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Thermodynamic Properties of Tc(IV) Oxides: Solubilities and the Electrode Potential of the Tc(VII)/Tc(IV)-Oxide Couple

R. E. Meyer
W. D. Arnold
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July 1987	The Solubility of Electrodeposited Tc(IV) Oxides, NUREG/CR-4865

ABSTRACT

Solubilities of precipitated Tc(IV) oxides have been determined in solutions of NaCl in the pH range 7 to 9. Technetium oxide was prepared by precipitation upon purified sand with a 30% excess of hydrazine. The oxide-covered sand was then transferred to a small column, and solutions of NaCl varying in concentration from 0.1 mol/L to 2.6 mol/L were continuously cycled through the column. The concentrations of total technetium and Tc(IV) species in the solutions were periodically determined by separating the oxidized and reduced technetium species with a solvent extraction procedure and counting the beta activity of the ^{99}Tc with a liquid scintillation counter. The concentrations of Tc(IV) species in equilibrium with the oxide were approximately constant in the NaCl concentration range 0.1 mol/L to 2.6 mol/L and averaged $(2.61 \pm 1.00) \times 10^{-9}$ mol/L. These Tc(IV) solubilities are very close to those measured for technetium oxide electrodeposited from basic solution, which averaged $(2.56 \pm 0.54) \times 10^{-9}$ mol/L (Meyer et al. 1987). A solubility product of $(1.63 \pm 0.62) \times 10^{-33}$ was calculated from the measured solubilities of Tc(IV) oxide. These data can be used to estimate Tc(IV) solubilities for cases where solubility limits transport of technetium in reducing environments of high-level waste repositories.

Because there is some disagreement among values of E^o for the Tc(VII) - Tc(IV) redox couple in the literature, a redetermination of the standard potential was completed. The slopes of the graphs of electrode potential vs pH and concentration were confirmed, and the value of E^o was determined to be 0.747 ± 0.004 V. Within the limits of error, this agrees most closely with the value $E^o = 0.741 \pm 0.004$ V reported by Cartledge and Smith (1955).

CONTENTS

	Page
ABSTRACT	iii
LIST OF FIGURES AND TABLES	vii
1. EXECUTIVE SUMMARY	1
2. INTRODUCTION	3
3. BACKGROUND	4
3.1 HYDROLYSIS REACTIONS	4
3.2 SOLUBILITY	5
3.3 ELECTRODE POTENTIALS	6
4. EXPERIMENTAL	8
4.1 INTRODUCTION TO EXPERIMENTATION	8
4.2 PROCEDURES	8
4.2.1 Maintenance of Anoxic Conditions	8
4.2.2 Valence State Determination	8
4.2.3 Determination of Solubilities	9
4.2.4 Estimates of Errors in Solubilities	9
4.2.5 Electrode Potential Measurements	11
4.3 RESULTS	12
4.3.1 Solubilities	12
4.3.2 Electrode Potentials	15
5. DISCUSSION	19
6. CONCLUSIONS	22
7. REFERENCES	23

LIST OF FIGURES

Figure — Page

1. Solubility of technetium under anoxic conditions as a function of NaCl concentration 14

2. Potential vs log $[TcO_4^-]$ 18

3. Potential vs pH 18

4. Calculated solubility of $TcO_2 \cdot nH_2O$ and concentrations of aqueous species in equilibrium with the amorphous solid as a function of pH, for Ksp = 1.63×10^{-33}. The open circles represent the seven values of the solubility listed in Table 1 20

LIST OF TABLES

Table — Page

1. Solubilities of $TcO_2 \cdot nH_2O$ in NaCl solutiions 13

2. Solubilities of $TcO_2 \cdot nH_2O$ electrodeposited from basic solutions 13

3. Effect of concentration on potential 15

4. Effect of concentration on potential 15

5. Effect of concentration on potential 16

6. Effect of pH on potential 16

7. Effect of pH on potential 16

THERMODYNAMIC PROPERTIES OF Tc(IV) OXIDES: SOLUBILITIES AND THE ELECTRODE POTENTIAL OF THE Tc(VII)/Tc(IV)-OXIDE COUPLE

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1. EXECUTIVE SUMMARY

The fission product ^{99}Tc is expected to occur in oxidizing environments as the anion TcO_4^- and in reducing environments as Tc(IV) oxide ($TcO_2 \cdot nH_2O$) plus the aqueous species in equilibrium with the oxide. The transport of technetium in reducing geologic environments may be limited to acceptable levels by the solubility of $TcO_2 \cdot nH_2O$ if it is low enough. Studies of the solubility of the oxide have been reported in solutions of low ionic strength (Meyer et al. 1986, 1987). To determine the solubility in solutions of higher ionic strength, solubility measurements were made in 0.1- to 2.6-mol/L sodium chloride solutions in the pH range 7 to 9.

Technetium oxide was prepared by precipitation upon purified sand with a 30% excess of hydrazine. The oxide-covered sand was then transferred to a small column in a controlled atmosphere box containing argon with <1 ppm oxygen, and NaCl solutions were continuously cycled through the column. The concentrations of total technetium and Tc(IV) species in the solution were periodically determined by separating the oxidized and reduced technetium species using a solvent extraction procedure and counting the beta particles of ^{99}Tc with a liquid scintillation counter. The concentrations of Tc(IV) species in equilibrium with the oxide were approximately constant in the NaCl concentration range 0.1 mol/L to 2.6 mol/L and averaged $(2.61 \pm 1.00) \times 10^{-9}$ mol/L. These Tc(IV) solubilities are very close to those measured for technetium oxide electrodeposited from basic solution, which averaged $(2.56 \pm 0.54) \times 10^{-9}$ mol/L (Meyer et al. 1987). A solubility product of $(1.63 \pm 0.62) \times 10^{-33}$ was calculated from the measured solubilities of Tc(IV) oxide. These data can be used to estimate solubilities for cases where solubility limits transport of technetium in reducing environments of high-level waste repositories.

The total concentration of technetium in the tested solutions include Tc(IV) species, which are in equilibrium with the oxide, and TcO_4^-. The concentration of TcO_4^- in contact with the oxide is dependent on the redox conditions in the system. Because no method was used to establish a redox potential in these experiments, the concentrations of TcO_4^- in the solutions varied considerably.

Because there is some disagreement among values of E^o for the Tc(VII) - Tc(IV) redox couple in the literature, a redetermination of the standard

potential was completed using electrodeposited technetium oxide. The slopes of the graphs of electrode potential vs pH and concentration were measured to be 0.0773 ± 0.0023 V/(pH unit) and 0.0211 ± 0.0050 V/(log [TcO_4^-] unit). These values agree with the theoretical values of 0.0788 V/(pH unit) and 0.0197 V/(log [TcO_4^-] unit) within the standard deviations of our measurements. The value of E^o was determined to be 0.747 ± 0.004 V. Within the limits of error, this agrees with the value E^o = 0.741 ± 0.004 V (Cartledge and Smith 1955). (Cartledge and Smith reported their value as 0.738 V using a value 0.242 V for the saturated calomel electrode (SCE). We have used the value of 0.244_5 V (Hills and Janz 1961), and we have converted Cartledge and Smith's value using this value for the SCE.)

