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Dana Isherwood

April 1985

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Application of the Ruthenium and Technetium Thermodynamic Data Bases Used in the EQ3/6 Geochemical Codes

Abstract

Based on a critical review of the available thermodynamic data, computerized data bases for technetium and ruthenium were created for use with the EQ3/6 geochemical computer codes. The technetium data base contains thermodynamic data for 8 aqueous species and 15 solids; 26 aqueous species and 9 solids were included in the ruthenium data base. The EQ3NR code was used to calculate solubility limits for ruthenium (8×10^{-16} M) in ground water from Yucca Mountain, a potential nuclear waste repository site near the Nevada Test Site (NTS). The code confirmed the essentially unlimited solubility of technetium in oxidizing conditions, such as those that are believed to exist in the unsaturated zone at Yucca Mountain and the Cambrian Nuclear event site at the NTS. Ruthenium migration observed from the Cambrian site was evaluated. The solubility limit for ruthenium (as the aqueous species RuO_4^-) when constrained by RuO_2 is approximately equal to the concentration of ruthenium found in the cavity ground water (i.e., 2.1×10^{-11} vs 4.5×10^{-11} M). Differences in ruthenium solubility limits between Yucca Mountain and Cambrian are primarily due to differences in ground-water pH. Technetium solubility (3×10^{-8} M) for moderately reducing conditions ($E_h = -0.1$ V) using the metastable oxide, $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, as the solubility constraint is within the range of experimental values recently published in a study of technetium sorption on basalt. Previously published technetium solubilities of 10^{-12} to 10^{-16} M were apparently based on a technetium data base that did not include aqueous species other than TcO_4^- . When $\text{TcO}(\text{OH})_2^0$ is included in the data base, the calculated values are much closer to the experimental results. Eh-pH diagrams were also generated for a variety of conditions using the SOLUPLOT code.

Introduction

Technetium-99 is an important radioisotope present in spent fuel from nuclear reactors and the debris from underground nuclear tests. Because of its very long half-life (2.1×10^5 years) and its potential for migration as the pertechnetate ion (TcO_4^-), it represents an implied threat to the biosphere if released into the ground-water system from a nuclear waste repository or nuclear event sites. Ruthenium is also present in spent fuel and nuclear test debris in both stable and radioisotope forms, although none of the isotopes has a half-

life sufficiently long to be of concern in nuclear waste disposal (the longest half-life is 357 days for ^{106}Ru). The ruthenium data base was developed primarily to evaluate the observed migration of ruthenium from the Cambrian nuclear event site at the NTS (Coles and Ramspott, 1982). The technetium data base was developed to study technetium geochemistry related to possible offsite migration at the NTS and to nuclear waste disposal.

The ruthenium and technetium data bases described in this report were incorporated into the

data base supporting the EQ3/6 geochemical codes. The EQ3/6 package is made up of two major codes. The EQ3NR code calculates from water sample analyses the distribution of ions, ion-pairs, and complexes, and determines whether the water sample is saturated with various minerals (Wolery, 1983). The EQ6 code calculates dynamic models of rock/water interactions, that is, minerals and other phases can be added to a chemical system such that the state of a new system is predicted (Wolery, to be published 1985).

The development of a comprehensive thermodynamic data base is an ongoing activity at the Lawrence Livermore National Laboratory (LLNL). These data can be used to determine the relative contribution of geochemical processes such as sorption or precipitation to radionuclide migration. The development and use of the ruthenium

and technetium data bases were funded by the Radionuclide Migration Project administered by the Department of Energy's Nevada Operations Office. The RNM Project is primarily concerned with radionuclide migration at NTS. The data base development work will also be useful in the data base upgrades planned for EQ3/6 as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) and the Office of Nuclear Waste Isolation (ONWI) (Isherwood and Wolery, 1984).

The purpose of this report is to document the thermodynamic data bases for ruthenium and technetium used in the 3245 version of the EQ3/6 code package and to apply this data base in studies related to nuclear waste disposal and radionuclide migration from an underground nuclear event at NTS.

Ruthenium and Technetium Data Bases

The ruthenium data base compiled for EQ3/6 was abstracted from Rard's (1985) critical review of ruthenium thermodynamic data. The 476 references listed by Rard contain essentially all of the thermodynamic data for ruthenium that was available in the literature at the time the document was written. Rard's recommended values were used to create MCRT data files for both solid phases and aqueous species. The MCRT code is a data-base-building program that uses the thermodynamic data to calculate a grid of stability constants as a function of temperature that can be inserted into the main EQ3/6 data base (DATA0).

In all, 9 ruthenium solids and 26 aqueous species were included in the data base. Appendix A contains the MCRT files for the solids (MDSOL) and the aqueous species (MDAQS) as well as the REAC file, which is used by MCRT to process the MDSOL and MDAQS files. For completeness, three ruthenium gases and one liquid are included in the data blocks that make up the MDSOL file, but are not included in the REAC file. The gases and liquid were omitted from the main EQ3/6 data base because they exist only at temperatures and conditions well outside the range of values

for geochemical applications involving aqueous solutions.

The technetium data base was similarly created using the compilation of technetium thermodynamic data by Rard (1983). The available thermodynamic data for 8 aqueous species and 15 solids were used to create the aqueous (MDAQS) and solid (MDSOL) data files along with the REAC file needed by MCRT to process the data files. Copies of these files are in Appendix B.

Both the technetium and ruthenium data bases suffer from a lack of high-temperature thermodynamic data. Only one of the 8 technetium aqueous species and 8 of the 15 solids have the necessary data for high temperature calculations (see discussion in Appendix A). Data are available for only 3 of the 26 ruthenium aqueous species. Thermodynamic values for the ruthenium solids are more complete—7 out of 9 solids have entropy, enthalpy, or heat capacity data; however, without the corresponding thermodynamic values for the aqueous species, reasonable predictions of solubility limits or speciation at elevated temperatures are not possible.

Eh-pH Diagrams

To test the effect of oxidation potential or pH on speciation and solubility over a wide range of Eh-pH conditions, Eh-pH diagrams for ruthenium

and technetium were generated using a version of the code SOLUPLOT, a code designed to calculate and plot complex Eh-pH diagrams for systems

with up to 35 aqueous species and solids containing a particular element (Bethke, 1978). The Eh-pH diagrams were used to evaluate ruthenium and technetium speciation in ground waters at two locations at NTS—Yucca Mountain and the Cambric site (Table 1). As stated in the introduction, the use of these sites as examples provides useful information to the NNWSI and RNM Projects.

Technetium

An Eh-pH diagram was created to predict the dominant aqueous species of technetium that will be present within the stability field of water [Fig. 1(a)]. Other aqueous species may be present in lesser amounts, but are not shown on the Eh-pH diagram. In Fig. 1(b), the stability fields for both the aqueous and solid phases are indicated. The boundary between the stable aqueous phase (e.g., TcO_4^-) and the solid phases is drawn where the concentration of technetium in solution ($2.0 \times 10^{-7} \text{ M}$) equals the maximum concentration of technetium-99 in drinking water as permitted by

Table 1. Ground-water analyses for the Cambric site (RNM2a) and J-13 well.

	RNM2a ^a (mg/l)	J-13 ^b (mg/l)
Na ⁺	61	45.1
K ⁺	9.9	5.3
Ca ²⁺	18	11.5
Mg ²⁺	5.5	1.8
Al ³⁺	—	0.025
Fe (total)	—	0.011
SiO ₂	66	68.2
HCO ₃ ⁻	170	170
Cl ⁻	15	6.4
SO ₄ ²⁻	40	10.1
F ⁻	0.5	2.1
NO ₃ ⁻	—	10.1
PO ₄ ³⁻	—	0.1
pH	8.1	6.9
O ₂	—	5.5

^a Values shown are averages of analyses for samples taken from January to December, 1982, provided by L. Benson (U.S.G.S.). Data for O₂, Al³⁺, Fe, NO₃⁻, and HPO₄²⁻ are not available.

^b Analyses for sample 6/81-51 reported by Daniels *et al.*, (1982).

Figure 1. Eh-pH diagrams generated for technetium by SOLUPLLOT. (a) Stability fields are shown only for the aqueous species of technetium. (b) Stability fields shown are for both aqueous and solid species at $[\text{Tc}] = 2.0 \times 10^{-7} \text{ M}$, the MPC_w for ⁹⁹Tc.

the Federal Government (10CFR60, App. B). Although the TcS_2 and Tc_2S_7 stability fields shown in this diagram are a function of the amount of sulfate or sulfide present in the ground waters, the range of sulfate concentrations (18 and 40 mg/l) at both the Yucca Mountain and Cambrian sites resulted in virtually identical Eh-pH diagrams.

The Eh-pH diagram [Fig. 1(a)] predicts that at equilibrium the dominant aqueous species of technetium will be TcO_4^- in an oxidizing to moderately reducing environment within a pH range of approximately 3 to 14. As the environment becomes more reducing, the dominant species is $\text{TcO}(\text{OH})_2^0$. Rard (1983), in his evaluation of the evidence cited for the hydrolysis of TcO^{3+} , suggests that $\text{TcO}(\text{OH})_2^0$ may form the dimer $[\text{TcO}(\text{OH})_2]_2^0$ above a pH of 2.7.

Figure 1(b) indicates that below an oxidation potential of approximately +0.2 V at pH = 7, the concentration of technetium in solution will be below the maximum permissible concentration in drinking water (MPC_w) required by the Federal Government. In the stability field for TcO_4^- , the concentration increases as the oxidation potential increases. The stable phase controlling the solubility limit for technetium will depend on the oxidation potential, pH, and the amount of sulfide in solution.

It is important to remember that Eh-pH diagrams are based on the assumption that the total system is at equilibrium. That is, all couples shown on the diagram as well as those couples considered, but not shown (e.g., $\text{S}^{2-}/\text{SO}_4^{2-}$), are in equilibrium with each other. Because of their dynamic nature, many natural systems do not achieve equilibrium. Eh-pH diagrams also tell us nothing about the rate of reaction. For example, if ground water moves from an oxidizing to a reducing environment and the rate of reduction of TcO_4^- and the subsequent precipitation of Tc_2O_7 are slow relative to the change in the environmental conditions, then the concentration of technetium could be higher than predicted along the flow path.

Like any model, an Eh-pH diagram depends on the number of species for which thermodynamic data are available and on the quality of that data. Uncertainties in the data must result in uncertainties in the boundaries shown on an Eh-pH diagram. Although an Eh-pH diagram can be useful in making predictions regarding speciation and solubility, these predictions must eventually be tested.

Ruthenium

Similar Eh-pH diagrams were constructed for ruthenium. Unlike technetium, where each dominant species contains only one technetium atom, ruthenium has dominant species containing either one or four ruthenium atoms [e.g., RuO_4^- and $\text{Ru}_4(\text{OH})_{12}^{4+}$]. This results in Eh-pH diagrams that depend on the concentration of ruthenium. Figure 2 shows the stability fields for the aqueous species at three ruthenium concentrations (10^{-6} , 10^{-11} , and 10^{-15} M). In each case, the boundary between $\text{Ru}_4(\text{OH})_{12}^{4+}$ and RuO_4^- is represented by the equation

where

$$\text{Eh} = \text{E}^0 + (2.303\text{RT}/12\text{F})(3\log[\text{RuO}_4^-] - 20\text{pH}).$$

Changes in the concentration of RuO_4^- result in changes in the Eh if the pH is held constant.

Similar equations can be written for the boundary between $\text{Ru}(\text{OH})_2^{2+}$ and $\text{Ru}_4(\text{OH})_{12}^{4+}$ and other pairs of aqueous species involving $\text{Ru}_4(\text{OH})_{12}^{4+}$. This relationship results in a decrease in the size of the stability field of $\text{Ru}_4(\text{OH})_{12}^{4+}$ as the total concentration of ruthenium decreases. Thus, in an oxidizing environment, the dominant aqueous species will depend not only on the oxidation potential and pH, but will also depend on the total amount of ruthenium in some cases.

Figure 3 is an Eh-pH diagram showing the stability fields of the solid phases where the concentration of ruthenium is equal to 3×10^{-14} M, the MPC_w for ruthenium-106 (10CFR60, App. B). Note that the oxidation potential strongly effects the ruthenium concentration below the MPC_w . For example, a decrease in the oxidation potential at a pH of seven first results in an increase in ruthenium solubility as the RuO_2 boundary is approached, then eventually in a decrease as $\text{Ru}(\text{OH})_2^+$ becomes more stable, followed by an increase as the $\text{Ru}(\text{c})$ boundary is approached.

