The thermodynamics of uranium salts and their hydrates – Estimating thermodynamic properties for nuclear and other actinoid materials using the Thermodynamic Difference Rule (TDR).

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Abstract

A comprehensive thermodynamic database of experimental standard enthalpy of formation, $\Delta_f H^o$ values, standard free energies of formation, $\Delta_f G^o$ and standard entropies, S^o_{298} for uranium salts and their hydrates at 298K and 1 bar pressure is assembled. For many of these materials there exist experimental uncertainties or else multiple values (often considerably different) are listed for the same material. The aim of this paper is to showcase the ability of the Thermodynamic Difference Rule (TDR) to provide quite accurate estimates of such data (usually errors are less than 1 %) and to provide guidance as to the most trusted value to adopt. In addition, where possible the TDR has been used to estimate missing literature values. 23 new thermochemical data values are predicted and TDR is not reliant on possession of knowledge of crystal structures.

Keywords: Thermodynamic difference rule; uranium (IV) salts; hydrates; actinoid;

1.   Introduction

The production of nuclear energy often involves a number of essentially chemical problems the solution of which may depend upon the thermodynamic analysis of an appropriate chemical interaction. The prediction of required reactor conditions can also demand a detailed knowledge of the thermodynamic properties of the nuclear fuels. Furthermore the reactions themselves can be thermochemically extremely complex, often requiring corrections to adjust for impurities present etc. This makes the TDR an ideal method to provide a ready means of providing an alternative assessment of much of the data.

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In order to provide tools for reactor engineers and physical chemists, critically evaluated compilations of thermodynamic data for uranium and other materials have, periodically, been assembled by the International Atomic Energy Agency in Vienna. This data coupled with a current literature survey of standard enthalpy of formation, $\Delta_f H^o$, free energy of formation, $\Delta_f G^o$ and standard entropy, S^o_{298} data provides the, sometimes conflicting, data given in the Appendix Tables for the listed uranium compounds.

Whilst all uranium compounds are radioactive, only a handful are involved in nuclear reactions.

However for all of them calorimetric measurements of their standard thermodynamic parameters can only be performed in specialised laboratories and can often involve complex adjustments when working up the data as is illustrated below. Possession of a suitable predictive tool such as the TDR available, which is facile to employ and which furnishes reliable estimates of thermochemical quantities is especially valuable for such compounds and is used in this paper to estimate unknown thermochemical parameters and also to help identify most trusted values. These latter values are identified in the appended tables and are indicated using Clarendon bold-faced) type.

 All thermochemical data considered in this paper refer to standard conditions (298K and 1 bar pressure). It is worth noting here that the TDR is capable of providing estimates for data at temperatures other than 298K with a precision comparable to that found in this work and this is the subject of a forthcoming paper.

1.1   The Thermodynamic Difference Rule (TDR) for Inorganic Hydrates.

A hydrate is defined as a material with formula $M_p X_q . n H_2 O$ which is derived, in turn, from an inorganic "parent" (unhydrated) compound of formula $M_p X_q$ for which n = 0.

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The TDR [1 – 7] is extremely powerful in its ability to estimate thermodynamic data in the absence of experimental data as a best estimate approximation. In its standard form it is represented by the equation:

$$[\Delta P(M_pX_q.nH_2O,s) - \Delta P(M_pX_q,s)] \approx n\Theta_P(H_2O, s\text{--}s) \qquad (1)$$

where $\Theta_P(H_2O, s\text{--}s)$ is a constant with s-s indicating that the hydrate and parent are both in their solid states indicated by s. $\Delta P(M_pX_q.nH_2O,s)$ is the thermodynamic property of the hydrate and $\Delta P(M_pX_q,s)$ the same thermodynamic property of the anhydrous "parent" material, whilst ΔP can be $\Delta_f H^o$/kJ mol^{-1}, $\Delta_f G^o$/kJ mol^{-1}, S^o_{298}/J K^{-1} mol^{-1}, $C_p^{\,o}$/J K^{-1} mol^{-1} *etc.* n is the number of water molecules possessed by the hydrate. Thus, for enthalpy of formation, in kJ mol^{-1}, of the inorganic hexahydrate of zinc sulfate, $ZnSO_4.6H_2O$ the rule takes the specific form:

$$[\Delta_f H^o(ZnSO_4.6H_2O,s) - \Delta_f H^o(ZnSO_4,s)]/\text{kJ mol}^{-1} \approx 6\Theta_{Hf}(H_2O, s\text{--}s) \qquad (2)$$

The rule can be applied to wide ranges of compounds so, for example, for the enthalpy of formation of 'parent' compound' uranium trioxide, UO_3, the enthalpy of formation, kJ mol^{-1}, corresponding dihydrate, $UO_3.2H_2O$ obeys the rule in the form:

$$[\Delta_f H^o(UO_3.2H_2O,s) - \Delta_f H^o(UO_3,s)] \approx 2\Theta_{Hf}(H_2O, s\text{--}s) \qquad (3)$$

The value of $\Theta_{Hf}(H_2O, s\text{--}s)$ is identical in magnitude in equations (2) and (3) and indeed for all similar expressions involving $\Delta_f H^o$ values.