2. INTRODUCTION

The nuclide ^{99}Tc, $t_{1/2}$ = 213,000 years, is present in large quantities in nuclear waste, and properties related to its migration in geological environments are therefore of considerable interest. Under oxidizing conditions, technetium is expected to exist in the oxidation state (VII) as the anion TcO_4^-. Technetium released into the groundwater surrounding a geologic high-level waste repository in the form of TcO_4^- is not expected to be sorbed significantly on the minerals and rocks present because of its negative charge. A number of studies have confirmed that little or no sorption occurs under oxic conditions (Salter et al. 1981, Barney 1982, Barney 1983, Palmer and Meyer 1981). However, if the technetium is reduced to a lower valence state, then it is possible that species may be formed that either are more highly sorbed or are insoluble enough to limit the maximum concentration of technetium in the groundwaters surrounding the repository. This solubility-limited concentration enters into the calculation of the release rate of technetium to the environment if the repository should be breached by groundwater. Other factors entering into this calculation are groundwater flow rate, length and nature of the path to the accessible environment, and possible dilution of the technetium-containing groundwater by non-contaminated groundwater. It is evident that the nature and solubility of reduced species of technetium compounds need to be known for the calculation of technetium releases from a repository in a reducing geological environment.

Based upon current knowledge of technetium chemistry, it is generally predicted that some form of Tc(IV) oxide will be formed if reducing conditions exist in a repository geological environment. However, technetium has an unusually complicated redox chemistry, and much is unknown about the chemistry of lower valence states. In particular, little is known about the solubilities of Tc(IV) oxides. Previously (Meyer et al. 1986, Meyer et al. 1987), we have reported solubilities of Tc(IV) oxides in pure solutions of NaCl and HCl and in synthetic groundwater formulations. These studies have been extended to higher concentrations of NaCl in this report. In addition, we have redetermined the standard electrode potential of the Tc(IV)-Tc(VII) couple because of disagreement in the literature among various investigators.

3. BACKGROUND

Because the chemistry of the oxy-compounds of technetium is extremely important to the safety analysis of technetium migration, a number of reviews have been written recently which deal with the chemistry and thermodynamics of technetium. A comprehensive review has been given by Rard (1982). This is probably the most complete review to date, and it has 240 references to technetium chemistry. In this work, judgments are given as to the reliability of the reported data. Another recent review, which is less comprehensive but presents the pertinent chemistry relative to nuclear waste disposal, is that of Paquette et al. (1980). A critical review of the data on electrode potentials, solubilities, and hydrolysis of Tc(IV) species is given in Meyer et al. (1986).

To calculate solubilities, the solubility product needs to be known in addition to equilibrium data for all species such as hydrolytic products in equilibrium with the solid. The thermodynamic data pertinent to calculation of solubilities are briefly summarized below.

3.1 HYDROLYSIS REACTIONS

Gorski and Koch (1969) have reported electromobility measurements from which they calculated equilibrium quotients for hydrolysis reactions which they write as follows:

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+ \qquad Q_{h1} = (4.3 \pm 0.4) \times 10^{-2} \qquad (3.1)$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2 + H^+ \qquad Q_{h2} = (3.7 \pm 4.0) \times 10^{-3} \qquad (3.2)$$

Their experiments were done by measuring the ionic mobility of Tc(IV) in columns composed of sea sand using solutions of pH 1 to 2.5 at an ionic strength of 0.1. Their data showed sharp decreases in mobility at about pH 1.3 and 2.2. At pH values above about 2.3, the mobility was approximately zero, which indicated an uncharged species. The height of the first step (pH 1 to 1.3) of the mobility vs pH curve was twice that of the second step (pH 1.3 to 2.2). This was taken as evidence of the migration of a doubly charged species in the first step and a singly charged species in the second step. The concentration of the technetium was not given. However, because ^{99}Tc was used as the tracer, it could have been in the range of 10^{-7} to 10^{-5} mol/L. The starting material in this study is reported to be technetium dioxide hydrate ($TcO_2 \cdot H_2O$) which was prepared by reduction of NH_4TcO_4 with hydrazine in a solution of perchloric acid. The hydrated dioxide was prepared immediately before each individual experiment because it is easily oxidized. If any significant fraction of the oxide had been oxidized to TcO_4^-, then reverse migration would have been observed in the column because of the negative charge of the TcO_4^- ion.

Since the hydrolysis studies of Gorski and Koch were reported, two

reports of unsuccessful attempts to repeat it have appeared (Sundrehagen 1979, Noll et al. 1975). A critical discussion of these experiments was given in Meyer et al. (1986). It appears that an important factor in these experiments is the initial concentration of technetium. If the concentration is too high, polymeric and/or colloidal forms of technetium may be present.

Support for Gorski and Koch's results comes from the work of Owunwanne et al. (1977), who worked with carrier-free ^{99m}Tc at low concentrations (10^{-7} to 10^{-9} mol/L). Using standard ion exchange techniques, they determined a charge of plus two for the Tc(IV) species at pH values <2. Owunwanne et al. suggest, on the basis of correlations with the formal charge of the metal and the pH, that the species in their experiment was actually $Tc(OH)_2^{2+}$ or possibly a mixture of $Tc(OH)_2^{2+}$ and TcO^{2+}.

Sundrehagen (1979) reports hydrolysis quotients from spectrophotometric measurements in the ultraviolet spectrum region for the reaction given in Eq. 3.2 and a quotient for a dimerization reaction (Eq. 3.3) postulated to account for the observation that their plot of molar absorbance with concentration was not constant.

$$2TcO(OH)_2 = [TcO(OH)_2]_2 \qquad (3.3)$$

The values for the quotients are $Q_{h2} = (9.3 \pm 2.0) \times 10^{-3}$, and $Q_{dim} = (3.14 \pm 0.28) \times 10^{6}$. These values were obtained by a computer program which fitted a plot of molar absorbance as a function of concentration of Tc(IV). The data were collected at 210 nm, a region in the ultraviolet spectrum where it is quite difficult to obtain reliable data. The dimerization reaction, Eq. 3.3, is postulated to account for the observation that the molar absorbance was constant above about 10^{-5} mol/L Tc(IV) but increased rapidly below this concentration. If the assumption is valid that the dimerization reaction occurs, then the change of molar absorbance with concentration implies that above this concentration (10^{-5} mol/L), dimerization is essentially complete, but below this concentration, the monomer is formed. In addition, it was assumed that a singly charge species hydrolyzed (as in Eq. 3.2) to form the monomer. The quotients from this study were obtained from the data-fitting routine assuming that the two reactions, Eqs. 3.2 and 3.3, occur. These experiments were done in 0.028-mol/L $HClO_4$ with added $NaClO_4$, and 0.05-mol/L $HClO_4$ with enough $NaClO_4$ to maintain the same ionic strength. The computer program did not produce a better fit when the first hydrolysis reaction (Eq. 3.1) was included. We have not seen any other spectroscopic study of this type or any confirmation of the spectrum at these wavelengths.

3.2 SOLUBILITY

On the basis of a single determination of solubility by Lefort (1963) and the data reported by Gorski and Koch (1969) and by Sundrehagen (1979), Rard (1983) calculated the solubility product for $TcO_2 \cdot H_2O$ Ksp $= 3.55 \times 10^{-34}$, or $\log_{10}$ Ksp $= -33.45 \pm 1.0$ at infinite dilution.

