Actinide Thermodynamics at Higher Temperatures

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Thermodynamic Parameters

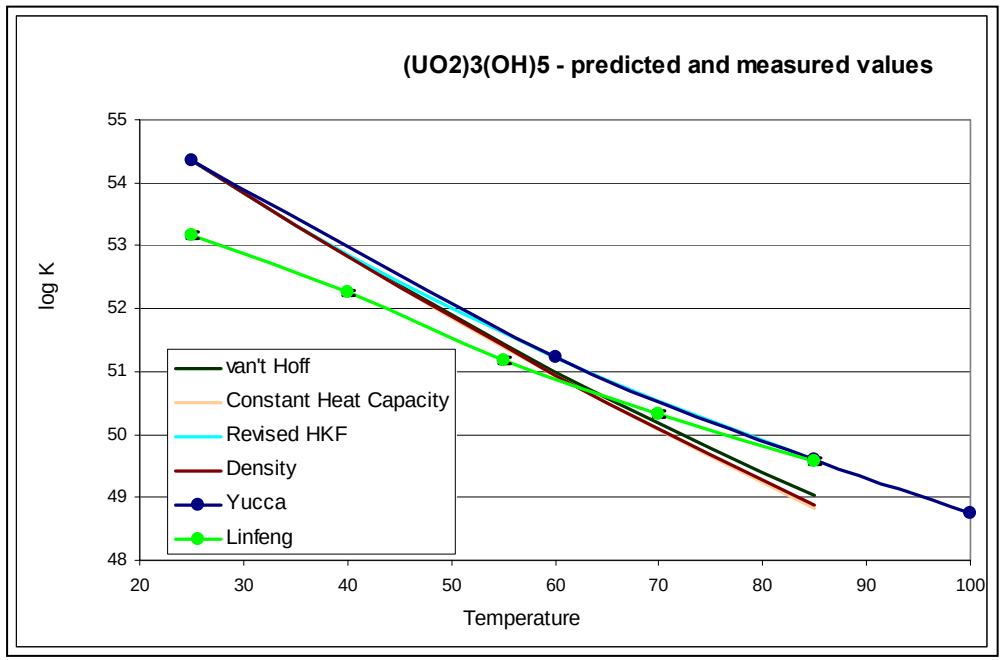
- **Thermodynamic database**
  - **Purpose and description**
- **Temperature extrapolation methods**
  - **Changes in speciation**
- **Enhanced data would reduce the need for conservatism**
- **Current experimental work**
  - **Calorimetric methods**
  - **Solvent extraction and Potentiometric methods**

Current Thermodynamic Database

- **Data0.ymp.r2 contains over 2000 values for an equal number of systems**
  - **Reviewed literature data is the source for the current database**
- **Modeling requires values ranging from 25°C to 100°C**
  - **Data is extrapolated and tabulated for higher temperature**
- **This database is the foundation for many models**
  - **Speciation calculations are necessary and all data needed is found in the Data0.ymp.r2 database**

