

Appendix D

The Gibbs energy minimisation and optimisation program, NONLINT-SIT

D.1 Introduction

A SIT fitting code, NONLINT-SIT (Personal communication, September 2004. A. R. Felmy, Pacific Northwest National Laboratory, Richland, WA, USA), was used in some systems to optimise $\Delta_f G_m^\circ / RT$ values of different solid and aqueous species and SIT ion-interaction parameters, using solubility, ion-exchange, and solvent extraction data. From these, the optimised values of the different quantities can be compared with the other reported values. The program NONLINT-SIT is an extended version of the parameter optimisation programs (NONLIN and NONLINT) developed by A. R. Felmy using the MINPACK nonlinear least-squares programs, in conjunction with a Gibbs energy minimisation program (GMIN, [1990FEL] and [1995FEL]). The mathematical development of the latter is based on the formulations described in [1981HAR], [1987HAR/GRE] and [1985GRE/WEA]. GMIN and NONLIN have also been the bases for the development of the related parameter optimisation code INSIGHT, [1997STE/FEL], which uses the same algorithms as NONLINT, but deals with fewer types of experimental data.

In this Appendix, no attempt will be made to present details of all the equations involved in calculations; we restrict ourselves to a very general description of the formulation of Gibbs-energy minimisation problem and the optimisation procedure, illustrated by an example. Readers interested in the details of the programs and the detailed equations involved should consult [1995FEL] and the very detailed user manual of INSIGHT, [1997STE/FEL].

The program can be used to analyse different types of experimental data (*e.g.*, solvent extraction, ion-exchange, potentiometric, solubility of pure phases, solubility of solid solutions) involving aqueous, solid, and gaseous phases at different temperatures.

The experimental data analysed in this review using the NONLINT-SIT program included solubility, solvent extraction and ion exchange measurements. Optimisation is carried out by minimising the penalty function, *viz.* the standard deviation, (σ), of the set of N experimental data points defined by:

$$\sigma^2 = \sum_{i=1}^N [\mu_i(\text{other}) - \mu_i(\text{aq})]^2 / N$$

where

- $\mu_i(\text{other})$ is the iteratively-fitted dimensionless Gibbs energy ($\Delta_f G_m^\circ / RT$) of the solid, organic phase, or exchange complex
- $\mu_i(\text{aq})$ is the dimensionless Gibbs energy calculated from the experimental aqueous phase data and the associated ion-interaction parameters (or equivalently, the chemical potential of the corresponding second phase).

The user can select different models (Pitzer, Davies, and SIT) for calculating the activity coefficients of aqueous solutions. All of the input data are user-defined. The code can be used just as a calculational tool where all of the inputs are defined and solution equilibria calculated, or as a tool to optimise values of chemical potentials for different species and/or ion-interaction parameters, based on best fits to given experimental data. Multiple data sets of a specific chemical system (*e.g.*, solubility of a solid phase) in different media can be evaluated simultaneously.

The inputs required include:

1. the analytical total concentration of the different components, *e.g.* thorium and sulphate, considered in modelling. The total concentration of a certain component is arbitrarily assigned to *one* of the species considered in the chemical model tested, *e.g.* Th^{4+} or $\text{Th}(\text{SO}_4)^{2+}$. The program then automatically calculates the speciation, that is the actual concentrations of all the species based on the modelling parameters (equilibrium constants and total concentrations of all components).
2. dimensionless Gibbs energies of formation ($\Delta_f G_m^\circ / RT$) of all of the species,
3. ion-interaction parameters, and
4. indication of the parameters to be varied.

The outputs include:

1. the new values of the parameters,
2. the molalities and activities of all of the species considered in modelling, based on the defined aqueous phase model,
3. the calculated differences in chemical potentials $[(\Delta_f G_m / RT)_{\text{predicted}}] - (\Delta_f G_m / RT)_{\text{experimental}}$ for each data point, where $(\Delta_f G_m / RT)_{\text{predicted}}$ is the fitted/predicted chemical potential of the solid phase and $(\Delta_f G_m / RT)_{\text{experimental}}$ is the value calculated by the program for the aqueous phase from the experimental

data (or equivalently also the chemical potential of the solid phase). From the fitted chemical potentials the user can calculate the corresponding equilibrium constants.

