

Ti(IV) Hydroxyfluoride Aqueous Complexes: Equilibrium Constants Derived From Rutile Solubility Measurements Made From 100° to 300°C

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**Ti(IV) Hydroxyfluoride Aqueous Complexes:
Equilibrium Constants Derived From Rutile
Solubility Measurements Made From 100° to 300°C**

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Abstract:

Using a Au-Ir hydrothermal reaction cell and dilute buffer solutions to control pH, the isobaric solubility of rutile (TiO_2) was measured over a range in fluoride concentration between 100° and 300°C. The solubility data were regressed to derive the equilibrium constant for the Ti(IV) mixed hydroxyfluoride complex $\text{Ti}(\text{OH})_4\text{F}_2^{2-}$.

These data are required to model the chemical behavior of Ti(IV) in aqueous solutions containing dissolved fluoride, e.g., that could result from evaporative concentration of normal ground water in the vicinity of a hot nuclear waste package, and provide a baseline for the Ti-solubility-limited dissolution of titanium metal and titanates, e.g., titanate-based ceramic waste forms for nuclear waste.

Introduction:

In prior work (Knauss et al., 2000) we described the need for thermodynamic data pertinent to the behavior of Ti(IV) in an aqueous environment at elevated temperature. Owing to the lack of directly useful thermodynamic data on Ti(IV) hydrolysis, particularly over a range in pH and temperature, we determined the cumulative and stepwise hydrolysis constants for Ti(IV) in aqueous solution. However, in some environments aqueous complexation by ligands other than the hydroxyl anion may afford a means to generate elevated Ti(IV) concentrations and, thus, increase the rate and extent to which titanates or titanium metal may dissolve.

In the vicinity of the proposed nuclear waste repository at Yucca Mtn., NV, typical ground waters are dilute Na- HCO_3 solutions, while perched waters in the unsaturated zone are typically less dilute Ca- SO_4 -Cl- HCO_3 solutions (Rosenberg et al., 2000). Using both thermodynamic-equilibrium-based geochemical modeling codes and actual experiments, the chemical evolution of these waters has been investigated as they are evaporatively concentrated. Both numerical (see below) and physical modeling (Rosenberg et al., 2000) suggest that the anions tend to become more concentrated in the remaining aqueous phase as evaporation proceeds. Eventually, CO_3^- and SO_4^- begin to decrease in solution as they become associated with alkaline earth minerals (e.g., calcite and gypsum) and F^- begins to decrease in solution as its concentration becomes limited by fluorite solubility. The Cl^- continues to increase in solution to a much higher concentration factor.

Prior work, although mostly limited to $< 37^\circ\text{C}$, suggests that of the anions likely to be present in evaporatively concentrated waters, F^- anion may have the highest affinity for dissolved titanium in aqueous solution (Cagliotti et al.,

1960; Ciavatta and Pirozzi, 1983; Pourbaix, 1963). A simple consideration of the Pearson Hard Acid – Soft Base concept would also suggest that F^- should form a stronger aqueous complex with Ti(IV) than Cl^- , SO_4^{2-} or CO_3^{2-} . The passivated titanium metal surface has long been recognized to be rutile (Hickman and Gulbransen, 1948). The corrosion behavior of passivated titanium metal shows that F^- anion has a more dramatic effect than Cl^- (Strietzel et al., 1998). In neutral pH solutions (pH 6-7) as little as 20 ppm F^- can produce strong localized corrosion of passivated titanium (rutile) (Reclaru and Meyer, 1998).

Given that low levels of F^- effectively corrode passivated titanium metal and rutile even at low temperature, one may ask what concentrations of F^- could possibly exist in a nuclear waste repository environment. A simple geochemical model calculation can be done by “titrating out” water from an appropriate ground water composition. This approximates low temperature (sub-boiling) evaporation.

The major limitation with modeling highly-concentrated salt solutions, however, is the limited choice of thermodynamic databases. Ideally, we would like to use a database that (1) includes all the aqueous species and minerals of interest, (2) is valid at high ionic strengths, and (3) is valid at elevated temperatures. There are several commonly used thermodynamic databases used with geochemical models like EQ3/6 (Wolery et al., 1990) and REACT (Bethke, 2000), but none has all of these desired features. Thus, we face a compromise in any calculation.

