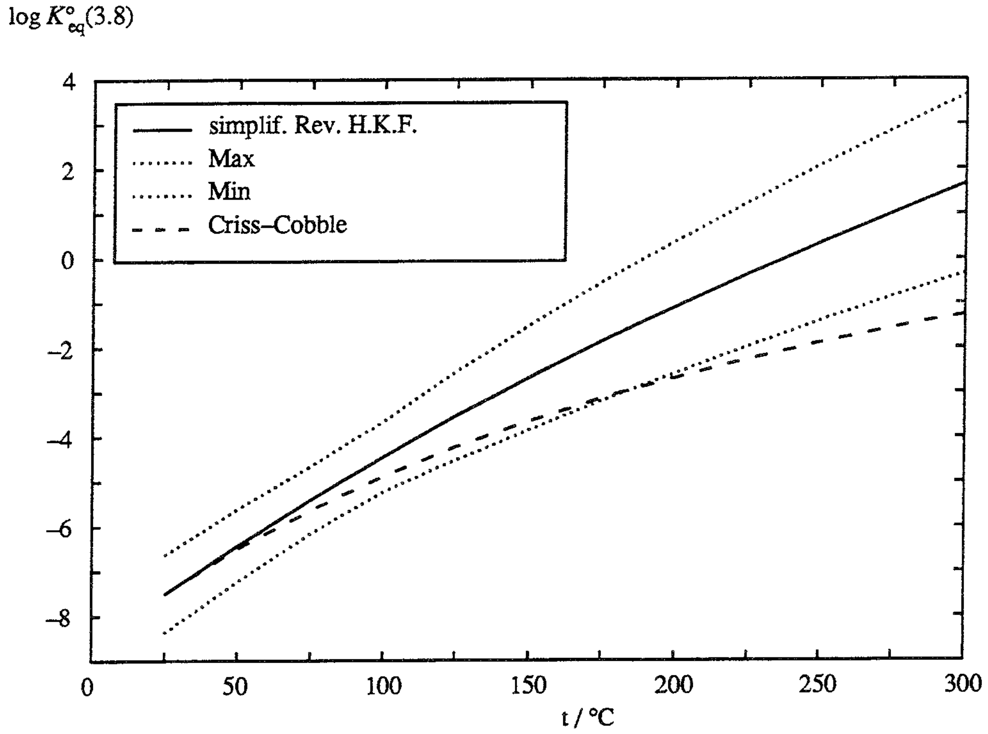

Figure 5: Calculated temperature dependence of $\log K^\circ_{eq}$ for the reaction: $TcO_2{\cdot}xH_2O(s) + HCO_3^- \rightleftarrows TcOCO_3OH^- + x\,H_2O(l)$. The graph shows results obtained with the equations of Criss-Cobble, and with the simplified version of the revised HKF model. The dotted lines show the uncertainty in the temperature extrapolation of the simplified revised HKF model using the data in Table 1.

4 RESULTS AND DISCUSSION

Two types of chemical equilibrium calculations have been performed in this work that are directly relevant to the performance assessment of a HLNW repository: speciation calculations (to highlight the important aspects of the aqueous chemistry of Tc, and consequently of its migration properties), and solubility calculations which define the Tc source term from the waste matrix.

Most of the calculations have been performed with a modification (Puigdomènech 1983) of the SOLGASWATER program (Eriksson 1979). This modified SOLGASWATER is specially adapted to draw chemical equilibrium diagrams, and has been extensively used for undergraduate courses in Stockholm. The results from SOLGASWATER, PHREEQE and EQ3/6 are essentially identical (Puigdomènech 1989, Puigdomènech and Emrén 1990)

Figure 6 shows a simulation of the reduction of Tc(VII) by aqueous solutions of HCl in a closed system, *i.e.* in a system where no oxidant or reductant are added along the reaction path. At high concentrations of hydrochloric acid, first Tc(V) and finally Tc(IV) are formed. The processes taking place are reactions of the following type:

$$TcO_4^- + 6\,Cl^- + 6\,H^+ \rightleftarrows TcOCl_4^- + Cl_2(aq) + 3\,H_2O(l).$$

It should be noted that the results given in Figure 6 are only qualitative, because an adequate correction for activity coefficients can not be made during the calculations. This is due to the high ionic concentration of the aqueous solutions involved. Nevertheless, the calculations show that the aqueous model is correct in reflecting the observed reduction of TcO_4^- by aqueous HCl. This has been possible by our estimation of the thermodynamic properties of $TcCl_6^{2-}$ and $TcOCl_5^{2-}$.

Calculated predominance area diagrams for a total concentration of technetium of 1µ mol/l, at 25, 150 and 300° C are shown in Figure 7. The metal appears to have at all temperatures a zone of potential/pH where it is immune to corrosion. However, there might exist some oxides or hydroxides of valence lower than (IV) not included in our model but which would affect the size of this area of corrosion immunity. Unfortunately, there is no reliable evidence or thermodynamic data for such solids.