The complex chemical behavior of ruthenium implies that site characterization, specifically, a reliable measurement of *in situ* oxidation potential and pH, will be needed to estimate solubility limits for those radionuclides that exhibit similar behavior. Theoretical studies such as the ones described in this report that use geochemical models to look at a variety of conditions are useful tools

Figure 3. Eh-pH diagram generated for ruthenium solids and aqueous species by SOLUPLOT. $[Ru] = 3.0 \times 10^{-14}$ M, the MPC_w for ¹⁰⁶Ru.

in establishing the priorities of an experimental program. However, as noted with technetium, interpretation of Eh-pH diagrams can be risky. The predictive capabilities of an Eh-pH diagram depend on the quality and interpretation of the available data and on whether the system being

modeled has reached equilibrium. There are many examples of natural systems that are not in equilibrium. The Eh-pH diagram is best used as an interpretive tool in combination with other models.

Solubility Limits in Yucca Mountain Ground Water

The EQ3NR computer code was used to calculate solubility limits and identify the aqueous species present in ground water at the Yucca Mountain site. The analysis of water samples (Table 1) collected from the J-13 well which intercepts the tuff aquifer below Yucca Mountain was used as input to EQ3NR. In the first run of EQ3NR, small amounts of ruthenium and technetium were added to the J-13 analysis to determine which of the solid phases in the data base would control technetium and ruthenium solubility in the Yucca Mountain environment. The calculated oxidation potential of the system, +0.808 V, was based on the 5.5 mg/l of dissolved oxygen in the J-13 water (Daniels *et al.*, 1982).

In this relatively strong oxidizing system, K₂TcO₄ and RuO₂ were identified as the solubility controls. The results of the EQ3NR run using these solid phases as constraints on the ruthenium

and technetium concentrations are summarized in Table 2. The solubility limit for ruthenium, 8.3×10^{-16} M, is below the MPC_w (3×10^{-14} M) for ruthenium-106 reported in the previous section. Essentially 100% of the ruthenium in solution is predicted to be RuO₄⁻.

The solubility for technetium when controlled by the very soluble K₂TcO₄ results in high concentrations of TcO₄⁻. Realistically, there is no solubility limit for technetium in an oxidizing environment. Maximum concentrations will always be below the solubility of K₂TcO₄ given the limited amount of technetium isotopes present in nuclear waste. Guzowski *et al.* (1983) also predict a high solubility for technetium in an oxidizing environment, but do not identify the solid phase. Guzowski *et al.* and numerous other studies have suggested that TcO₄⁻ is the aqueous species present in an oxidizing environment.

Table 2. EQ3NR-calculated solubility limits and dominant Ru and Tc species predicted for J-13 and Cambric (RNM2s) ground waters.

Water	Element	Solid phase constrained	Dominant species	%	Solubility (moles/l)
J-13	Tc	KTcO ₄	TcO ₄ ⁻	100	>1
Eh = +0.8	Ru	RuO ₂	RuO ₄ ⁻	99.9	8.3 × 10 ⁻¹⁶
RNM2s	Tc	KTcO ₄	TcO ₄ ⁻	100	>1
Oxidizing	Ru	RuO ₂	RuO ₄ ⁻	99.9	2.1 × 10 ⁻¹¹
Eh = +0.8	Tc	Tc ₂ O ₄	TcO(OH) ₂ ⁰	99.5	1.8 × 10 ⁻¹⁴
RNM2s	Ru	TcO ₃ ·2H ₂ O	TcO(OH) ₂ ⁰	84	3.0 × 10 ⁻⁶
Reducing	Ru	Ru(c)	Ru(OH) ₂ ⁺	100	1.5 × 10 ⁻²³
Eh = -0.1					

The Cambric Site—A Field Study

At the location of the Cambric nuclear test at NTS, a field study of radionuclide migration has been ongoing since 1975. The Cambric device was detonated at a depth of 294 m in tuffaceous alluvium in May 1965. In 1974, two wells were drilled—one into the Cambric cavity region and a satellite well (RNM2s) 91 m to the south (Fig. 4). The objective of the study was to determine the potential for radionuclide migration from an underground nuclear test.

Pumping of the satellite well began in October 1975 and has continued since that time. No radioactivity was observed for the first two years. With further pumping, tritium concentrations began to increase in samples from the satellite well and to decrease in the cavity (Hoffman *et al.*, 1977). Attempts were made to measure radionuclides other than tritium using large volume samples that were evaporated in the field using a distillation apparatus. Ruthenium-106 and several other radionuclides were observed in the samples (Coles and Ramspott, 1982). The ¹⁰⁶Ru/³H ratios were nearly the same for all water samples from both wells. Coles and Ramspott suggest that ruthenium and tritium traveled at the same rate from the Cambric cavity to the satellite well. Their finding contradicts the prediction, based on laboratory sorption measurements, that ruthenium-106 would migrate at a slower rate than tritium.

Ruthenium

This study of the Cambric site offers an opportunity to apply the ruthenium data base to a

field problem. Water analyses of samples taken from the satellite well (RNM2s) were used as input to EQ3NR. Ruthenium was added as a component. Since the oxidation potential of the system is unknown, the system was assumed to be oxidizing (Eh = +0.8 V) based on the work of Winograd and Robertson (1982). They report that dissolved oxygen has been observed in a variety of aquifers in the south-central Great Basin, Nevada, and in all valley-fill aquifers in the southern Arizona portion of the Basin and Range Province.

The results of the EQ3NR runs are summarized in Table 2. To compare the effects of oxidation potential, a series of runs were also made assuming a reducing environment (Eh = -0.1 V). Under oxidizing conditions, where the solid-phase controlling solubility is RuO₂, the calculated solubility limit is 2.1 × 10⁻¹¹ M. In reducing conditions, the solubility is controlled by Ru(c) at 1.5 × 10⁻²³ M. The solubility in oxidizing conditions reported earlier for the J-13 water is lower (i.e., 10⁻¹⁵ M) as a result of the difference in pH. The effect of pH on ruthenium solubility is shown in Fig. 5. As the pH is lowered at Eh = 0.8 V, the solubility decreases to a lower limit of 10⁻¹⁸ M at pH = 6.3. Below that pH value, the solubility again increases and the dominant stable aqueous species becomes Ru(OH)₂⁺ instead of RuO₄⁻. This effect on speciation is also illustrated in Fig. 2.

How does the solubility limit calculated for the Cambric ground water compare with the ruthenium concentration in the cavity before pumping? To make this comparison we must first assume that: (1) the chemical composition of ground

Figure 4. Cross section of Cambric Experiment Site shows position of cavity and satellite wells.

water in the satellite well represents the composition of ground water in the cavity well, and (2) the pH at the bottom of the cavity at approximately the depth of the perforations in the satellite well is also the same (i.e., 8.3).*

To calculate the total ruthenium content at the Cambric site, we must know the total of all ruthenium isotopes generated at the time of the nuclear detonation (Table 3). Based on the ^{106}Ru found in a sample collected from the bottom of

the cavity (8.3 dpm/ml, which is equivalent to $3.4 \times 10^{-16} \text{ M}$ at 15 years after detonation)* and the percent of total ruthenium represented by the ^{106}Ru isotope (0.0007%) also at $T = 15$ years, the concentration of ruthenium in solution is $4.5 \times 10^{-11} \text{ M}$. The EQ3NR code predicts that ruthenium solubility in an oxidizing environment where RuO_2 is the stable solid phase is $2.1 \times 10^{-11} \text{ M}$. Given the uncertainties in the data base and the assumptions regarding the composition and pH of the cavity water, the two numbers are remarkably close.

* A second sample from the bottom of the cavity had a pH = 11, but was apparently contaminated with drilling fluid (high calcium and lithium values were reported) and was not used in this evaluation.

* Fifteen years was chosen for comparison with the Coles and Ramspott (1982) work.

Figure 5. Both the speciation and solubility of ruthenium are dependent on pH. Graph drawn from calculations using successive runs of EQ3NR.

The EQ3NR code predictions coincide with the field observations. The calculated ruthenium solubility matches the observed values when corrected for the presence of other ruthenium isotopes. The dominant aqueous ion, RuO_4^- , is negatively charged and therefore likely to migrate. Clues to the reasons for the apparent discrepancy between the laboratory and field measurements can be found in the Eh-pH diagrams.

In Fig. 2, the stability fields for the dominant aqueous ions are highly dependent on the concentration of ruthenium in solution as well as the Eh-pH of the system. The boundaries between

positively and negatively charged species shift with changes in concentration. If the experimental conditions were at concentrations or pH's different from those in the field, then one of the positively charged species shown in the diagrams could be dominant and sorption onto the solid would occur. The most likely species are $\text{Ru}(\text{OH})_2^{++}$ and $\text{Ru}_4(\text{OH})_{12}^{++}$.

As concentrations decrease, the stability field of the negatively charged ion RuO_4^- increases. This may explain the migration of ruthenium since the ruthenium will become more dilute (and therefore more negatively charged) as water moves into and away from the cavity (assuming that negative ions will migrate and positively charged ions will likely be sorbed onto the rock). Kinetics could also affect the results of laboratory sorption experiments using ruthenium. For example, if the conversion of the positively charged to negatively charged species is slow relative to the time of the laboratory experiments, the decrease in concentration of the ruthenium remaining in solution as the positively charged ruthenium species is sorbed onto the solid phase would not favor the formation of RuO_4^- . In this case, the laboratory conditions would not be representative of field conditions.

The interpretation of the results of the geochemical modeling relies heavily on theory and the reliability of the data base. Ruthenium experiments that combined leaching and sorption on crushed alluvium gave distribution coefficients (K_d 's) of 1000 to 3400 ml/g (Wolfsberg, 1978). Given the low solubility of ruthenium in the Cambrian ground water, the K_d 's could be a measure of precipitation rather than sorption. In a reducing environment ($\text{Eh} = -0.1 \text{ V}$), the solubility of ruthenium in the +3 oxidation state (i.e., $1.5 \times 10^{-23} \text{ M}$) is much less than in oxidizing conditions. The formation of positively charged ions could also be a contributing or a major factor.

Table 3. Ruthenium isotopes generated at Cambrian event.^a

Isotope ^b	%	Half-life	Atoms at T = 0	Atoms at T = 15 years
Ru-101	6.75	Stable	8.1×10^{21}	8.1×10^{21}
Ru-102	6.65	Stable	8.0×10^{21}	8.0×10^{21}
Ru-104	5.86	Stable	7.0×10^{21}	7.0×10^{21}
Ru-106	4.64	357 d	5.6×10^{21}	1.7×10^{17}

^a Yield = 0.75 kilotons.

^b Isotope percentages are from Fleming (1967). Because of their short half-lives, ruthenium isotopes 103, 105, 107, and 108 are not included in the calculations.

Given the complexity of ruthenium chemistry, the geochemical models used in this study provide new answers, but not the only answers.

Tchnetium

Tchnetium solubilities were calculated for the Cambrian ground water using EQ3NR (Table 2). In oxidizing conditions, solubility was virtually unlimited. In a reducing environment ($E_h = -0.1$ V), the calculated solubility was 1.8×10^{-14} M using Tc_2O_4 as the solubility constraint. Using the thermodynamic data base developed by Rard (1983), EQ3NR predicts that Tc_2O_4 is the most stable solid phase for a reduced form of technetium. However, the use of Tc_2O_4 is a source of uncertainty in the calculations because there is no direct chemical evidence that it exists. There is strong (but indirect) electrochemical evidence for its existence in surface films on technetium metal in acid solutions. Although Rard (1984) considers his calculated Gibbs free energy for Tc_2O_4 to be reliable, the differences in the free energies of reaction for the disproportionation of Tc_2O_4 and that of several other hydrated oxides and hydroxides is approximately 1 kcal, which is within the error limits of the free energy of formation reported by Rard. Given our current state of knowledge, we cannot predict with certainty the solid phase controlling the solubility limit of technetium in reducing conditions. Added to this problem is the difficulty in determining the oxidation potential of the system (Lindberg and Runnells, 1984; Hostettler, 1984).