All these caveats notwithstanding, the correspondence between our modeling simulations done using the EQ3/6 cmp database and experimental data are (perhaps) surprisingly good. In Fig. 1 we show the results of a geochemical model simulation in which J-13 ground water from the Nevada Test Site (NTS) is evaporatively concentrated at 85°C while constantly equilibrated with the atmosphere. Note that we define the initial system to have 1 kg H_2O , so that the x-axis values in the plot are equivalent to the negative log of the concentration factor as evaporation proceeds. This plot shows that the simulated free F^- concentration increases over 1000-fold from 1.1×10^{-4} molal (2.2 ppm) to 1.8×10^{-1} molal (2351 ppm) before it becomes limited by fluorite solubility. In an experiment designed to be closely analogous to this simulation we found that after an estimated 956-fold concentration of a synthetic J-13 water, the F^- concentration had risen to 1550 ppm and its concentration factor (final concentration/original concentration) was identical to that of Cl^- , an anion that would be expected to be a conservative indicator of the degree of evaporation. It is also important to note that the simulated evaporation results in an increase in pH from approximately 7 to 9.4, as seen in Fig. 2. This is pertinent

to the pH chosen for these experiments.

Given these preliminary calculations and experimental results we concluded that it was necessary to investigate the importance of mixed hydroxyfluoride Ti(IV) aqueous complexes. In particular, a range in F^- concentration and temperature needed to be studied. Based on the likely pH range to be generated during evaporative concentration of NTS waters, a neutral to slightly alkaline pH (~pH 9) was appropriate. In this work we measure the solubility of rutile at an essentially fixed pH (~pH 9) over a range in F^- concentration from 0.1 to 0.7 m (in KF) and over a temperature range from 100° to 300°C.

Unfortunately, other than the references cited above, there is only one reference available that provides information on the equilibrium constants for mixed hydroxyfluoride Ti(IV) aqueous complexes (Barsukova et al., 1980). It is the only reference containing data acquired at elevated temperatures. However, because the primary interest in this earlier work was in the hydrothermal formation of titanium ore bodies, the range in both temperature (400° and 450°C) and F^- concentration (0.5 – 2.1 m KF) was somewhat higher than appropriate for nuclear waste studies. These workers also focused on the determination of ligand number, by running a large number of F^- concentrations, at the expense of measurements made at a greater number of temperatures. The results of the earlier work, however, should extend the range obtained here.

Experimental and Analytical Methods

The rutile used in these experiments was a split of the material used in our earlier work on Ti(IV) hydrolysis constants and the information on characterization and preparation is contained in that reference (Knauss et al., 2000).

The dilute buffer solutions used to control pH have recipes designed using the geochemical modeling code EQ3/6 v.7.2c (Wolery et al., 1990). We used the $B(OH)_3$ - NaOH buffer system to achieve a pH ~9. The exact solution compositions and the measured and calculated room temperature pH values are contained in Table 1. In order to be more nearly equivalent to the solutions used in the earlier work on Ti(IV) hydrolysis constants, in each solution 0.1m $NaNO_3$ was added as a background electrolyte. Ultrapure reagents were used whenever available, and in every case reagents were analytical reagent grade or better. The water used was Milli-Q™ 18MΩ deionized water. All concentrations are reported on the molal scale for convenience. The EQ3/6 code is used to calculate the in situ pH at each temperature using a 1-step temperature jump and the charge-balance constraint.

We used a pure Au-Ir reaction cell based on our modification of a design by Rosenbauer et al. (1993). This flexible reactor and the entire hydrothermal apparatus, including sampling valves, furnaces, etc., has been described in detail in our earlier work (Knauss et al., 2000).

Isobaric measurements were made at 200 bar pressure at the following temperatures: 100, 150, 200, 250, 300 and approx. 325°C. The excursion to approximately 325°C was made to allow for a reversed measurement at 300°C. The pressure chosen was conveniently high to maintain the system as a single liquid phase at all temperatures. All measurements at 100, 150, 200, 250 and 300°C were reversed, i.e., steady state was approached from both under- and over-saturation. At the highest temperature (325°C), steady state was approached from undersaturation only. After each temperature change, the cells were allowed to equilibrate for at least a week prior to sampling. From 3 to 12 samples were taken following each temperature change, with at least 1 day between each sampling. Thus, 7 to 18 analyses were available to determine the equilibrium concentration at each temperature. The mean values at each temperature calculated for these measurements represent from one to several weeks of equilibration time at that condition.

In order to minimize analytical blanks, plastic, rather than glass, syringes and sample tubes were used (Hansson et al., 1988; Stetzenbach et al., 1994). The sample tubes were acid-washed prior to use. The syringes were rinsed with the diluting fluid (1 m HNO₃) prior to use. Sampling of the equilibrated fluid was accomplished by connecting a Nalgene™ syringe with attached 0.45-µm disposable filter directly to the vessel's high-pressure valve. This filter size should be sufficient to exclude particulate rutile in this system (Pokrovski and Schott, 1998). The sample syringe was preloaded with 1 g of 1m HNO₃ to maintain Ti in solution in the quenched sample.

