



U.S. Department of Energy
Office of Civilian Radioactive Waste Management



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



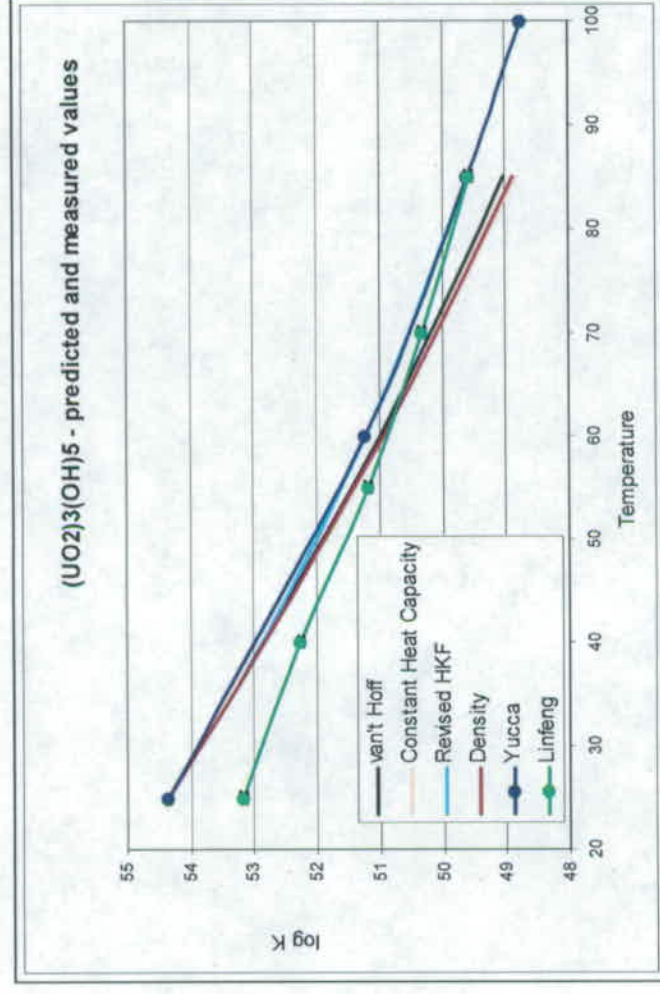
Current Thermodynamic Database

- 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