The technetium solubility limit of 1.8×10^{-14} M predicted by EQ3NR is similar to values reported by Salter and Jacobs (1982), Wildung *et al.* (1979), and Guzowski *et al.* (1983). All of these studies assumed that TcO_4^- was the dominant ion in solution and used $TcO_2(c)$ as the solubility constraint. The thermodynamic data for $TcO_2(c)$ came from a study by Cartledge and Smith (1955). $TcO_2(c)$ is not included in the EQ3NR thermodynamic data base because these data are now believed to be incorrect. Cartledge and Smith measured the electrochemical potential for the half-cell TcO_2/TcO_4^- . The half-cell reaction was written as

The electrodes were prepared by reduction of TcO_4^- on platinum and gold. No x-ray analysis was performed to see whether the material was

crystalline or amorphous. However, amorphous hydrated $TcO_2 \cdot 2H_2O$ is usually obtained following electrolytic reduction of TcO_4^- (Spitsyn *et al.*, 1976). If we assume that $TcO_2 \cdot 2H_2O$ was the technetium oxide produced in Cartledge and Smith's experiments, then the data they reported can only be used to calculate the Gibbs free energy for $TcO_2 \cdot 2H_2O$, not $TcO_2(c)$, unless we assume for the purpose of the calculation that the free energy of the dehydration reaction is zero. We can expect $TcO_2 \cdot 2H_2O$ to be metastable relative to $TcO_2(c)$.

The calculated technetium solubility limit using $TcO_2 \cdot 2H_2O$ as the solubility constraint is much greater (3.0×10^{-8} M). This value is very similar to the technetium concentrations measured by Kelmers *et al.* (1984a) in carefully controlled laboratory experiments. Kelmers *et al.* measured technetium concentrations of 10^{-6} to 10^{-7} M in synthetic basalt ground water in contact with basalt in anoxic conditions for 10 days. Anoxic conditions were simulated with hydrazine (0.05 and 0.07 M N_2H_4). In later experiments, hydrazine was rejected as an inadequate redox buffer. Using instead a controlled atmosphere glove box to simulate an anoxic environment, Kelmers *et al.* (1984b) measured slightly higher technetium concentrations (10^{-5} to 10^{-6} M).

In the technetium solubility studies, the hydrated form of TcO_2 is the most likely product. To convert $TcO_2 \cdot 2H_2O$ to $TcO_2(c)$, the amorphous oxide must be dehydrated in a vacuum at 300°C (Nelson *et al.*, 1954). Kelmers *et al.*'s experiments, which were designed to test the validity of the technetium solubilities reported in the literature, cannot be expected to give the same results as the calculations based on $TcO_2(c)$. First, the calculations were based on the solubility of $TcO_2(c)$ in equilibrium with TcO_4^- , a condition that may not be representative of the experimental conditions. Second, the oxidation potential of the experimental system is believed to be reducing, but the actual E_h value needed to calculate a solubility to compare with the experimental value is not available.

What is the solubility of technetium in a reducing environment? The predicted solubility limits for technetium calculated by EQ3NR (Table 2) are based on the assumption that the system is at equilibrium and that the master variables, E_h and pH, are known. Although pH measurements are generally reliable, E_h measurements are not. In Figs. 6(a) and 6(b), the solubilities of Tc_2O_4 and $TcO_2 \cdot 2H_2O$ are plotted at pH = 7.1 and 8.1 as a

Figure 6. Relatively small changes in Eh strongly affect the solubility of technetium in mildly to moderately reducing conditions ($E_h = +0.20$ to -0.10 V). Solubility calculated using (a) Tc_3O_4 and (b) $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ as the solubility constraint. The solubility for pH = 8.1 represents the Cambrian site ground water. A pH of 7.1 was chosen to show the affect on solubility of a change of one pH unit.

function of oxidation potential. In Fig. 6(a), the solubility of Tc_3O_4 is highly dependent on oxidation potential. A 0.1-V increase in the Eh value increases technetium solubility by five orders of magnitude. In Fig. 6(b), $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ controls solubility. The total technetium concentration is dependent on Eh only until $\text{TcO}(\text{OH})_2$ becomes the dominant aqueous ion. The solubility limit for technetium under these conditions is 3.2×10^{-8} M. It is independent of Eh or pH.

When TcO_4^- is assumed to be the only aqueous ion present in solution, calculated solubilities are much lower than the solubility limit when $\text{TcO}(\text{OH})_2$ is used in the calculations. This can be shown in Fig. 6(b) by extending the line representing Eq. (1) at pH 8.1 to lower Eh values. For example, at $E_h = 0.15$, technetium solubility (ignoring the presence of $\text{TcO}(\text{OH})_2$) is approximately 10^{-12} M, a value close to calculated values previously reported in the literature. Studies such as these illustrate the need to consider all species and phases when making predictions of solubility.

The above calculations do not take into account metastable phases other than $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$, supersaturated solutions, colloid formation, or sorption processes. The model predictions are also

hampered by the lack of thermodynamic data for $\text{TcO}_2(\text{c})$. In contrast, the laboratory experiments are hampered by the problems of artificially creating an anoxic environment. For example, Kelmers *et al.*'s (1984b) anoxic experiments were done in a controlled atmosphere glove box. However, the amount of oxygen they calculated to be present in the solutions (1.6×10^{-5} ppm) is theoretically equivalent to an oxidation potential of 0.6 V, which is relatively oxidizing. The technetium concentrations they measured suggest a much lower oxidation potential was achieved, although the actual Eh value is unknown. The experimental work reported by Kelmers *et al.* (1984a,b) is regarded by the authors as a progress report. Future experiments are planned.

If ruthenium migrates, the technetium that also exists as a negative ion in an oxidizing environment should also migrate. Seven technetium isotopes are produced in a nuclear detonation (Fleming, 1967). With the exception of ^{99}Tc , none of the technetium isotopes have half-lives that would result in measurable concentrations given the time of the Cambrian study. Approximately one-third as many ^{99}Tc atoms are produced as stable ruthenium atoms. However, technetium is not

limited by solubility in an oxidizing environment and should be present, albeit in small concentrations. At the present time, the lack of sensitivity in our analytical techniques prevents the study of technetium migration. More sensitive methods are currently being developed by both LLNL and the

Los Alamos National Laboratory, a co-participant in the RNM Project. Until the archived samples from the cavity and satellite wells have been analyzed for technetium, we are limited to predictions using geochemical models.

Summary

The thermodynamic data bases constructed for ruthenium and technetium are based on the best data currently available. The information most missing from the data base is the thermodynamic data needed to make high temperature predictions. It will be necessary to apply the geochemical model at temperatures above 25°C (the temperature for which most of the data are valid) to model geochemical processes in the region around the waste package where temperatures are predicted to exceed 100°C for extended periods of time. However, the current data base is applicable for far-field studies (i.e., the undisturbed region away from the repository) where the relatively low temperatures will depend on the thermal gradient of the host rock and the depth of the repository.

The species missing from the data bases are (especially for Ru) primarily complexes of chloride, sulfate, phosphate, and other oxy-anions and halides. Given that many ground waters are dilute solutions with respect to these ions, it is unlikely that ruthenium or technetium speciation or solubility will be much different in most ground waters from what is predicted in the Yucca Mountain and Cambric site studies. For example, the EQ3NR code predicts that the ruthenium chloride and sulfate complexes now in the data base will exist in only trace amounts; however, this may not be true everywhere. Exceptions would be brines associated with either salt sites or brines found in deep ground waters from some granitic sites.

Since much of the data represent calculated values that are based on data reported for related species (e.g., the Gibbs free energy for NaTcO_4 was based in part on the Gibbs free energies reported for TcO_4^- and Na^+), the adequacy of the overall data set is best determined by validation studies using field and laboratory measurements. Unfortunately, opportunities for modeling real life situations are rare. In the case of the Cambric site, the observed migration of ruthenium was successfully predicted by the model. The solubility of ruthenium in the cavity water was approximately

equal to the predicted value. The negative ion predicted as the dominant species has potential for migration. The behavior of ruthenium in laboratory experiments that conflicts with the observed behavior of ruthenium can be explained by differences in speciation between laboratory and field conditions.

Similar studies for technetium do not exist. In oxidizing conditions, both the model predictions and the experimental results show high technetium solubility. In reducing conditions the solubility limits reported in the laboratory (10^{-5} to 10^{-6} M) are close to those predicted by EQ3NR when the metastable phase $\text{TcO}_2 \cdot 2\text{H}_2\text{O}$ in equilibrium with $\text{TcO}(\text{OH})_2^0$ is used to control solubility (10^{-5} to 10^{-6} M vs 10^{-8} M). Given the lack of field evidence for technetium mobility in the natural environment, the model predictions cannot be validated. However, when analytical techniques are improved, there is hope that technetium migration may yet be measured at the Cambric site, thus providing for a comparison of the field results and model predictions.

Like most elements with complex chemical behavior, the solubility and speciation of ruthenium and technetium depend on the Eh-pH conditions. Improvements are needed in field measurement techniques, in particular, measurement techniques used to characterize the unsaturated zone where oxidation potential and pH operate on a microscale and are not easily defined.

Documentation and verification/validation of the computer codes required by the NRC to meet their licensing requirements include the evaluation of the supporting data bases. To successfully apply a geochemical code's abilities, all the necessary species must be represented in the data file, and their equilibrium constants must be correct. Application studies such as the ones described in this report are necessary to determine the validity of data bases developed for individual elements considered important to the performance assessment of waste disposal sites.

Appendix A. MCRT Files for Ruthenium

Appendices A and B contain the MCRT data files constructed using the thermodynamic reviews of Rard (1983 and 1985). Gibbs free energies, enthalpies, entropies, and heat capacities given by Rard in SI units of joules or kJ were converted to calories or kcal, the units used by the EQ3/6 codes.

Data blocks, in the format required by the MCRT code, were created for each of the aqueous species and solid phases. The data blocks make up two MCRT files, MDAQS and MDSOL, for the aqueous species and for solids, respectively. A third file, called the REAC file, was also created. It specifies the reactions that must be considered in generating the data base using the two MCRT files. EQTL, a companion code to MCRT, processes the main data base, DATA0, and creates especially formatted data files for use either by EQ3NR or EQ6. For additional information on the EQ3/6 data base, see Chapter 3 in Wolery, 1983.

For both the technetium and ruthenium data, the quality of the Gibbs free energy value for each aqueous species and solid was estimated based on the criteria given at the end of each data file. For example, the Gibbs free energy was rated "good" if the likely error was considered less than 1 kcal by Rard. The quality of the data is based on an estimate of the likely error in kcal rather than as a percentage, since free energy is a relative value rather than an absolute value.