4. the standard deviation (one sigma) in the predicted and experimental chemical potentials for the entire data set, and from these the uncertainties in the various equilibrium constants (the uncertainties quoted in text and appendices are two sigma).
5. In addition one can obtain the molalities and activities of all of the species in accordance with the aqueous phase model and in equilibrium with the solid phase or the other phases involved (solid, organic or ion exchanger).

D.2 Uncertainties in NONLINT-SIT calculations

There are three different types of uncertainties: those based in 1) the experimental data, 2) the ion-interaction parameters used in the SIT model, and 3) the Gibbs energies of the species which are not optimised. These uncertainties are briefly discussed below.

D.2.1 Uncertainties in experimental data

The NONLINT-SIT program has been used to interpret the available experimental data in order to find the “best” chemical model, including the most important species and their equilibrium constants based on the fixed values of the Gibbs energies of other participating species and values of the ion-interaction parameters. The latter were only varied in the optimisation in a few cases. The program provides uncertainty values for the fitted equilibrium constants based solely on the uncertainties in the experimental data. These are the values reported in the text of the review.

D.2.2 Accounting for uncertainties in ion-interaction parameters

The uncertainty values quoted from NONLINT-SIT calculations are based on the average values of the selected interaction parameters, but without taking into consideration their uncertainty. The most rigorous method of determining how these errors influence the uncertainty in $\Delta_f G_m^o / RT$ of the different species and the equilibrium constants of the different reactions would be to describe the error in interaction parameters with a probability distribution function and then make a large number of Monte Carlo samplings to calculate $\Delta_f G_m^o / RT$ values. The average of these and their associated statistical uncertainty would provide the effects of uncertainties in the interaction parameters. Such calculations are time consuming and beyond the scope of this review. Thus for the uncertainties values quoted from the NONLINT-SIT calculations this review has not been able to implement strictly the procedures implied in Appendix C. However, to estimate the maximum effects of the interaction uncertainties for a few important species/reactions in the sulphate system, this review has made sample NONLINT-SIT calculations using maximum and minimum values for all interaction parameters.

The calculated uncertainties in $\Delta_f G_m^\circ / RT$ will increase with the uncertainty in the interaction parameters and with increasing ionic strength. We have used the studies of [1963ALL/MCD] and the solubility investigations of many sulphate solids (see Section IX.1.3.3) to explore this effect, because the chemical system is simple, with $\text{Th}(\text{SO}_4)_3^{2-}$ as the dominant species. The solvent extraction data of [1963ALL/MCD], where the ionic strength varies from a very low value up to 4.5 m, were used as a first test of the impact of uncertainties in interaction parameters on the fitted values of $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_3^{2-}$), as it is expected that this system will provide maximum variability in the calculated values. The values of all of the ion-interaction parameters involved in this system are listed in Table D-1 and the $\Delta_f G_m^\circ / RT$ values of all of the species considered in interpretation are listed in Table D-2. The fitted $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_3^{2-}$) value was found to be $-(1209.511 \pm 0.086)$ when maximum values of all the ion interaction parameters, based on the uncertainties reported in Table D-1, were used and $-(1209.348 \pm 0.088)$ when the minimum values were used. These compare with the value of $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_3^{2-}$) = $-(1209.432 \pm 0.086)$ found when the mean values of the ion interaction parameters were used (see Section IX.1.3.2).

The mean and uncertainty based on the mean of the maximum and minimum values are $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_3^{2-}$) = $-(1209.430 \pm 0.123)$.

Thus the optimised value is not significantly different from the value based on the mean epsilon values, but the uncertainty is slightly larger. The value including the uncertainty in the epsilon values would translate into $\log_{10} K^\circ$ (D.1) = (10.748 ± 0.053) for Reaction (D.1) as compared to $\log_{10} K^\circ$ (D.1) = (10.748 ± 0.038) based only on the mean epsilon values (Table IX-6).



Table D-1: Ion interaction parameters used in calculations involving $\text{Th}(\text{SO}_4)_3^{2-}$.