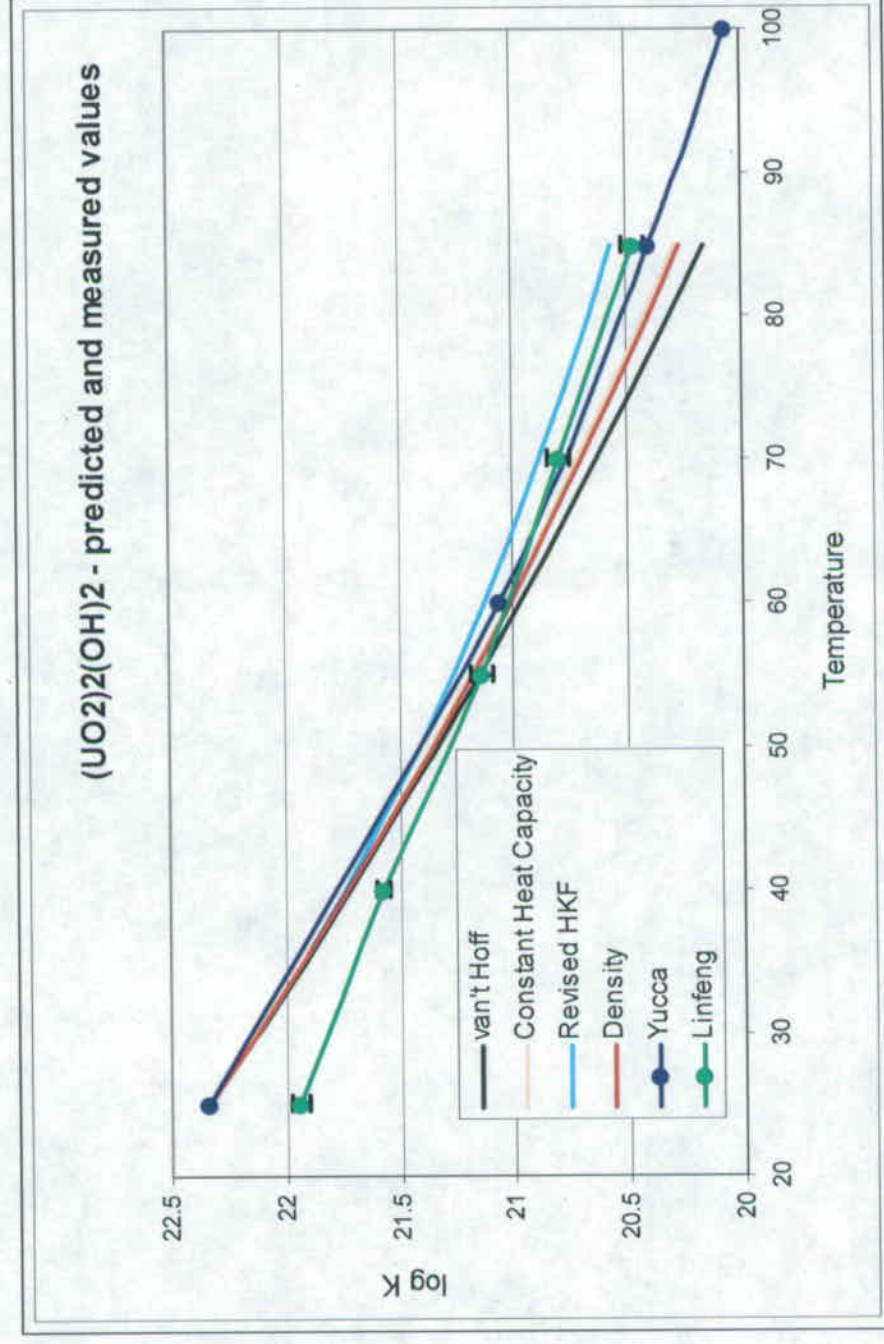
Temperature Extrapolation Methods

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

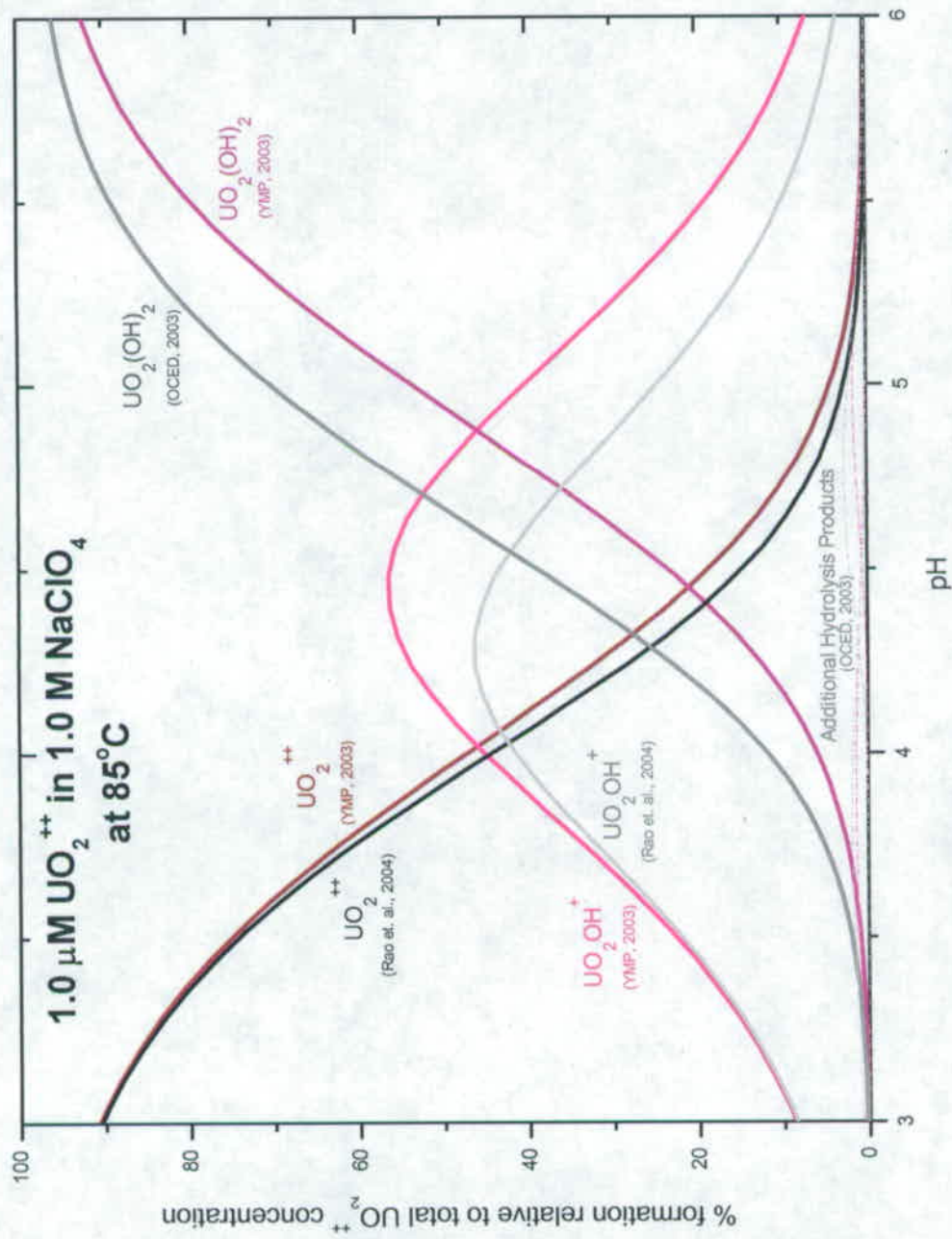


Temperature Extrapolation Methods

- Uranium hydrolysis 2:2 constants



Uranium Hydrolysis 85°C Speciation Plot



Thermodynamic Measurements

<i>Technique</i>	<i>Measured properties</i>	<i>Scientific information</i>
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Calorimetry → **Q** → ΔH^0 → ΔC_p^0
(LBNL)

Potentiometry

Spectroscopy

Distribution methods

Solubility measurements

(PNNL)