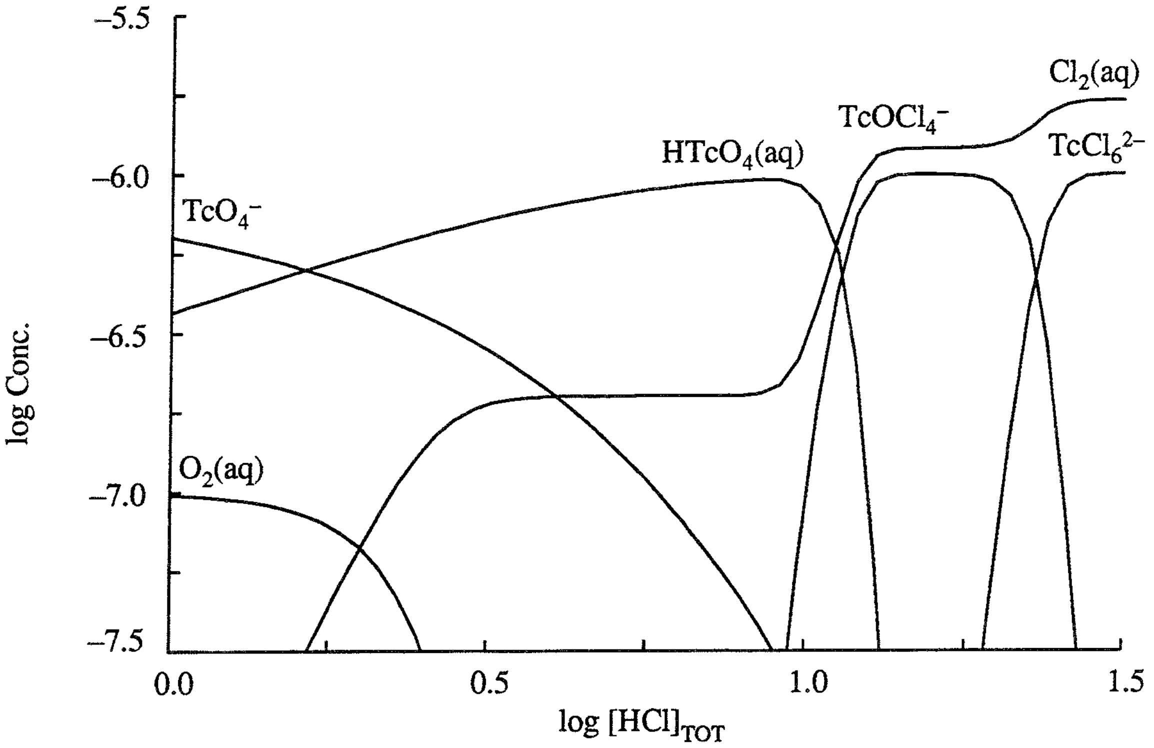

Figure 6: Calculated effect of increasing HCl concentration on the concentrations of aqueous species of technetium at 25°C. The redox capacity and the total amount of technetium of the system are kept constant.

Figure 7 also shows that the solubility of $TcO_2 \cdot xH_2O(s)$ increases with temperature, because the predominance area of this solid disappears (at the 1µ mol/l level) between 25 and 150°C.

The effect of increasing total carbonate concentration on the speciation of Tc at 25°C, is shown in Figure 8. The calculations were made by setting the partial pressure of $H_2(g)$ to a constant value, which results in a variation of the redox potential, Eh, with increasing pH, according to the following reaction,

$$H^+ + e^- \rightleftarrows \tfrac{1}{2} H_2(g)$$

by definition, the equilibrium constant is unity for the reaction above:

$$\log K^\circ_{eq} = 0 = \log p(H_2) - \log\{e^-\} - \log\{H^+\}$$

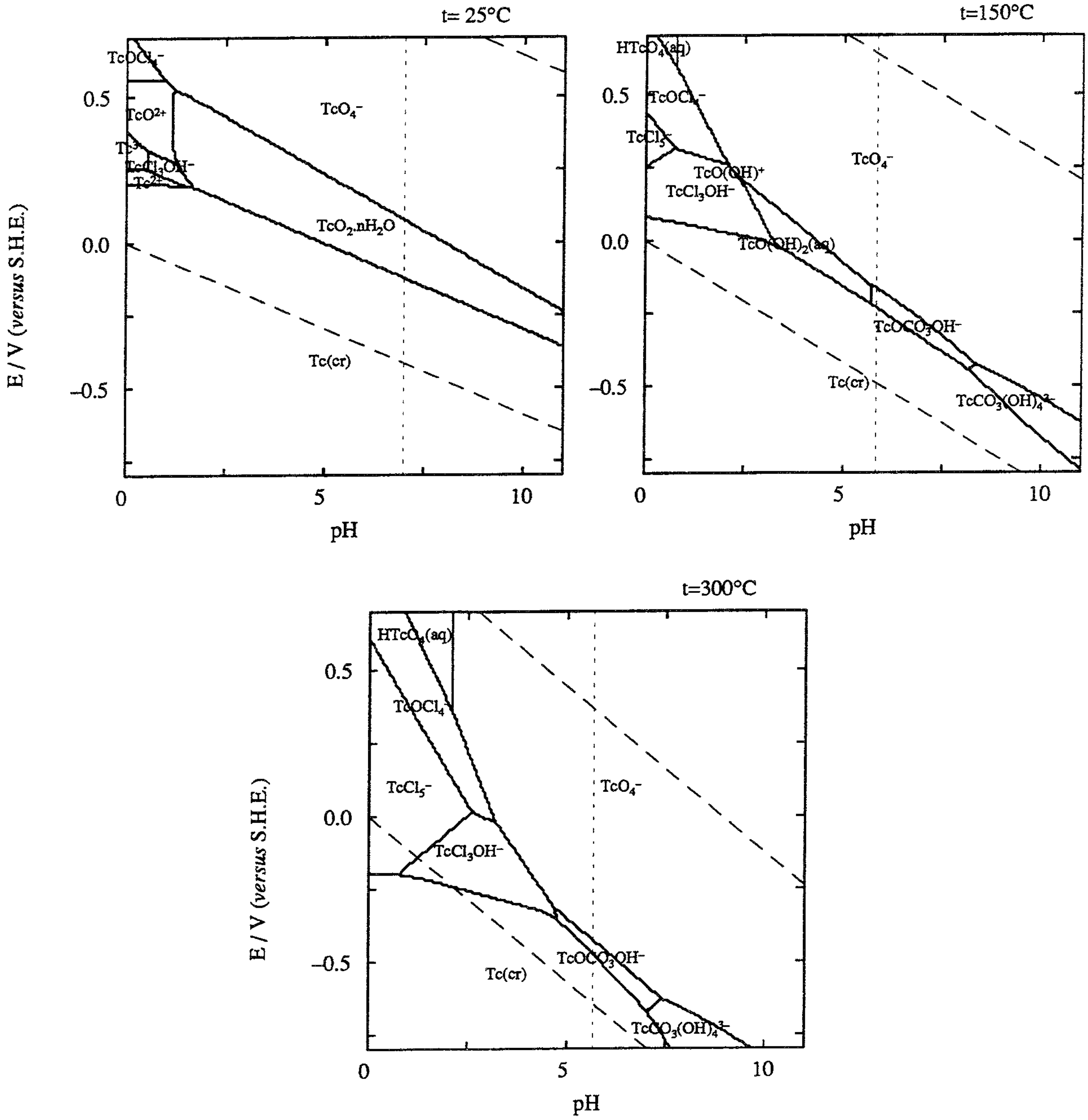

Figure 7: Calculated predominance area diagrams for technetium at $[Tc]_T = 1\mu$ m, $[Cl^-]_T = 0.5$ m, and $[CO_3^{2-}]_T = 0.005$ m, and at 25, 150 and 300°C. The upper and lower discontinuous lines show the limits of stability of water at each T: the fugacity of $O_2(g)$ and $H_2(g)$ are >1 bar above and below the upper and lower dash lines respectively. The vertical dotted lines show the neutral pH of pure water at each temperature.

i.e.,

$$pe = -(\log p(H_2) + pH).$$

Now, because

$$pe = Eh \cdot (F/R \cdot T \cdot \ln(10))$$

we have at 25° C:

$$\begin{aligned} Eh &= -(R \cdot T \cdot \ln(10)/F) \cdot (\log p(H_2) + pH) \\ &= -0.05916\,(pH + \log p(H_2)). \end{aligned}$$

Therefore, at constant $H_2(g)$ fugacity, the redox potential can be easily calculated with this equation.

Figure 8 shows that in a closed system, and according to the calculations, carbonate complexation of Tc in reducing aqueous solutions is increasingly important with decreasing pH. At pH=8 (Eh between +90 and +240 mV), carbonate complexes dominate over hydrolysis products when $[CO_3^{2-}]_T \geq 0.2$ mol/l, but at pH=7 (Eh between +150 and +300 mV) carbonate complexes predominate when $[CO_3^{2-}]_T \geq 0.02$ mol/l. At lower reduction potentials, *i.e.*, at lower $p(H_2(g))$, the calculations show that technetium metal becomes thermodynamically stable (*cf.* Figure 7).

Figure 9 shows the calculated effect of $[CO_3^{2-}]_T$ on the solubility of technetium at pH=8 as a function of the redox potential at 25°C. The sudden drop in the calculated solubility at Eh<–180mV is due to the stability of Tc(cr), *cf.* Figure 7.