Meyer et al. (1986, 1987) have reported solubility measurements of electrodeposited and precipitated Tc(IV) oxides. Oxides were deposited both from acidic and basic solutions onto a platinum gauze electrode using a procedure similar to that used by Cartledge and Smith (1955) for electrode potential measurements. The precipitated oxides were formed by reduction with hydrazine onto washed sea sand; the resulting product was placed into a column, and solution was recirculated through the column until the concentrations in solution stabilized. The technetium in solution was composed of Tc(VII) in the form of TcO_4^- and reduced technetium, which was assumed to be Tc(IV). The TcO_4^- was removed by a solvent extraction technique, and the reduced technetium was left in solution. Concentrations of total and reduced technetium were determined by liquid scintillation counting of the separated solutions. There was always a small and variable amount of TcO_4^- in the solution, possibly formed by oxidation by radiolytic products or residual oxygen. The solubilities in basic solutions depended upon the method of preparation and the history of the oxide. In general, the results could be correlated with calculations from the hydrolysis quotients of Gorski and Koch (1969) and solubility products in the range 10^{-32} to 10^{-33} according to the equations given by Rard (1982). The assumed values for the solubility products are close to the estimate, $\log_{10} Ksp = -33.45 \pm 1.0$ given by Rard (1982). Although the precision of the experiments may not be sufficient to make a distinction of 1.0 in the $\log_{10}$ of the solubility product, there does appear to be a consistent difference between the oxides formed by electrodeposition and those formed by precipitation.

3.3 ELECTRODE POTENTIALS

A number of measurements have been reported in the literature for the standard potential of the Tc(IV)-Tc(VII) couple, which for acid solutions is represented by Eq. 3.4.

$$TcO_2 + 2H_2O = TcO_4^- + 4H^+ + 3e^- \qquad (3.4)$$

The usual value quoted in the literature for the standard potential, $E^o = 0.738$ V, is that of Cartledge and Smith (1955). The procedure used to form the oxide was to electrodeposit a "brown adherent deposit" of what was assumed to be TcO_2 from a solution of potassium pertechnetate acidified with sulfuric acid. No further description is given of the solution from which the technetium was deposited. No analysis of the brown deposit is given in this reference. A total of eight measurements were made in mixed solutions of sulfuric acid and potassium pertechnetate. However, seven of the eight solutions were in the pH range 2.49 to 3.10. The only other measurement, taken at pH 6.65, was reported as slowly becoming more positive, and so may not have represented a stable potential. Of the seven measurements between pH 2.49 and 3.10, there was a spread in values from 0.733 to 0.743 V. The average of the measurements was reported to be 0.738 ± 0.003 V (using 0.242 V for the potential of the saturated calomel reference electrode). The concentration range of the $KTcO_4$ used was 1.00×10^{-3} to 1.82 x

10^{-3} mol/L in these solutions. Thus, limited ranges of pH and concentration were investigated, and the ranges were not large enough to determine accurately the slopes of the plots of the potential vs concentration of TcO_4^- and the potential vs pH.

An earlier measurement by Cobble et al. (1952) gives the result E^o = 0.782 ± 0.011 V. Cartledge and Smith suggested that this result was higher than their value of 0.738 V because the presence of oxygen in the cell used by Cobble et al. tended to polarize the electrode in the positive direction. Although this is a possible explanation, there is also the possibility that the oxides were prepared differently, and differences in composition and/or structure accounted for the difference. A well-defined thermodynamic potential can be obtained only from a well-defined solid and solution, and the methods used to prepare the oxides may differ sufficiently to cause these differences in the standard potential. Spitsyn et al. (1964) calculated a value of 0.71 V from electrodeposition experiments, and the most recent investigation (Liebscher and Münze 1975) gives directly measured values as a function of pH as follows:

pH	1.05	1.85	2.90	3.85	4.50
E^o (V)	0.769	0.766	0.769	0.745	0.728

At the higher pH values, the potential seems to be dropping somewhat, perhaps due to a change in composition or structure of the solid which here is reported to be hydrated $TcO_2 \cdot H_2O$. This work seems to be carefully done with proper consideration to corrections from activity coefficients and junction potentials. The value of 0.769 V at pH 1.05 is closer to the value given by Cobble et al. (0.782 V) than the value 0.738 V.

As pointed out by Isherwood (1985), the potential for the Tc(IV) - Tc(VII) couple (Eq. 3.4) probably refers to a hydrated oxide rather than the anhydrous oxide, TcO_2. In a later publication, Cartledge (1971) refers to oxide electrodeposited by the method used in his 1955 determinations as the hydrated form, $TcO_2 \cdot 2H_2O$ or possibly $Tc(OH)_4$. Thus, thermodynamic calculations based on the 0.738 V potential should probably refer to the hydrated form of Tc(IV) oxide. Some of the differences observed in the standard potential reported in the literature may therefore be due to differences in hydration. Experiments to determine the stoichiometry of electrodeposited oxides indicated that they had the composition $TcO_2 \cdot nH_2O$, where n is equal to 1.63 ± 0.28 (Meyer et al. 1986).

4. EXPERIMENTAL

4.1 INTRODUCTION TO EXPERIMENTATION

Determination of the concentration of technetium in equilibrium with Tc(IV) oxides is a difficult experiment at high pH levels because the concentration levels are low. Furthermore, Tc(IV) is easily oxidized, and experiments must be protected from oxygen and other possible oxidizing agents. A good method for determination of these low concentration levels is liquid scintillation counting of the beta particles emitted by ^{99}Tc.

To lend more confidence to the data, several methods of preparing Tc(IV) oxides were used by Meyer et al. (1986). In the first of these, Tc(IV) oxide was formed by precipitation with hydrazine from a solution containing TcO_4^-. This is a procedure reported in the literature to produce $TcO_2 \cdot nH_2O$ (Gorski and Koch 1969, Sundrehagen 1979). When Tc(IV) oxide is precipitated from solution, it is generally believed that a hydrated form of the oxide is produced. The second procedure was electrodeposition of Tc(IV) oxide from a solution of TcO_4^- (Cartledge and Smith 1955). With the third procedure, Tc(IV) oxide was precipitated with hydrazine onto sand that had been carefully purified, and a column of the resulting material was placed in a closed system in which the solution was continuously recirculated through the column. For each experiment, the concentration of Tc in solution was monitored as a function of time. The solution was centrifuged, the centrifugate was treated by solvent extraction, and the ^{99}Tc in the separated phases was counted to determine the concentrations of total and reduced technetium. Each individual experiment was continued until measured concentration levels were constant within experimental error. In the work reported here, we have emphasized the use of oxide precipitated onto purified sand.

4.2 PROCEDURES

4.2.1 Maintenance of Anoxic Conditions

Because Tc(IV) is so easily oxidized, all operations were carried out in a controlled atmosphere box filled with high purity argon. The oxygen level in the argon was constantly monitored and was maintained at < 1 ppm. Sampling, centrifugation, and solvent extraction were carried out within the box. Exposure to air occurred only when the final samples were removed for counting.

4.2.2 Valence State Determination

The valence state of the species in equilibrium with Tc(IV) oxides must be determined for an accurate measure of the true solubility of the oxide. The procedure followed is one that we have used previously (Meyer et al. 1986) to determine the valence state of technetium sorbed

on various minerals. The procedure consists of solvent extraction of the solution with 0.05-mol/L tetraphenyl arsonium chloride dissolved in chloroform. The organic phase removes the TcO_4^- very efficiently, leaving reduced species in the solution. If the ratio of Tc(VII) to Tc(IV) is very high, two extractions are done to insure that all of the Tc(VII) is removed before determining the concentration of Tc(IV) in the aqueous solution.