Species	SIT ion interaction parameters ($\text{kg}\cdot\text{mol}^{-1}$)		Reference
	ϵ_1	ϵ_2	
$\text{H}^+ - \text{HSO}_4^-$	0.14 ± 0.02	0.00	This review ^a
$\text{H}^+ - \text{Th}(\text{SO}_4)_3^{2-}$	-0.068 ± 0.003	0.093 ± 0.007	This review ^b
$\text{Na}^+ - \text{SO}_4^{2-}$	-0.184 ± 0.002	0.139 ± 0.006	Table B-6
$\text{Na}^+ - \text{HSO}_4^-$	-0.01 ± 0.02	0.00	Table B-5
$\text{Na}^+ - \text{Th}(\text{SO}_4)_3^{2-}$	-0.091 ± 0.038	0.00	This review ^c
$\text{Th}^{4+} - \text{HSO}_4^-$	0.70 ± 0.10	0.00	This review ^d

a: Assumed to be identical to that for $\text{H}^+ - \text{ClO}_4^-$ (Table B-4).

b: Assumed to be identical to that for $\text{Li}^+ - \text{SO}_4^{2-}$ (Table B-6).

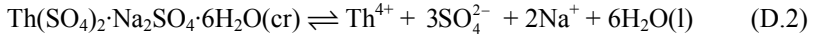
c: Based on experimental data interpretations (see Section IX.1.3.2 for details).

d: Assumed to be identical to that for $\text{Th}^{4+} - \text{ClO}_4^-$.

Table D-2: Dimensionless molar Gibbs energies of formation at 298.15 K used in calculations involving $\text{Th}(\text{SO}_4)_3^{2-}$.

Species	$\Delta_f G_m^\circ / RT$
$\text{H}_2\text{O}(\text{l})$	-95.6607
H^+	0
Na^+	-105.67
Th^{4+}	-284.305
SO_4^{2-}	-300.126
HSO_4^-	-304.689
ThSO_4^{2+}	-598.638
$\text{Th}(\text{SO}_4)_2(\text{aq})$	-906.869

In a similar fashion, the solubility data for $\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(\text{cr})$ and the parameters listed in Table D-3 and Table D-4 were used to explore how the optimised value of $\Delta_f G_m^\circ / RT$ for $\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(\text{cr})$ and the solubility product for Reaction (D.2) varied for changes in the ion interaction parameters. The fitted $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, cr) values were found to be $-(2006.078 \pm 0.460)$ when the maximum values of all of the ion interaction parameters, based on the uncertainties reported in Table D-3 were used and $-(2006.184 \pm 0.348)$ when the minimum values were used, compared with the value of $-(2006.131 \pm 0.402)$ found when the mean values of the ion interaction parameters were used (see Sections IX.1.3.3 and IX.1.3.4). The average and uncertainties based on the maximum and minimum values of ion-interaction parameters are $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$, cr) = $-(2006.131 \pm 0.577)$, where the calculated $\Delta_f G_m^\circ / RT$ is identical to that from the value based on the average epsilon values $-(2006.131 \pm 0.402)$ (Table IX-5). The uncertainty based on maximum and minimum epsilon values is slightly larger than that calculated from the average epsilon values. Thus, the calculated solubility product for Reaction (D.2) is unchanged from that reported in Table IX-6.

Table D-3: Ion interaction parameters used in calculations involving $\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(\text{cr})$.

Species	SIT ion interaction parameters ($\text{kg} \cdot \text{mol}^{-1}$)		Reference
	ϵ_1	ϵ_2	
$\text{Na}^+ - \text{SO}_4^{2-}$	-0.184 ± 0.002	0.139 ± 0.006	Table B-6
$\text{Na}^+ - \text{Th}(\text{SO}_4)_3^{2-}$	-0.091 ± 0.038	0.00	This review ^a

a: Based on experimental data interpretations (see Section IX.1.3.2 for details).

Table D-4: Dimensionless molar Gibbs free energies of formation at 298.15 K, unless otherwise identified, used in calculations involving $\text{Th}(\text{SO}_4)_2 \cdot \text{Na}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}(\text{cr})$.

Species	$\Delta_f G_m^\circ / RT$
$\text{H}_2\text{O}(\text{l})$	-96.375 ^a
H^+	0
Na^+	-105.670
Th^{4+}	-284.305
SO_4^{2-}	-300.126
HSO_4^-	-304.689
ThSO_4^{2+}	-598.638
$\text{Th}(\text{SO}_4)_2(\text{aq})$	-906.869
$\text{Th}(\text{SO}_4)_3^{2-}$	-1209.432

a: Value at 16°C.