K → ΔG^0

ΔS^0

-T effect

-Nature of complex

-Solvent effect

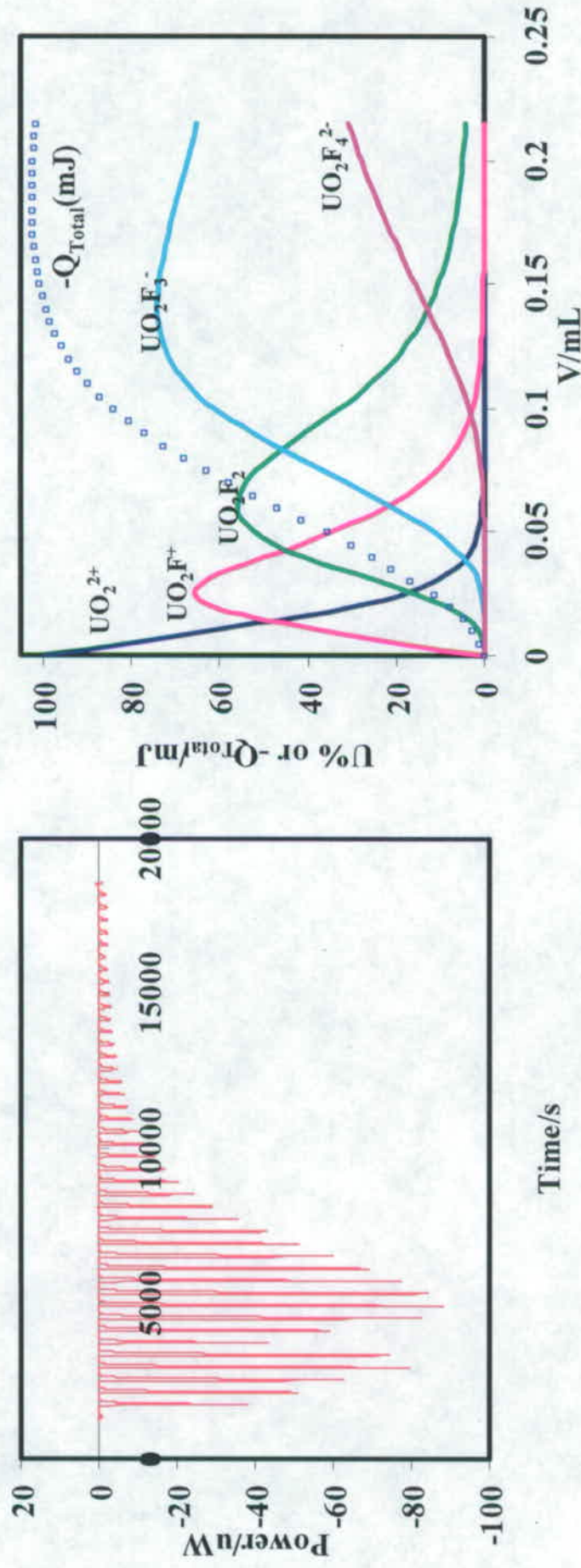
effect



Isothermal Micro Calorimeter



Enthalpy of Complexation ($\text{UO}_2\text{F}_j^{(2-j)+}$)



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 , $t = 25^\circ\text{C}$).

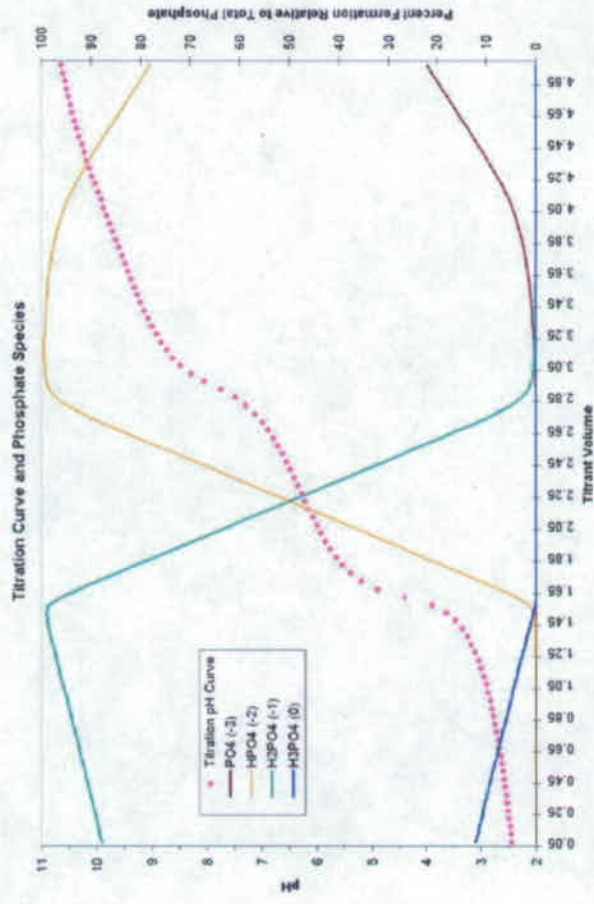


The Fluoride System at 25°C

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



Potentiometric Titrations



Potentiometric Data

Equation	Measured value in 1M NaClO ₄		Literature value corrected to 1M NaClO ₄ using SIT	
	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	
	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