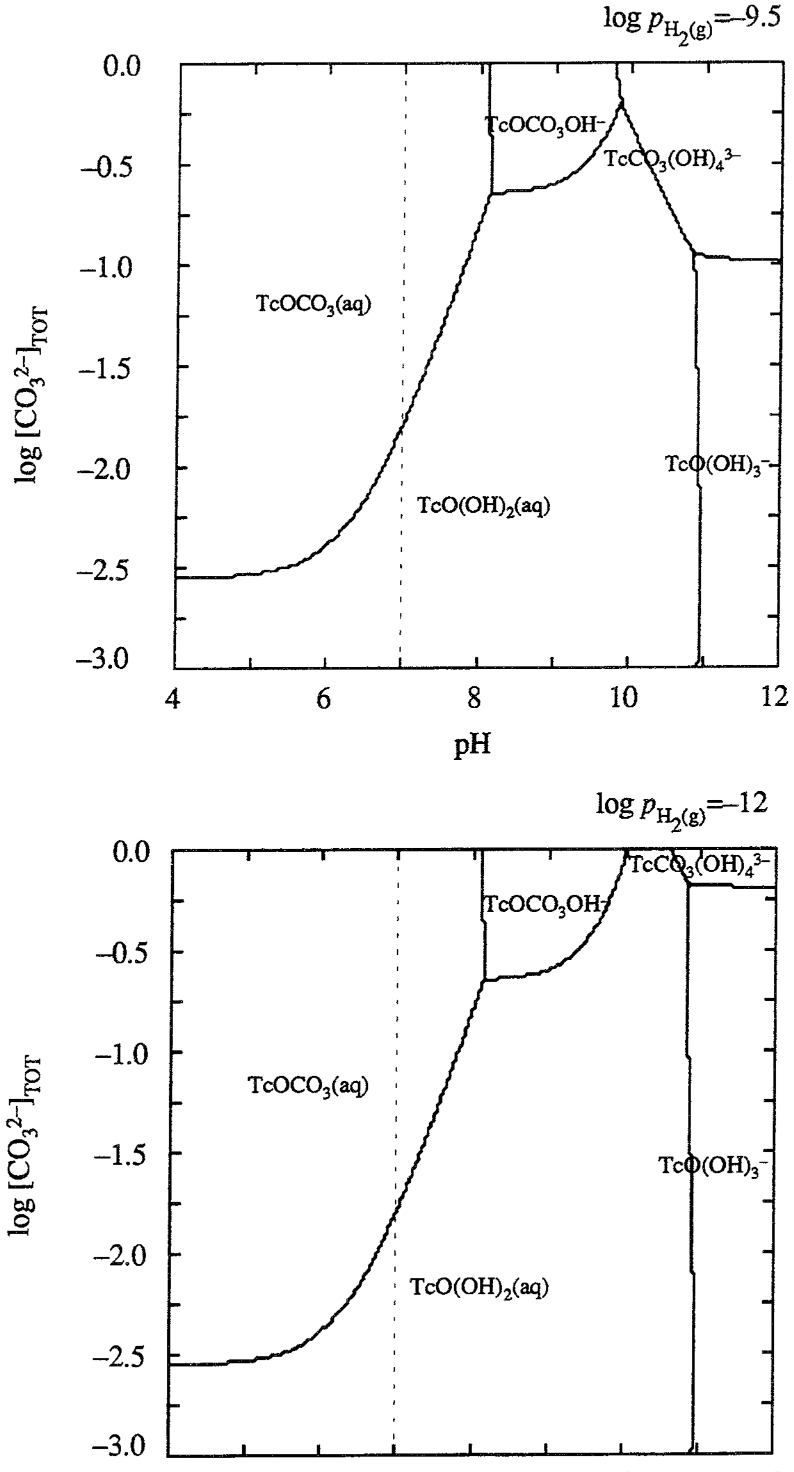

Figure 8: Influence of the total carbonate concentration on the calculated predominance of aqueous complexes of technetium at two fixed fugacities of $H_2(g)$ and at 25°C. The total technetium concentration is set to 10^{-9} mol/l to avoid the precipitation of $TcO_2 \cdot xH_2O(s)$.

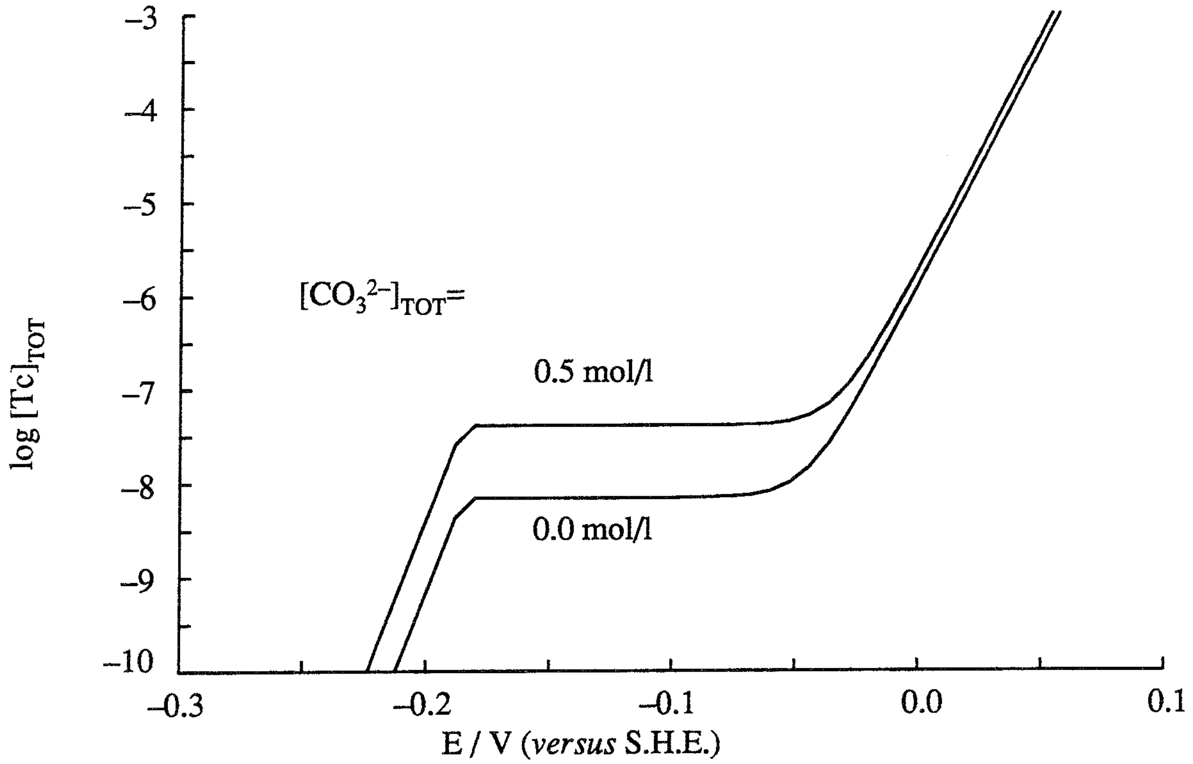

Figure 9: The calculated influence of the total carbonate concentration on the solubility of technetium at pH=8 and 25°C as a function of Eh.

The calculated effect of temperature on the solubility of technetium solutions is shown in Figure 10. The form of the curves is due to two main factors: **a**) that the reduction from Tc(VII) to Tc(IV) takes place at lower values of Eh as temperature increases, and **b**) that the solids Tc(cr) and $TcO_2 \cdot xH_2O(s)$ become unstable as temperature increases. This results agree, at least qualitatively, with the conclusions reached by Lemire and Garisto (1989, Figure 11 and p.44)

This instability of Tc(cr) and $TcO_2 \cdot xH_2O(s)$ with temperature has important implications on the near-field design. Depending on the temperature of disposal, the release of Tc may be large even under anoxic conditions.