Graphite Furnace Atomic Absorption Spectroscopy (GFAAS) was used as the primary Ti analytical method (Hansson et al., 1988) for the RUTS15 and RUTS16 samples. However, for the lowest temperatures (100, 150 and 200°C) in the lowest F⁻ containing run (RUTS15), we also analyzed the samples using quadrupole-based Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using an HP4500 (Stetzenbach et al., 1994) to confirm the GFAAS analyses. Five Ti isotopes (46, 47, 48, 49 & 50) were scanned and it was found that the most precise analyses were obtained using ⁴⁷Ti and ⁴⁸Ti. Quantification was achieved via external calibration and ⁴⁵Sc and ⁸⁹Y internal standards were used to improve reproducibility. The RUTS17 samples displayed significant matrix effects in the GFAAS, so for this run Inductively-Coupled Plasma Atomic Emission Spectrometry was used. In all three analytical methods, the calibration standards were matrix-matched, being made up in each buffer

diluted just as each sample was diluted by the preloaded Ultrex HNO₃. The sampling blanks, determined by running each buffer solution through the entire sampling process, were found to be similar to the analytical blanks (diluted buffer solutions).

Results

The mean measured values for the blank-corrected equilibrium Ti concentration at each temperature and their standard deviations are contained in Tables 2 through 4. The calculated in situ pH, free F⁻ molality and activity, H₂O activity and true ionic strength of the buffer solutions at the appropriate temperatures are contained in Tables 5 through 7. These latter quantities are required to calculate the activity coefficients for the mixed hydroxyfluoride complexes of Ti(IV). The Ti concentrations are so low that the products of Ti hydrolysis have little impact on the calculated in situ pH, F⁻, or ionic strength of these buffer solutions. The blanks are usually less than 5% of the uncorrected concentration and more typically less than 1%.

In Fig. 3 the mean concentrations contained in Tables 2 through 4 are plotted vs. temperature. Although the mean Ti concentration measured at 100°C in the 0.5 m F run (RUTS16) clearly looks anomalous, there was no justification (no sampling or analytical problems) for ignoring it in the data reduction so it has been retained.

Note that these Ti concentrations are significantly higher than one obtains in F⁻-free solutions over this temperature range (Knauss et al., 2000). For example, at the mid-point of the temperature range (200°C) the Ti concentration in the presence of F⁻ at the same pH ranges from 3 times (in 0.1 m F), to 16 times (in 0.5 m F) to 52 times higher (in 0.7 m F) than in F⁻-free solutions. These results indicate that F⁻ is a good complexing ligand for Ti(IV), as expected.

Calculation of Hydrolysis Constants

The work of Barsukova et al. (1980) showed clearly that in weakly alkaline F⁻-containing solutions (pH 8-9) the dominant Ti-F aqueous complex is Ti(OH)₄F₂²⁻. This complex is formed via the reaction:



The thermodynamic equilibrium constant (K_{s42}) for the formation of this mixed hydroxyfluoride complex of Ti(IV) is given by:

$$K_{s42} = \frac{a_{\text{Ti}(\text{OH})_4\text{F}_2^{2-}}}{a_{\text{F}^-}^2 \cdot a_{\text{H}_2\text{O}}^2} \quad (2)$$

where: a_i = activity of the i^{th} species.

Substituting $a_i = \lambda_i m_i$, where m_i = molality and λ_i = molal activity coefficient of the i^{th} species:

$$K_{s42} = \frac{\lambda_{\text{Ti(OH)}_4\text{F}_2^{2-}} m_{\text{Ti(OH)}_4\text{F}_2^{2-}}}{a_{\text{F}^-}^2 a_{\text{H}_2\text{O}}^2} \quad (3)$$

The measured solution Ti concentration at each temperature and F^- concentration is taken as $m_{\text{Ti(OH)}_4\text{F}_2^{2-}}$, by assuming that the contribution to total Ti(IV) from the simple hydrolysis species is negligible. The activities of F^- and H_2O have been calculated and tabulated in Tables 5 through 7.

The activity coefficient (λ) for the species $\text{Ti(OH)}_4\text{F}_2^{2-}$ in each sample solution may be calculated using the Helgeson b-dot extrapolation (Helgeson, 1969):

$$\log \lambda_i = - \frac{Az_i^2 \sqrt{I}}{1 + aB\sqrt{I}} + B \quad (4)$$

where A = the Debye-Hückel A , z = the species charge, I = ionic strength, the ion size parameter (a) for this species is assumed to be 5, B = the Debye-Hückel B , and B is the extended Debye-Hückel term of Helgeson (1969). The values for these latter terms required to calculate λ at each temperature are tabulated in Table 8.

Once the λ 's have been calculated for each buffer solution at each temperature using Eqn. 4, the $\log K_{s42}$'s can be calculated using Eqn. 3. The mean values (and their uncertainties) for $\log K_{s42}$ at each temperature are tabulated in Table 9 and plotted in Fig. 4. In this figure we have included the $\log K_{s42}$ values determined by Barsukova et al. (1980). The data, including those of Barsukov et al., have been fit to a polynomial of the form:

$$\text{Log } K_{s42} = a + b \cdot \log T + c/T \quad (5)$$

The polynomial coefficients provided in this figure allow convenient calculation of $\log K_{s42}$ values at any desired temperature.