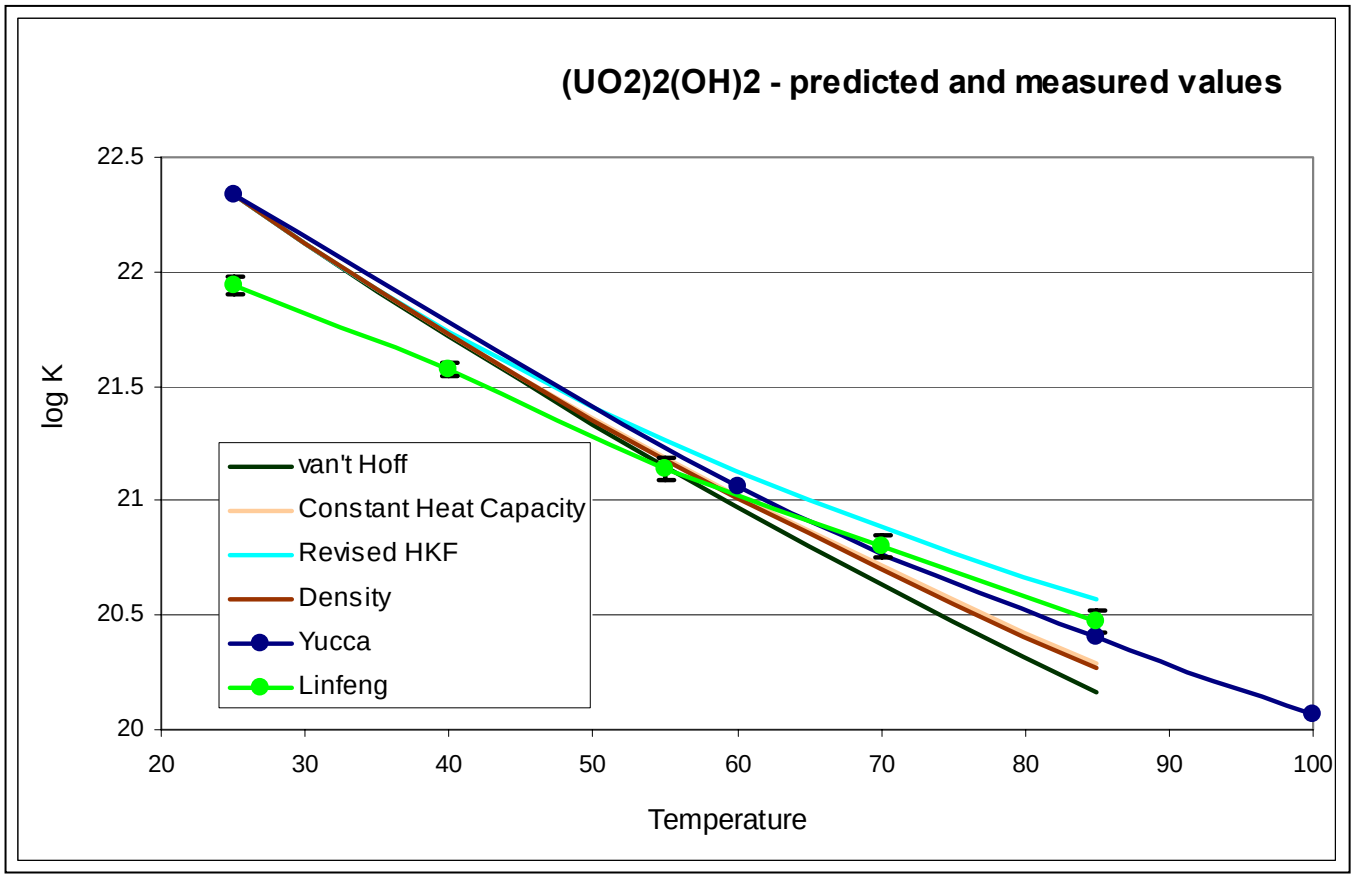
Temperature Extrapolation Methods

- **3:5 uranium hydrolysis constants**
- **Various extrapolation methods yield different values**
- **Enhanced data would likely reduce need for conservatism in extrapolation to higher temperature**