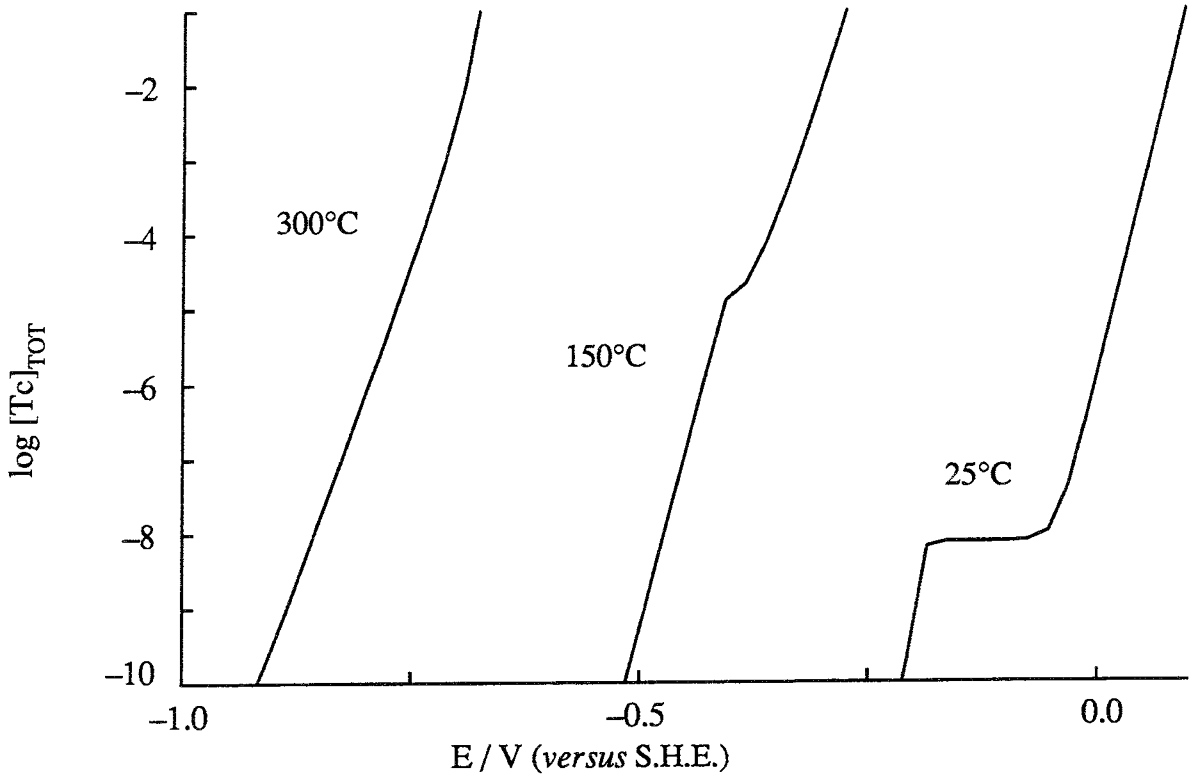

Figure 10: Technetium solubility calculated at the temperatures 25, 150 and 300°C as a function of redox potential, at pH= 8 and $[CO_3^{2-}]_T$= 0.005m.

To inprove the technetium data base presented in this report, and in order to decrease the uncertainties associated with calculations using the estimated values in this data base, it is strongly recommended that the following experimental work should be undertaken in the future:

- The hydration of Tc(IV) oxide(s) should be studied as a function of temperature. This might be performed with a DTA technique.
- The solubility of Tc(cr) in reducing conditions should be determined to confirm its calculated low solubilities (*c.f.* Figures 9 and 10).
- The solubility of TcO_2(cr) and/or Tc(cr) should be studied at some high temperature to confirm the calculated increase in solubility with temperature predicted by our work (*c.f.* Figure 10) and by Lemire and Garisto (1989).

5 CONCLUSIONS

The technetium data base presented here is constituted by both reliable experimental data and estimations. When the NEA-TDB technetium review is finished (Rard *et al.* 1993), the data base presented here will have to be revised, although much larger changes are expected when more experimental studies are published on thermodynamic data of the aqueous chemistry of this element, specially at high temperatures.

Due to the uncertainties in the estimates of entropies and heat capacities, there is an increasing incertitude at high temperatures in the calculated solubilities and speciations. Nevertheless, the available evidence strongly suggests that for a given set of chemical conditions, solubilities increase with temperature.

The redox potential at which Tc(VII) is reduced to lower oxidation states, decreases with increasing temperature. That is, more reducing conditions are needed at higher temperatures for the formation of Tc(IV).

The thermodynamic calculations show that increasing temperature decreases the area of corrosion immunity for metallic technetium, and it also decreases the predominance areas of Tc(IV) species.

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APPENDIX

Data blocks to be used in the DATA0 file of the EQ3/6 geochemical code package, are given here. This data blocks were produced by the "TePeX" code described in the text, with the thermodynamic data listed in Table 1. The DATA0 file has to be reformatted by the EQPT program into DATA1, DATA2 and DATA3 files before the equilibrium constants may be used as input for the EQ3NR and EQ6 programs.

For users requiring redox reactions involving "e^-" rather than "$O_2(g)$", the necessary reactions and equilibrium constants may be obtained from the EQ6/6 data blocks listed below. The procedure described in Puigdomènech and Bruno (1991) was incorrect, and the correct method is given here.

As an example, the following reaction,

$$TcO_4^- + 3\,H^+ \rightleftarrows TcO^{2+} + 3/4\,O_2(g) + 3/2\,H_2O(l) \qquad (A.1)$$

will be converted to

$$TcO_4^- + 3\,e^- + 6\,H^+ \rightleftarrows TcO^{2+} + 3\,H_2O(l). \qquad (A.2)$$

At this point, it must be reminded that "e^-" is a species that does not exist. In fact, reaction (A.2) is a convenient rewriting of the equation:

$$TcO_4^- + 3/2\,H_2(g) + 3\,H^+ \rightleftarrows TcO^{2+} + 3\,H_2O(l). \qquad (A.3)$$

Reaction (A.2) is written from (A.3) by use of the convention, that defines $\log K^\circ_{eq}=0$ at all temperatures for reaction:

$$H^+ + e^- \rightleftarrows \tfrac{1}{2}\,H_2(g). \qquad (A.4)$$

Reaction (A.2), which might be of interest for example for PHREEQE users, is obtained from $\log K^\circ_{eq}(A.1)$ listed later in this Appendix, by using the equilibrium

$$3/2\,H_2O(l) \rightleftarrows 3/4\,O_2(g) + 3\,H^+ + 3\,e^-. \qquad (A.5)$$

Now again, because of the presence of "e⁻", it must be reminded that by the convention expressed in reaction (A.4), reaction (A.5) is equivalent to:

$$3/2\ H_2O(l) \rightleftarrows 3/4\ O_2(g) + 3/2\ H_2(g). \qquad (A.6)$$

The equilibrium constant for the last reaction may be obtained from the apparent standard partial molar Gibbs free energies of formation of the reactants involved, $\Delta_a G^\circ_m$, *cf.* Eq.(3.1). For H^+ $\Delta_a G^\circ_m$ is zero at all T, while for $H_2O(l)$ it can be obtained from the CODATA tables (Cox *et al.* 1989), and for $H_2(g)$ and $O_2(g)$, it can be obtained from Eqs. (3.2) and (3.5). The equilibrium constant is then obtained from Eqs. (3.3) and (3.4). Table A.1 contains the necessary $\Delta_a G^\circ_m$ to calculate $\log K^\circ_{eq}(A.6)$ as a function of temperature, and this value will be equal to $\log K^\circ_{eq}(A.5)$.