MCRT uses the Gibbs free energy of formation at a given temperature to calculate the stability constant for a solid or aqueous species. Usually the free energy value at 25°C is known and reported in the literature. Extrapolation to higher temperatures requires knowledge of the enthalpy at 25°C (or equivalently, the 25°C entropy), plus the heat capacity as a function of temperature (Helgeson *et al.*, 1978). If the heat capacity is not known, then one may either assume the heat capacity is zero, giving rise to the constant enthalpy method, or, in the case of aqueous species, use one of several algorithms that estimate the heat capacity from the entropy. For example, extrapolations of the free energies for the aqueous species of ruthenium and technetium, where entropy values were available, used the Criss and Cobble (1964a,b) method for ionic species as well as the method suggested by Helgeson (1967) for neutrals. The ability to extrapolate free energies to higher temperatures is particularly important in applications involving nuclear waste disposal where elevated temperatures in the vicinity of the repository are expected as a result of radioactive decay.

mdaqsr.3245u01 data for aqueous complexes of ruthenium (see bottom of file)
last revised 2/28/84 by dana isherwood

*
* reformatted 08/24/83 by tjw
*

+-----
ru(so4)2-

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= -1.0 titr. factor=
ion type= 2 ion size=
hydr. no.=
3 chemical elements=
1.000 ru 2.000 s 8.000 o
temp= 298.15 k press= 1.013 bars
delg0= -318.60 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(so4)2- 1.000 ru+++ 2.000 so4--
log k= -8.72 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol
* ru+++ salts are generally easily oxidized
* log k = -4.61 at i = 2.0. log k recalculated using bdot
* equation for i = 0.
+-----

hruo5-

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= fair
charge= -1.0 titr. factor=
ion type= 4 ion size=
hydr. no.=
3 chemical elements=
1.000 ru 1.000 h 5.000 o
temp= 298.15 k press= 1.013 bars
delg0= -77.8 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 hruo5- -1.000 h+ 1.000 h2ruo5
log k= 11.59 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation
* equilibrium constant uncertain by 50%
* there is a report that h2ruo5 behaves as a base
* in very acidic solutions but this is probably in error
* delgo refers to formation from the elements and an electron;
* hruo5- can oxidize water. ionic strength unknown.
+-----

ru(oh)2so4

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= poor
charge= 0.0 titr.factor=
ion type= ion size=
hydr. no.=
4 chemical elements=
1.000 ru 1.000 s 6.000 o
2.000 h
temp= 298.15 k press= 1.013 bars
delg0= -233.35 kcal/mol delh0= 500.000 kcal/mol
s0= 500.000 cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(oh)2so4 1.000 ru(oh)2++ 1.000 so4--
log k= -1.79 delh0r= -9.26 kcal/mol
dels0r= -39.3 cal/mol/k

* rard evaluation
* the species ru(oh)2++ could well be ruo++. there is evidence that in
* sulfate solutions ru exists as the polymer ru4(oh)12++++ rather than
* ru(oh)2++. the calculations will not be effected by assuming the
* monomer since its concentration and the stability constant will each
* be off by a factor of 4 which will cancel in any calculations
* original data at 20,25, and 35c log k extrapolated to i = 0.

ruso4+

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= 1.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
3 chemical elements=
1.000 ru 1.000 s 4.000 o
temp= 298.15 k press= 1.013 bars
delg0= -139.10 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ruso4+ 1.000 ru+++ 1.000 so4--
log k= -5.16 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol
* ru+++ salts are generally easily oxidized
* log k = -2.04 at i = 2.0. log k at i = 0 calculated using bdot equation.

ru4(oh)12++++

entered by= d.j. isherwood

date= 03/03/83

source= rard, 1984

quality= poor

charge= 4.0

titr. factor=

ion type= 1

ion size=

hydr. no.=

3 chemical elements=

4.000 ru

12.000 o

12.000 h

temp= 298.15 k

press=

1.013 bars

delg0= -448.60 kcal/mol

delh0=

500.000 kcal/mol

s0= 500. cal/mol/k

se=

cal/mol/k

v0=

cc/mol

cp=

cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ru4(oh)12++++ -4.000 oh-

4.000 ruo2.2h2o(s)

log k= 47.08

delh0r=

500. kcal/mol

dels0r= 500. cal/mol/k

* rard evaluation

* for solid phase usually about 2 waters. this is the thermodynamically
* stable species in non-complexing media. ru(oh)2++ is metastable in non
* -complexing media and gradually forms the tetramer. in cl- and so4--
* media use ru(oh)2++ instead solubility known within a factor of two.
* log k = 43.3 at i = 0.5. log k at i = 0 calculated using bdot equation.

ru(oh)2cl+

entered by= d.j. isherwood

date= 03/03/83

source= rard, 1984

quality= poor

charge= 1.0

titr. factor=

ion type= 1

ion size=

hydr. no.=

4 chemical elements=

1.000 ru

2.000 o

2.000 h

1.000 cl

temp= 298.15 k

press=

1.013 bars

delg0= -86.30 kcal/mol

delh0=

500.000 kcal/mol

s0= 500. cal/mol/k

se=

cal/mol/k

v0=

cc/mol

cp=

cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ru(oh)2cl+

1.000 ru(oh)2++

1.000 cl-

log k= -1.72

delh0r=

500. kcal/mol

dels0r= 500. cal/mol/k

* this species takes several days to reach equilibrium

* ru(oh)2++ could also be ruo++

* rard evaluation log k = -0.91 at i = 0.7. log k at i = 0

* calculated using bdot equation.

ru(oh)2(cl)4--

entered by= d.j. isherwood date= 03/03/83

source= rard, 1984 quality= poor

charge= -2.0 titr. factor=

ion type= 2 ion size=

hydr. no.=

4 chemical elements=

1.000 ru 2.000 o '2.000 h

4.000 cl

temp= 298.15 k press= 1.013 bars

delg0= -182.20 kcal/mol delh0= 500.000 kcal/mol

s0= 500. cal/mol/k se= cal/mol/k

v0= cc/mol

cp= cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ru(oh)2(cl)4-- 1.000 ru(oh)2++ 4.000 cl-

log k= -1.18 delh0r= 500. kcal/mol

dels0r= 500. cal/mol/k

* rard evaluation

* this species takes several days to reach equilibrium

* ru(oh)2++ could also be ruo++

* there is a stepwise constant at 90c and one ionic strength but

* there is not enough related data to utilize it.

* log k given is at i = 6.2

+-----

ruso4

entered by= d.j. isherwood date= 02/28/84

source= rard, 1984 quality=

charge= 0.0 titr. factor=

ion type= ion size=

hydr. no.=

3 chemical elements=

1.000 ru 1.000 s 4.000 o

temp= 298.15 k press= 1.013 bars

delg0= -145.20 kcal/mol delh0= 500.000 kcal/mol

s0= 500. cal/mol/k se= cal/mol/k

v0= cc/mol

cp= cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ruso4 1.000 ru++ 1.000 so4--

log k= -2.35 delh0r= 0.0 kcal/mol

dels0r= -10.75 cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol

* most ru++ salts are easily oxidized

* original data at 20,25, and 35c

* log k extrapolated to i = 0.

+-----

ru(oh)2(cl)2

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= poor
charge= 0.0 titr. factor=
ion type= ion size=
hydr. no.=
4 chemical elements=
1.000 ru 2.000 o 2.000 h
2.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -118.20 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(oh)2(cl)2 1.000 ru(oh)2++ 2.000 cl-
log k= -2.25 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation
* this species takes several days to reach equilibrium
* ru(oh)2++ could also be ruo++.
* log k = -1.08 at i = 0.7. log k at i = 0 calculated using
* bdot equation.

ru(oh)2(cl)3-

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= poor
charge= -1.0 titr. factor=
ion type= 2 ion size=
hydr. no.=
4 chemical elements=
1.000 ru 2.000 o 2.000 h
3.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -149.40 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(oh)2(cl)3- 1.000 ru(oh)2++ 3.000 cl-
log k= -2.03 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation
* this species takes several days to reach equilibrium
* ru(oh)2++ could also be ruo++.
* log k = -0.86 at i = 0.7. log k at i = 0
* calculated using bdot equation.

ru(oh)++

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= 2.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
3 chemical elements=
1.000 ru 1.000 o 1.000 h
temp= 298.15 k press= 1.013 bars
delg0= -12.2 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

4 species in reaction=

-1.000 ru(oh)++ -1.000 h+ 1.000 ru+++

1.000 h2o

log k= 1.62 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol
* most species containing ru+++ are easily oxidized
* log k = 2.59 at i = 1.0. value uncertain by 50%.
* log k at i = 0 calculated using bdot equation.

ru(oh)2+

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= poor
charge= 1.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
3 chemical elements=
1.000 ru 2.000 o 2.000 h
temp= 298.15 k press= 1.013 bars
delg0= -67.1 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ru(oh)2+ 1.000 ru(oh)3(s) -1.000 oh-
log k= 15.9 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation
* most species containing ru+++ are easily oxidized
* ru(oh)3(s) is either ru(oh)3.nh2o or ruo(oh).nh2o
* the solubility is known within a factor of two.
* log k = 15.6 at i = 0.5. log k at i = 0 calculated using bdot equation.

ruo4

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= fair
charge= 0.0 titr. factor=
ion type= ion size=
hydr. no.=
2 chemical elements=
1.000 ru 4.000 o
temp= 298.15 k press= 1.013 bars
delg0= -36.8 kcal/mol delh0= -56.9 kcal/mol
s0= 37.5 cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

2 species in reaction=

-1.000 ruo4 1.000 ruo4(s)
log k= 0.88 delh0r= 1.5 kcal/mol
dels0r= 0.6 cal/mol/k

* rard evaluation

* the reaction refers to the formation of a saturated solution of ruo4 in
* equilibrium with solid ruo4. ruo4 is a strong oxidizing agent and can
* oxidize h2o. ruo4 (s) melts at 25.5 + or - 0.1c so reaction applies
* only from 0 to 25.5c.
* doppelganger of h2ruo5 = ruo4 + h2o

h2ruo5

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= fair
charge= 0.0 titr. factor=
ion type= ion size=
hydr. no.=
3 chemical elements=
1.000 ru 2.000 h 5.000 o
temp= 298.15 k press= 1.013 bars
delg0= -93.5 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction=

* rard evaluation

* formed by hydration of aqueous ruo4
* hydrated ruo4 is a weak actd
* doppelganger of aqueous ruo4

ruo4-

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= fair
charge= -1.0 titr. factor=
ion type= 3 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 4.000 o
temp= 298.15 k press= 1.013 bars
delg0= -59.8 kcal/mol delh0= -79.4 kcal/mol
s0= 54.5 cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction=

* rard evaluation s0 uncertain by 19 eu
* thermodynamic data refer to formation from the elements and ie-
* ruo4- is more nearly stable in alkaline media, but upon acidification
* get ruo4 , ruo2.2h2o and h2o
* some authors claim ru2o5.nh2o rather than ruo2.2h2o
* ruo4- is a strong oxidizing agent.

ruo4--

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= poor
charge= -2.0 titr. factor=
ion type= 3 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 4.000 o
temp= 298.15 k press= 1.013 bars
delg0= -73.3 kcal/mol delh0= -109.2 kcal/mol;
s0= 15.5 cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction=

* rard evaluation
* s0 uncertain by 8 eu
* thermodynamic data refer to formation from the elements and ie-
* ruo4-- is more nearly stable in alkaline media, but upon acidification
* get ruo4- , ruo2.2h2o and h2o some authors claim ru2o5.nh2o rather than
* ruo2.2h2o. ruo4-- is a fairly strong oxidizing agent.

rucl+

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= 1.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 1.000 cl
temp= 298.15 k press= 1.013 bars
delg0= +5.20 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 rucl+ 1.000 ru++ 1.000 cl-
log k= 0.49 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol

* k is known to about 30%

* this species is formed by the reduction of rucl++ and within a few

* minutes it polymerizes to form ru blue neither the chemistry nor

* thermodynamics of ru blue are understood very well.

ru(oh)2++

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality= poor
charge= 2.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
3 chemical elements=
1.000 ru 2.000 o 2.000 h
temp= 298.15 k press= 1.013 bars
delg0= -53.00 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction=

* rard evaluation

* for solid phase usually about 2 waters but variable ru(oh)2++ or

* ruo++ is a metastable species and polymerizes to ru4(oh)12+++

* over a several month period in non-complexing media.

* in complexing media like cl- or so4-- this species should be used

* and not the tetramer. log k=27.21 for reaction ru(oh)2++ + oh- = ruo2.2h2o.