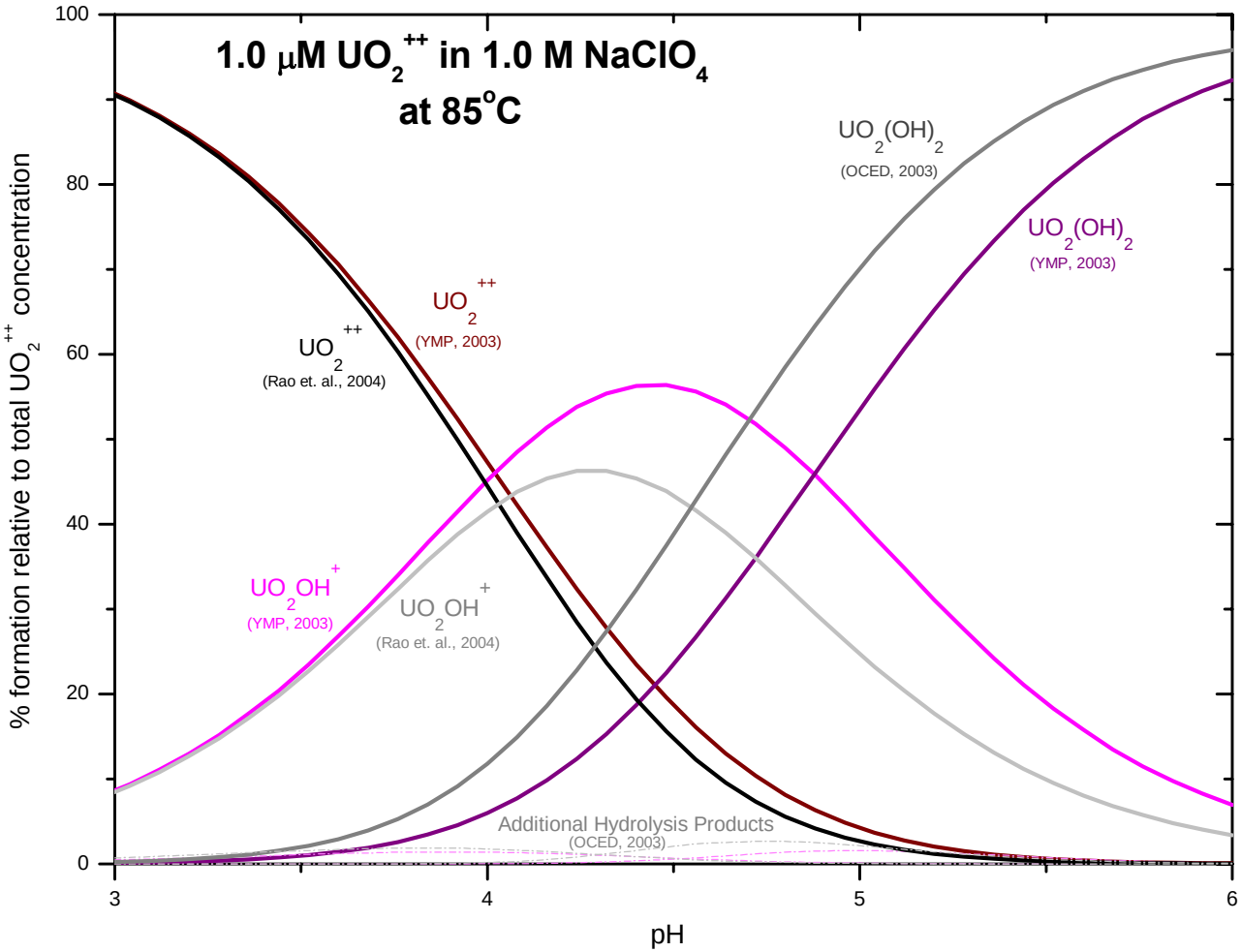


Temperature Extrapolation Methods

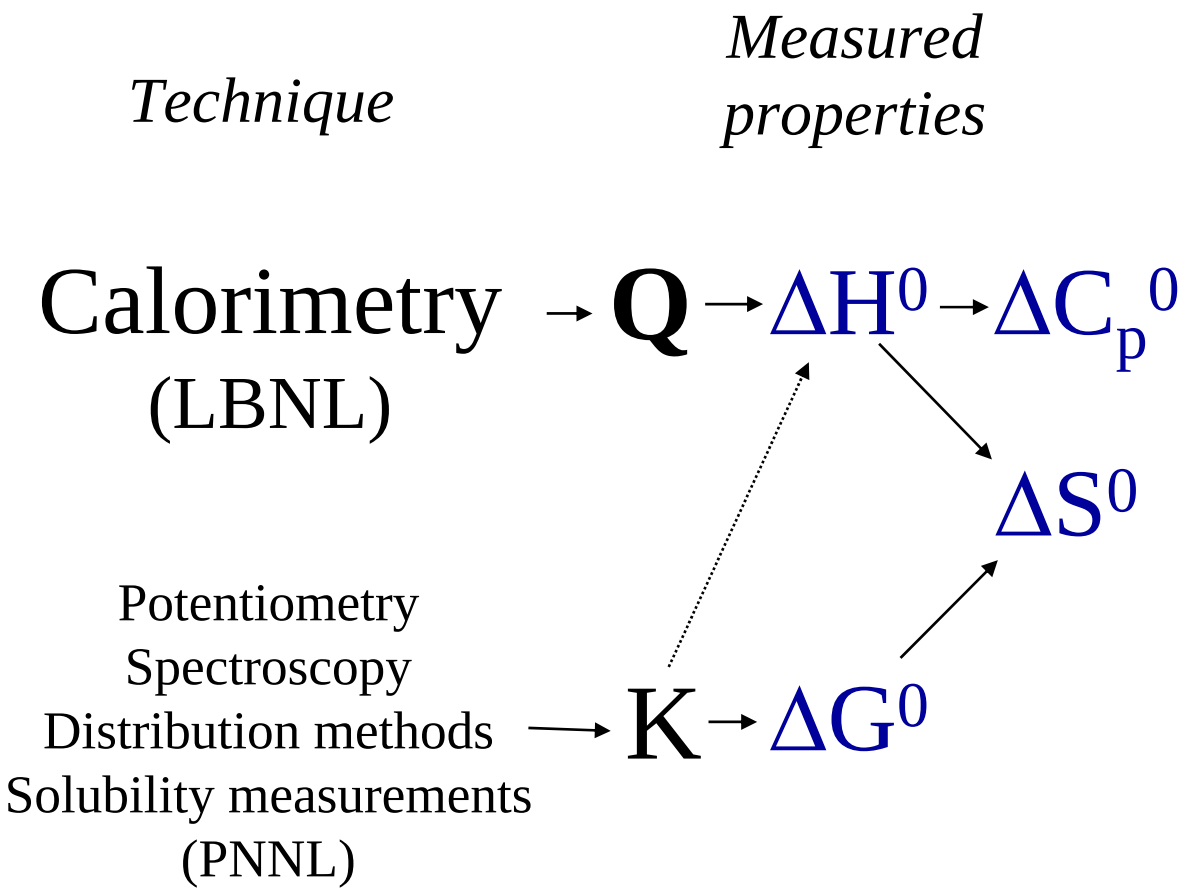
- **Uranium hydrolysis 2:2 constants**



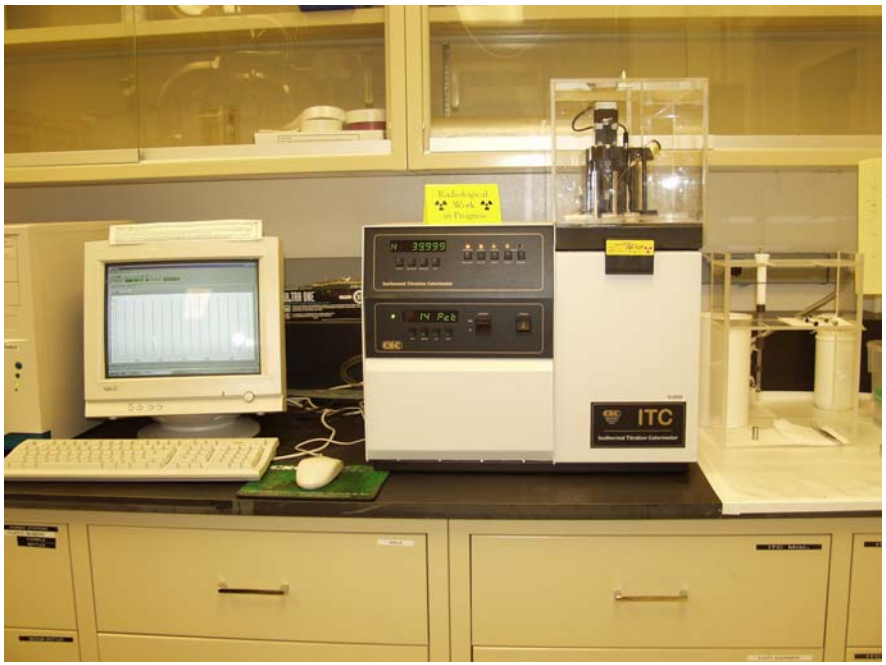
Uranium Hydrolysis 85°C Speciation Plot

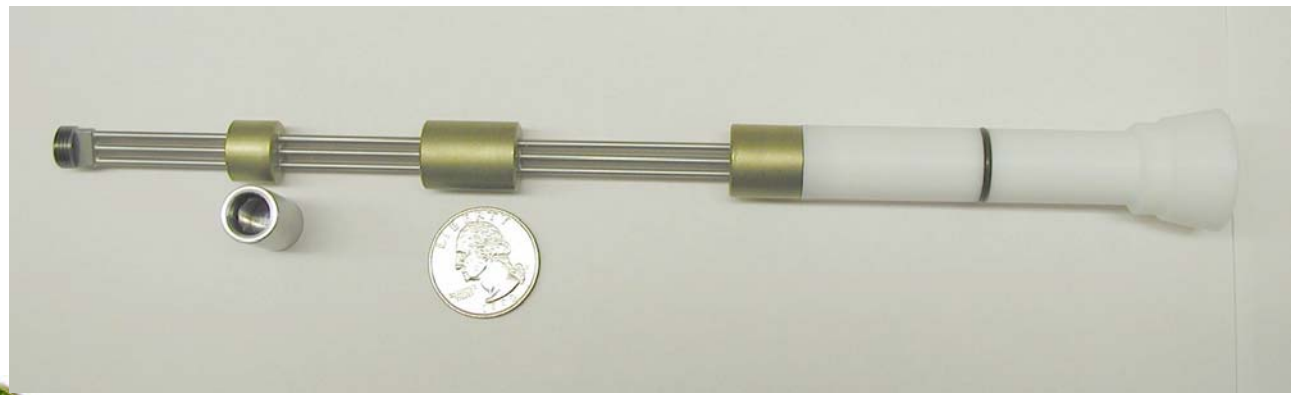


Thermodynamic Measurements

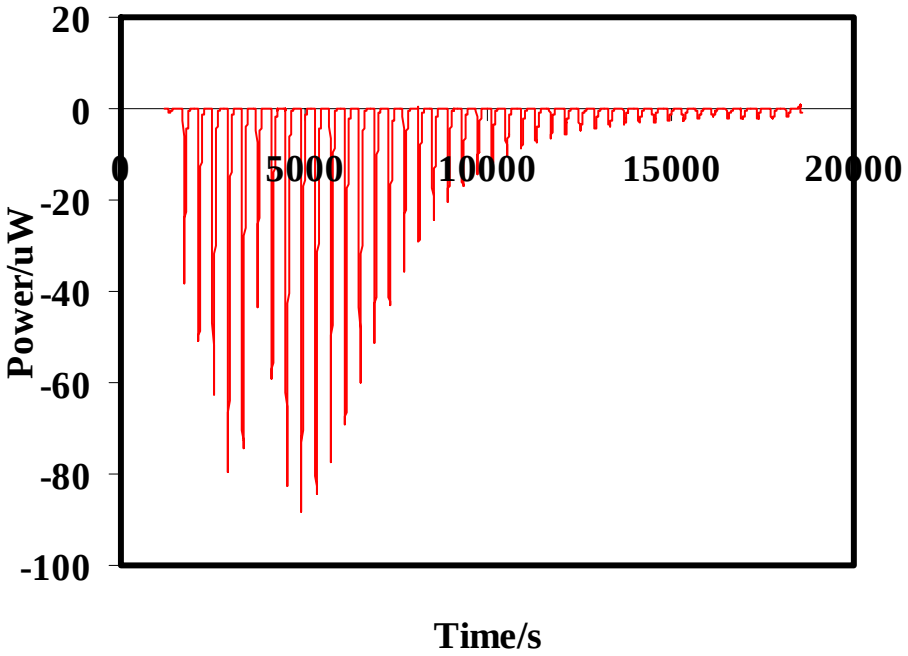