4.2.3 Determination of Solubilities

Technetium oxide was precipitated onto purified sand with a 30% excess of hydrazine. The precipitate was transferred to a 0.3-cm diameter column and washed thoroughly with dilute NaCl solution to remove the excess hydrazine. The solubility measurements were made with NaCl solutions that had been conditioned electrolytically to remove traces of oxygen. For the solubility measurements, the solution of interest was pumped upflow through the bed of technetium oxide-sand at a flow rate of 0.20 mL/min and recycled to the reservoir. At intervals of two to three days, triplicate samples of the reservoir solution were centrifuged and analyzed for total and reduced technetium by use of the solvent extraction procedure and liquid scintillation counting of aliquots from the separated phases. Most of the tests included seven or eight sample sets, taken over a period of about three weeks. For subsequent tests with the same column, as much of the solution as practical was pumped from the column and lines, and then the system was flushed with the new solution of interest by pumping solution upflow through the column from a clean reservoir and discarding the effluent. The solubility measurement with the new solution was then carried out by recycling and analyzing the solution as described above.

In a typical run, three 0.8-mL samples were removed three times a week immediately after the pH was monitored. Each sample was centrifuged at 12,000 rcf for 15 minutes. A 0.2-mL portion from each sample was saved as a head solution, and a 0.5-mL portion was treated by the solvent extraction process described above to distinguish between Tc(VII) and lower valence states, which we assume to be Tc(IV). The concentrations of ^{99}Tc were determined in the 0.2-mL head solution and in aliquots of the aqueous and organic phases from the valence state determination. A material balance was calculated by comparing the total amount of technetium present as calculated from the head solution with the sum of the technetium from the organic and aqueous phases from the solvent extraction procedure. If the material balance was satisfactory, the concentrations of Tc(VII) and Tc(IV) in the original reservoir were calculated for each of the three samples, and the results were averaged. The experiment was continued until the concentrations stabilized.

4.2.4. Estimation of Errors in Solubilities

The experimental errors associated with the values for the solubilities of total and reduced technetium were estimated by a computer program which analyzed all of the data from each solubility experiment carried out by the procedures described in Section 4.2.3. Each solubility value

was obtained by computing the arithmetic mean, or first moment, of the last five values determined:

$$AVG = (1/n)*Summation(x_i), \tag{4.1}$$

where AVG represents the arithmetic mean, x_i is the i th measured value, and n is the number of determinations (5 in the present case). The standard deviation s of x about the value AVG was computed by the n-method, sometimes called the "biased" method:

$$s = [(1/n)*Summation(x_i - AVG)^2]^{1/2}. \tag{4.2}$$

For small numbers of determinations, statisticians generally prefer the n - 1 method, also called the "unbiased" method, which substitutes n - 1 for n in Eq. 4.2. Use of the n - 1 method in calculating the standard deviations for the solubilities would increase the values of s by a factor of $(5/4)^{1/2} = 1.118$, or about 12%.

It was recognized at the outset that a determination of the solubility of reduced technetium would be very difficult because the sample counting rates due to the ^{99}Tc beta particles would be relatively close to the background counting rate of the liquid scintillation counter. Thus, the design of experiments to measure technetium solubility required great care, with particular emphasis on replicate measurements of backgrounds, ^{99}Tc standards, and samples. Counting times were 120 minutes, which was estimated to yield reasonable statistical accuracy for the samples of low counting rate, but short enough to be practical when as many as 39 samples needed to be counted for one experiment over a period of 3.25 days.

Although the standard deviations did not seem to be unreasonably large, especially considering the very low concentrations of reduced technetium measured, the role of nuclear counting statistics in the overall experimental error was a matter of some concern. If errors due to counting statistics were found to contribute greatly to the overall errors in the experiments, then it was felt that it might be necessary to make appropriate changes in our procedures to improve precision. To investigate this issue, a complete analysis of the errors due to counting statistics was carried out for a measurement of technetium solubility, taking into account the certified error of $\leq$ 1.2% in the Amersham technetium standard solution, together with statistical counting errors in the background, standard, and sample counts. The method was rather lengthy, and made use of standard formulae for calculation and propagation of statistical errors in radioactivity determinations (e.g., Friedlander et al. 1981; NCRP 1978). A few of the considerations used will be discussed below.

If a large number of radioactive atoms are observed for a time short with respect to their half lives, then repeated counts for equal intervals of time follow a Poisson distribution. Then, for a reasonably large number of counts N, measured in a time t, at a counting rate R = N/t, the following relationships are obtained:

$$\text{standard deviation in the number of counts} = s = N^{1/2} \quad (4.3)$$

$$\text{standard deviation in the counting rate} = s_R = N^{1/2}/t \quad (4.4)$$

$$N^{1/2}/t = (Rt)^{1/2}/t = (R/t)^{1/2}. \quad (4.5)$$

Once values of s have been determined for a series of counting measurements, then counting or other errors can be combined by using standard formulae for error propagation, as described in NCRP (1978) or in works on statistics. For example, if we consider two numbers and their uncertainties (standard deviations), $A \pm s_a$, $B \pm s_b$, the standard deviation in the result of either addition or subtraction, $A \pm B$, is

$$s = (s_a^2 + s_b^2)^{1/2}. \quad (4.6)$$

An example of a useful application of this equation is in computing the error in the net counting rate of a sample R_s when the background counting rate R_B is subtracted from the gross counting rate measured for the sample plus the background R_G: $R_s = R_G - R_B$.

The propagation of errors in other functions, such as multiplication, division, or raising an expression to a power, are more complicated but are readily calculated.

In the case for which a detailed analysis was made, the standard deviation calculated in a manner similar to those given below in Table 1 was 7.05% for the solubility of total technetium, while the overall standard deviation due to counting statistics alone was only 0.58%. The standard deviation in the solubility of reduced technetium was 11.1%, but for counting errors alone was 2.30%. Thus, it appears that counting errors can account only for a small part of the errors in measuring technetium solubility. Although counting errors can be estimated with considerable accuracy, the magnitude of other types of errors, such as incomplete extraction, errors associated with pipetting the small volumes used, and variations in experimental conditions from one determination to another, are more difficult to estimate.

4.2.5 Electrode Potential Measurements

For the studies of the electrode potential, technetium oxide was electrodeposited onto a platinum mesh electrode. The platinum mesh electrode was placed in a Princeton Applied Research (PAR) electrolytic cell which contained 100 mL of a 0.005-mol/L solution of technetium at pH 2. The electrode has a cross-sectional area of about 6 cm^2 and an estimated actual area of 3 - 4 cm^2. The electrode potential was controlled by a PAR Model 173 Potentiostat/Galvanostat; significant electrolysis occurred at -200 mV vs the saturated calomel electrode (SCE). With respect to the hydrogen scale, the potential was +44.5 mV. The current density was approximately 1.0 mA/cm^2. A black solid gradually formed on the electrode, and deposition was stopped after about five hours.

The electrode measurements were made with a Hewlett Packard 3490A Multimeter capable of reading potentials to within ±20 uV. Before use it was calibrated by the Oak Ridge National Laboratory (ORNL) Instrumentation and Controls Division. The PAR cell had a jacket through which water thermostatted to 25 ± 0.1°C was circulated. Potential measurements were made with respect to a saturated calomel electrode (SCE) which was checked by periodic comparison to two SCE electrodes maintained as standards. Generally all of the electrodes were within a few tenths of a millivolt of each other. The potential of the SCE is 0.244_5 V with respect to the standard hydrogen electrode. This is the value recommended by Hills and Ives (1961) and Janz and Kelly (1964) for the case where a liquid junction is established with a dilute solution. A value of 0.242 V was used by Cartledge and Smith (1955).