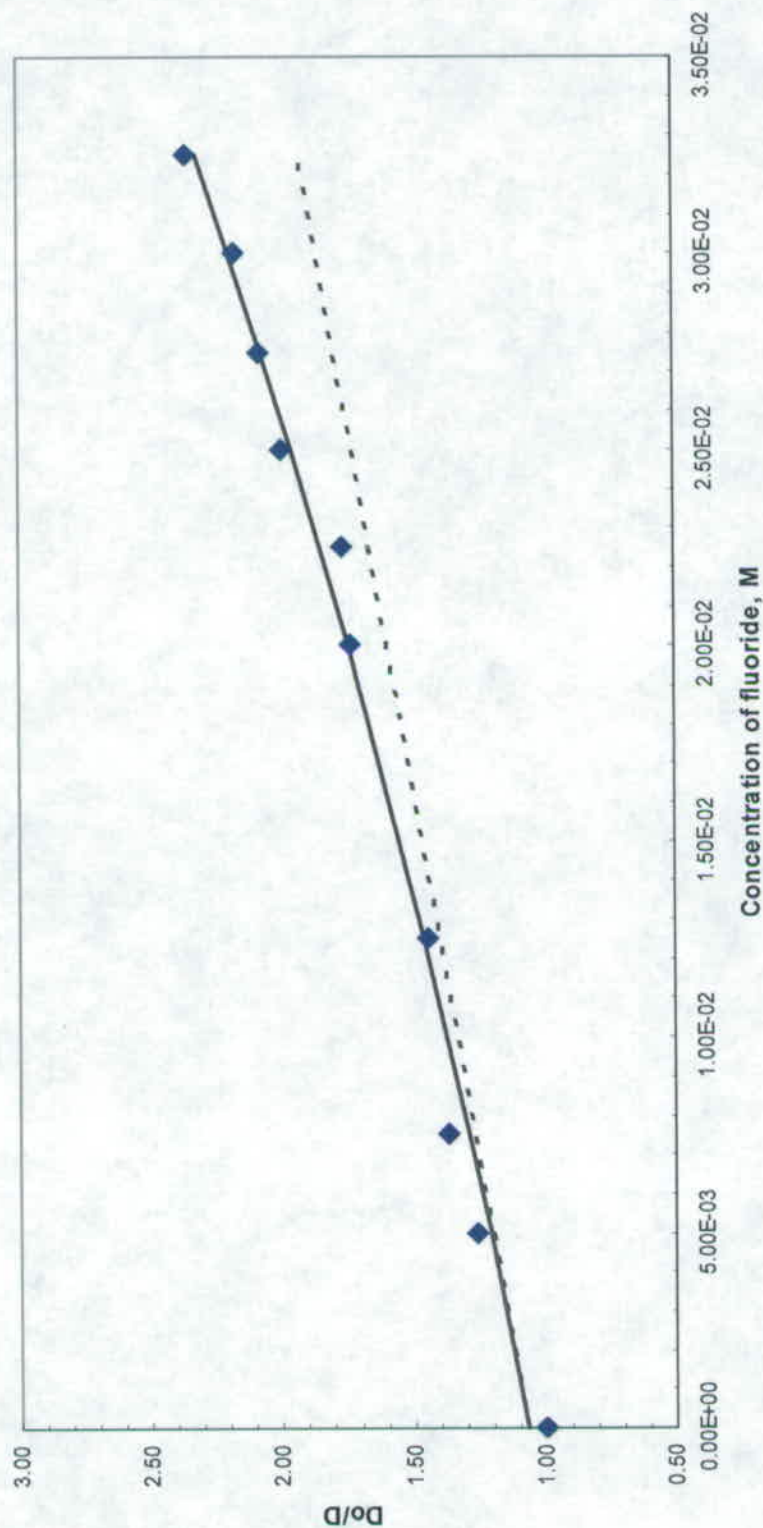


Fig.1. Extraction of Np(V) by 0.01 M HDEHP in heptane at pH 5.0 and 24°C from 1.0 M NaClO_4 . The solid line represents the contributions of both NpO_2F^+ and NpO_2F_2^- complexes, while the dashed line represents the contribution of only NpO_2F^+ .