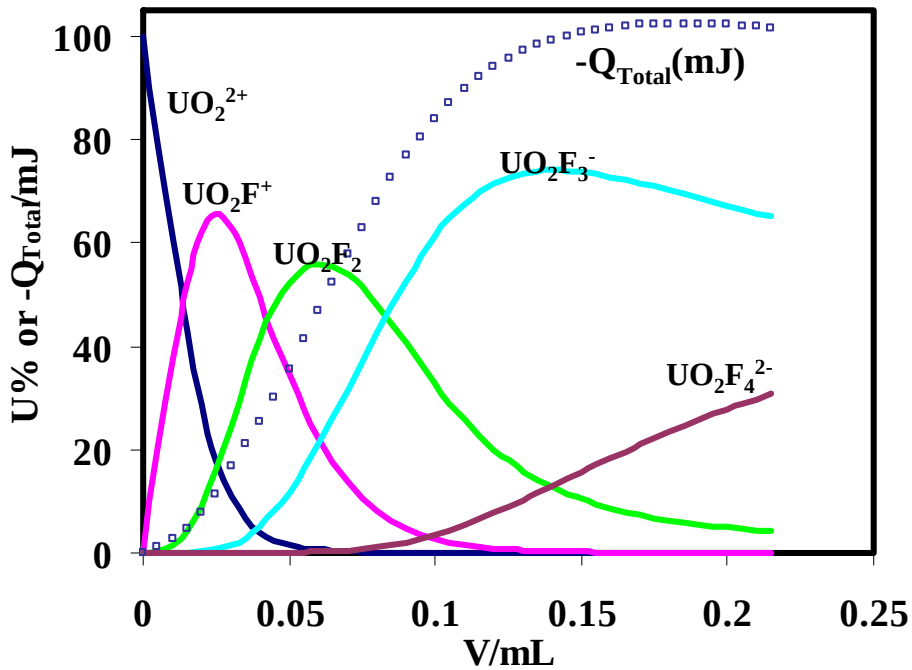
Isothermal Micro Calorimeter





Enthalpy of Complexation ($UO_2F_j^{(2-j)+}$)



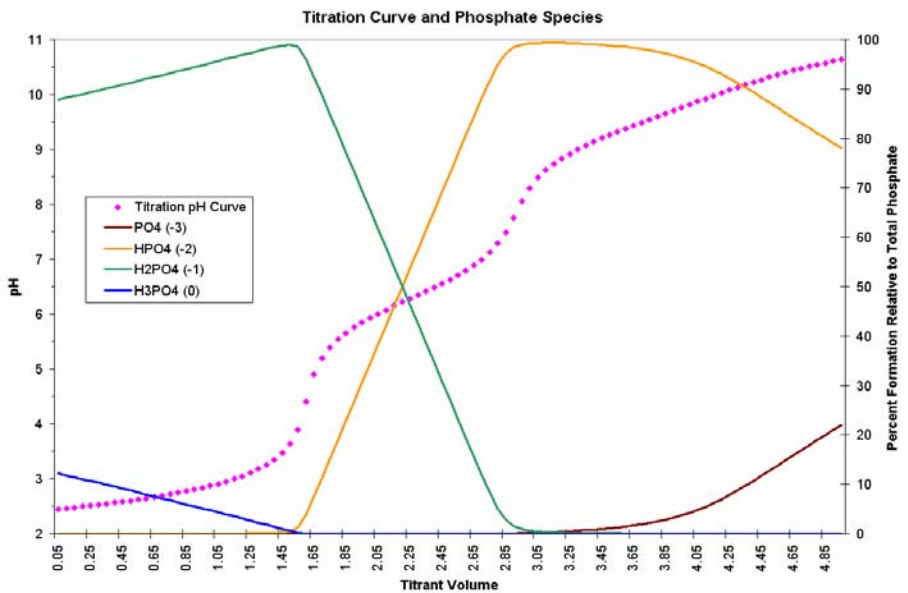


Cup: 0.900 mL 7.87/9.42 mM C_U/C_H; titrant: 0.300/0.0333 M C_F/C_H, 0.220 mL added. (left) Thermogram; (right) Total heat and speciation of U(VI) *vs.* $V_{titrant}$ (I = 1.0 M $NaClO_4$, t = 25 °C).