1.2   The Key Features of the Difference Rule.

The key features of the Thermodynamic Difference Rule [1-7] are that:

- Equation (1) applies whenever ΔP represents *any* standard thermodynamic property, which can extend to the standard enthalpy of formation, $\Delta_f H^o$/kJ mol^{-1}, free energy of formation, $\Delta_f G^o$/kJ mol^{-1}, standard entropy of formation, $\Delta_f S^o$/J K^{-1} mol^{-1}, standard

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entropy, S_{298}^{o}/J K^{-1} mol^{-1}, heat capacity, C_p^{o}/J K^{-1} mol^{-1}, lattice energy, U_{POT}/kJ mol^{-1}, formula unit volume, V_m/nm^3 etc.;

- It works for *any* hydrate, $M_pX_q.nH_2O$ irrespective of the nature of M_pX_q whilst retaining the same constant value of $\Theta_P(H_2O$, s–s) in respect of thermodynamic property, *P*;

- It also works for any solvate that is non-aqueous, e.g. $M_pX_q.nNH_3$ or $M_pX_q.nSO_2$ where the solvate replaces the water;

- It works for *any* value of n, the number of water molecules within the hydrate;

- n need not be an exact integer;

- The value of $\Theta_P(H_2O$, s–s) remains constant throughout for all hydrates independent of the value of *n*, being dependent *only* on the thermodynamic property, *P*, which is being studied - irrespective of the nature of the inorganic component involved (see Table 1). Thus $\Theta_P(H_2O$, s–s) has the same constant value in the Difference Rule equation (1) in accordance with Table 1;

- A great strength of the TDR approach is that it is not concerned with the absence of structural information;

- The values for $\Theta_P(H_2O$, s–s) for individual properties are listed in Table 1.

< Table 1 about here >

Table 1. Values for Difference Rule constants, $\Theta_P(H_2O$, s–s) Jenkins and Glasser [1] corresponding to thermodynamic property, ΔP, appropriate for any material and for use in equations of types (1), (2) and (3).

ΔP	$\Delta_f H^o$	$\Delta_f G^o$	$S^o{}_{298}$
$\Theta_P(H_2O$, s–s)	-299 ± 11 kJ mol^{-1}	-242 ± 10 kJ mol^{-1}	41 ± 7 J K^{-1} mol^{-1}

1.3   General Generation of Data using the TDR.

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The TDR is capable of estimating thermodynamic data for any hydrate for which ΔP is known for its parent or vice-versa for any parent given possession of a value for *at least one* of its hydrates. Further consider two different inorganic compounds, A_pB_q and C_rD_s, and suppose that the thermodynamic value of $\Delta P(A_pB_q,s)$ is known for compound A_pB_q and that a value for $\Delta P(A_pB_q.mH_2O,s)$ for the hydrate, $A_pB_q.mH_2O$ is sought. We have for the n hydrate of a completely different compound, $C_rD_s.nH_2O$ (which could be a different actinoid material):

$$\Delta P(C_rD_s.nH_2O,s) - \Delta P(C_rD_s,s) \approx n.\Theta_P(H_2O, s–s) \quad (4)$$

Also for the n hydrate of $A_pB_q.nH_2O$:

$$\Delta P(A_pB_q.nH_2O,s) - \Delta P(A_pB_q,s) \approx n.\Theta_P(H_2O, s–s) \quad (5)$$

so that, since the right hand sides of equations (4) and (5) are identical :

$$\Delta P(C_rD_s.nH_2O,s) - \Delta P(C_rD_s,s) \approx \Delta P(A_pB_q.nH_2O,s) - \Delta P(A_pB_q,s) \quad (6)$$

and hence, for the *m* hydrate, $A_pB_q.mH_2O$:

$$\Delta P(A_pB_q.mH_2O,s) \approx \Delta P(C_rD_s.mH_2O,s) - \Delta P(C_rD_s,s) + \Delta P(A_pB_q,s) \quad (7)$$

In a similar way, possession of a single thermodynamic property for a hydrate, $\Delta P(A_pB_q.mH_2O,s)$ can lead to the estimation of the value of the same thermodynamic property ΔP of its parent, $\Delta P(A_pB_q,s)$, by use of the values for another hydrate, $\Delta P(C_rD_s.mH_2O,s)$ and *its* parent, $\Delta P(C_rD_s,s)$. Thus:

$$\Delta P(A_pB_q,s) \approx \Delta P(A_pB_q.mH_2O,s) - \Delta P(C_rD_s.mH_2O,s) + \Delta P(C_rD_s,s) \quad (8)$$

Thus equations (6), (7) and (8) can, for example, provide data for an actinoid material, say a uranium salt, A_pB_q, using data for a completely different compound, including one derived

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from a different actinoid element, say a thorium compound, C_rD_s. This facility is useful when data are difficult to determine, as perhaps for a radioactive material etc.