Using the example given above (reactions A.1 and A.2), and the values in Table 1 for 100° C,

$$\begin{aligned}\Delta_r G^\circ_m(373.15,A.5) &= \Delta_r G^\circ_m(373.15,A.6)\\ &= 0.75\cdot(-15.644) + 1.5\cdot(-10.054) - 1.5\cdot(-243.066) = +337.785\ \mathrm{kJ\cdot mol^{-1}}\end{aligned}$$

$$\log K^\circ_{eq}(373.15,A.5) = -337.785 \cdot 1000 / (R\cdot T\cdot \ln(10)) = -47.283$$

where $R = 8.31451\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$, and for reaction (A.2), which is equivalent to reaction (A.3):

$$\log K^\circ_{eq}(A.2) = \log K^\circ_{eq}(A.3) = \log K^\circ_{eq}(A.1) + \log K^\circ_{eq}(A.5)$$

and at 100° C, after inspection of the EQ3/6 data block for

$$\log K^\circ_{eq}(A.2) = -23.676 + 47.283 = +23.607.$$

Table A.1 Apparent standard molar Gibbs free energies of formation for O_2(g), H_2(g) and H_2O(l). Note that the standard state of the gaseous species is the ideal gas at 1 bar of fugacity, while for H_2O(l), it is pure water at the temperature and pressure indicated. This table superseedes Table B.1 in Puigdomènech and Bruno (1991).

Temp. (° C)	Press. (bar)	$\Delta_a G^\circ_m$ / (kJ·mol^{-1}) H_2O(l)	 O_2(g)	 H_2(g)
0	1	−235.467	5.097	3.236
25	1	−237.140	0	0
60	1	−239.746	−7.239	−4.631
100	1.013	−243.066	−15.644	−10.054
150	4.8	−247.668	−26.329	−17.008
200	15.5	−252.719	−37.195	−24.134
250	39.8	−258.170	−48.224	−31.416
300	85.9	−263.981	−59.403	−38.837