The Fluoride System at 25°C

Reaction	logβ	ΔH, kJ·mol^{-1}
$H^+ + F^- = HF(aq)$	2.93 *	12.0 ± 0.1
$NpO_2^+ + F^- = NpO_2F(aq)$	1.25 ± 0.01	8.1 ± 0.1
$NpO_2^+ + 2F^- = NpO_2F_2^-$	1.77 ± 0.01	19.2 ± 0.3
$UO_2^{2+} + F^- = UO_2F^+$	4.82 ± 0.01	2.4 ± 0.1
$UO_2^{2+} + 2F^- = UO_2F_2(aq)$	8.47 ± 0.02	5.5 ± 0.2
$UO_2^{2+} + 3F^- = UO_2F_3^-$	11.29 ± 0.02	2.4 ± 0.3
$UO_2^{2+} + 4F^- = UO_2F_4^{2-}$	12.59 ± 0.02	-1.6 ± 0.9

Potentiometric Titrations



Potentiometric Data

	Measured value in 1M $NaClO_4$		Literature value corrected to 1M $NaClO_4$ using SIT	
Equation	**Log K**	**±**	**Log K**	**±**
$H^+ + PO_4^{3-} = HPO_4^{2-}$	11.21	0.15	11.14	0.06
$2H^+ + PO_4^{3-} = H_2PO_4^-$	17.44	0.15	17.6	0.04
$3H^+ + PO_4^{3-} = H_3PO_4$	19.07	0.24	19.39	0.06