* delg0 calculated from log k.

rucl++

entered by= d.j. isherwood date= 03/03/83
source= rard, 1984 quality=
charge= 2.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 1.000 cl
temp= 298.15 k press= 1.013 bars
delg0= +7.1 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 rucl++ 1.000 ru+++ 1.000 cl-
log k= -2.17 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k
* rard evaluation-corrected for $\Delta_i = 35.5$ kcal/mol
* uncatalyzed reaction takes several months to reach equilibrium
* log k extrapolated to $i = 0$.

ru(cl)2+

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= 1.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 2.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -26.40 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(cl)2+ 1.000 ru+++ 2.000 cl-
log k= -3.74 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for $\Delta_i = 35.5$ kcal/mol
* uncatalyzed reaction takes several weeks to months to
* reach equilibrium. log k extrapolated to $i = 0$.

ru(c1)3

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= 0.0 titr. factor=
ion type= ion size=
hydr. no.=
2 chemical elements=
1.000 ru 3.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -58.60 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ru(c1)3 1.000 ru+++ 3.000 cl-
log k= -4.28 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol

* uncatalyzed reaction takes several days to weeks to

* reach equilibrium. log k extrapolated to i = 0.

ru(c1)4-

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= -1.0 titr. factor=
ion type= 2 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 4.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -89.70 kcal/mol delh0= 500. kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

3 species in reaction=

-1.000 ru(c1)4- 1.000 ru+++ 4.000 cl-
log k= -4.13 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol

* uncatalyzed reaction takes several days to reach equilibrium

* log k extrapolated to i = 0.

ru(cl)5--

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= -2.0 titr. factor=
ion type= 2 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 5.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -120.70 kcal/mol delh0= 500.000 kcal/mol
s0= 500.00 cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(cl)5-- 1.000 ru+++ 5.000 cl-
log k= -3.27 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol

* reaction reaches equilibrium rapidly

* approximately known k at i = 5.0.

ru(cl)6---

entered by= d.j. isherwood date= 02/28/84
source= rard, 1984 quality=
charge= -3.0 titr. factor=
ion type= 2 ion size=
hydr. no.=
2 chemical elements=
1.000 ru 6.000 cl
temp= 298.15 k press= 1.013 bars
delg0= -151.50 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
3 species in reaction=
-1.000 ru(cl)6--- 1.000 ru+++ 6.000 cl-
log k= -2.27 delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-corrected for xi=35.5 kcal/mol

* reaction reaches equilibrium rapidly

* approximately known k at i = 5.0.

ru+++

entered by= d.j. isherwood date= 03/03/83
source= see below quality=
charge= 3.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
1 chemical elements=
1.000 ru
temp= 298.15 k press= 1.013 bars
delg0= 41.4 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction=

* rard evaluation
* there is no experimental value for this due to the complicated chemistry
* and irreversible thermodynamics. this is an estimate. unfortunately we
* need its value to get delg0 for ru++ , ru(oh)++ and all the chloride and
* sulfate complexes of ru+++ and ru++++ the estimate comes from ru++
*

ru++

entered by= d.j. isherwood date= 03/03/83
source= see below quality=
charge= 2.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
1 chemical elements=
1.000 ru
temp= 298.15 k press= 1.013 bars
delg0= 35.9 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction=

* rard evaluation
* the ru++/ru+++ electrode potential is very accurately known, but
* there is no experimental data to assign either ru+++ or ru++.

stop.

notation--

-- delg0 = gibbs energy of formation
-- delg0r = gibbs energy of reaction
-- delh0 = enthalpy of formation
-- delh0r = enthalpy of reaction
-- s0 = conventional entropy
-- se = internal electronic entropy
-- delh0r = entropy of reaction

note that "500." is entered to mean "no data" for ΔG^0 , ΔH^0 , ΔS^0 , $\log K$, ΔH^0 , and ΔS^0 . never enter zero or leave blank for these parameters unless you mean to use an actual value of zero.

data for aqueous species=

name= an alphabetic or alphanumeric string
entered by= name of person who entered data or last revised it
date= data of entering or revising data
source= alphanumeric string identifying a major source of data. use
"see below" for minor sources
quality= alphanumeric string describing the probable error in gibbs energy
or its equivalent, based on subjective judgement and chosen from
among the following (in order of increasing value)
bad - demonstrably bad data- do not use except in illustrative
calculations
poor - likely error exceeds a couple of kcal
restricted - ad hoc fit to a particular situation; see notes
speculative - species not shown conclusively to exist
uncertain - chosen rather arbitrarily from divergent reported
values
unspecified - no quality information
(blank) - equivalent to unspecified
fair - likely error less than a couple of kcal
good - likely error less than about one kcal

the code must be modified to allow other quality parameter inputs.
unrecognized inputs are set to "error". data for which the quality
is "restricted", "speculative", or "uncertain" may numerically be
"fair" to "good". the major uncertainty associated with these values
is qualitative (i.e., uncertainty of interpretation). data for which
the quality is "poor" may be quite sufficient for making "good"
calculations- this depends on the sensitivity of the results to it in
any particular application.

charge= electrical charge

titration factor= weighting factor for ph 4.5 (methyl orange)

alkalinity

ion type= criss-cobble ion type

- 0 neutral complex (may be left blank)
- 1 cation (may be left blank)
- 2 simple anion (may be left blank)
- 3 oxyanion
- 4 acid oxyanion

ion size= debye-huckel hydrated ion size (for activity coefficient
estimation)

hydration number= number of bound water molecules not explicitly
shown in the assumed molecular formula (for activity coefficient
estimation)

temp= the base point temperature (K), usually 298.15 K

press= the base point pressure (bars), usually 1 bar

ΔG^0 = the apparent standard partial molal gibbs energy at the
base point

Δh_0 = the apparent standard partial molal enthalpy at the base point
 s_0 = the conventional entropy at the base point
 s_e = the internal electronic entropy; this function is zero except for some actinide and rare earth species (it is used in criss-cobble method temperature extrapolations)
 v_0 = the partial molal volume at the base point; there is no current provision for using this input in the current mcrt (as of 12/16/82)
 cp = the partial molal heat capacity at the base point; there is no current provision for using this input in the current mcrt (as of 12/16/82)
 $\log k$ = log of the equilibrium constant of the given reaction at the base point
 Δh_{0r} = enthalpy of the given reaction at the base point
 Δs_{0r} = entropy of the given reaction at the base point

references

rard, j., 1985, chemistry and thermodynamics of ruthenium and some of its inorganic compounds and aqueous species, lawrence livermore national laboratory, ucrl-90254, chem reviews, 85, p. 1-39.

mdsolru.3245u02 data for solids of ruthenium (see bottom of file)
last revised 02/29/84 by dji

*

ruo2.2h2o(am)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= poor

3 chemical elements=

1.000 ru

4.000 o

4.000 h

temp= 298.15 k

press=

1.013 bars

delg0= -165.1 kcal/mol

delh0=

500. kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* hydrated ruthenium dioxide is an amorphous solid with usually about

* two waters; two waters were used to calculate the free

* energy of formation. this is the solid phase to be used in aqueous

* solubility calculations and not ruo2(s).

* there is no evidence that the hydrate is a definite stoichiometric

* compound.

ru(oh)3.h2o(am)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= poor

3 chemical elements=

1.000 ru

4.000 o

5.000 h

temp= 298.15 k

press=

1.013 bars

delg0= -183.1 kcal/mol

delh0=

500. kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* the available data can not tell ru(oh)3 from ruo(oh).h2o

* the above species should be used in solubility calculations

* although the actual number of waters of hydration is in doubt.

route2(s)

entered by= d.j. isherwood

date= 02/28/84

source= rard, 1984

quality= good

2 chemical elements=

1.000 ru 2.000 te

temp= 298.15 k

press= 1.013 bars

delg0= -30.8 kcal/mol delh0= -33.5 kcal/mol

s0= 21.4 cal/mol/k v0= cc/mol

1 heat capacity range(s) follow=

equation= 0 cp or a= 17.09 cal/mol/k

b= 2.46

c=

d=

e=

limit= 600. k

no t-p grid data

no reaction given

* rard evaluation

* these results from decomposition pressure and relative enthalpy

* measurements to high t. a four term heat capacity equation is

* available to 1500k but the simpler equation works to 600k.

* second and third law extrapolations give identical results.

* thermodynamic data for formation from ru(s) and te(s).

* this compound is not included in reacru or data0 files

ruse2(s)

entered by= d.j. isherwood

date= 03/03/83

source= rard, 1984

quality= good

2 chemical elements=

1.000 ru 2.000 se

temp= 298.15 k

press= 1.013 bars

delg0= -33.0 kcal/mol delh0= -35.0 kcal/mol

s0= 20.4 cal/mol/k v0= cc/mol

1 heat capacity range(s) follow=

equation= 0 cp or a= 15.79 cal/mol/k

b= 3.915

c=

d=

e=

limit= 600. k

no t-p grid data

no reaction given

* rard evaluation

* these results from high t decomposition pressure data heat capacities

* average of values for ruse2(s) and route(s) since no experimental

* values for ruse(s).

* second and third law extrapolations give identical results.

* thermodynamic data for formation from ru(s) and te(s).

* this compound is not included in reacru and data0 files

rus2(s)

entered by= d.j. isherwood

date= 03/03/83

source= see below

quality= good

2 chemical elements=

1.000 ru

2.000 s

temp=

298.15 k

press=

1.013 bars

delg0=

-45.0 kcal

delh0=

-47.7 kcal

s0=

13.2 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

14.49 cal/mol/k

b=

5.37

c=

d=

e=

limit=

600. k

no t-p grid data

no reaction given

* rard evaluation. rus2 mineral name is laurite.

* these results from decomposition pressure are relative enthalpy

* measurements to high t. a four term heat capacity equation is

* available to 1500k, but this simpler equation works to 600k.

* the formation energies refer to ru(s) and rhombahedral sulfur.

* second and third law extrapolations give identical results.

rucl3(g)

entered by= d.j. isherwood

date= 03/03/83

source= see below

quality= poor

2 chemical elements=

1.000 ru

3.000 cl

temp=

298.15 k

press=

1.013 bars

delg0=

4.3 kcal/mol

delh0=

4.8 kcal/mol

s0=

88.8 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

19.5 cal/mol/k

b=

c=

d=

e=

limit=

1000. k

no t-p grid data

no reaction given

* rard evaluation

* these data-from sublimation pressures - are fairly uncertain since

* two available studies are in poor agreement. heat capacity was

* estimated. rucl3(g) important only at very high temperatures.

* rucl4(g) is also known at very high temperatures and cl2

* pressures but does not exist as a solid above -30c.

* this gas is not included in data0

rucl3(s)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= poor

2 chemical elements=

1.000 ru

3.000 cl

temp= 298.15 k

press=

1.013 bars

delg0= -37.9 kcal/mol

delh0=

-52.9 kcal/mol

s0= 36.6 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

26.0 cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* the data based on decomposition pressure measurements for rucl3(s)

* from about 800 - 1100k and three studies in fair agreement.

* the heat capacity of 26.0 + or - 1.6 cal/mol/k is an estimate based

* on values for other mcl3(s) compounds.

* results based on a second law extrapolation of high t data and refer

* to formation from ru(s) and cl2(g).

rubr3(s)

entered by= d.j. isherwood

date= 03/03/83

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru

3.000 br

temp= 298.15 k

press=

1.013 bars

delg0= -28.9 kcal

delh0=

-35.3 kcal

s0= 39.8 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

27.5 cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* the data based on decomposition pressure measurements for rubr3(s)

* from 781 - 870k.

* the heat capacity of 27.5 + or - 3.9 cal/mol/k is an estimate

* based on values for other mbr3(s) compounds.

* results based on a second law extrapolation of high t data and

* refer to formation from ru(s) and br2(l).

rui3(s)

entered by= d.j. isherwood

date= 03/03/83

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru

3.000 i

temp= 298.15 k

press=

1.013 bars

delg0= -13.5 kcal

delh0=

-13.8 kcal

s0=

47.5 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

25.6 cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* the data based on decomposition pressure measurements for rui3(s)

* from 590 - 660k and direct combustion enthalpy measurements.

* the heat capacity of 25.6 + or - 1.0 cal/mol/k is an estimate based

* on values for other mi3(s) compounds. results based on a second law

* extrapolation of high t data and refer to formation from ru(s) and i2(s).

ruo2(s)

entered by= d.j. isherwood

date= 03/03/83

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru

2.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -60.5 kcal/mol

delh0=

-73.4 kcal/mol

s0=

12.5 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

18.2934 cal/mol/k

b= 2.6341

c=

-5.788

d=

e=

limit= 1175. k

no t-p grid data

no reaction given

* rard evaluation

* data at 298 k obtained by a modified third-law extrapolation of

* high temperature free energy of formation data and relative

* enthalpies delg0 average of 5 determinations and delh0 average

* of 6 determinations in fairly good agreement. most of the problems

* with pourbaix's calculations come from bad data for ruo2(s).

* this compound unknown as liquid.

ruo4(g)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru 4.000 o

temp= 298.15 k

press= 1.013 bars

delg0= -35.5 kcal/mol

delh0= -46.1 kcal/mol

s0= 69.5 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a= 22.13 cal/mol/k

b= 2.94

c= -4.33

d=

e=

limit= 1200. k

no t-p grid data

no reaction given

* rard evaluation

* thermodynamic data for formation from ru(5) and o2(g).

* thermodynamic data for ruo4 g,l,s and aq have been forced to self

* consistency using phase transition thermodynamic data.

* gas phase experimental entropies and value from statistical mechanical

* calculation in good agreement.