2   Results and Discussion

2.1   Application of the TDR to Actinoid Chemistry for Uranium Compounds by involving data for other actinoid materials.

The parent actinoid thorium nitrate has a known enthalpy of formation [8]:

$$\Delta_f H^{\circ}(Th(NO_3)_4, s)/kJ \ mol^{-1} = -1446 \pm 13 \qquad (9)$$

Knowledge of $\Delta_f H^{\circ}$ for the parent compound $U(SO_4)_2$, $\Delta_f H^{\circ}(U(SO_4)_2, s)/kJ \ mol^{-1} = -2309.6 \pm 12.6$ [8] can enable direct estimate of the standard enthalpy of formation values for both the tetra- and octa- hydrates of $U(SO_4)_2$.

2.1.1   Prediction of Standard Enthalpy of Formation of $U(SO_4)_2.4H_2O$.

Using the TDR an estimate can be made of the enthalpy of formation of the tetra-hydrate of thorium nitrate:

$$\Delta_f H^{\circ}(Th(NO_3)_4.4H_2O, s) \approx \Delta_f H^{\circ}(Th(NO_3)_4, s) + 4\Theta_{Hf}(H_2O, s-s) = -2642 \pm 24 \ kJ \ mol^{-1} \ (10)$$

using equation (7):

$\Delta_f H^{\circ}(U(SO_4)_2.4H_2O, s)$

$\approx \Delta_f H^{\circ}(Th(NO_3)_4.4H_2O, s) - \Delta_f H^{\circ}(Th(NO_3)_4, s) + \Delta_f H^{\circ}(U(SO_4)_2, s) = -3506 \pm 29 \ kJ \ mol^{-1} \quad (11)$

2.1.2   Prediction of Standard Enthalpy of Formation of $U(SO_4)_2.8H_2O$.

Using the TDR we have for the enthalpy of formation of the octa-hydrate of thorium nitrate:

$$\Delta_f H^{\circ}(Th(NO_3)_4.8H_2O, s) \approx \Delta_f H^{\circ}(Th(NO_3)_4, s) + 8\Theta_{Hf}(H_2O, s-s) = -3838 \pm 34 \ kJ \ mol^{-1} \qquad (12)$$

and then using equation (7) leads to:

$\Delta_f H^{\circ}(U(SO_4)_2.8H_2O, s)$

$\approx \Delta_f H^{\circ}(Th(NO_3)_4.8H_2O, s) - \Delta_f H^{\circ}(Th(NO_3)_4, s) + \Delta_f H^{\circ}(U(SO_4)_2, s) = -4702 \pm 39 \ kJ \ mol^{-1} \quad (13)$

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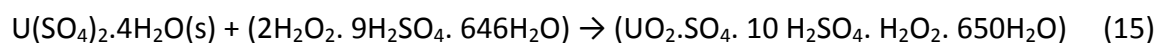## 2.2   Comparison of Predicted Values with Experimental Values

The corresponding experimental values for the standard enthalpy of formation for the above two hydrates are experimentally known. The discussion below gives some insight as to how these experimental values are actually determined and the processes and corrections that one is required to make in order to do this.

2.2.1 Experimental Determination of the Enthalpy of Formation of the tetrahydrate, $\Delta_f H^o(U(SO_4)_2.4H_2O,s)/kJ\ mol^{-1}$

The experimental value for $\Delta_f H^o(U(SO_4)_2.4H_2O,s)$ is -3483.2 ± 6.3 kJ mol^{-1} [8], reasonably close (0.66% error) to the value estimated in equation (11). The experimental value was obtained by combining the enthalpy of oxidation of this tetrahydrate with H_2O_2 (see below) reported by Vidavskij et. al. [9] with the enthalpy of reaction of amorphous UO_3 with aqueous H_2SO_4 (reaction 14) as determined by the same workers [10]. These latter experiments were carried out using two samples of amorphous (am) UO_3; one containing some H_2O as hydrate, the other containing α-UO_3 as well as water. Appropriate thermochemical corrections were then applied by Vidavskij and Ippolitova [11] who found ΔH^o for the reaction in equation (14):