4.3. RESULTS

4.3.1 Solubilities

The results of the measurements are given numerically in Table 1 and graphically in Figure 1. All results are the average of the last five measurements over the period of the experiment, and the errors given are the standard deviations calculated by the n-method. During the experiments the pH generally drifted to less basic values. The range and value of the average pH for the last five determinations are given in Table 1.

Total solubilities include Tc(VII) as TcO_4^- and reduced technetium. There appears to be no trend in the concentration of reduced technetium with increase of the concentration of NaCl. Up to 2-mol/L NaCl, there appears to be a consistent decrease of total technetium; however, at 2.6-mol/L NaCl the total technetium appears to increase again. Further solubility determinations with new columns are planned for higher concentrations of NaCl and for confirmation of some of the data obtained so far. The concentration levels of both reduced and total technetium are relatively low in the NaCl solutions studied. The concentrations of reduced technetium are about as low as any determined in our previous measurements. For example, they are of the same order of magnitude as those for technetium oxide electrolytically deposited from basic solutions, as shown in Table 2 (Meyer et al. 1987).

The average solubility for reduced technetium from Table 1 is (2.61 ± 1.00) x 10^{-9} mol/L, and the average value for the reduced technetium from Table 2 is (2.56 ± 0.54) x 10^{-9} mol/L. However, there are considerable variations in total solubilities both within each table and between the two tables.

Table 1. Solubility of $TcO_2 \cdot nH_2O$ in NaCl solutions

NaCl Conc. (mol/L)	Solubility (mol/L) Reduced	Solubility (mol/L) Total	pH Range	pH Avg.
0.1	$(2.52 \pm 0.84) \times 10^{-9}$	$(4.03 \pm 0.87) \times 10^{-7}$	7.2 - 6.6	6.9
0.5	$(1.11 \pm 0.57) \times 10^{-9}$	$(2.24 \pm 0.16) \times 10^{-7}$	7.9 - 7.5	7.7
1.0	$(3.49 \pm 0.90) \times 10^{-9}$	$(1.84 \pm 0.08) \times 10^{-7}$	9.1 - 8.8	8.9
1.2	$(3.88 \pm 0.20) \times 10^{-9}$	$(2.20 \pm 0.06) \times 10^{-8}$	9.3 - 9.1	9.2
1.6	$(3.59 \pm 0.26) \times 10^{-9}$	$(2.58 \pm 0.31) \times 10^{-8}$	9.3 - 9.1	9.2
2.0	$(1.47 \pm 0.37) \times 10^{-9}$	$(6.90 \pm 1.70) \times 10^{-9}$	9.2 - 9.1	9.2
2.6	$(2.24 \pm 0.14) \times 10^{-9}$	$(7.57 \pm 0.53) \times 10^{-8}$	9.1 - 9.0	9.0

Table 2. Solubility of $TcO_2 \cdot nH_2O$ electrodeposited from basic solutions[a]

NaCl Conc. (mol/L)	Solubility (mol/L) Reduced	Solubility (mol/L) Total	pH Range	pH Avg.
GR-4[b]	$(2.94 \pm 2.80) \times 10^{-9}$	$(8.87 \pm 0.50) \times 10^{-8}$	9.3 - 9.5	9.4
0.01	$(3.14 \pm 1.54) \times 10^{-9}$	$(1.41 \pm 0.10) \times 10^{-7}$	8.7 - 8.7	8.7
0.01	$(3.20 \pm 1.69) \times 10^{-9}$	$(4.25 \pm 0.59) \times 10^{-8}$	7.4 - 7.5	7.5
0.01	$(1.70 \pm 1.29) \times 10^{-9}$	$(3.76 \pm 0.75) \times 10^{-8}$	5.4 - 5.6	5.6
0.01	$(2.20 \pm 0.78) \times 10^{-9}$	$(8.35 \pm 2.22) \times 10^{-9}$	5.3 - 5.4	5.3

[a] Meyer et al. (1987).
[b] Basalt groundwater GR-4 (Salter, 1984)

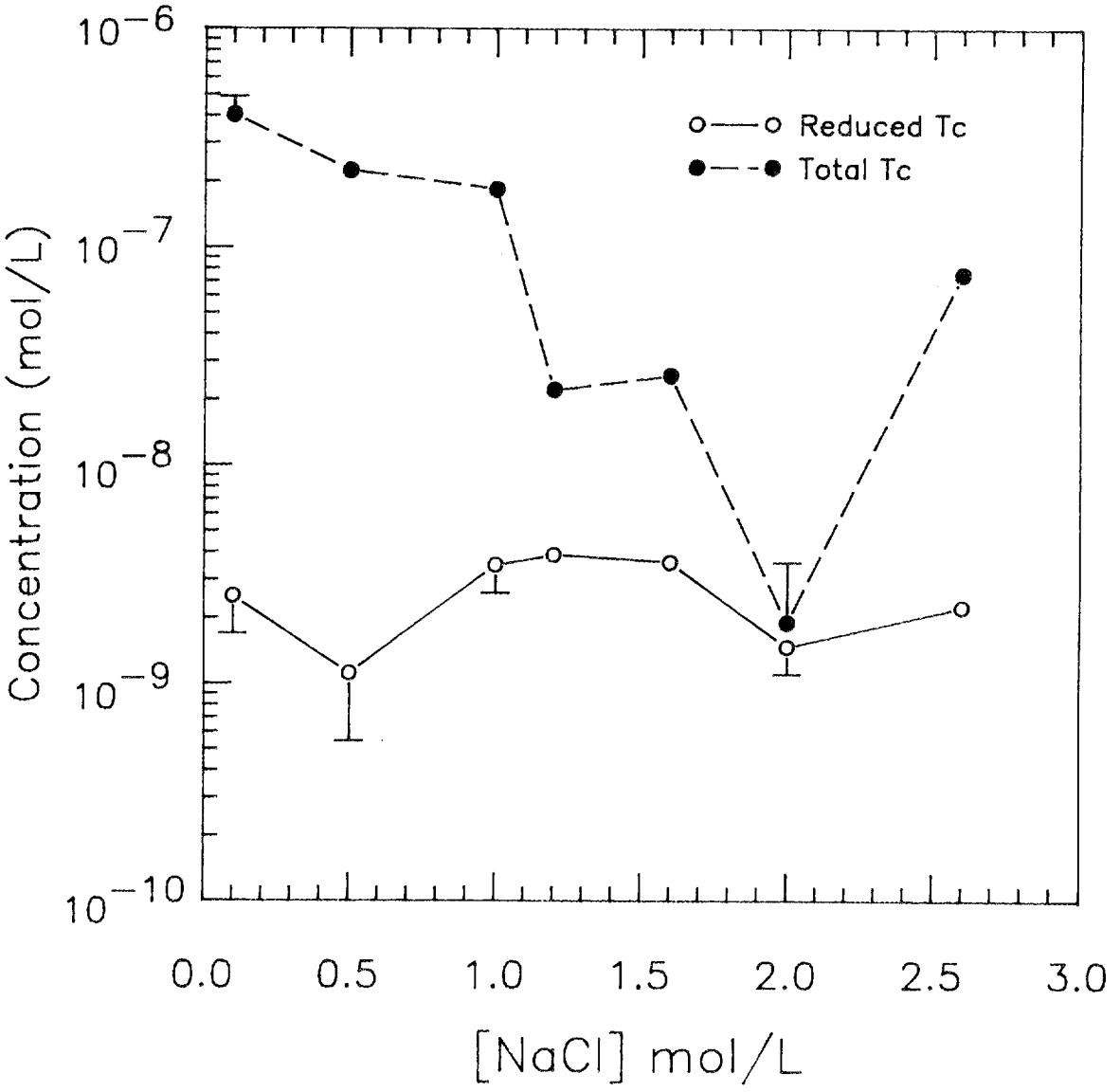

Fig. 1. Solubility of technetium under anoxic conditions as a function of NaCl concentration.