The data of Barsukova et al. (1980) were generated using a greater number of F^- concentrations at the expense of a smaller number of temperatures. This allowed more confident determination of ligand number ($n = 2$ for F^-) in the mixed hydroxyfluoride Ti(IV) aqueous complex that forms in weakly alkaline (pH 9) solutions. The ligand number (n) is determined at each temperature by plotting $\log \text{Ti} (m)$ vs. $\log \text{F}^- (m)$, where the slope is the ligand number. In this work we have generated data over a greater number of temperatures at the expense of a smaller number of F^- concentrations. Although tenuous, we have estimated the ligand number at each temperature independently using our own

data, realizing that these are 3-point plots. The results of this exercise are presented in Fig. 5. Although the ligand number is an integer, the apparent (or average) ligand number does appear to be decreasing towards one, as the temperature lowers. In spite of the large uncertainty inherent in regressing sparse data, it would seem prudent to evaluate the possible existence of a mixed hydroxyfluoride Ti(IV) aqueous complex with a single fluoride ($n = 1$) that may become more significant at low temperatures. Such a complex could form as the result of the following reaction:



Concluding Remarks

In this study solubility data for rutile measured over a broad range in temperature and a range in F^- concentrations were used to calculate thermodynamic equilibrium constants for the formation of a mixed hydroxyfluoride Ti(IV) aqueous complex. These thermodynamic data are a key requirement for the successful modeling of the behavior of Ti(IV) in an aqueous environment containing F^- anion. Such an environment could form in a hot nuclear waste repository where normal tuffaceous ground water could be evaporatively concentrated. Given that the ceramic waste form being considered for defense wastes is a titanate and that the current repository design invokes a titanium metal “drip shield” to meet performance assessment containment requirements, understanding the behavior of Ti(IV) in aqueous solutions containing dissolved F^- is critically important. Although inconclusive, results obtained here suggest the possible existence of yet another mixed hydroxyfluoride Ti(IV) aqueous complex. A more complete thermodynamic investigation of this system seems warranted.

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Table 1. Buffer Compositions and 25°C pH (measured and calculated)

recipes	experiment number	measured pH (°C)	calculated pH (°C)
0.100 m NaNO ₃ + 0.100 m H ₃ BO ₃ + 0.100 m KF + 0.04670 m NaOH	RUTS15	9.15 (19)	9.06 (19)
0.100 m NaNO ₃ + 0.100 m H ₃ BO ₃ + 0.500 m KF + 0.04811 m NaOH	RUTS16	9.23 (22)	9.03 (22)
0.100 m NaNO ₃ + 0.100 m H ₃ BO ₃ + 0.700 m KF + 0.04855 m NaOH	RUTS17	9.31 (22)	9.02 (22)

Table 2. Mean Ti Concentrations for RUTS15 (0.1 m F)

T (°C)	approach direction	mean Ti (log molal)	st dev Ti (log molal)	n (#samples)
101	u	-7.31	.0481	3
	o	-7.07	.0464	4
	mean	-7.26	.1160	7
150	u	-7.00	.0233	4
	o	-7.07	.0464	4
	mean	-7.01	.0537	8
200	u	-7.00	.0671	4
	o	-6.81	.0461	4
	mean	-6.91	.1109	8
250	u	-6.80	.0943	4
	o	-6.75	.0390	4
	mean	-6.77	.0721	8
301	u	-6.60	.1004	4
	o	-6.66	.1031	4
	mean	-6.63	.1010	8
324	u	-6.33	.0014	2

u = under-saturation

o = over-saturation

Table 3. Mean Ti Concentrations for RUTS16 (0.5 m F)

T (°C)	approach direction	mean Ti (log molal)	st dev Ti (log molal)	n (#samples)
100	u	-6.32	.0067	3
	o	-6.17	.0570	5
	mean	-6.23	.0933	8
150	u	-6.25	.0094	3
	o	-6.46	.0063	6
	mean	-6.40	.1421	9
200	u	-6.34	.0962	4
	o	-6.07	.0032	6
	mean	-6.18	.1493	10
250	u	-5.90	.0035	6
	o	-5.90	.0025	6
	mean	-5.90	.0799	12
300	u	-5.77	.0010	6
	o	-5.61	.0088	12
	mean	-5.66	.0913	18
325	u	-5.32	.0050	3

u = under-saturation

o = over-saturation

Table 4. Mean Ti Concentrations for RUTS17 (0.7 m F)