$$UO_3(am) + (11\ H_2SO_4.\ 649\ H_2O) \rightarrow UO_2.SO_4.\ 10\ H_2SO_4.\ 650H_2O \qquad (14)$$
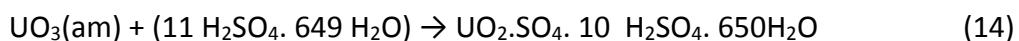
to be -97.53 ± 0.33 kJ mol^{-1} later corrected (because of a small change in molar mass) to -97.40 ± 0.33 kJ mol^{-1} by Cordfunke and O'Hare [8]. Vidavskij and Ippolitova[11] later revised their original data for the enthalpy of oxidation of the tetrahydrate, U(SO$_4$)$_2$.4H$_2$O, by applying a correction to allow for a small H_2SO_4 impurity (reaction 14). As a result of this, and a change in the molar mass, ΔH^o yields, for the reaction (15):

$$U(SO_4)_2.4H_2O(s) + (2H_2O_2.\ 9H_2SO_4.\ 646H_2O) \rightarrow (UO_2.SO_4.\ 10\ H_2SO_4.\ H_2O_2.\ 650H_2O) \quad (15)$$
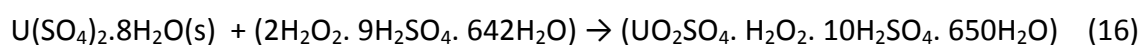
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−260.66 ± 1.13 kJ mol^{-1}. The enthalpy of formation of H_2O_2 in the above reaction was shown

to be very close to the value for $H_2O_2.\infty H_2O$ where ∞ represents infinite dilution (just as

though a single molecule of H_2O_2 was not present) and the product solutions formed in

reactions (14) and (15) were thus assumed to be identical. The oxidation experiments were

performed at 293 K; however a correction to 298 K is considered to be within the limits of

uncertainty in ΔH^o. Cordfunke and O'Hare [8] took $\Delta_f H^o(UO_3,am) = -1207.9 \pm 1.2$ kJ mol^{-1},

based on the results of Cordfunke [12, 13] in order to generate the experimental result above,

which differs from the TDR result (Table A3) by a mere 28 kJ

mol^{-1} (or 0.80% in error).

2.2.2 Experimental Determination of the Enthalpy of Formation of $U(SO_4)_2.8H_2O(s)$.

The experimental result [8] for the octahydrate is $\Delta_f H^o(U(SO_4)_2.8H_2O,s) = -4662.6 \pm 6.3$ kJ

mol^{-1} is fairly close (0.84% error) to the value estimated by equation (13) and results from a

revision of calorimetric data obtained earlier for the oxidation of $U(SO_4)_2.8H_2O$ in order to

allow for presence of a small H_2SO_4 impurity [11]. This, coupled with a slight adjustment in

the molar mass, gives a value $\Delta H = -226.54 \pm 0.29$ kJ mol^{-1} at 293 K for the reaction shown

in equ. (16):

$$U(SO_4)_2.8H_2O(s) + (2H_2O_2. 9H_2SO_4. 642H_2O) \rightarrow (UO_2SO_4. H_2O_2. 10H_2SO_4. 650H_2O) \quad (16)$$

Again, taking $\Delta_f H^o(H_2O_2)$ in the solution to be the same as $\Delta_f H^o(H_2O_2.\infty H_2O)$ and neglecting

the correction to 298 K and combining the result with ΔH for equ (14) gives rise to the result

quoted above, which differs from the TDR result (in Table A3) by only 12 kJ mol^{-1} (or 0.25

% in error). Once again this confirms the virtue of this alternative TDR route for estimating

thermochemical data.

2.3 Estimation of other Thermodynamic Properties for the Tetra and Octa Hydrates.

In the case of $U(SO_4)_2.4H_2O$ and $U(SO_4)_2.8H_2O$, neither the standard Gibbs energy, $\Delta_f G°$ nor the standard entropy, $S°_{298}$ of these hydrates are known, whilst $\Delta_f G^o$ and $S°_{298}$ are both known experimentally for the parent [8], $U(SO_4)_2$. Since:

$$\Delta_f G^o(U(SO_4)_2,s) = -2084.9 \pm 14.6 \text{ kJ mol}^{-1} \quad (17)$$

and

$$S°_{298}(U(SO_4)_2,s) = 180 \pm 21 \text{ J K}^{-1} \text{ mol}^{-1} \quad (18)$$

then writing the TDR corresponding to $\Delta_f G^o$ and $S°_{298}$ allows access to the thermodynamic functions for the hydrates.