Equation	**Log K**	**±**	**Log K**	**±**
$H^+ + F^- = HF$	2.97	0.02	2.93	
$H^+ + 2F^- = HF_2^-$	3.93	0.06	3.66	0.15

Solvent Extraction

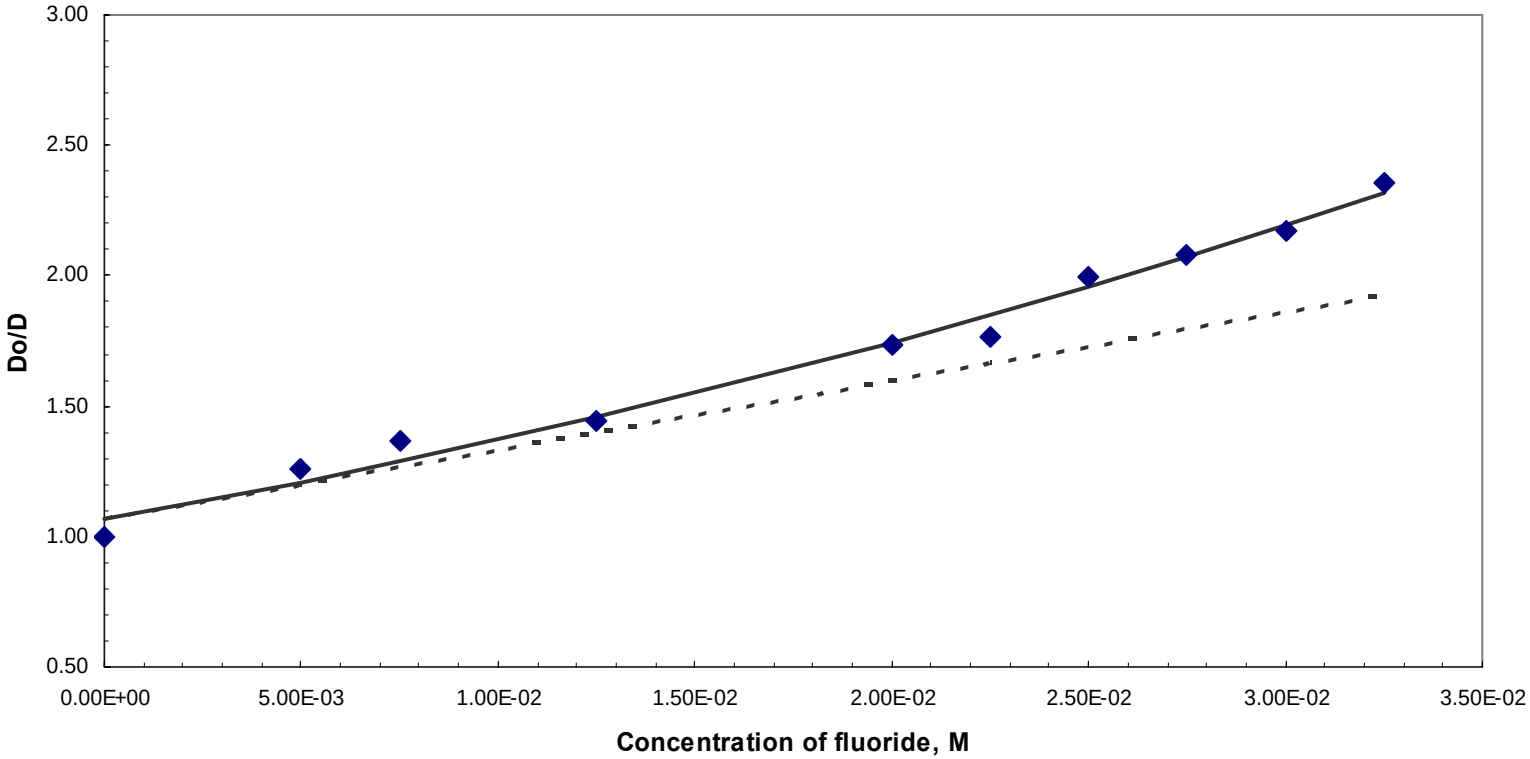


Fig.1. Extraction of Np(V) by 0.01 M HDEHP in heptane at pcH 5.0 and 24°C from 1.0 M $NaClO_4$. The solid line represents the contributions of both NpO_2F and $NpO_2F_2^-$ complexes, while the dashed line represents the contribution of only NpO_2F