T (°C)	approach direction	mean Ti (log molal)	st dev Ti (log molal)	n (#samples)
100	u	-6.05	.0144	2
	o	-6.30	.0064	2
	mean	-6.18	.1512	4
150	u	-5.73	.0028	3
	o	-6.14	.0267	2
	mean	-5.90	.2237	5
200	u	-5.65	.0057	2
	o	-5.68	.0010	2
	mean	-5.66	.0250	4
250	u	-5.41	.0010	2
	o	-5.36	.0030	2
	mean	-5.39	.0393	4
300	u	-5.02	.0007	2
	o	-5.03	.0007	2
	mean	-5.02	.0321	4

u = under-saturation

o = over-saturation

Table 5. Calculated Quantities for RUTS15 (0.1 m F)

T (°C)	pH	F ⁻ concentration (log molal)	F ⁻ activity (log molal)	H ₂ O activity (log molal)	I (molal)
101	8.59	-1.01	-1.17	-.00392	.245
150	8.48	-1.01	-1.19	-.00388	.244
200	8.47	-1.02	-1.23	-.00381	.242
250	8.55	-1.04	-1.29	-.00371	.237
301	8.76	-1.09	-1.41	-.00352	.224
324	8.89	-1.14	-1.50	-.00341	.210

Table 6. Calculated Quantities for RUTS16 (0.5 m F)

T (°C)	pH	F ⁻ concentration (log molal)	F ⁻ activity (log molal)	H ₂ O activity (log molal)	I (molal)
100	8.57	-.307	-.506	-.00966	.6401
150	8.46	-.310	-.538	-.00952	.6377
200	8.44	-.316	-.582	-.00932	.6307
250	8.52	-.327	-.645	-.00893	.6184
300	8.74	-.348	-.747	-.00826	.5955
325	8.90	-.363	-.823	-.00780	.5772

Table 7. Calculated Quantities for RUTS17 (0.7 m F)

T (°C)	pH	F ⁻ concentration (log molal)	F ⁻ activity (log molal)	H ₂ O activity (log molal)	I (molal)
100	8.57	-.160	-.371	-.0126	.838
150	8.46	-.164	-.404	-.0125	.835
200	8.43	-.169	-.449	-.0122	.826
250	8.51	-.178	-.513	-.0116	.812
300	8.73	-.193	-.616	-.0107	.788

Table 8. Terms for Activity Coefficient (λ) Calculation

T (°C)	A	B	\dot{B}
100	0.5995	0.3421	0.0460
150	0.6855	0.3525	0.0470
200	0.7994	0.3639	0.0470
250	0.9593	0.3766	0.0340
300	1.2180	0.3925	0.0000

Table 9. Mean Calculated $\log K_{s42}$

T (°C)	$\log K_{s42}$	std dev
100	-5.92	0.34
150	-5.83	0.45
200	-5.68	0.39
250	-5.34	0.27
300	-5.33	0.32

Figures

Fig 1. Calculated aqueous F speciation resulting from the evaporative concentration of tuffaceous ground water.

Fig 2. Calculated in situ pH resulting from the evaporative concentration of tuffaceous ground water.

Fig 3. Measured titanium concentration vs temperature.

Fig 4. Log K_{s42} vs . temperature

Fig 5. Ligand number (n) vs . temperature.