* heat capacity equation based on least-squares fit to statistical

* mechanical calculations. ruo4(g) coexists in vapor phase with

* ruo3(g) at high t. not included in data0.

ruo3(g)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru 3.000 o

temp= 298.15 k

press= 1.013 bars

delg0= -13.3 kcal/mol

delh0= -16.9 kcal/mol

s0= 68.3 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a= 18.13 cal/mol/k

b= 1.16

c= -3.32

d=

e=

limit= 1200. k

no t-p grid data

no reaction given

* rard evaluation

* ruo3(g) coexists in the vapor phase with ruo4(g) at high t

* ruo3 is unknown as a condensed phase owing to its thermodynamic

* instability.

* heat capacity equation based on least-squares fit to statistical

* mechanical calculations.

* the experimental measurements involve vapor pressures of ruo4(g)

* and ruo3(g) formed from heating ruo2(s) and o2(g), so data for

* ruo3(g) and ruo4(g) depend on ruo2(s). not included in data0.

ruo4(s)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru 4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -38.1 kcal/mol

delh0=

-58.4 kcal/mol

s0= 36.8 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* thermodynamic data for formation from ru and o2

* data for ruo4 g,l,s and aq have been forced to self consistency

* using phase transition thermodynamic data.

* the melting point of ruo4(s) is 25.5 + or - 0.1c

ruo4(l)

entered by= d.j. isherwood

date= 02/29/84

source= rard, 1984

quality= fair

2 chemical elements=

1.000 ru 4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -38.0 kcal/mol

delh0=

-56.3 kcal/mol

s0= 43.4 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a=

cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* thermodynamic data for formation from ru and o2(g) data for ruo4

* g,l,s and aq have been forced to self consistency using phase

* transition thermodynamic data. the melting point of ruo4(s) is

* 25.5 + or - 0.1c

* the boiling temperature of ruo4(l) is about 133 + or - 5c and

* this temperature is uncertain because ruo4(l) decomposes around 108c.

* not included in data0.

ru(c)

entered by= d.j. isherwood
source= rard, 1984

date= 03/03/83
quality= fair

1 chemical elements=

1.000 ru

temp= 298.15 k

press= 1.013 bars

delg0= 0.0 kcal/mol

delh0= 0.0 kcal/mol

s0= 6.840 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a= 5.25 cal/mol/k

b= 1.45

c= 0.0

d=

e=

limit= 1200. k

no t-p grid data

no reaction given

* rard evaluation

* heat capacity equation valid from 298k to 1200k but still fairly good
* at 1400k.

* melting point 2550k, boiling point about 4285k

* the enthalpy of fusion is 9.3 + or - kcal/mol

ru(g)

entered by= d.j. isherwood
source= see below

date= 03/03/83
quality=

1 chemical elements=

1.000 ru

temp= 298.15 k

press= 1.013 bars

delg0= 143.1 kcal/mol

delh0= 154.4 kcal/mol

s0= 44.55 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a= cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

2 species in reaction=

-1.000 ru(g)

1.000 ru(s)

log k= 104.9

delh0r= 154.4 kcal/mol

dels0r= 37.71 cal/mol/k

* rard evaluation

* this species is significant only at extreme temperatures.

stop.

notation--

- delg0 = gibbs energy of formation
- delg0r = gibbs energy of reaction
- delh0 = enthalpy of formation
- delh0r = enthalpy of reaction
- s0 = conventional entropy
- dels0r = entropy of reaction

note that "500." is entered to mean "no data" for delg0, delh0, s0, delhtr, delstr, log k, delh0, and dels0r. never enter zero for these parameters or leave them blank unless you mean to use an actual value of zero. 1000 k is the default for the "limit" parameter.

data for solid/gas species=

name= an alphabetic or alphanumeric string; e.g., calcite, bischofite.
the formula may also be used as the name.

formula= an alphanumeric string denoting the formula of the species;
e.g., caco3, mgcl2.6h2o.

entered by= name of person who entered data or last revised it

date= data of entering or revising data

source= alphanumeric string identifying a major source of data. use
"see below" for minor sources

quality= alphanumeric string describing the probable error in gibbs energy
or its equivalent, based on subjective judgement and chosen from
among the following (in order of increasing value)

bad - demonstrably bad data- do not use except in illustrative
calculations

poor - likely error exceeds a couple of kcal

restricted - ad hoc fit to a particular situation; see notes

speculative - species not shown conclusively to exist

uncertain - chosen rather arbitrarily from divergent reported
values

unspecified - no quality information

(blank) - equivalent to unspecified

fair - likely error less than a couple of kcal

good - likely error less than about one kcal

the code must be modified to allow other quality parameter inputs.

unrecognized inputs are set to "error". data for which the quality
is "restricted", "speculative", or "uncertain" may numerically be
"fair" to "good". the major uncertainty associated with these values
is qualitative (i.e., uncertainty of interpretation). data for which
the quality is "poor" may be quite sufficient for making "good"
calculations- this depends on the sensitivity of the results to it in
any particular application.

number of chemical elements per mole

number of moles of element per mole of substance

symbol of chemical element

temp= the base point temperature (k); usually 298.15 k

press= the base point pressure (bars), usually 1 bar

delg0= the apparent standard partial molal gibbs energy at the
base point

Δh_0 = the apparent standard partial molal enthalpy at the base point
 s_0 = the conventional entropy at the base point
 v_0 = the molar volume at the base point
 number of heat capacity ranges that follow
 equation = heat capacity equation code
 0- $cp = a + 1.e-3*b*t + 1.e+5*c*t^{**(-2)} + 1.e-6*d*t^{**2}$
 1- $cp = a + 1.e-3*b*t + 1.e+5*c*t^{**(-2)} + 1.e+8*d*t^{**(-3)}$
 cp = the molar heat capacity, assumed to be a constant
 a = first heat capacity coefficient
 b = second heat capacity coefficient
 c = third heat capacity coefficient
 d = fourth heat capacity coefficient
 e = fifth heat capacity coefficient
 $limit$ = upper limit (k) of the preceding set of heat capacity parameters;
 no t-p data grid
 this is either the upper limit of use based on the range of measurement
 or the temperature of a phase transition
 Δh_{tr} = enthalpy of a phase transition, if any
 Δs_{tr} = entropy of a phase transition, if any
 t-p data grid indication line, followed by t-p data grid, if any
 temp, press, Δg_0 , Δh_0 , s_0 , v_0
 number of species appearing in a reaction, if a reaction follows
 number of moles of a species appearing in the reaction
 the name of the corresponding species
 $\log k$ = log of the equilibrium constant of the given reaction at the
 base point
 Δh_{0r} = enthalpy of the given reaction at the base point
 Δs_{0r} = entropy of the given reaction at the base point

REFERENCES

Rard, J. (1985), Chemistry and Thermodynamics of Ruthenium and
 Some of its Inorganic Compounds and Aqueous Species,
 Lawrence Livermore National Laboratory, Livermore, CA,
 UCRL-90254, Chem. Reviews, 85, p. 1-39.

stop.

run by= d.j. isherwood

date= 03/05/84

0 0 0 0 0 0 0 0

aqueous species of ruthenium

ru+++	1	
1.00000 ru+++		
ru++	5	
-1.00000 ru++		-0.25000 o2(g)
-1.00000 h+		1.00000 ru+++
0.50000 h2o		
ruo4	5	
-1.00000 ruo4		-3.00000 h+
1.00000 ru+++		1.50000 h2o
1.25000 o2(g)		
ruo4-	5	
-1.00000 ruo4-		-4.00000 h+
1.00000 o2(g)		1.00000 ru+++
2.00000 h2o		
ruo4--	5	
-1.00000 ruo4--		-5.00000 h+
0.75000 o2(g)		1.00000 ru+++
2.50000 h2o		
ru(oh)2++	5	
-1.00000 ru(oh)2++		1.00000 ru+++
1.50000 h2o		0.25000 o2(g)
-1.00000 h+		
ru(oh)++	4	
-1.00000 ru(oh)++		-1.00000 h+
1.00000 ru+++		1.00000 h2o
ru(oh)2+	4	
-1.00000 ru(oh)2+		-2.00000 h+
1.00000 ru+++		2.00000 h2o
h2ruo5	3	
-1.00000 h2ruo5		1.00000 ruo4
1.00000 h2o		
rucl+	3	
-1.00000 rucl+		1.00000 cl-
1.00000 ru++		
rucl++	3	
-1.00000 rucl++		1.00000 cl-
1.00000 ru+++		
ru(cl)2+	3	
-1.00000 ru(cl)2+		2.00000 cl-
1.00000 ru+++		
ru(cl)3	3	
-1.00000 ru(cl)3		3.00000 cl-
1.00000 ru+++		
ru(cl)4-	3	
-1.00000 ru(cl)4-		4.00000 cl-
1.00000 ru+++		
ru(cl)5--	3	
-1.00000 ru(cl)5--		1.00000 ru+++
5.00000 cl-		

ru(c1)6---	3	
-1.00000 ru(c1)6---		1.00000 ru+++
6.00000 cl-		
hruo5-	4	
-1.00000 hruo5-		-1.00000 h+
1.00000 h2o		1.00000 ruo4
ru(so4)2-	3	
-1.00000 ru(so4)2-		1.00000 ru+++
2.00000 so4--		
ruso4+	3	
-1.00000 ruso4+		1.00000 ru+++
1.00000 so4--		
ruso4	3	
-1.00000 ruso4		1.00000 ru++
1.00000 so4--		
ru(oh)2so4	3	
-1.00000 ru(oh)2so4		1.00000 ru(oh)2++
1.00000 so4--		
ru4(oh)12++++	4	
-1.00000 ru4(oh)12++++		-4.00000 h+
4.00000 ru(oh)2++		4.00000 h2o
ru(oh)2cl+	3	
-1.00000 ru(oh)2cl+		1.00000 cl-
1.00000 ru(oh)2++		
ru(oh)2(c1)4--	3	
-1.00000 ru(oh)2(c1)4--		4.00000 cl-
1.00000 ru(oh)2++		
ru(oh)2(c1)2	3	
-1.00000 ru(oh)2(c1)2		2.00000 cl-
1.00000 ru(oh)2++		
ru(oh)2(c1)3-	3	
-1.00000 ru(oh)2(c1)3-		3.00000 cl-
1.00000 ru(oh)2++		
solids of ruthenium		
ru(c)	4	
-1.00000 ru(c)		-2.00000 h+
-1.00000 o2(g)		1.00000 ru(oh)2++
ruo2.2h2o(am)	4	
-1.00000 ruo2.2h2o(am)		-2.00000 h+
1.00000 ru(oh)2++		2.00000 h2o
ru(oh)3.h2o(am)	4	
-1.00000 ru(oh)3.h2o(am)		-3.00000 h+
4.00000 h2o		1.00000 ru+++
rui3(s)	3	
-1.00000 rui3(s)		1.00000 ru+++
3.00000 i-		
ruc13(s)	3	
-1.00000 ruc13(s)		1.00000 ru+++
3.00000 cl-		
ruo2(s)	3	
-1.00000 ruo2(s)		1.00000 ru(oh)2++
-2.00000 h+		

rus2(s)	4	
-1.00000 rus2(s)		-2.00000 h2o
1.00000 ru(oh)2++		2.00000 hs-
rubr3(s)	3	
-1.00000 rubr3(s)		1.00000 ru+++
3.00000 br-		
ruo4(s)	2	
-1.00000 ruo4(s)		1.00000 ruo4
stop.		

Acknowledgments

The author is grateful to reviewers of a draft version of this document for their helpful suggestions and comments. I especially wish to thank Thomas Wolery, Joan Delany, Ken Jackson, Ignasi Puigdomenech, and Larry Ramspott. The final version of the document incorporates most of their recommendations. I also wish to thank Joe Rard for his evaluations of the thermodynamic data and for our many helpful discussions. Both the reviews of the thermodynamics data and the modelling studies were funded by the Radionuclide Migration Project administered by the Department of Energy's Nevada Operations Office.