Based on the analyses of these two cases discussed above, it is expected that the additional uncertainties in $\Delta_f G_m^\circ / RT$ of different species and in the calculated equilibrium constants due to uncertainties in the epsilon values will not be large.

D.2.3 Accounting for uncertainties in $\Delta_f G_m^\circ / RT$ values of auxiliary input data

The NONLINT-SIT and most other chemical equilibrium programs fix the chemical potential of the basal species (“master species”) of the various components (in this review the master species for thorium is always the aquo-ion, $\text{Th}^{4+}(\text{aq})$), and the chemical potentials of all other thorium species are calculated relative to these. For the example discussed in this Appendix, the values of $\Delta_f G_m^\circ / RT$ for Th^{4+} , H^+ , Na^+ , H_2O , HSO_4^- and SO_4^{2-} were fixed to the selected values given in Table D-4 and the values calculated by NONLINT-SIT for other species are referred to these values when calculating the equilibrium constant for a given reaction and its uncertainty. Note that the uncertainty in the Gibbs energy data for different species must not be included in the calculation of the equilibrium constants, because the Gibbs energies of both sides of such a reaction ‘float’ by exactly the same amount. To exemplify, we may use the results from the optimisation of the data [1963ALL/MCD] as discussed above. Based on a value of $\Delta_f G_m^\circ / RT(\text{Th}^{4+}) = -284.305$, an optimised value of $\Delta_f G_m^\circ / RT(\text{Th}(\text{SO}_4)_3^{2-}) = -(1209.432 \pm 0.086)$ was obtained. If $\Delta_f G_m^\circ / RT(\text{Th}^{4+})$ values of -282.168 or -286.442 (corresponding to the upper and lower limit of the uncertainties selected for Th^{4+}) were used, the optimised $\Delta_f G_m^\circ / RT(\text{Th}(\text{SO}_4)_3^{2-})$ values would have changed by the same amounts to $-(1207.295 \pm 0.086)$ and $-(1211.569 \pm 0.086)$. Hence the calculated value and uncertainty of $-\ln K^\circ(\text{D.1}) = -(24.749 \pm 0.086)$ would not change at all as is clear from Equation (D.3):



$$-\ln K^\circ = \Delta_f G_m^\circ / RT(\text{Th}(\text{SO}_4)_3^{2-}) - \Delta_f G_m^\circ / RT(\text{Th}^{4+}) - 3 [\Delta_f G_m^\circ / RT(\text{SO}_4^{2-})] \quad (\text{D.3})$$

In this respect, one may also regard the optimisation program as a convenient means of fitting equilibrium constants, through the formal use of equations such as (D.3).

To conclude: the derived values of $\log_{10} K^\circ$ and their associated uncertainties are based only on the aqueous phase model and the experimental data, and not on the selected values or uncertainties of the $\Delta_f G_m^\circ / RT$ values of Th^{4+} or other auxiliary species used in the modelling. This holds true for all the other cases where values of equilibrium constants are determined directly from the experimental data. NONLIN-SIT is a comprehensive program that uses ion interaction parameters and chemical potentials of all of the species expected in a given system, but it may be regarded as a method to optimise equilibrium constants, even if it operates *via* $\Delta_f G_m^\circ / RT$ values.

To avoid the disparities discussed in this Section, when analysing a system with NONLIN-SIT, this review has selected some well studied equilibrium values of $\log_{10} K^\circ$. The uncertainties associated with these $\log_{10} K^\circ$ values have been estimated from the uncertainty of the Gibbs energy of relevant reaction calculated from the combined uncertainties of $\Delta_f G_m^\circ / RT$ for the species and compounds involved in the corresponding equilibria as reported or used by NONLIN-SIT, not by following the error propagation rules for the formal calculation leading from $\Delta_f G_m^\circ$ to $\log_{10} K^\circ$. Hence the inherent uncertainties in the auxiliary data, including that of Th^{4+} , are not included in the uncertainties of the $\log_{10} K^\circ$ values.