2.3.1 TDR Prediction of Standard Gibbs Energy of Formation for $U(SO_4)_2.nH_2O,s),(n = 4, 8)$

Using the value of $\Theta_{Gf}(H_2O, s\text{–}s) = -242 \pm 10$ kJ mol^{-1} from Table 1 one can compute values for the tetra- and octa-hydrates:

$$\Delta_f G^o(U(SO_4)_2.4H_2O,s) \approx -3054 \pm 25 \text{ kJ mol}^{-1} \quad (19)$$

$$\Delta_f G^o(U(SO_4)_2.8H_2O,s) \approx \Delta_f G^o(U(SO_4)_2,s) + 8\Theta_{Gf}(H_2O, s\text{–}s) = -4022 \pm 32 \text{ kJ mol}^{-1} \quad (20)$$

2.3.2 TDR Prediction of Standard Entropy, $S°_{298}(U(SO_4)_2.nH_2O,s)/J K^{-1} mol^{-1}$ (n = 4, 8)

Using the value of $\Theta_S(H_2O, s\text{–}s) = 41 \pm 7$ J K^{-1} mol^{-1} from Table 1, one can compute values for the tetra- and octa-hydrates:

$$S°_{298}(U(SO_4)_2.4H_2O,s) \approx S°_{298}(U(SO_4)_2,s) + 4\Theta_S(H_2O, s\text{–}s) = 344 \pm 25 \text{ J K}^{-1} \text{ mol}^{-1} \quad (21)$$

$$S°_{298}(U(SO_4)_2.8H_2O,s) \approx S°_{298}(U(SO_4)_2,s) + 8\Theta_S(H_2O, s\text{–}s) = 499 \pm 29 \text{ J K}^{-1} \text{ mol}^{-1} \quad (22)$$

2.3.3. Alternative Approach via Yoder's Simple Sum Approximation (SSA) [41]

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As has been discussed in previous papers [3, 4, 5], additivity relationships can also emerge directly from the TDR. One example is Yoder's [41] simple sum approximation, which can take the generalised form:

$$\Delta P(U(SO_4)_2.8H_2O,s) + \Delta P(U(SO_4)_2,s) \approx 2\Delta P(U(SO_4)_2.4H_2O,s) \qquad (23)$$

and the data already obtained above can be shown to obey such relationships of which there are many based on the simple additivity principle shown in equation (23). When $\Delta P = \Delta_f H^o$, using the data above the left hand side of equation (23) sums to:

$$\Delta_f H^o(U(SO_4)_2.8H_2O,s) + \Delta_f H^o(U(SO_4)_2,s) = -6972.2 \pm 14.1 \text{ kJ mol}^{-1} \quad (24)$$

whilst the right hand side is equal to:

$$2 \Delta_f H^o(U(SO_4)_2.4H_2O,s) = -6966.4 \pm 8.9 \text{ kJ mol}^{-1} \quad (25)$$

so confirming the relationship (23) since the two values are in range (within 0.09%) of one another and also being close (0.57% error) to the value in equ (11). Similarly when $\Delta P = \Delta_f G^o$:

$$\Delta_f G^o(U(SO_4)_2.8H_2O,s) + \Delta_f G^o(U(SO_4)_2,s) = -6106 \pm 35 \text{ kJ mol}^{-1} \quad (26)$$

and

$$2 \Delta_f G^o(U(SO_4)_2.4H_2O,s) = -6106 \pm 35 \text{ kJ mol}^{-1} \quad (27)$$

again in conformity with equation (23). Here (and below) the match is exact because the data has been derived using TDR whereas the data used in the first example (equations (24) and (25)) is experimentally derived. Finally when $\Delta P = S^o_{298}$ we have:

$$S^o_{298}(U(SO_4)_2.8H_2O,s) + S^o_{298}(U(SO_4)_2,s) = 688 \pm 36 \text{ J K}^{-1} \text{ mol}^{-1} \quad (28)$$

and

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$$2\ S^o_{298}(U(SO_4)_2.4H_2O,s) =\ 688 \pm 35\ J\ K^{-1}\ mol^{-1} \quad (29)$$

once again confirming general relationship (23). Relationships of the type (23) provide an alternative route for deriving missing data or confirming experimental data.

3. Examination of Cordfunke/O'Hare [8], Karapet'yants and Karapet'yants [16] and other databases [12, 14, 22, 24-33, 36, 38-40] of thermodynamic data for Uranium Compounds.