Stability Constants of Monofluoro Complexes of Np(V)

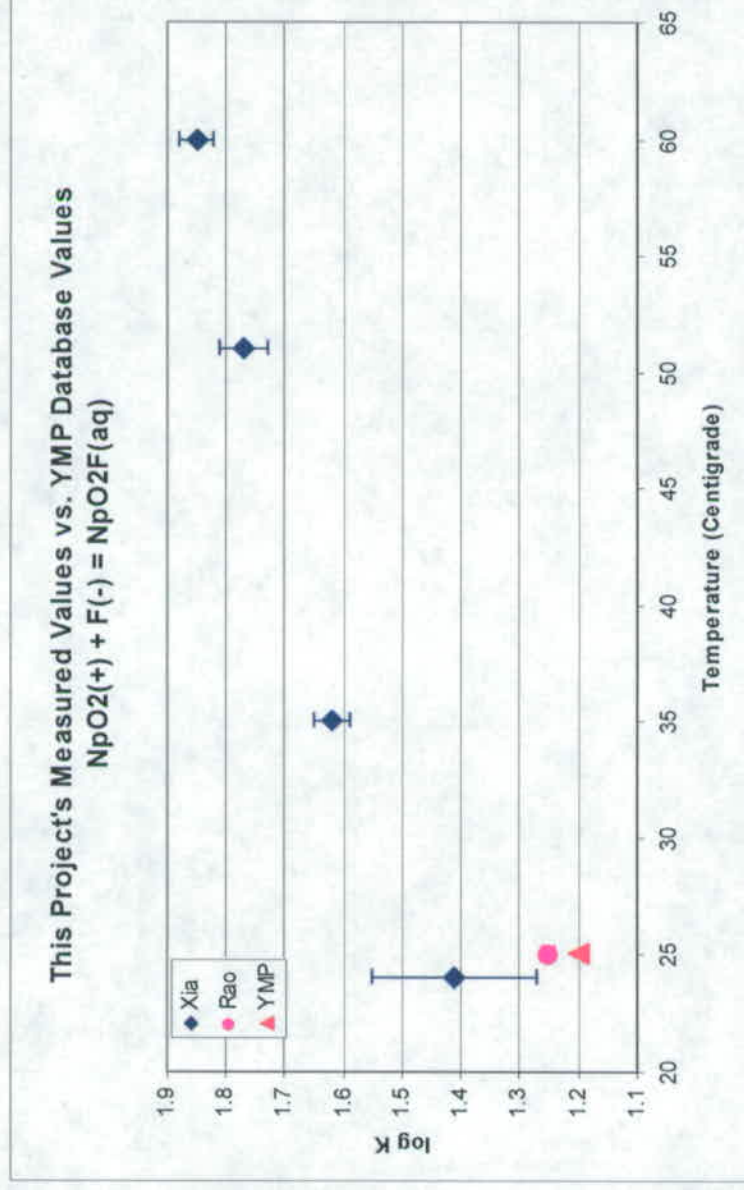
Table 1. Stability constants of Np(V) with fluoride
($\text{NpO}_2^{2+} + \text{F}^- = \text{NpO}_2\text{F}$)

Method	Ionic medium	t (°C)	log β_1	Reference
sp	2 M NaClO ₄	25	(1.35 ± 0.30)	[78RAO/PAT]
dis	2 M NaClO ₄	25	(0.99 ± 0.10)	[79RAO/GUD]
dis	1 M NaClO ₄	23	(1.26 ± 0.30)	[84CHO/RAO]
dis	1 M NaClO ₄	25	(1.39 ± 0.30)	[85INO/TOC2]
ise-F-	0.1 M NaClO ₄	21	(1.51 ± 0.50)	[85SAW/RIZ]
	1 M NaClO ₄		(1.15 ± 0.80)	
dis	1 M NaClO ₄	24	(1.41 ± 0.14)	[this work]
dis	1 M NaClO ₄	35	(1.62 ± 0.03)	[this work]
dis	1 M NaClO ₄	51	(1.77 ± 0.04)	[this work]
dis	1 M NaClO ₄	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