A list of technetium data blocks for the DATA0 file of the EQ3/6 geochemical computer code is given in the next pages.

```
D-file in EQ3/6 format.   05-Feb92   10:59:30
Generated by code TePeX
+------------------------------------------------------------------------
*
*            auxiliary-basis species for technetium:
*------------------------------------------------------------------------
TcO4-2
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -2.0           titr. factor=    1.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     2 chemical elements=
       1.000 tc              4.000 o
     5 species in reaction=
     -1.0000 TcO4-2          .5000 h2o             -.2500 o2(g)
     -1.0000 h+                1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        33.5529   31.0917   28.3995   26.0769
        23.9611   22.4753   21.4730   20.9154
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       19.134     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+------------------------------------------------------------------------
TcO4-3
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -3.0           titr. factor=    2.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     2 chemical elements=
       1.000 tc              4.000 o
     5 species in reaction=
     -1.0000 TcO4-3            1.0 h2o             -.5000 o2(g)
     -2.0000 h+                1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        66.4322   61.8330   56.7764   52.3933
        48.3842   45.5607   43.6500   42.5749
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       65.168     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+------------------------------------------------------------------------
TcO+2
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=   2.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     2 chemical elements=
       1.000 tc              1.000 o
     5 species in reaction=
     -1.0000 TcO+2             3.0 h+              -.7500 o2(g)
     -1.5000 h2o               1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        31.3973   29.0541   26.2871   23.6757
        21.0145   18.8391   17.0055   15.3884
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       19.998     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
*------------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
Tc+3
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=   3.0          titr. factor=     .00 eq/mol
      ion size=   3.0 A        hydr. number=   0.0
     1 chemical elements=
       1.000 tc
     5 species in reaction=
     -1.0000 Tc+3             4.0 h+            -1.0000 o2(g)
     -2.0000 h2o              1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        47.7941   44.4362   40.5527   36.9663
        33.4030   30.5799   28.2819   26.3321
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       10.964     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
Tc+2
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=   2.0          titr. factor=     .00 eq/mol
      ion size=   3.0 A        hydr. number=   0.0
     1 chemical elements=
       1.000 tc
     5 species in reaction=
     -1.0000 Tc+2             3.0 h+            -1.2500 o2(g)
     -1.5000 h2o              1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        65.7857   60.0196   53.3291   47.1375
        40.9529   35.9971   31.9127   28.4367
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       19.998     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
*
*            non-basis aqueous species of technetium:
*-----------------------------------------------------------------------
HTcO4(aq)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=    .0          titr. factor=     .00 eq/mol
      ion size=   3.0 A        hydr. number=   0.0
     3 chemical elements=
       1.000 tc             4.000 o             1.000 h
     3 species in reaction=
     -1.0000 HTcO4(aq)        1.0 h+               1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
          .0081    -.0999    -.3103    -.5888
         -.9712   -1.3951   -1.8868   -2.5256
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       47.100     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
*-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
HTcO4-
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -1.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc             4.000 o              1.000 h
     3 species in reaction=
     -1.0000 HTcO4-           1.0 h+               1.0 TcO4-2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -9.0313   -8.7072   -8.4965   -8.4608
        -8.6152   -8.9351   -9.4054  -10.0743
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       37.000     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
H2TcO4(aq)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=    .0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc             4.000 o              2.000 h
     3 species in reaction=
     -1.0000 H2TcO4(aq)       2.0 h+               1.0 TcO4-2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -9.0617   -9.0051   -9.1752   -9.5633
       -10.2341  -11.0794  -12.1260  -13.5182
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       37.000     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcOCl5-2
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -2.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc             1.000 o              5.000 cl
     5 species in reaction=
     -1.0000 TcOCl5-2         6.0 h+               5.0 cl-
     -3.0000 h2o              1.0 TcO4-3
*    log K grid (0-25-60-100/150-200-250-300 C) =
       -44.3579  -41.3671  -38.5841  -36.7196
       -35.7398  -35.8912  -37.0207  -39.3118
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       34.736     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
*-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
TcOCl4-
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -1.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              1.000 o              4.000 cl
     5 species in reaction=
     -1.0000 TcOCl4-           6.0 h+               4.0 cl-
     -3.0000 h2o               1.0 TcO4-3
*    log K grid (0-25-60-100/150-200-250-300 C) =
       -49.2207  -46.6668  -44.3390  -42.8530
       -42.2156  -42.6264  -43.9833  -46.5311
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       16.948     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcO2Cl4-3
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -3.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              2.000 o              4.000 cl
     5 species in reaction=
     -1.0000 TcO2Cl4-3         4.0 h+               4.0 cl-
     -2.0000 h2o               1.0 TcO4-3
*    log K grid (0-25-60-100/150-200-250-300 C) =
       -41.8263  -38.4570  -35.0862  -32.5143
       -30.6072  -29.7595  -29.7716  -30.6995
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       35.016     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcCl5-
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -1.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     2 chemical elements=
       1.000 tc              5.000 cl
     5 species in reaction=
     -1.0000 TcCl5-            5.0 cl-              2.0 h+
     -1.0000 h2o               1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
         -.0882   -1.0165   -2.5894   -4.5438
        -7.1245   -9.8798  -12.9041  -16.4864
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.       70.873     0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
*-----------------------------------------------------------------------
```

```
+-------------------------------------------------------------------------
TcCl6-2
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -2.0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     2 chemical elements=
       1.000 tc              6.000 cl
     5 species in reaction=
     -1.0000 TcCl6-2           6.0 cl-                 2.0 h+
     -1.0000 h2o               1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -1.0110   -1.0217   -1.5875   -2.6596
        -4.4021   -6.5070   -8.9883  -12.0542
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        88.661     0.         0.
         0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
+-------------------------------------------------------------------------
TcO(OH)+
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=   1.0           titr. factor=    1.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              2.000 o                1.000 h
     4 species in reaction=
     -1.0000 TcO(OH)+          1.0 h2o            -1.0000 h+
         1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
         1.5645    1.1282     .6286     .1777
         -.2682    -.6350    -.9541   -1.2461
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        18.068     0.         0.
         0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
+-------------------------------------------------------------------------
TcO(OH)2(aq)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=    .0           titr. factor=    2.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              3.000 o                2.000 h
     4 species in reaction=
     -1.0000 TcO(OH)2(a        2.0 h2o            -2.0000 h+
         1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
         4.1103    3.5546    2.9412    2.4154
         1.9271    1.5497    1.2367     .9580
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        36.136     0.         0.
         0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
*-------------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
TcO(OH)3-
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -1.0           titr. factor=    3.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              4.000 o                 3.000 h