In the Appendix is collected thermodynamic data (in Tables A1- A3) for uranium materials and their hydrates and alongside this compilation given also (where possible) are predictions of the data made using the TDR. When TDR data is given, the relative percentage error (listed in parentheses) found for the prediction as compared to the most trusted value (highlighted in Clarendon bold-faced type) and calculated using equation (32). The tables in the Appendix contain 41 (in Table A1), 20 (in Table A2), 53 for $\Delta_f H^o$, 30 for $\Delta_f G^o$ and 31 for S^o_{298} (in Table A3) individual listings of thermodynamic data for crystalline uranium compounds derived mainly from the databases of Cordfunke and O'Hare [8], Karapet'yants and Karapet'yants [6] and the sundry sources further indicated [12, 14, 22, 24-33, 36, 38-40]. The decision as to which of the experimental data is the more reliable is guided by our estimates made using the TDR. Usually the experimental value in closest proximity to the TDR value is selected (see for example the UF$_4$ data0.

At the foot of each of the three separate tables combined within Table A3 are given the average percentage error found in the predictions made by TDR for the 49 predicitons of $\Delta_f H^o$ and the 22 predictions of $\Delta_f G^o$ (both equal 0.29%) and for 24 predictions of S^o_{298} (= 2.03%). It will be noted just how small these errors are and that they are, in the majority of cases, comparable with experimental errors and therefore serve to illustrate the reliability of the TDR when used for estimation. In Table A2 the average error found in the TDR estimates amount to 0.02%, smaller still.

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3.1 Thermodynamic data for parent materials (n = 0) for which there are no known hydrates.

In cases where parent data only is known and no hydrates are known to exist the TDR has no value except to estimate data for hypothetical hydrates using the general equation (30) where the thermodynamic property, $\Delta P = \Delta_f H^o$, $\Delta_f G^o$, or S^o_{298} and:

$$\Delta P(\text{n-hydrate,s}) = n.\Theta_P(H_2O, \text{s–s}) + \Delta P(\text{parent, n} = 0,\text{s}) \quad (30)$$

To take a specific example (in kJ mol^{-1}):

$$\Delta_f H^o(UO_2SeO_4.nH_2O,s) = -299\ n + \Delta_f H^o(UO_2SeO_4,s) \quad (31)$$

In order to ensure that this paper gives a complete overview of the thermodynamics of uranium compounds, data in this class is listed in table A1 of the Appendix. 38 values are listed for $\Delta_f H^o$, 32 values are listed for $\Delta_f G^o$ and 35 values for S^o_{298} In the case where multiple values are cited a sample averaging is employed to identify the most trusted values (in bold-faced type) with selection being guided by TDR.

3.2 Thermodynamic data for hydrate materials for which there is no data for the parent salts.

In Table A2 11 uranium salt hydrates are listed for which there is no experimental $\Delta_f H^o$ data for any of their parent salts. In the case of the parent salts (column 5, table A2) we estimate their $\Delta_f H^o$ values (in Clarendon, bold-faced type) using the TDR and also test the capability of the TDR (column 4) to predict the hydrate values of $\Delta_f H^o$ which are already known.

3.3 Error calculation

What is most important is the *relative difference* between thermodynamic data since the values are not absolute but are relative in the sense that they are represented with respect to a

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standard state. The percentage error recorded in Tables A2 and A3 by means of parentheses following the value predicted is calculated using the formula:

% age error =

$\underline{\text{[Most trusted value (column 1) – TDR predicted value (column 4 or 5)] x 100}}$ (32)
$\qquad\qquad$ Most trusted value (column 1)

In cases where the experimental data are uncertain (i.e. enclosed within parentheses) or there are multiple values listed an average is often taken to establish a preferred value. In cases where there are several experimental values, the TDR estimate error is calculated using the predicted value *closest* in magnitude to the most trusted value.

3.4 New Predictions made using TDR

In cases where data were uncertain or simply not known and where TDR could be employed to give estimates, the following values were established and possess errors similar to those averages listed in Table A3 at the foot of each individual table.

$$\Delta_f H^o(UO_2(OH)Br,s) \approx -1360 \text{ kJ mol}^{-1} \quad (33)$$

$$\Delta_f H^o(UO_2(OH)Cl,s) \approx -1413 \text{ kJ mol}^{-1} \quad (34)$$

$$\Delta_f H^o(UO_2NH_4(CH_3COO)_3,s) \approx -2549 \text{ kJ mol}^{-1} \quad (35)$$

$$\Delta_f H^o(UO_2CrO_4,s) \approx -1854 \text{ kJ mol}^{-1} \quad (36)$$

$$\Delta_f H^o(UO_{2.86},s) \approx -1217 \text{ kJ mol}^{-1} \quad (37)$$

$$\Delta_f H^o(NH_3(UO_3)_2,s) \approx -2593 \text{ kJ mol}^{-1} \quad (38)$$

$$\Delta_f H^o(NH_3(UO_3)_3,s) \approx -3816 \text{ kJ mol}^{-1} \quad (39)$$

[Type here]