D.3 Example: Determining the $\Delta_f G_m^\circ / RT$ value of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ from its solubility in H_2SO_4 solutions [1912BAR]

D.3.1 General equations and schematic approach to calculations

The experimental data consists of measured thorium concentrations at different given H_2SO_4 concentrations in equilibrium with $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$. The total measured aqueous thorium concentration is the sum of all the major aqueous thorium species (D.4) and the total experimental sulphate concentration is the sum of all the aqueous sulphate species (D.5).

$$m_{\text{Th, total}} = m_{\text{Th}^{4+}} + m_{\text{ThSO}_4^{2-}} + m_{\text{Th}(\text{SO}_4)_2(\text{aq})} + m_{\text{Th}(\text{SO}_4)_3^{-}} \quad (\text{D.4})$$

$$m_{\text{SO}_4^{2-}, \text{total}} = m_{\text{SO}_4^{2-}} + m_{\text{HSO}_4^{-}} + m_{\text{ThSO}_4^{2-}} + 2 m_{\text{Th}(\text{SO}_4)_2(\text{aq})} + 3 m_{\text{Th}(\text{SO}_4)_3^{-}} \quad (\text{D.5})$$

The $\Delta_f G_m^\circ / RT$ values of all the aqueous species in this system are known (Table D-6). The $\Delta_f G_m^\circ / RT$ value of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ is the unknown which we need to optimise. The NONLIN-SIT program starts out with an estimated $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$, cr) value and calculates the total $\Delta_f G_m^\circ / RT$ of the solution phase (D.6) and the concentrations and activities of all of the species defined in the problem (Table D-6). Multiple iterations with different $\Delta_f G_m^\circ / RT$ ($\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$, cr)

estimates are done in order to minimise the differences between the total chemical potential of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ ($\Delta_f G_m / RT$) and the total chemical potential of the solution phase while meeting the mass and charge balance constraints,

$$(\Delta_f G_m / RT)_{\text{solution}} = \sum_j n_j (\Delta_f G_m / RT)_j \quad (\text{D.6})$$

where n_j is the number of moles of solute and solvent species j [relevant species in this case are H_2O , H^+ , Th^{4+} , SO_4^{2-} , ThSO_4^{2+} , $\text{Th}(\text{SO}_4)_2$ and $\text{Th}(\text{SO}_4)_3^{2-}$]. On a molality basis, the $\Delta_f G_m / RT$ of different phase species is related to molalities and activity coefficients (γ) as depicted in Table D-5. For example:

$$\Delta_f G_m / RT = \Delta_f G_m^\circ / RT + \ln m_i + \ln \gamma_i$$

for solute species, where m_i is the molality of the species calculated by the program from model inputs and solution composition, and γ_i is the activity coefficients based on SIT ion-interaction parameters (for details see Appendix B).

The actual quantity minimised by NONLINT-SIT for this example is the penalty function:

$$\sigma^2 = \sum_{i=1}^N f(x)^2 / N$$

where $f(x)$ is given by the phase equilibrium condition as:

$$f(x) = [\Delta_f G_m / RT]_{\text{solid}} - [\Delta_f G_m / RT]_{\text{solution}}$$

where $[\Delta_f G_m / RT]_{\text{solution}}$ is the sum of the contributions of all the relevant species in the aqueous phase. This quantity can also be regarded as the chemical potential of the solid, calculated from the current set of parameters.

Table D-5: General equations for different phase species.

Phase	Equation
Aqueous phase	
Solvent (H_2O)	$\Delta_f G_m / RT = (\Delta_f G_m^\circ / RT) - (RT \cdot W / 1000) \left(\sum_{i=1}^{ns} m_i \right) \phi$
Solute species	$\Delta_f G_m / RT = (\Delta_f G_m^\circ / RT) + \ln m_i + \ln \gamma_i$
Pure solid phase	$\Delta_f G_m / RT = \Delta_f G_m^\circ / RT$
Solid-solution species	$\Delta_f G_m / RT = (\Delta_f G_m^\circ / RT) + \ln x_i + \ln \gamma_i$
Gaseous species	$\Delta_f G_m / RT = (\Delta_f G_m^\circ / RT) + \ln f_i$

W = molecular weight of water ($18.016 \text{ g} \cdot \text{mol}^{-1}$),

γ_i = activity coefficient of species i ,

ϕ = osmotic coefficient of the solution

x_i = mole fraction of species i ,

f_i = fugacity of species i .