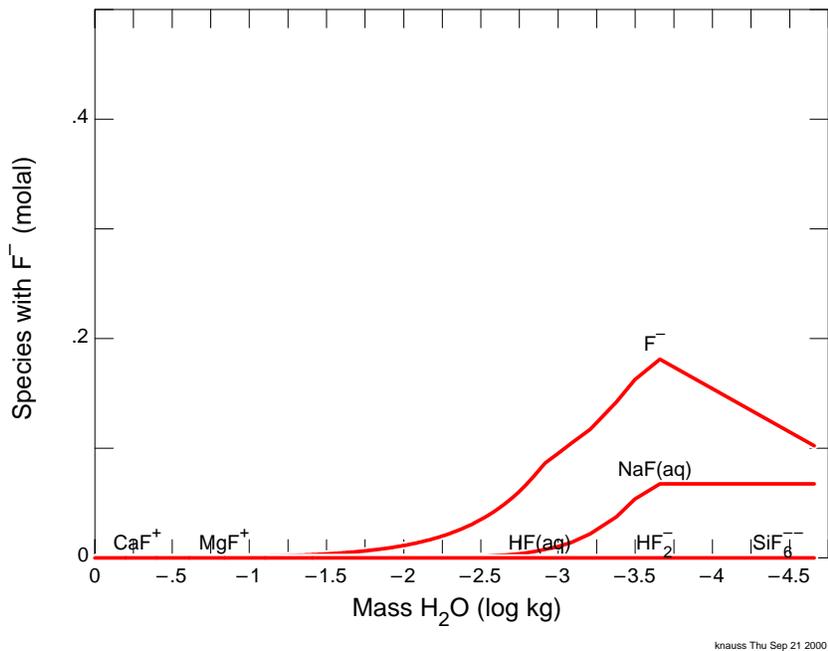


Fig. 1a

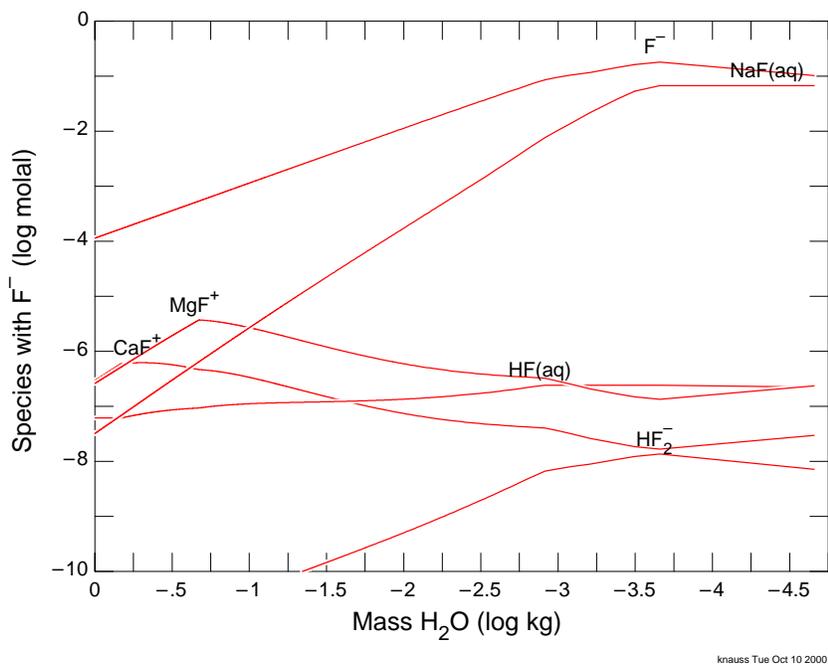
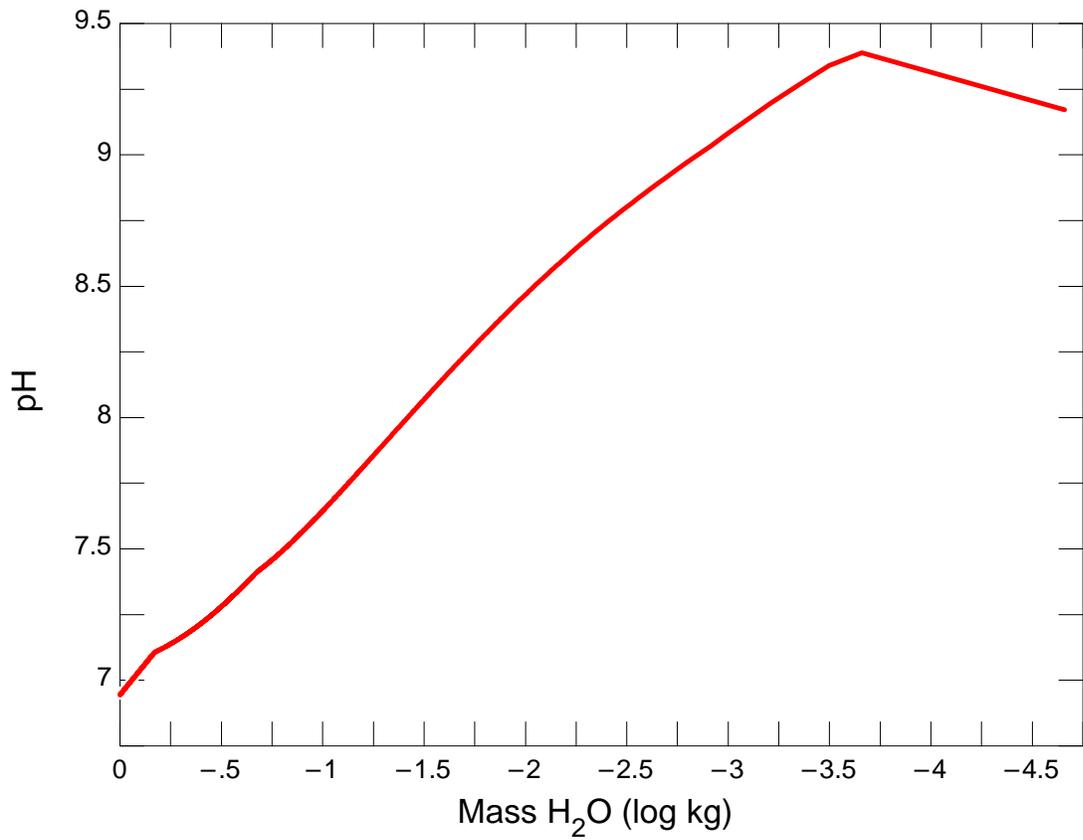