$$\Delta_f H^o((NH_3)_2(UO_3)_3,s) \approx -3917 \text{ kJ mol}^{-1} \quad (40)$$

$$\Delta_f H^o(UO_{2.86},s) \approx -1217 \text{ kJ mol}^{-1} \quad (41)$$

$$\Delta_f H^o(UO_2CrO_4,s) \approx -1854 \text{ kJ mol}^{-1} \quad (42)$$

$$\Delta_f H^o(UO_2C_2O_4,s) \approx -1815 \text{ kJ mol}^{-1} \quad (43)$$

$$\Delta_f H^o(UO_2Cl_2,s) \approx -1267 \text{ kJ mol}^{-1} \quad (44)$$

$$\Delta_f H^o(UO_2Br_2,s) \approx -1159 \text{ kJ mol}^{-1} \quad (45)$$

$$\Delta_f G^o(UO_2(NO_3)_2,s) \approx -1130 \text{ kJ mol}^{-1} \quad (46)$$

$$\Delta_f G^o(U(SO_4)_2.4H_2O,s) \approx -3054 \pm 25 \text{ kJ mol}^{-1} \quad (47)$$

$$\Delta_f G^o(U(SO_4)_2.8H_2O,s) \approx -4022 \pm 32 \text{ kJ mol}^{-1} \quad (48)$$

$$\Delta_f G^o(UO_2Cl_2,s) \approx -1166 \text{ kJ mol}^{-1} \quad (49)$$

$$\Delta_f G^o(UO_2Br_2,s) \approx -1087 \text{ kJ mol}^{-1} \quad (50)$$

$$S^o_{298}(UO_3.0.5H_2O,s) \approx 116 \text{ J K}^{-1} \text{ mol}^{-1} \quad (51)$$

$$S^o_{298}(UO_3.0.85H_2O,s) \approx 131 \text{ J K}^{-1} \text{ mol}^{-1} \quad (52)$$

$$S^o_{298}(U(SO_4)_2.4H_2O,s) \approx 325 \pm 25 \text{ J K}^{-1} \text{ mol}^{-1} \quad (53)$$

$$S^o_{298}(U(SO_4)_2.8H_2O,s) \approx 499 \pm 29 \text{ J K}^{-1} \text{ mol}^{-1} \quad (54)$$

3.5. Results and Discussion.

Here we discuss a few of the individual compounds. Table A3 provides (column 2) experimental values of $\Delta_f H^0$ for the parent trioxide, UO_3, in its numerous phases. These values, which range from −1220 to −1237.6 kJ mol^{-1}, are predicted in column 5 of Table A3 for UO_3 using TDR equation (30) based on the hydrate values lower down in the table. Thus $\Delta_f H^0$ values for the parent are

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estimated using the TDR from the 6 experimental values of $\Delta_f H^0$ recorded for the 6 hydrates of UO_3 (n = ½, 0.85, 1 and 2) in column 1. The most trusted $\Delta_f H^0$ value for $UO_3(\gamma)$ is taken to be the average of 4 values, for $UO_3(\epsilon)$ the average of 7 values and for $UO_3(\alpha)$ the average of 3. For estimation of the hydrate values by TDR the average of the three UO_3 parent values (= -1226 kJ mol^{-1}) is used in column 4 of Table A3.

Four hydrates exist also for $UO_2(NO_3)_2$ (n = 1,2, 3 and 6) the most preferred experimental values of $\Delta_f H^0$ (column 1) are utilised with the TDR (equation (30)) to predict $\Delta_f H^0$ for the parent (column 5). The average value of -1381 kJ mol^{-1} of these 4 values corresponds within 0.58% to average value given in column 1 for $UO_2(NO_3)_2$ and we assign the latter (-1374 kJ mol^{-1}) this to be the most likely value of $\Delta_f H^0(UO_2(NO_3)_2,c)$. The relative percentage error in the prediction of the hydrate values using TDR ranges from 0.05 % to 0.48 %.

For $UO_2CrO_4(s)$ the TDR estimate made for the parent (-1854 kJ mol^{-1}) gives good account of the value [8,14] assigned to the hydrate and we take this to be our preferred value. Cordfunke and O'Hare [8] contend that "because of the computational uncertainties the data are regarded as tentative" and further, because the $\Delta_f H^0$ value for the parent is calculated by assessing the enthalpy of hydration then both the parent and the hydrate would be affected by any error.