Appendix B. MCRT Files for Technetium

mdaqstc.3245u03 data for aqueous complexes of technetium (see bottom of file)
last revised 02/21/84

*
* all thermodynamic values and evaluations are from rard, 1983
*

* reformatted 08/24/83 by tjw
*

*-----

tco4-

entered by= d.j. isherwood date= 07/20/83
source= see below quality= good
charge= -1.0 titr. factor=
ion type= 3 ion size=
hydr. no.=
2 chemical elements=
1.000 tc 4.000 o
temp= 298.15 k press= 1.013 bars
delg0= -149.1 kcal/mol delh0= -171.2 kcal/mol
s0= 47.6 cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
0 species in reaction
-1.000 xx 1.000 xx 1.000 xx
log k= 500. delh0r= 500. kcal/mol
dels0r= 500. cal/mol/k

* rard evaluation-delg0 corrected according to errata sheet

* these values are based on good thermodynamic data

* ionic strength=0
+-----

tco4--

entered by= d.j. isherwood date= 07/20/83
source= see below quality= uncertain
charge= -2.0 titr. factor=
ion type= 3 ion size=
hydr. no.=
2 chemical elements=
1.000 tc 4.000 o
temp= 298.15 k press= 1.013 bars
delg0= -135.0 kcal/mol delh0= 500. kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k
no t-p data grid
0 species in reaction

* rard evaluation-delg0 corrected according to errata sheet

* this value is based on a difficult to measure redox potential

* owing to the instability of tco4--. ionic strength=0.12
+-----

htco4-

entered by= d.j. isherwood

date= 07/20/83

source= see below

quality= bad

charge= -1.0

titr. factor=

ion type= 2

ion size=

hydr. no.=

3 chemical elements=

1.000 tc

1.000 h

4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -146.89 kcal/mol

delh0=

500. kcal/mol

s0= 500.0 cal/mol/k

se=

cal/mol/k

v0= cc/mol

cp=

cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation-delg0 corrected according to errata sheet

* this value based on difficult to measure quantities owing to

* the instability of tco4-- in aqueous solution. ionic strength=8.

* do not use.

h2tco4

entered by= d.j. isherwood

date= 07/20/83

source= see below

quality= speculative

charge= 0.0

titr. factor=

ion type=

ion size=

hydr. no.=

3 chemical elements=

1.000 tc

2.000 h

4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -147.3 kcal/mol

delh0=

500. kcal/mol

s0= 500. cal/mol/k

se=

cal/mol/k

v0= cc/mol

cp=

cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation-delg0 corrected according to errata sheet

* h2tco4 is a fairly strong acid with regard to its first ionization.

* it might be better to ignore this species since its free energy

* of formation is well within experimental error of h+ + htco4-.

* ionic strength=8. do not use.

tco4---

entered by= d.j. isherwood

date= 07/20/83

source= see below

quality= fair

charge= -3.0

titr. factor=

ion type= 3

ion size=

hydr. no.=

2 chemical elements=

1.000 tc

4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -121.4 kcal/mol

delh0=

500. kcal/mol

s0= 500. cal/mol/k

se=

cal/mol/k

v0= cc/mol

cp=

cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation-delg0 corrected according to errata sheet

* this is based on tco4- and 5 determinations of the reduction

* potential which are in fair agreement (,- 0.024). this species

* is probably unstable. ionic strength=0. delg0 uncertainty is +/- 2.6.

tco++

entered by= d.j. isherwood date= 07/20/83
source= see below quality= poor
charge= 2.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
2 chemical elements=
1.000 tc 1.000 o
temp= 298.15 k press= 1.013 bars
delg0= -24.04 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation

* tco++ could well be tc(oh)2++ instead. this value is based on

* tco2.2h2o which is well characterized, and on its solubility

* which is very poorly determined. unfortunately its value is

* needed for tco(oh)+, tco(oh)2++, and [tco(oh)2]2. ionic

* strength is probably 1.0. delg0 uncertainty is +/- 2.5.

* delg0 corrected to zero ionic strength using bdot equation.

+-----

tco(oh)+

entered by= d.j. isherwood date= 07/20/83
source= see below quality= uncertain
charge= 1.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
3 chemical elements=
1.000 tc 2.000 o 1.000 h
temp= 298.15 k press= 1.013 bars
delg0= -79.2 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation

* this is based on tco++ which is uncertain. i=0.1.

* delg0 uncertainty is +/- 2.5. delg0 corrected to i=0 using bdot equation.

+-----

tco(oh)2

entered by= d.j. isherwood date= 07/20/83
source= see below quality= uncertain
charge= 0.0 titr. factor=
ion type= ion size=
hydr. no.=
3 chemical elements=
1.000 tc 3.000 o 2.000 h
temp= 298.15 k press= 1.013 bars
delg0= -132.9 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation

* this is based on tco++ which is uncertain. i=0.15.

* delg0 uncertainty is +/- 2.5. delg0 corrected to i=0 using bdot equation.

+-----
[tco(oh)2]2

entered by= d.j. isherwood date= 07/20/83
source= see below quality= poor
charge= 0.0 titr. factor=
ion type= ion size=
hydr. no.=
3 chemical elements=
2.000 tc 6.000 o 4.000 h
temp= 298.15 k press= 1.013 bars
delg0= -274.7 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation

* this is a dimer of tc(oh)2 and it further polymerizes to form

* colloidal tco2.2h2o. this based on tco++ which is uncertain. i=0.2.

* delg0 corrected to i=0 using bdot equation. delg0 uncertainty is

* +/- 5.1.

+-----
tc++

entered by= d.j. isherwood date= 07/20/83
source= see below quality= uncertain
charge= 3.0 titr. factor=
ion type= 1 ion size=
hydr. no.=
1 chemical elements=
1.000 tc
temp= 298.15 k press= 1.013 bars
delg0= 25.3 kcal/mol delh0= 500.000 kcal/mol
s0= 500. cal/mol/k se= cal/mol/k
v0= cc/mol
cp= cal/mol/k

no t-p data grid

0 species in reaction

* rard evaluation

* this is an estimated delgo and should be used with caution.

* assumed i=0.

```

tc++
  entered by= d.j. isherwood      date= 07/20/83
    source= see below            quality= speculative
    charge= 2.0                  titr. factor=
    ion type= 1                   ion size=
  hydr. no.=
  1 chemical elements=
    1.000 tc
      temp=      298.15 k          press=      1.013 bars
    delg0=      18.5 kcal/mol      delh0=      500.000 kcal/mol
      s0=        500. cal/mol/k    se=          cal/mol/k
      v0=          cc/mol
      cp=          cal/mol/k
    no t-p data grid
    0 species in reaction
* rard evaluation
* this is an estimated value based on latimer estimate (see rard,1983)
* of the tc++/tc(o) potential. i=0.0. tc++ exists in theory only.
* do not use.
+-----

```

stop.

reference

rard, j., 1983, critical review of the chemistry and thermodynamics of technetium and omse of its inorganic compounds and aqueous species, lawrence livermore national laboratory report ucrl-53440.

notation--

```

-- delg0 = gibbs energy of formation
-- delg0r = gibbs energy of reaction
-- delh0 = enthalpy of formation
-- delh0r = enthalpy of reaction
-- s0 = conventional entropy
-- se = internal electronic entropy
-- dels0r = entropy of reaction

```

note that "500." is entered to mean "no data" for delg0, delh0, s0, log k, delh0, and dels0r. never enter zero or leave blank for these parameters unless you mean to use an actual value of zero.

data for aqueous species=

```

name= an alphabetic or alphanumeric string
entered by= name of person who entered data or last revised it
date= data of entering or revising data
source= alphanumeric string identifying a major source of data. use
"see below" for minor sources

```

```

quality= alphanumeric string describing the probable error in gibbs energy
or its equivalent, based on subjective judgement and chosen from
among the following (in order of increasing value)

```

bad - demonstrably bad data- do not use except in illustrative calculations

poor - likely error exceeds a couple of kcal

restricted - ad hoc fit to a particular situation; see notes

speculative - species not shown conclusively to exist

uncertain - chosen rather arbitrarily from divergent reported values

unspecified - no quality information

(blank) - equivalent to unspecified

fair - likely error less than a couple of kcal

good - likely error less than about one kcal or four kj

the code must be modified to allow other quality parameter inputs. unrecognized inputs are set to "error". data for which the quality is "restricted", "speculative", or "uncertain" may numerically be "fair" to "good". the major uncertainty associated with these values is qualitative (i.e., uncertainty of interpretation). data for which the quality is "poor" may be quite sufficient for making "good" calculations- this depends on the sensitivity of the results to it in any particular application.

charge= electrical charge

titration factor= weighting factor for ph 4.5 (methyl orange)
alkalinity

ion type= criss-cobble ion type

0 neutral complex (may be left blank)

1 cation (may be left blank)

2 simple anion (may be left blank)

3 oxyanion

4 acid oxyanion

ion size= debye-huckel hydrated ion size (for activity coefficient estimation)

hydration number= number of bound water molecules not explicitly shown in the assumed molecular formula (for activity coefficient estimation)

temp= the base point temperature (k), usually 298.15 k

press= the base point pressure (bars), usually 1 bar

delg0= the apparent standard partial molal gibbs energy at the base point

delh0= the apparent standard partial molal enthalpy at the base point

s0= the conventional entropy at the base point

se= the internal electronic entropy; this function is zero except for some actinide and rare earth species (it is used in criss-cobble method temperature extrapolations)

v0= the partial molal volume at the base point; there is no current provision for using this input in the current mcrt (as of 12/16/82)

cp= the partial molal heat capacity at the base point; there is no current provision for using this input in the current mcrt (as of 12/16/82)

log k= log of the equilibrium constant of the given reaction at the base point

delh0r= enthalpy of the given reaction at the base point

delS0r= entropy of the given reaction at the base point

the following species have been identified by researchers, but are not included in the mdaqstc file as there is no thermodynamic data for them.

tcocl4-

tcocl5--

tcobr4-

tcobr5--

tcoi4-

tci6--

tco(so4)2--

hydrolysis products of tc+5 may exist

tc+3 and tc+4 phosphate and polyphosphate complexes

stop.

mdsoltc.3245u02 data for solids of technetium (see bottom of file)
last revised 01/26/84 by dji

*
* all thermodynamic data and evaluations are from rard, 1983
*

htco4(s)

entered by= d.j. isherwood date= 07/14/83
source= rard, 1983 quality= fair
3 chemical elements=
1.000 tc 4.000 o 1.000 h
temp= 298.15 k press= 1.013 bars
delg0= -141.0 kcal/mol delh0= -168.3 kcal/mol
s0= 30.2 cal/mol/k v0= cc/mol
1 heat capacity range(s) follow=
equation= cp or a= cal/mol/k
b= c=
d= e=
limit= 1000. k
no t-p grid data
0 species in reaction=
0.000 xx 0.000 xx 0.000 xx
log k= 500.000 delh0r= 500.000 kcal/mol
dels0r= 500.000 cal/mol/k

* rard evaluation
* the enthalpy data is experimental but the entropy is an estimate from
* ktco4(s) and additivity relations.

ktco4(s)

entered by= d.j. isherwood date= 07/14/83
source= rard, 1983 quality= fair
3 chemical elements=
1.000 tc 4.000 o 1.000 k
temp= 298.15 k press= 1.013 bars
delg0= -219.70 kcal/mol delh0= -244.3 kcal/mol
s0= 39.38 cal/mol/k v0= cc/mol
1 heat capacity range(s) follow=
equation= 0 cp or a= 17.84 cal/mol/k
b= 39.0 c= 0.0
d= e=
limit= 309. k
no t-p grid data
no reaction given

* rard evaluation
* these data are based on heat capacity measurements and should be
* reliable. delgo value is +/- 2.4 kcal/mol.

tc4o7(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= speculative

2 chemical elements=

4.000 tc 7.000 o

temp= 298.15 k

press= 1.013 bars

delg0= -316.4 kcal/mol

delh0= 500.0 kcal/mol

s0= 500.0 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation= 0

cp or a= cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* identification of tc4o7 as an existing solid species is not certain

* use with caution

tc3(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= speculative

2 chemical elements=

1.000 tc 3.000 o

temp= 298.15 k

press= 1.013 bars

delg0= -110. kcal/mol

delh0= -129.0 kcal/mol

s0= 17.3 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* these values are estimates of cobble, smith, and boyd, 1953 (see

* rard, 1983). delg0 value calculated to be consistent with s0 and delh0.

tc2o7(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

2 chemical elements=

2.000 tc 7.000 o

temp= 298.15 k

press= 1.013 bars

delg0= -223.6 kcal/mol

delh0= -267.8 kcal/mol

s0= 39.7 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* the enthalpy is an average of two values in good agreement.

