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Author

Marcalo, Joaquim

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Gas-phase energetics of actinide oxides – an assessment of neutral and cationic monoxides and dioxides from thorium to curium

Joaquim Marçalo[a,*] and John K. Gibson[b,*]

[a] Unidade de Ciências Químicas e Radiofarmacêuticas, Instituto Tecnológico e Nuclear, 2686-953 Sacavém, Portugal
[b] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

*Corresponding authors: jmarcalo@itn.pt; JKGibson@lbl.gov.

Abstract
An assessment of the gas-phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides of thorium, protactinium, uranium, neptunium, plutonium, americium, and curium is presented. A consistent set of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation, including new or revised values, is proposed, mainly based on recent experimental data and on correlations with the electronic energetics of the atoms or cations and with condensed-phase thermochemistry.

Introduction
The thermodynamic properties of actinide (An) oxides are of paramount importance to nuclear science at both the fundamental and applied levels. In the most recent, comprehensive overview of the thermodynamics of actinides and actinide compounds [1], the history of the field and the most reliable current data can be found. As concerns the actinide oxides, that work appropriately indicates that, while a significant number of studies of the solid compounds have been undertaken, gas-phase data are still incomplete. An earlier compilation devoted to the gas-phase thermochemistry of the actinides [2], as well as others of a more general nature [3], are now more than twenty years old and do not reflect the experimental data gathered since then. For instance, recent high-quality spectroscopic studies of thorium and uranium oxides [4] have afforded exceedingly reliable values for the ionization energies IE[ThO], IE[UO], and IE[UO$_2$], which showed significant differences relative to the older accepted values included in the compilations.
In recent years, we have carried out a systematic study of the gas-phase thermochemistry of neutral and cationic actinide oxides from thorium to curium using Fourier transform ion cyclotron resonance mass spectrometry (FTICR/MS) [5,6]. This experimental work was based on the observation of exothermic reactions of An metal or metal-oxide cations with various inorganic and organic molecules. Reactions of singly or doubly charged An cations with oxidizing reagents with a large range of oxygen dissociation energies provided metal-oxygen bond dissociation enthalpies, D[An$^+$-O], D[OAn$^+$-O], D[An^{2+}-O], and D[OAn^{2+}-O]. Reactions of singly or doubly charged An monoxide and dioxide cations, produced via the oxidation reactions, yielded ionization energies of the corresponding neutral and monopositive monoxides and dioxides, IE[AnO], IE[AnO$_2$], IE[AnO$^+$], and IE[AnO$_2^+$]. The values of D and IE determined by these procedures were either unknown or could be used to verify or correct literature values obtained by other methods.
The gas-phase data acquired from these studies justifies an overall assessment of gas-phase actinide oxide energetics. Besides evaluating the consistency of the data from our experimental work [5,6], which were obtained in several stages, this assessment compares them with corresponding values from the standard literature sources [1-3]. This assessment also tests the evaluation of the bond dissociation energies of neutral and singly charged actinide monoxides

carried out not long ago by one of us [7], based on correlations with the electronic structures and energetics of the isolated metal atoms and ions. Therefore, in the present work, we perform an assessment of the gas-phase energetics of neutral, and singly and doubly charged cationic actinide monoxides and dioxides from thorium to curium based on experimental data and on correlations with the electronic energetics of the atoms or cations and with condensed-phase thermochemistry. A prospective outcome of the assessment is the unraveling of variations across the actinide series that can be of value for evaluating or predicting the properties of other actinide oxides.

Methodology
The approach used in this assessment is the following:
1. Identification of the more reliable experimental data from existing sources.
2. In the absence of data of confidence, selection of existing estimates as a starting point for the analysis.
3. Evaluation of the data based on the Hess's law equations (1) to (4).

$$D[An^+\text{-}O] = D[An\text{-}O] + IE[An] - IE[AnO] \qquad (1)$$
$$D[OAn^+\text{-}O] = D[OAn\text{-}O] + IE[AnO] - IE[AnO_2] \qquad (2)$$
$$D[An^{2+}\text{-}O] = D[An^+\text{-}O] + IE[An^+] - IE[AnO^+] \qquad (3)$$
$$D[OAn^{2+}\text{-}O] = D[OAn^+\text{-}O] + IE[AnO^+] - IE[AnO_2^+] \qquad (4)$$

4. Trial-and-error adjustment of the less reliable values based on experimental restraints and on correlations with independent data.
5. Estimation of the uncertainties of the final values based on experimental restraints, and on the uncertainties of the selected data.
A detailed explanation of each step of the procedure is presented in the following sections; additional data can be found in the Supporting Information.