The monohydrate of UO_2Cl_2 and the dihydrate and trihydrates of UO_2Br_2 have been discussed in the literature [42,43] as not being a "true" hydrates. which could explain firstly the wide discrepancy in $\Delta_f H^0$ values assigned for the monohydrate and the 0.37% difference found in the TDR prediction. $\Delta_f G^0$ for UO_2Cl_2 is predicted by TDR to be much lower than the two (agreeing) experimental values [14,40] discussed and their hydrates. This makes selection of preferred value difficult and these results should be treated with caution. Thermochemistry of UO_2Br_2 has been discussed by Prins[44.]

[Type here]

Standard entropy data, at 298K, for uranium salts generally lie in the range: $511 > S^o_{298}$ /J K^{-1} mol^{-1} > 90 with errors arising from TDR prediction usually in the range: 3 – 34 J K^{-1} mol^{-1}. Clearly if we calculate percentage errors via equation (32) then because of the magnitude of the numbers involved these will generally lie above the 1% level. This is found in the Table A3. However this does not imply that the TDR is any less accurate in its prediction of standard entropy than it is for $\Delta_f H^o$ or for $\Delta_f G^o$

The error of 4.4% in column 4 of Table A3 for $UO_2SO_4.2.5H_2O$ is one of the largest found in the Tables. Considering the difference [8] between $S^o_{298}(UO_2SO_4.3\frac{1}{2}H_2O,s)$ and

$S^o_{298}(UO_2SO_4.2\frac{1}{2}H_2O,s) = 292.9 – 247.7 = 45.23$ J K^{-1} mol^{-1} should, according to our TDR (Table 1) be 41. Accordingly the two hydrate values 287.9 and 245.6 J K^{-1} mol^{-1} which offer a 42.3 J K^{-1} mol^{-1} difference might offer a better choice of preferred values.

Just to take one final example, to estimate the enthalpy of formation for the octahydrate, $\Delta_f H(U(SO_4)_2.8H_2O,s)$/kJ mol^{-1} we could use equation (2) in the form of equation (21) and incorporate the value of $\Theta_{Hf}(H_2O, s-s)$ from Table 1 to give:

$[\Delta_f H(ZnSO_4.6H_2O,s) – \Delta_f H(ZnSO_4,s)]$/kJ mol$^{-1} \approx 6\Theta_{Hf}(H_2O, s-s) = -1794 \pm 66$ \hfill (56)

so that for the octahydrate, $ZnSO_4.8H_2O$ we can also write:

$[\Delta_f H(ZnSO_4.8H_2O,s) – \Delta_f H(ZnSO_4,s)]$/kJ mol$^{-1} \approx 8\Theta_{Hf}(H_2O, s-s) = -2392 \pm 88$ \hfill (57)

$\Delta_f H^o(ZnSO_4.8H_2O,s)$ is not listed in standard thermochemical tables[14]. However data for the heptahydrate *is* listed as $\Delta_f H^o(ZnSO_4.7H_2O,s)$/kJ mol$^{-1} = -3077.8$ and $\Delta_f H^o(ZnSO_4,s)$/kJ mol$^{-1} = -982.8$ [14], so that, using TDR:

$\Delta_f H(ZnSO_4.8H_2O,s)$/kJ mol$^{-1} \approx \Delta_f H(ZnSO_4.7H_2O,s) + \Theta_{Hf}(H_2O, s-s) = -3377 \pm 11$ \hfill (61)

thus:

$\Delta_f H(U(SO_4)_2.8H_2O,s)$/kJ mol$^{-1} \approx -4704 \pm 17$ \hfill (62)

[Type here]

This prediction should be compared with that made in equation (13) and also with the experimental value [8] of -4662 k mol^{-1}, showing an error of some 42 kJ mol^{-1} or less than 1% relative error. Any number of similar procedures could be used to estimate $\Delta_f H$(U(SO$_4$)$_2$.8H$_2$O,s) and one assumes, the greater the number of variants used would yield more accurate average predictions.

4. Conclusions

From the brief description of the procedure needed to obtain experimentally based results for these actinoid materials as described in section 2.2.1. above, one can see how complex the experimental determination process is and how dependent it is on identifying correctly the products (usually of hydrolysis reactions) of the reactions involved. This requires considerable expertise. Contrasted with this, when carefully and simply applied, the TDR can offer - in many cases - an alternative route to obtaining such data as well as providing guidance as to preferred values. In one example shown above we invoked some *thorium* data to apply the rule to establish thermodynamic values for *uranium* bearing species. What was not shown - although hinted at in the early part of the manuscript - was the fact that a virtually limitless series of data (hydrate and parent) could have been used in order to carry out multiple estimates of the target data and in this way errors could be reduced possibly even further by averaging the results. The errors obtained from our examples are, however, highly satisfactory. The TDR is also shown to be well capable of extending the existing databases for uranium materials in a reliable way.

5   Supplementary Information

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Supplementary data containing Tables A1–A3 are available for this paper online.

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