* however the entropy is based on an estimate for htco4(s) and

* the entropy of decomposition.

tc2o7(g)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

2 chemical elements=

2.000 tc 7.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -212.4 kcal/mol

delh0=

-236.1 kcal/mol

s0= 107.5 cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* these data are based on tc2o7(s) and sublimation thermodynamics.

tc(oh)3(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

3 chemical elements=

1.000 tc 3.000 h

3.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -157.4 kcal/mol

delh0=

500.0 kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* the data is from cartledge, 1971 (see rard, 1983) this compound

* could well be tco(oh).h2o or tc2o3.3h2o.

tc3o4(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

2 chemical elements=

3.000 tc 4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -206.5 kcal/mol

delh0=

500. kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

tc(oh)(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

2 chemical elements=

1.000 tc

1.000 o

1.000 h

temp= 298.15 k

press=

1.013 bars

delg0= -56.1 kcal/mol

delh0=

500.0 kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

tc(oh)2(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

3 chemical elements=

1.000 tc

2.000 o

2.000 h

temp= 298.15 k

press=

1.013 bars

delg0= -110.2 kcal/mol

delh0=

500.0 kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

natco4(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= fair

3 chemical elements=

1.000 tc

1.000 na

4.000 o

temp= 298.15 k

press=

1.013 bars

delg0= -209.6 kcal/mol

delh0=

500.0 kcal/mol

s0= 500. cal/mol/k

v0=

cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* this value was calculated from ionic data and activity coefficient

* and solubility data.

tco2.2h2o(am)
 entered by= d.j. isherwood date= 07/14/83
 source= rard, 1983 quality= fair
 3 chemical elements=
 1.000 tc 4.000 h 4.000 o
 temp= 298.15 k press= 1.013 bars
 delg0= -199.9 kcal/mol delh0= 500.0 kcal/mol
 s0= 500. cal/mol/k v0= cc/mol
 1 heat capacity range(s) follow=
 equation= cp or a=
 b= c=
 d= e=
 limit= 1000. k
 no t-p grid data
 no reaction given
 * rard evaluation
 * tco2.2h2o(am) could well be tc(oh)4(am). this is based on two
 * experimental values in good agreement.

tc(c)
 entered by= d.j. isherwood date= 07/14/83
 source= rard, 1983 quality= fair
 1 chemical elements=
 1.000 tc
 temp= 298.15 k press= 1.013 bars
 delg0= 0.0 kcal/mol delh0= 0.0 kcal/mol
 s0= 8.0 cal/mol/k v0= cc/mol
 1 heat capacity range(s) follow=
 equation= 0 cp or a= 5.20 cal/mol/k
 b= 2.0 c=
 d= e=
 limit= 1000. k
 no t-p grid data
 no reaction given
 * rard evaluation
 * there are experimental heat capacities from 3 to 15 k only.
 * the values above are estimates from fitting the experimental
 * values to 1000 deg °k.
 * the melting point is 2440 +/- 30 k. the enthalpy of vaporization
 * is 155.4 +/- 3.1 kcal/g-atom.

tcs2(s)
 entered by= d.j. isherwood date= 07/14/83
 source= rard, 1983 quality= poor
 2 chemical elements=
 1.000 tc 2.000 s
 temp= 298.15 k press= 1.013 bars
 delg0= -51.63 kcal/mol delh0= -53.5 kcal/mol
 s0= 17. cal/mol/k v0= cc/mol
 1 heat capacity range(s) follow=
 equation= cp or a= cal/mol/k
 b= c=
 d= e=
 limit= 1000. k
 no t-p grid data
 no reaction given
 * rard evaluation
 * delg0 calculated from delh0 and dels0 using values from mills, 1974
 * (see rard, 1983). delh0=-53.5 +/- 5, s0=17 +/- 3.

tcs3(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= poor

2 chemical elements=

1.000 tc 3.000 s

temp= 298.15 k

press= 1.013 bars

delg0= -62.9 kcal/mol

delh0= -66.0 kcal/mol

s0= 20.1 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* delg0 calculated from delh0 and dels0 using values from mills, 1974

* (see rard, 1983). delh0=-66.0 +/- 5, s0=20.1 +/- 3.

tc2s7(s)

entered by= d.j. isherwood

date= 07/14/83

source= rard, 1983

quality= poor

2 chemical elements=

2.000 tc 7.000 s

temp= 298.15 k

press= 1.013 bars

delg0= -138.90 kcal/mol

delh0= -147.0 kcal/mol

s0= 42.1 cal/mol/k

v0= cc/mol

1 heat capacity range(s) follow=

equation=

cp or a=

cal/mol/k

b=

c=

d=

e=

limit= 1000. k

no t-p grid data

no reaction given

* rard evaluation

* delg0 calculated from delh0 and dels0 using values from mills, 1974

* (see rard, 1983). delh0=-138.9 +/-14, s0=42 +/-6.

stop.

references

rard, j. 1983. chemistry and thermodynamics of technetium and some of its inorganic and aqueous species. lawrence livermore national laboratory, ucr1-53440.

notation--

- delg0 = gibbs energy of formation
- delg0r = gibbs energy of reaction
- delh0 = enthalpy of formation
- delh0r = enthalpy of reaction
- s0 = conventional entropy
- dels0r = entropy of reaction

note that "500." is entered to mean "no data" for delg0, delh0, s0, delhtr, delstr, log k, delh0, and dels0r. never enter zero for these parameters or leave them blank unless you mean to use an actual value of zero. 1000 k is the default for the "limit" parameter.

data for solid/gas species=

name= an alphabetic or alphanumeric string; e.g., calcite, bischofite.

the formula may also be used as the name.

formula= an alphanumeric string denoting the formula of the species;

e.g., caco3, mgcl2.6h2o.

entered by= name of person who entered data or last revised it

date= data of entering or revising data

source= alphanumeric string identifying a major source of data. use

"see below" for minor sources

quality= alphanumeric string describing the probable error in gibbs energy or its equivalent, based on subjective judgement and chosen from among the following (in order of increasing value)

bad - demonstrably bad data- do not use except in illustrative calculations

poor - likely error exceeds a couple of kcal or several kj

restricted - ad hoc fit to a particular situation; see notes

speculative - species not shown conclusively to exist

uncertain - chosen rather arbitrarily from divergent reported values

unspecified - no quality information

(blank) - equivalent to unspecified

fair - likely error less than a couple of kcal or a few kj

good - likely error less than about one kcal or four kj

the code must be modified to allow other quality parameter inputs.

unrecognized inputs are set to "error". data for which the quality

is "restricted", "speculative", or "uncertain" may numerically be

"fair" to "good". the major uncertainty associated with these values

is qualitative (i.e., uncertainty of interpretation). data for which

the quality is "poor" may be quite sufficient for making "good"

calculations- this depends on the sensitivity of the results to it in any particular application.

number of chemical elements per mole

number of moles of element per mole of substance

symbol of chemical element

temp= the base point temperature (k), usually 298.15 k

press= the base point pressure (bars), usually 1 bar

delg0= the apparent standard partial molal gibbs energy at the
 base point
 delh0= the apparent standard partial molal enthalpy at the base point
 s0= the conventional entropy at the base point
 v0= the molar volume at the base point
 number of heat capacity ranges that follow
 equation= heat capacity equation code
 0- $cp = a + 1.e-3*b*t + 1.e+5*c*t**(-2) + 1.e-6*d*t**2$
 1- $cp = a + 1.e-3*b*t + 1.e+5*c*t**(-2) + 1.e+8*d*t**(-3)$
 cp= the molar heat capacity, assumed to be a constant
 a= first heat capacity coefficient
 b= second heat capacity coefficient
 c= third heat capacity coefficient
 d= fourth heat capacity coefficient
 e= fifth heat capacity coefficient
 limit= upper limit (k) of the preceding set of heat capacity parameters;
 no t-p data grid
 this is either the upper limit of use based on the range of measurement
 or the temperature of a phase transition
 delhtr= enthalpy of a phase transition, if any
 delstr= entropy of a phase transition, if any
 t-p data grid indication line, followed by t-p data grid, if any
 temp, press, delg0, delh0, s0, v0
 number of species appearing in a reaction, if a reaction follows
 number of moles of a species appearing in the reaction
 the name of the corresponding species
 log k= log of the equilibrium constant of the given reaction at the
 base point
 delh0r= enthalpy of the given reaction at the base point
 dels0r= entropy of the given reaction at the base point

the following solid and gas technetium compounds are not included
 in the mdsoltc file because there is insufficient thermodynamic
 data. at this time only entropies have been measured (see rard,1983).

tcf6(c)
 tcf6(g)
 tco3cl(g)
 k2tccl6(c)

stop.

run by= d.j. isherwood

date= 02/02/84

0 0 0 0 0 0 0 0

aqueous species of technetium

tco4-	1	
1.00000 tco4-		
tco4--	5	
-1.00000 tco4--		-0.25000 o2(g)
-1.00000 h+		1.00000 tco4-
0.50000 h2o		
tco4---	5	
-1.00000 tco4---		-2.00000 h+
1.00000 tco4-		1.00000 h2o
-0.50000 o2(g)		
tco++	5	
-1.00000 tco++		3.00000 h+
-0.75000 o2(g)		1.00000 tco4-
-1.50000 h2o		
tc+++	5	
-1.00000 tc+++		1.00000 tco4-
-2.00000 h2o		-1.00000 o2(g)
4.00000 h+		
[tco(oh)2]2	4	
-1.00000 [tco(oh)2]2		-4.00000 h+
2.00000 tco++		4.00000 h2o
tco(oh)2	4	
-1.00000 tco(oh)2		-2.00000 h+
1.00000 tco++		2.00000 h2o
tco(oh)+	4	
-1.00000 tco(oh)+		1.00000 tco++
-1.00000 h+		1.00000 h2o

solids of technetium

tc(c)	5	
-1.00000 tc(c)		1.00000 h+
-1.75000 o2(g)		1.00000 tco4-
-0.50000 h2o		
ktco4(s)	3	
-1.00000 ktco4(s)		1.00000 k+
1.00000 tco4-		
htco4(s)	3	
-1.00000 htco4(s)		1.00000 h+
1.00000 tco4-		
tc2o7(s)	4	
-1.00000 tc2o7(s)		2.00000 tco4-
-1.00000 h2o		2.00000 h+
tc(oh)3(s)	4	
-1.00000 tc(oh)3(s)		1.00000 tc+++
3.00000 h2o		-3.00000 h+
tc3o4(s)	5	
-1.00000 tc3o4(s)		3.00000 tc+++
-9.00000 h+		-0.25000 o2(g)
4.50000 h2o		

tco3(s)	4	
-1.00000 tco3(s)		1.00000 tco4--
-1.00000 h2o		2.00000 h+
tc4o7(s)	5	
-1.00000 tc4o7(s)		2.00000 tco++
-10.00000 h+		2.00000 tco+++
5.00000 h2o		
natco4(s)	3	
-1.00000 natco4(s)		1.00000 na+
1.00000 tco4-		
tc(oh)2(s)	5	
-1.00000 tc(oh)2(s)		1.00000 tco+++
-3.00000 h+		2.50000 h2o
-0.25000 o2(g)		
tc(oh)(s)	5	
-1.00000 tc(oh)(s)		-2.00000 h+
-0.50000 o2(g)		1.00000 tco++
1.00000 h2o		
tc2s7(s)	5	
-1.00000 tc2s7(s)		-8.00000 h2o
9.00000 h+		2.00000 tco4-
7.00000 hs-		
tcs2(s)	4	
-1.00000 tcs2(s)		-1.00000 h2o
1.00000 tco++		2.00000 hs-
tcs5(s)	5	
-1.00000 tcs3(s)		1.00000 tco4--
3.00000 hs-		-4.00000 h2o
5.00000 h+		
tco2.2h2o(am)	4	
-1.00000 tco2.2h2o(am)		-2.00000 h+
1.00000 tco++		3.00000 h2o

stop.

the following species are not included in data0

htco4-	3	
-1.00000 htco4-		1.00000 tco4--
1.00000 h+		
h2tco4	3	
-1.00000 h2tco4		1.00000 tco4--
2.00000 h+		

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