4.3.2 Electrode Potentials

To reduce uncertainties related to the unavoidable presence of liquid junction potentials and the estimation of activity coefficients which could be significant, electrode potentials were measured in 5 x 10^{-3} mol/L HCl at relatively low concentrations of the TcO_4^- ion. Despite these precautions there will always be an uncertainty of a few millivolts due to these effects. Calculation of the activity coefficient correction using the Debye-Hückel limiting law at these low concentrations resulted in values no greater than a millivolt in the calculation of E^o.

In Tables 3 to 5, results are given for the potential as a function of concentration at constant pH for three different electrodeposits of the oxide. Because there were slight variations in pH, the values in the potential column labeled "E pH 2.3" were normalized to a value at pH 2.3 using the coefficient 0.0788 V/(pH unit). The columns labeled "log activ." contain values of the logarithms of the activities obtained by multiplying each concentration by the appropriate activity coefficient.

Table 3. Effect of concentration on potential

E (V)	E pH 2.3 (V)	$[TcO_4^-]$ (mol/L)	pH	E^o (V)	log activ.
0.243	0.242	9.66 x 10^{-5}	2.31	0.749	-4.049
0.258	0.258	2.78 x 10^{-4}	2.30	0.755	-3.590
0.262	0.265	9.39 x 10^{-4}	2.27	0.746	-3.063
0.273	0.276	2.88 x 10^{-3}	2.27	0.748	-2.582
0.274	0.274	2.95 x 10^{-3}	2.30	0.751	-2.572

Table 4. Effect of concentration on potential

E (V)	E pH 2.3 (V)	[TcO4-] (mol/L)	pH	E^o (V)	log activ.
0.253	0.251	1.01 x 10^{-4}	2.32	0.760	-4.028
0.258	0.256	2.85 x 10^{-4}	2.33	0.757	-3.579
0.266	0.265	9.78 x 10^{-4}	2.32	0.754	-3.046
0.275	0.275	2.93 x 10^{-3}	2.31	0.753	-2.575

Table 5. Effect of concentration on potential

E (V)	E pH 2.3 (V)	[TcO4-] (mol/L)	pH	E° (V)	log activ.
0.224	0.224	1.06×10^{-4}	2.31	0.730	-4.007
0.237	0.235	3.15×10^{-4}	2.33	0.735	-3.536
0.252	0.248	1.13×10^{-3}	2.35	0.740	-2.984
0.263	0.262	3.51×10^{-3}	2.32	0.740	-2.497

In Tables 6 and 7, the results from experiments to measure the effect of pH on potential at constant technetium concentration are shown. The technetium concentrations varied slightly and were normalized using the theoretical coefficient 0.0197 V/log unit of concentration. Experiments were done at TcO_4^- concentrations of ca 10^{-4} mol/L and 10^{-3} mol/L.

Table 6. Effect of pH on potential

E (V)	E(norm.) (V)	[TcO4-] (mol/L)	pH	E° (V)
0.127	0.126	1.14×10^{-4}	3.99	0.764
0.165	0.164	1.20×10^{-4}	3.40	0.755
0.201	0.200	1.12×10^{-4}	2.83	0.747
0.239	0.239	1.07×10^{-4}	2.30	0.744
0.272	0.273	9.11×10^{-5}	1.90	0.747

Table 7. Effect of pH on potential

E (V)	E(norm.) (V)	[TcO4-] (mol/L)	pH	E° (V)
0.146	0.145	1.14×10^{-3}	3.81	0.749
0.165	0.164	1.15×10^{-3}	3.56	0.748
0.203	0.202	1.16×10^{-3}	3.00	0.743
0.246	0.245	1.15×10^{-3}	2.46	0.743
0.286	0.285	1.13×10^{-3}	2.01	0.748

The data from Tables 3-5 on potential as a function of concentration are plotted in Fig. 2. The slope of the line in Fig. 2 is 0.0211 $\pm$ 0.005 V/(log unit). The theoretical slope at 25°C is 0.0197 V/(log unit). While the agreement between measured and theoretical slopes seems satisfactory, it appears that one of the electrodes exhibited somewhat lower values of potential than the other two.

The data from Tables 6 and 7 on potential vs pH are plotted in Fig. 3. The straight lines shown were fitted to the respective data sets by the method of least squares. The slope of the line in Fig. 3 for approximately 10^{-4} mol/L TcO_4^- is -0.0700 $\pm$ 0.0024 V/pH unit, and the theoretical value is -0.0788 V/pH unit. There appears to be a slight curvature to the data as plotted; in fact, the slope appears to be approaching the theoretical slope at the lower pH values. Initially, at 10^{-4} mol/L TcO_4^-, concentration and pH were adjusted, and the potential was followed with time. However, the potentials tended to drift with time, and it was not possible to determine a steady potential. Therefore, the potential was adjusted to a suitable value and fixed by a potentiostat; the concentration and pH were then allowed to change with time until a steady state was observed. Because of the difficulty in obtaining steady states at 10^{-4} mol/L Tc, the concentration was increased to 10^{-3} mol/L. In this case the potentials were allowed to change with time after the pH and concentration were adjusted, and they came to a steady state after about 4 hr at the lower pH values and about a day at the highest pH value. The slope of the line at approximately 10^{-3} mol/L TcO_4^- is -0.0773 $\pm$ 0.0023 V/pH unit, which is very close to the theoretical slope of -0.0788 V/pH unit. Values of the standard potential in the tables were computed with the assumptions that the theoretical slopes were applicable. Because values of the potential were less reliable at the lower Tc concentrations, we used only measurements at concentrations >9 x 10^{-4} mol/L to determine the average E^o value of 0.747 $\pm$ 0.004 V vs the standard hydrogen electrode from the data in Tables 3 to 6.