D.3.2 Input data

The input $\Delta_f G_m^\circ / RT$ values are reported in Table D-6 and SIT ion-interaction parameters in Table D-7. The raw experimental data for the solubility of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ in H_2SO_4 solutions given by [1912BAR] and summarised in [1965LIN2] are listed in Table D-8. These experimental data were used to calculate the total molalities of H^+ , sulphate, and thorium, and are listed in Table D-9 as the experimental data used as a part of the input to the NONLINT-SIT program. The species used in the model were: H^+ , Th^{4+} , ThSO_4^{2+} , $\text{Th}(\text{SO}_4)_2(\text{aq})$, $\text{Th}(\text{SO}_4)_3^{2-}$, SO_4^{2-} , HSO_4^- , and $\text{H}_2\text{O}(\text{l})$. The input molalities of H^+ , Th^{4+} , and SO_4^{2-} were assigned equal to the analytical total concentrations. The input values of the other species were set to a very low value (1.0×10^{-9}).

Table D-6: Dimensionless molar Gibbs energies of formation at 25°C used in calculations.

Species	$\Delta_f G_m^\circ / RT$	Reference
$\text{H}_2\text{O}(\text{l})$	-95.661	Table VI-1
SO_4^{2-}	-300.126	Table VI-1
HSO_4^-	-304.689	Table VI-1
H^+	0.00	Table VI-1
OH^-	63.421	Table VI-1
Th^{4+}	-284.305	This Review
ThSO_4^{2+}	-598.638 ± 0.737	This Review
$\text{Th}(\text{SO}_4)_2(\text{aq})$	-906.869 ± 0.622	This Review
$\text{Th}(\text{SO}_4)_3^{2-}$	-1209.432 ± 0.086	This Review
	-1745.5	Estimated, input ^a
$\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}$	-1771.410 ± 0.232	Optimised value

a: Sum of $\Delta_f G_m^\circ / RT$ values of constituent species.

Table D-7: SIT ion interaction parameters used in calculations.

Species	Ion interaction coefficients ($\text{kg} \cdot \text{mol}^{-1}$)		References
	ϵ_1	ϵ_2	
$\text{H}^+ - \text{Th}(\text{SO}_4)_3^{2-}$	-0.068 ± 0.003	0.093 ± 0.007	This review ^a
$\text{Th}^{4+} - \text{HSO}_4^-$	0.70 ± 0.10	0.00	This review ^b
$\text{H}^+ - \text{HSO}_4^-$	0.14 ± 0.02	0.00	This review ^c

a: It is assumed that the values for $\text{Li}^+ - \text{SO}_4^{2-}$ (Table B-6) are applicable to this interaction.

b: It is assumed that the values for $\text{Th}^{4+} - \text{ClO}_4^-$ (this review) are applicable to this interaction.

c: It is assumed that the values for $\text{H}^+ - \text{ClO}_4^-$ (Table B-4) are applicable to this interaction.

Table D-8: The solubility of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ in aqueous solutions of sulphuric acid [1912BAR].

Concentrations (g per 100 g H_2O)		Molarities ^a	
H_2SO_4	Total Th	H_2SO_4	Total Th
0.00	1.722	0.000	0.041
1.072	1.919	0.109	0.045
1.941	2.017	0.198	0.047
2.821	2.060	0.288	0.0486
3.843	2.061	0.392	0.0486
5.212	2.035	0.532	0.0480

a: Calculated from columns 1 and 2.

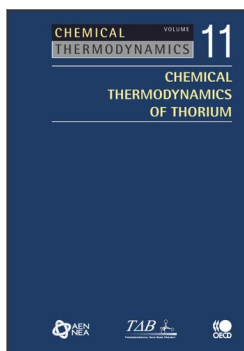
D.3.3 Outputs

An optimised value of $\Delta_f G_m^\circ / RT = -(1771.410 \pm 0.232)$ was obtained for $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$. Using this fitted value and other inputs (chemical potentials, ion-interaction parameters, and analytical molalities of different species) described above, the program calculates:

1. the equilibrium aqueous concentrations for all of the species included in the model, as listed in Table D-9 and plotted in Figure IX-6,
2. the uncertainty (0.232, two sigma) for the optimised parameter from the data set used in these calculations. The fitted $\Delta_f G_m^\circ / RT$ value of $-(1771.410 \pm 0.232)$ for $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ when combined with the $\Delta_f G_m^\circ / RT$ values of other species given in Table D-6 gives a $\log_{10} K^\circ$ value of $-(11.250 \pm 0.096)$ for the following solubility reaction:

Table D-9: Experimental [1912BAR] and predicted concentrations for the solubility of $\text{Th}(\text{SO}_4)_2 \cdot 9\text{H}_2\text{O}(\text{cr})$ in H_2SO_4 solutions.