Fig. 1b



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Fig. 2

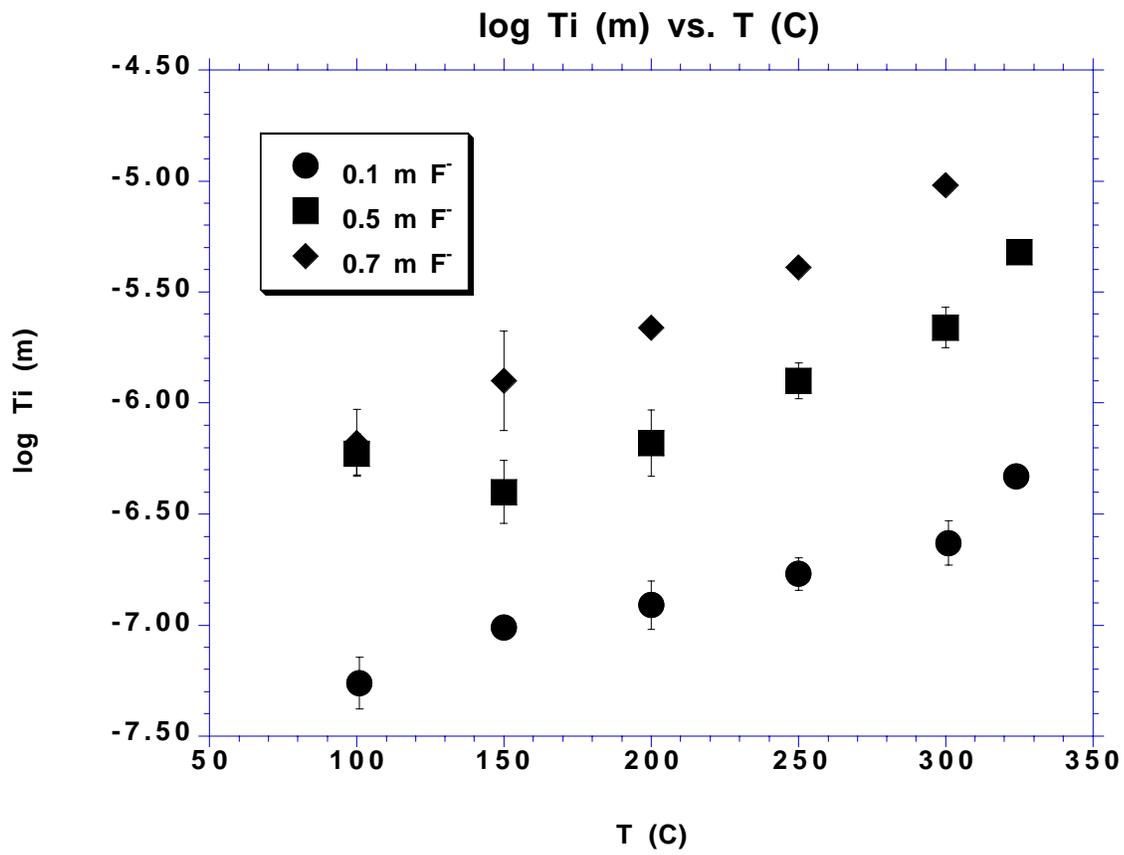


Fig. 3

$\log K_{s_{42}}$ vs T(K)