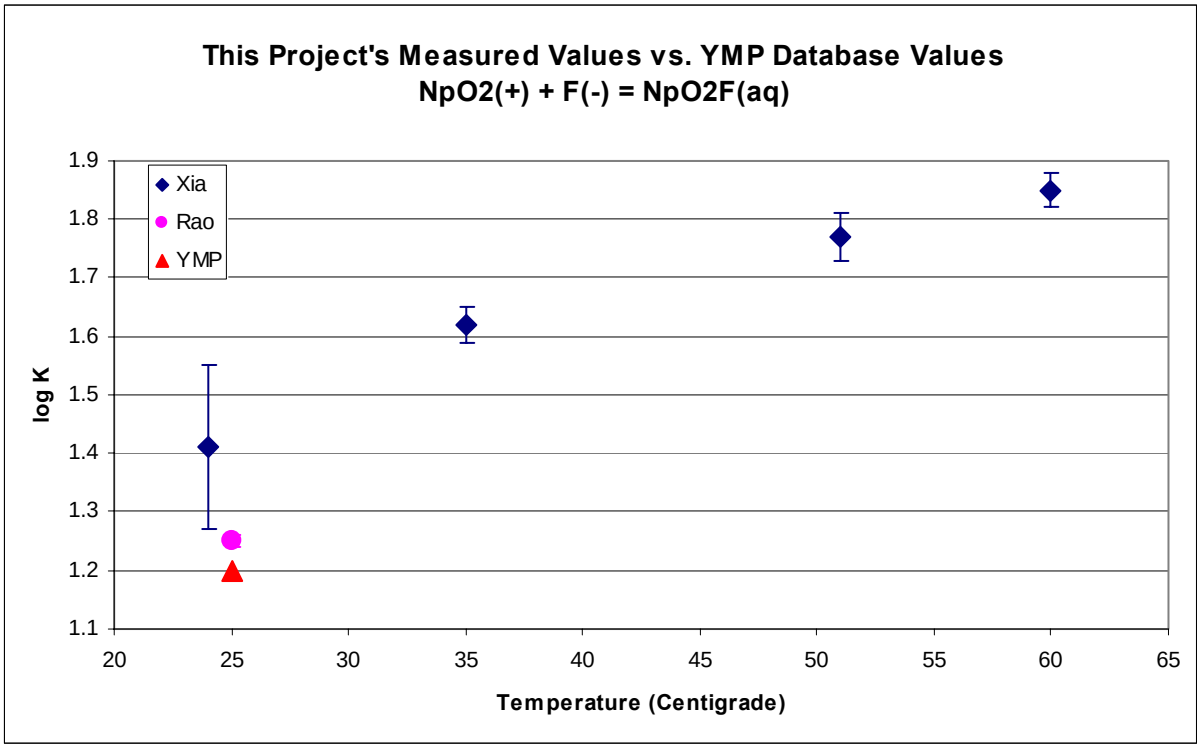
Stability Constants of Monofluoro Complexes of Np(V)

Table 1. Stability constants of Np(V) with fluoride ($NpO2^{+} + F^{-} = NpO_2F$)

Method	Ionic medium	t (^{0}C)	log β_1	Reference
sp	2 M NaClO4	25	(1.35 ± 0.30)	[78RAO/PAT]
dis	2 M NaClO4	25	(0.99 ± 0.10)	[79RAO/GUD]
dis	1 M NaClO4	23	(1.26 ± 0.30)	[84CHO/RAO]
dis	1 M NaClO4	25	(1.39 ± 0.30)	[85INO/TOC2]
ise-F-	0.1 M NaClO4	21	(1.51 ± 0.50)	[85SAW/RIZ]
	1 M NaClO4		(1.15 ± 0.80)	
dis	1 M NaClO4	24	(1.41 ± 0.14)	[this work]
dis	1 M NaClO4	35	(1.62 ± 0.03)	[this work]
dis	1 M NaClO4	51	(1.77 ± 0.04)	[this work]
dis	1 M NaClO4	60	(1.85 ± 0.03)	[this work]

Note: sp- spectrophotometric; dis- solvent extraction; ise-F^--potentiometric.

Neptunium Fluoride System



YMP data point from Data0.ymp.r2