     4 species in reaction=
     -1.0000 TcO(OH)3-        3.0 h2o             -3.0000 h+
         1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        15.7499   14.5323   13.2053   12.0882
        11.1050   10.4401   10.0153    9.8204
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        54.204     0.         0.
         0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
[TcO(OH)2]2
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=    .0           titr. factor=    4.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       2.000 tc              6.000 o                 4.000 h
     4 species in reaction=
     -1.0000 [TcO(OH)2]       4.0 h2o             -4.0000 h+
         2.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
         1.4316     .6235    -.2552    -.9843
        -1.6404   -2.1509   -2.6092   -3.1033
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        72.272     0.         0.
         0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcOCO3(aq)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=    .0           titr. factor=    2.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              4.000 o                 1.000 c
     4 species in reaction=
     -1.0000 TcOCO3(aq)       1.0 hco3-           -1.0000 h+
         1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -5.6848   -5.3698   -5.1951   -5.2094
        -5.4319   -5.8250   -6.3641   -7.0739
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        24.602     0.         0.
         0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
*-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
TcOCO3OH-
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -1.0           titr. factor=    3.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     4 chemical elements=
       1.000 tc              5.000 o                1.000 c
       1.000 h
     5 species in reaction=
     -1.0000 TcOCO3OH-         1.0 hco3-              1.0 h2o
     -2.0000 h+                1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
         3.8911    2.8889    1.5531     .1756
        -1.3569   -2.7406   -4.0265   -5.2676
*    delVr grid (0-25-60-100/150-200-250-300 C) =
        0.        42.670     0.         0.
        0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcOSO4(aq)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=    .0           titr. factor=     .00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     3 chemical elements=
       1.000 tc              5.000 o                1.000 s
     3 species in reaction=
     -1.0000 TcOSO4(aq)        1.0 so4--              1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -2.8040   -2.2391   -1.6773   -1.2494
         -.9564    -.8949   -1.0466   -1.4470
*    delVr grid (0-25-60-100/150-200-250-300 C) =
        0.        13.884     0.         0.
        0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcCl3OH-
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -1.0           titr. factor=   1.00 eq/mol
      ion size=   3.0 A         hydr. number=   0.0
     4 chemical elements=
       1.000 tc              3.000 cl               1.000 o
       1.000 h
     5 species in reaction=
     -1.0000 TcCl3OH-          1.0 h2o                3.0 cl-
     -1.0000 h+                1.0 Tc+3
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -1.1513   -2.4232   -4.1202   -5.9121
        -8.0073  -10.0535  -12.1571  -14.5011
*    delVr grid (0-25-60-100/150-200-250-300 C) =
        0.        71.432     0.         0.
        0.         0.        0.         0.
* T-extrapolation method: simplified Revised HKF
*-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
TcCO3(OH)4-3
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        charge=  -3.0          titr. factor=    6.00 eq/mol
      ion size=   3.0 A        hydr. number=   0.0
     4 chemical elements=
       1.000 tc              7.000 o              1.000 c
       4.000 h
     5 species in reaction=
     -1.0000 TcCO3(OH)4        1.0 hco3-            4.0 h2o
     -5.0000 h+                1.0 Tc+3
*    log K grid (0-25-60-100/150-200-250-300 C) =
        28.1065   25.1823   21.6897   18.4317
        15.1874   12.6275   10.6165    9.1508
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        96.874     0.        0.
         0.         0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
*
*            solid compounds of technetium:
*-----------------------------------------------------------------------
Tc(cr)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        volume=       .000 cc/mol
     1 chemical elements=
       1.000 tc
     5 species in reaction=
     -1.0000 Tc(cr)            1.0 h+           -1.7500 o2(g)
      -.5000 h2o               1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        97.1634   88.0400   77.4985   67.7973
        58.1546   50.4476   44.1001   38.7008
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        38.066     0.        0.
         0.         0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
HTcO4(cr)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        volume=       .000 cc/mol
     3 chemical elements=
       1.000 tc              4.000 o              1.000 h
     3 species in reaction=
     -1.0000 HTcO4(cr)         1.0 h+              1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
         5.6118    5.4835    5.2708    5.0058
         4.6554    4.2826    3.8728    3.3800
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        47.100     0.        0.
         0.         0.        0.        0.
* T-extrapolation method: Cp constant
*-----------------------------------------------------------------------
```

```
+-----------------------------------------------------------------------
Tc2O7(cr)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        volume=       .000 cc/mol
     2 chemical elements=
       2.000 tc               7.000 o
     4 species in reaction=
     -1.0000 Tc2O7(cr)          2.0 h+             -1.0000 h2o
         2.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        12.5296   12.1689   11.5848   10.8576
         9.8905    8.8599    7.7399    6.4413
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        76.132    0.        0.
         0.        0.        0.        0.
* T-extrapolation method: simplified Revised HKF
+-----------------------------------------------------------------------
TcO2.1.63H2O(cr)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        volume=       .000 cc/mol
     3 chemical elements=
       1.000 tc               3.630 o                  3.260 h
     4 species in reaction=
     -1.0000 TcO2.1.63H     2.6300 h2o             -2.0000 h+
         1.0 TcO+2
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -4.7226   -4.6132   -4.4515   -4.2622
        -4.0423   -3.8603   -3.7250   -3.6459
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        47.519    0.        0.
         0.        0.        0.        0.
* T-extrapolation method: Cp constant
+-----------------------------------------------------------------------
KTcO4(cr)
    entered by= I.Puigdomenech          date= 05-Feb92
        source= TePeX                quality=
        volume=       .000 cc/mol
     3 chemical elements=
       1.000 tc               4.000 o                  1.000 k
     3 species in reaction=
     -1.0000 KTcO4(cr)          1.0 k+                 1.0 tco4-
*    log K grid (0-25-60-100/150-200-250-300 C) =
        -3.6588   -2.7331   -1.7394    -.9028
         -.1692     .3105     .5845     .6442
*    delVr grid (0-25-60-100/150-200-250-300 C) =
         0.        56.168    0.        0.
         0.        0.        0.        0.
* T-extrapolation method: Cp constant
+-----------------------------------------------------------------------
stop.
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Annual Research and Development Report 1985
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Stockholm, May 1994

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TR 95-01

Biotite and chlorite weathering at 25°C. The dependence of pH and (bi) carbonate on weathering kinetics, dissolution stoichiometry, and solubility; and the relation to redox conditions in granitic aquifers

Maria Malmström[1], Steven Banwart[1], Lara Duro[2], Paul Wersin[3], Jordi Bruno[3]
[1] Royal Institute of Technology, Department of Inorganic Chemistry, Stockholm, Sweden
[2] Universidad Politécnica de Cataluña, Departmento de Inginería Química, Barcelona, Spain
[3] MBT Tecnología Ambiental, Cerdanyola, Spain
January 1995

TR 95-02

Copper canister with cast inner component. Amendment to project on Alternative Systems Study (PASS), SKB TR 93-04

Lars Werme, Joachim Eriksson
Swedish Nuclear Fuel and Waste Management Co, Stockholm, Sweden
March 1995

TR 95-03

Prestudy of final disposal of long-lived low and intermediate level waste

Marie Wiborgh (ed.)
Kemakta Konsult AB, Stockholm, Sweden
January 1995

TR 95-04

Spent nuclear fuel corrosion: The application of ICP-MS to direct actinide analysis

R S Forsyth[1], U-B Eklund[2]
[1] Caledon-Consult AB, Nyköping, Sweden
[2] Studsvik Nuclear AB, Nyköping, Sweden
March 1995

TR 95-05

Groundwater sampling and chemical characterisation of the Laxemar deep borehole KLX02

Marcus Laaksoharju[1], John Smellie[2]
Ann-Chatrin Nilsson[3], Christina Skårman[1]
[1] GeoPoint AB, Sollentuna, Sweden
[2] Conterra AB, Uppsala, Sweden
[3] KTH, Stockholm, Sweden
February 1995

TR 95-06

Palaeohydrological implications in the Baltic area and its relation to the groundwater at Äspö, south-eastern Sweden – A literature study

Bill Wallin
Geokema AB, Lidingö, Sweden
March, 1995

TR 95-07

Äspö Hard Rock Laboratory Annual Report 1994

SKB
April 1995

TR 95-08

Feasibility study for siting of a deep repository within the Storuman municipality

Swedish Nuclear Fuel and Waste Management Co., Stockholm
January 1995