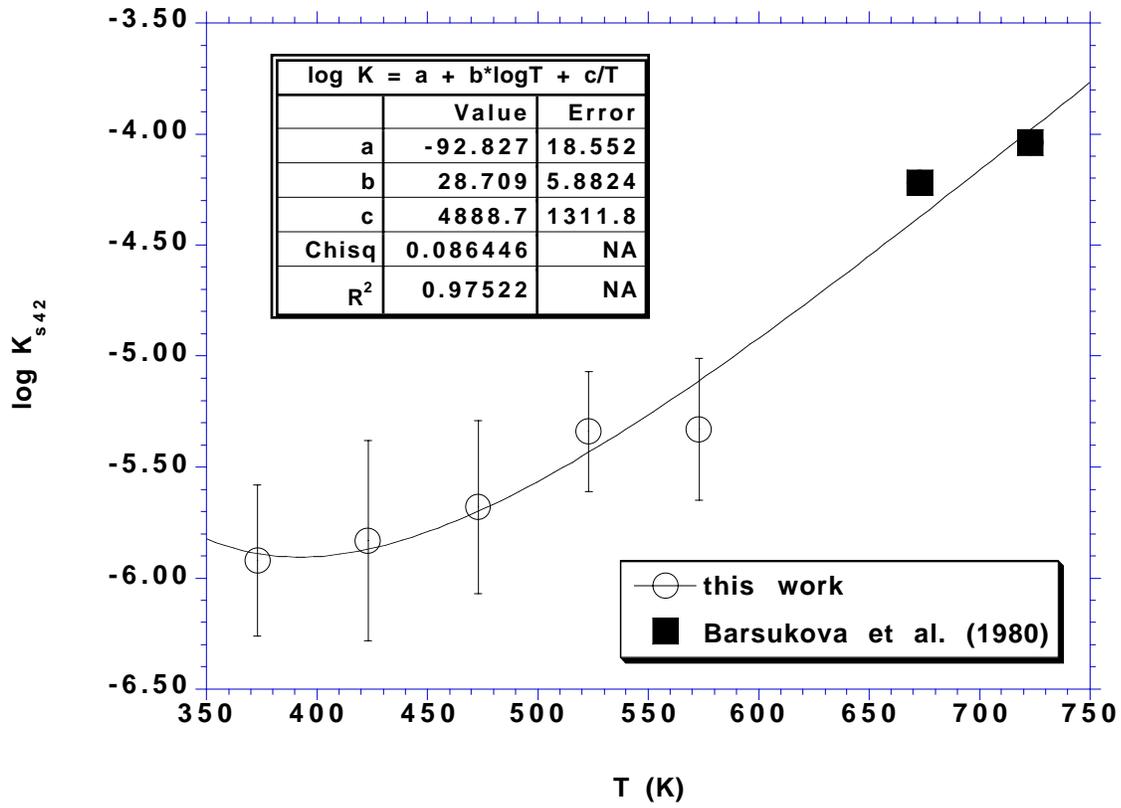
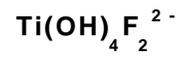


Fig. 4

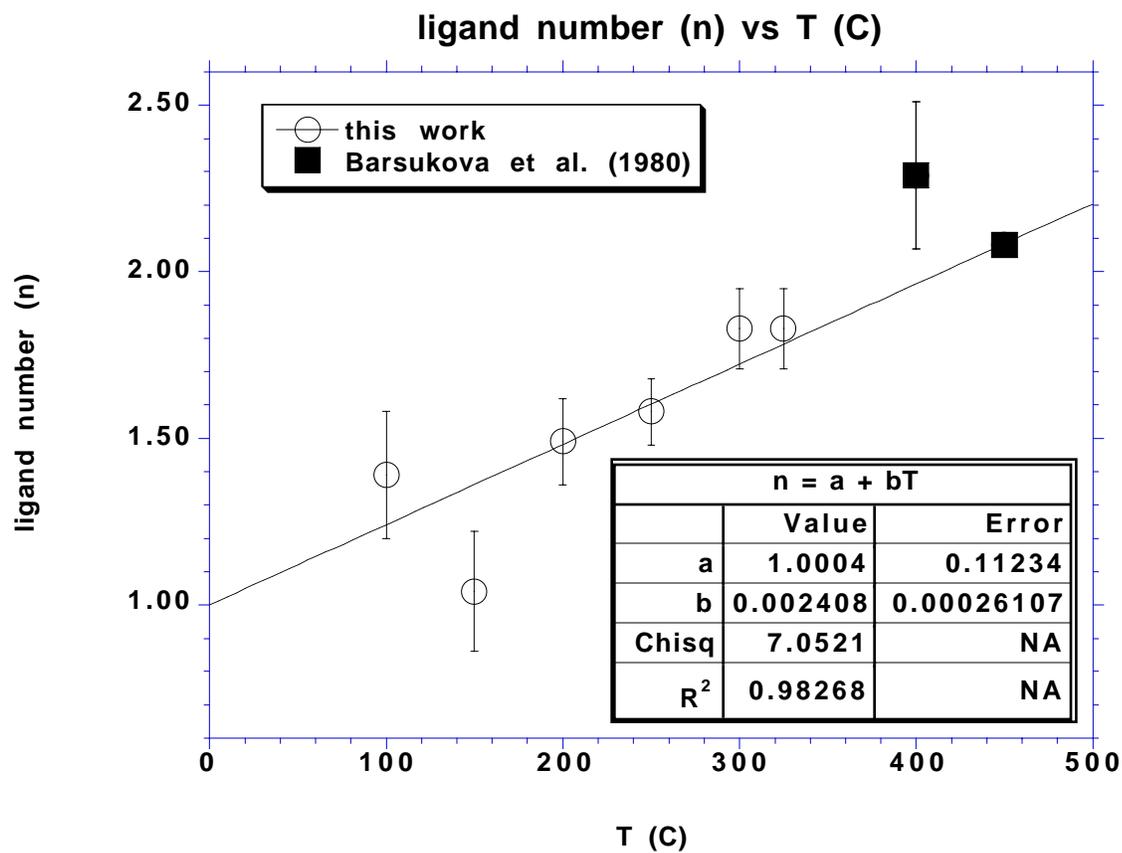


Fig. 5