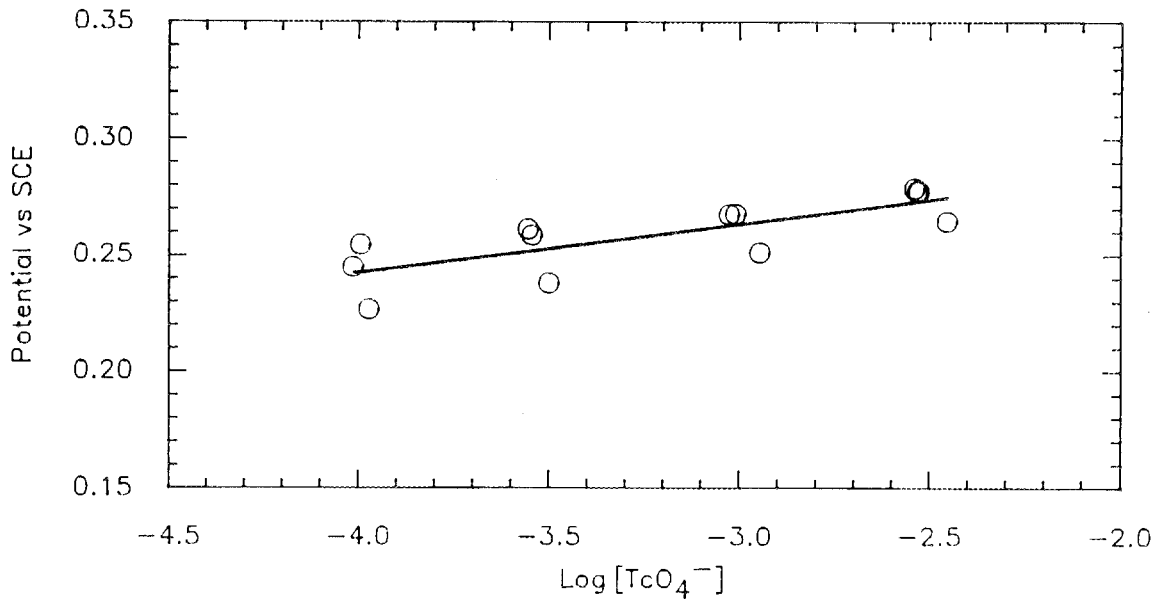

Fig. 2. Potential vs log $[TcO_4^-]$

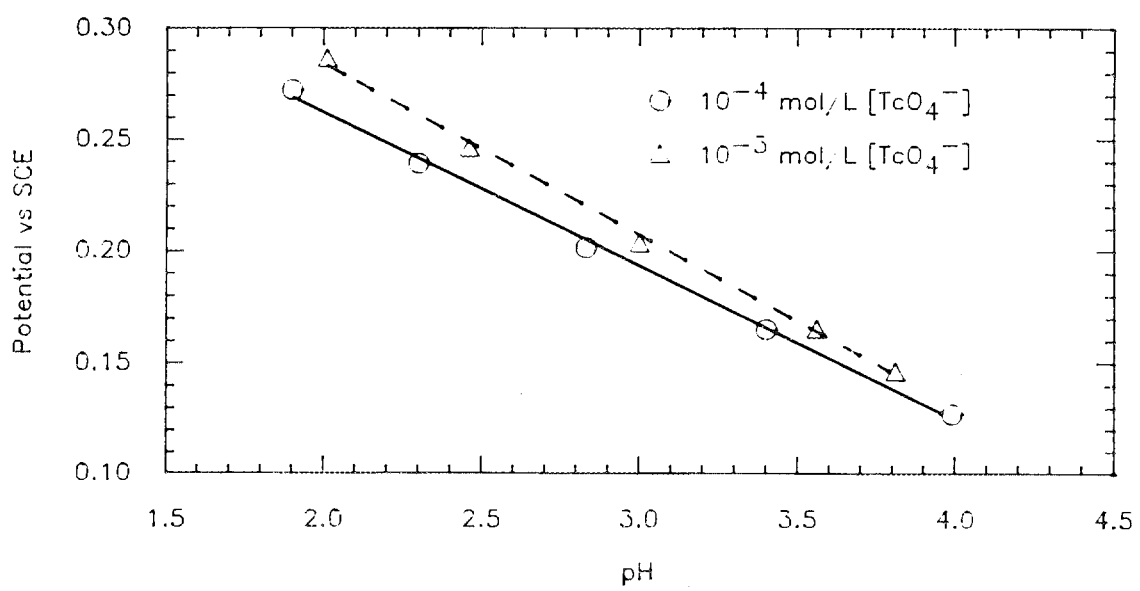

Fig. 3. Potential vs pH

5. DISCUSSION

The results of the solubility experiments shown in Table 1 are plotted in Fig. 4, where the data are compared to a theoretical line calculated using Eqs. 5.1 to 5.4; activity coefficients are assumed to be one. These equations follow the solubility discussion given by Rard (1982). A solubility product of (1.63 $\pm$ 0.63) x 10^{-33} was calculated from the average solubility of those shown in Table 1 (2.61 x 10^{-9} mol/L) at the average pH of the determinations (8.6). In Rard's discussion the solid is assumed to be $TcO(OH)_2$ which corresponds to $TcO_2 \cdot H_2O$. We have modified Rard's equations slightly to show the oxide as $TcO_2 \cdot nH_2O$; in our experiments, n has an average value of 1.63 $\pm$ 0.28 (Meyer et al. 1987)

$$TcO_2 \cdot nH_2O(solid) + (1-n)H_2O = TcO^{2+} + 2(OH)^- \qquad Ksp = 1.63 \times 10^{-33} \qquad (5.1)$$

$$TcO^{2+} + H_2O = TcO(OH)^+ + H^+ \qquad K_{h1} = 4.3 \times 10^{-2} \qquad (5.2)$$

$$TcO(OH)^+ + H_2O = TcO(OH)_2(aqueous) + H^+ \qquad K_{h2} = 3.7 \times 10^{-3} \qquad (5.3)$$

$$2TcO(OH)_2(aq.) = [TcO(OH)_2]_2(aq.) \qquad K_{dim} = 3.14 \times 10^{6} \qquad (5.4)$$

This scheme assumes the existence in solution of neutral monomers and dimers of $TcO(OH)_2$. The concentrations of the aqueous species of Tc(IV) are shown in Fig. 4 along with the total solubility. It is shown that in basic solution the only significant species in equilibrium with the oxide is the neutral species $TcO(OH)_2$.

The solubilities of reduced technetium shown in Table 1 are similar in magnitude to those that we found for oxides electrodeposited from basic solution (Meyer et al. 1987) which averaged (2.56 $\pm$ 0.54) x 10^{-9} mol/L. However, they are about a factor of four lower than those found in solutions of lower ionic strength for the oxide precipitated on sand (Meyer et al. 1987), the preparation technique used for the experiments shown in Table 1. To check these differences, we plan repeat experiments at lower ionic strengths.

The differences in total solubility at the different concentrations of NaCl are due to variable concentrations of TcO_4^-, and the reasons for these variations are not clear. Generally, the concentration of TcO_4^- stays relatively constant or deceases slightly with time during an experiment. The concentration of reduced technetium is determined by thermodynamic equilibrium with the oxide; the concentration of TcO_4^- in the presence of the reduced oxide would be controlled by the Tc(IV)/Tc(VII) redox equilibrium if some means were used to establish the equilibrium. Thus, when the oxide was deposited on an electrode controlled by a potentiostat, redox equilibrium was established, and the concentration of TcO_4^- was determined by this equilibrium (Meyer et al. 1986, 1987). Possibly, the concentration of TcO_4^- is controlled by variable small concentrations of oxygen or other oxidizing agents. The