Experimental data			Predicted concentrations							
Concentrations of species (m)			Concentrations of species (m)							
H^+	Total SO_4^{2-}	Total Th	Total Th	Th^{4+}	ThSO_4^{2+}	$\text{Th}(\text{SO}_4)_2\text{aq}$	$\text{Th}(\text{SO}_4)_3^{2-}$	SO_4^{2-}	HSO_4^-	H^+
$1.000 \cdot 10^{-9}$	$8.200 \cdot 10^{-2}$	$4.100 \cdot 10^{-2}$	$3.515 \cdot 10^{-2}$	$9.393 \cdot 10^{-6}$	$5.979 \cdot 10^{-3}$	$2.772 \cdot 10^{-2}$	$1.445 \cdot 10^{-3}$	$4.553 \cdot 10^{-3}$	$3.897 \cdot 10^{-10}$	$1.610 \cdot 10^{-9}$
0.220	$2.000 \cdot 10^{-1}$	$4.500 \cdot 10^{-2}$	$4.072 \cdot 10^{-2}$	$1.490 \cdot 10^{-5}$	$4.396 \cdot 10^{-3}$	$2.867 \cdot 10^{-2}$	$7.636 \cdot 10^{-3}$	$2.229 \cdot 10^{-2}$	$8.450 \cdot 10^{-2}$	$1.355 \cdot 10^{-1}$
0.440	$2.940 \cdot 10^{-1}$	$4.700 \cdot 10^{-2}$	$4.508 \cdot 10^{-2}$	$2.247 \cdot 10^{-5}$	$4.840 \cdot 10^{-3}$	$2.941 \cdot 10^{-2}$	$1.081 \cdot 10^{-2}$	$3.013 \cdot 10^{-2}$	$1.639 \cdot 10^{-1}$	$2.361 \cdot 10^{-1}$
0.580	$3.870 \cdot 10^{-1}$	$4.860 \cdot 10^{-2}$	$4.900 \cdot 10^{-2}$	$2.927 \cdot 10^{-5}$	$5.282 \cdot 10^{-3}$	$3.015 \cdot 10^{-2}$	$1.354 \cdot 10^{-2}$	$3.620 \cdot 10^{-2}$	$2.454 \cdot 10^{-1}$	$3.346 \cdot 10^{-1}$
0.780	$4.870 \cdot 10^{-1}$	$4.860 \cdot 10^{-2}$	$5.310 \cdot 10^{-2}$	$3.551 \cdot 10^{-5}$	$5.743 \cdot 10^{-3}$	$3.099 \cdot 10^{-2}$	$1.633 \cdot 10^{-2}$	$4.186 \cdot 10^{-2}$	$3.374 \cdot 10^{-1}$	$4.426 \cdot 10^{-1}$
1.060	$6.260 \cdot 10^{-1}$	$4.800 \cdot 10^{-2}$	$5.855 \cdot 10^{-2}$	$4.189 \cdot 10^{-5}$	$6.351 \cdot 10^{-3}$	$3.217 \cdot 10^{-2}$	$1.999 \cdot 10^{-2}$	$4.856 \cdot 10^{-2}$	$4.679 \cdot 10^{-1}$	$5.921 \cdot 10^{-1}$



From:
Chemical Thermodynamics of Thorium, Volume 11

Access the complete publication at:
<https://doi.org/10.1787/9789264056688-en>

Please cite this chapter as:

OECD/Nuclear Energy Agency (2008), "Appendix D: The Gibbs energy minimisation and optimisation program, NONLINT-SIT", in *Chemical Thermodynamics of Thorium, Volume 11*, OECD Publishing, Paris.

DOI: <https://doi.org/10.1787/9789264056688-17-en>

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