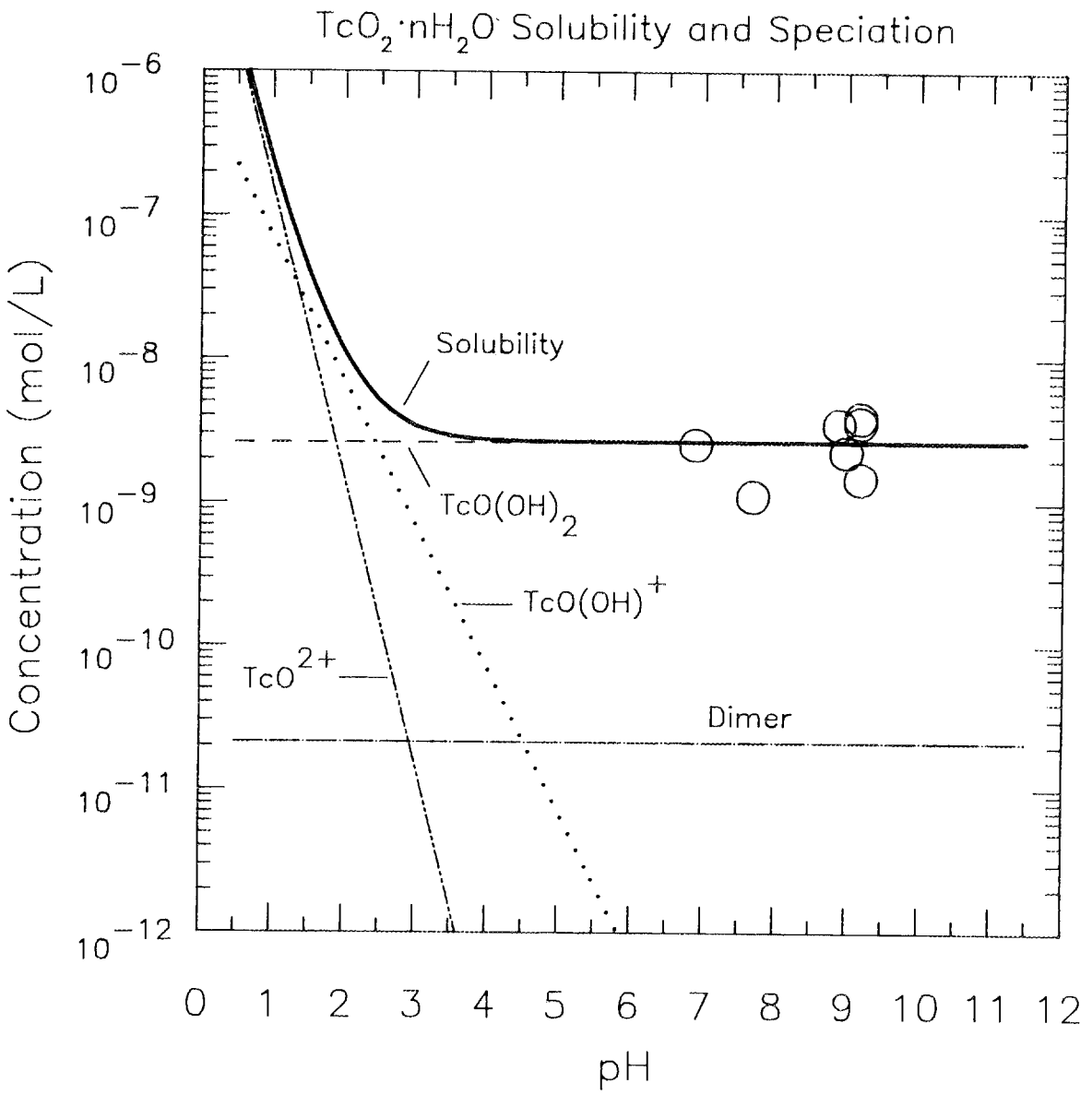

Fig. 4. Calculated solubility of $TcO_2 \cdot nH_2O$ and concentrations of aqueous species in equilibrium with the amorphous solid as a function of pH, for Ksp = 1.63×10^{-33}. The open circles represent the seven values of the solubility listed in Table 1.

oxygen in the solution could be from residual amounts in the controlled-atmosphere box. Also, oxygen and peroxides could be formed by radiolysis caused by the emission of ^{99}Tc beta particles in the column.

Cartledge and Smith (1955) used techniques similar to ours to measure potentials, and they reported the standard potential as 0.738 $\pm$ 0.003 V. Cartedge and Smith measured their potentials with respect to the SCE as we did, but they used a value of 0.242 V for the potential of the SCE, and we used the more recent value 0.244_5 V (Hills and Janz 1961, Janz and Kelly 1964). We recalculated the values for E^o from Cartledge and Smith's data using the same computer program that we used; this resulted in the value 0.741 $\pm$ 0.004 V. There appears to be agreement between our value of 0.747 $\pm$ 0.004 V and that of Cartledge and Smith (1955), but not with the value 0.782 $\pm$ 0.011 V of Cobble et al. (1953) or the more recent values of Liebscher and Münze (1955), which varied with pH.

5. CONCLUSIONS

(1) Solubilities of precipitated Tc(IV) oxides were determined in solutions of NaCl from 0.1 mol/L to 2.6 mol/L in the pH range 7 to 9. The concentrations of Tc(IV) species in equilibrium with the oxide were approximately constant in the NaCl concentration range studied and averaged $(2.61 \pm 1.00) \times 10^{-9}$ mol/L.

(2) These Tc(IV) solubilities are very close to those measured for technetium oxide electrodeposited from basic solution, which averaged $(2.56 \pm 0.54) \times 10^{-9}$ mol/L (Meyer et al. 1987).

(3) A value of $(1.63 \pm 0.62) \times 10^{-33}$ was determined for the solubility product of $TcO_2 \cdot nH_2O$.
was calculated from the data.

(4) A redetermination of the standard potential E^o for the Tc(VII) - Tc(IV) redox couple was completed. The slopes of the electrode potential vs pH and concentration were confirmed, and the value of E^o was determined to be 0.747 ± 0.004 V.

(5) Our value for the standard potential, 0.747 ± 0.004 V, agrees most closely with the value of 0.741 ± 0.004 V reported by Cartledge and Smith (1955).

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12. SUPPLEMENTARY NOTES

13. ABSTRACT (200 words or less)

Solubilities of precipitated Tc(IV) oxides have been determined in solutions of NaCl in the pH range 7 to 9. Technetium oxide was prepared by precipitation upon purified sand with a 30% excess of hydrazine. The oxide-covered sand was then transferred to a small column, and solutions of NaCl varying in concentration from 0.1 mol/L to 2.6 mol/L were continuously cycled through the column. The concentrations of Tc(IV) species in equilibrium with the oxide were determined and found to be approximately constant in the NaCl concentration range 0.1 mol/L to 2.6 mol/L and averaged $(2.61 \pm 1.00) \times 10^{-9}$ mol/L. A solubility product of $(1.63 \pm 0.62) \times 10^{-33}$ was calculated from the measured solubilities of Tc(IV) oxide. Because there is some disagreement among values of E^{o} for the Tc(VII) - Tc(IV) redox couple in the literature, a redetermination of the standard potential was completed. The slopes of the graphs of electrode potential vs pH and concentration were confirmed, and the value of E^{o} was determined to be 0.747 ± 0.004 V. These data can be used to estimate Tc(IV) solubilities for cases where solubility limits transport of technetium in reducing environments of high-level waste repositories.

14. DOCUMENT ANALYSIS - a. KEYWORDS/DESCRIPTORS

Sorption
Solubility
Technetium
Migration of Nuclides
Hydrolysis
Redox Process
Electrode Potential

b. IDENTIFIERS/OPEN-ENDED TERMS

15. AVAILABILITY STATEMENT

Unlimited

16. SECURITY CLASSIFICATION

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17. NUMBER OF PAGES

18. PRICE