Key data
The main sources of the An data selected as key for the evaluation are those indicated in the Introduction [1-6]; other sources of An data are cited when needed. Ancillary thermodynamic values are from the NIST Chemistry WebBook [8] (see Table S1). The source for condensed-phase (solution and solid) thermodynamic data, used in correlations with the gas-phase data during the evaluation, was also Konings et al. [1]. 298.15 K values have been used throughout the work, with the exception of spectroscopically determined IEs which correspond to 0 K values; no thermal corrections were applied when combining 298.15 and 0 K values as the differences of a few kJ mol^{-1} are significantly smaller than the uncertainties involved.

An metals. The enthalpies of formation of the gaseous An metals were retrieved from the review of Konings et al. [1] (see Table S2). The first ionization energies of the An metals were obtained from the review of Worden et al. [9] (see Table S2); with the exception of Pa, all the values are from highly reliable spectroscopic determinations.
For the second ionization energies of the An metals there are no commonly accepted values. There are scattered values obtained from spectroscopic data [10] but more complete sets were only derived from estimates [2,11] or theoretical calculations [12]. The estimates made by Sugar (see Table S3), as cited by Hildenbrand et al. [2] and also by Morss [13], seemed to be reliable (as typical of Sugar's estimates) and we have used them in previous studies [5d-f].
Recent work in our laboratories in which we have examined the gas-phase reactions of hydrocarbons with Ln^{2+} [14] have indicated that a correlation exists between the aggregate rates of electron transfer from hydrocarbons and the IE[Ln$^+$]; the same type of correlation was observed in reactions of other M^{2+} ions with different reagents (see Figures S1 and S2 for details). However, our recent examination of the gas-phase reactions of hydrocarbons with An^{2+} [15] has

shown that a poor correlation is obtained between the aggregate rates of electron transfer from hydrocarbons and the IE[An$^+$] estimated by Sugar (see Figure S3). Therefore, our first suggestion here is that an adjustment of the set of IE[An$^+$] estimated by Sugar be made. For this, an anchor value within Sugar's set is needed. Known systematics of the ionization energies of the metallic elements tells us that, depending on the ground-state configuration of the M$^{0/+/2+}$ and the electron being removed, IE[M$^+$]/IE[M] is in many instances close to 2 [16]. This is rather clear in the case of the lanthanides and we suggest here that for the more "lanthanide-like" actinides the same relationship applies. The more common ground state configurations of the lanthanides are $4f^n6s^2$ for the element, $4f^n6s^1$ for the singly charged cation, and $4f^n$ for the doubly charged [17]. Considering Am and also Bk, Cf, and Es, which all have ground sates similar to those of the more typical lanthanides, and also very reliable IE[An] [9] (see Table S4 for the IE[An] for Bk, Cf, and Es), we can multiply these IE[An] by 2, obtaining IE[Am$^+$] = 11.95 eV; extrapolating linearly the values of IE[An$^+$] for Bk, Cf, and Es back to Am, a value of IE[Am$^+$] = 12.05 eV is obtained. The two values for IE[Am$^+$] derived here average to 12.0 eV which is also the value estimated by Sugar [2].

Summarizing, in the present work we propose an adjustment to Sugar's estimates of the IE[An$^+$] based on these considerations on the relationship between the IE[M] and the IE[M$^+$], taking IE[Am$^+$] = 12.0 eV as an anchor value, and on the experimental reactivity data obtained by us [14,15]. In Table 1 we present the new values of IE[An$^+$], with our suggested uncertainty of ±0.3 eV, and in Figure 1 a graphical representation of the correlation of these new values with electron-transfer reaction efficiencies of the An^{2+} ions with hydrocarbons [14,15] (see Figure S3 for the same representation when using Sugar's values). It should be noted that our new suggested values for IE[An$^+$] are in general accord with Sugar's values when our rather large assigned uncertainty (i.e., ±0.3 eV) and the uncertainties in Sugar's values [2] (see Table S3) are considered. A comparison of our new IE[An$^+$] estimates with the high-level theoretical values from Dolg and co-workers [12] shows that the computed values are higher for Th, Pa, and U (particularly in the case of Th, 0.5 eV), are lower for Pu and Am, and are identical for Np and Cm. Similar trends can, however, be seen in a decrease of IE[An$^+$] from Th to Np followed by an increase from Pu to Cm. These differences clearly indicate the need of reliable experimental determinations of the IE[An$^+$].

We use the new IE[An$^+$] values (Table 1) in our assessment with the proviso that if reliable experimental values become available, a revision of this assessment will be necessary; corrections implied by new, reliable values of the IE[An$^+$] would require adjustment to the IE[AnO$^+$] which came out of this assessment with large uncertainties.

Other data pertaining to the An metals that will be used in this assessment are the promotion energies from the ground levels of the An, An$^+$, and An^{2+} species to relevant, low-lying excited configurations; these data were retrieved from the standard sources [9,10a] (the values are collected in Tables S5, S6, and S7). It should be noted that the energies of the excited levels of the An^{2+}, other than for Th^{2+} and U^{2+}, have significant uncertainties.

Neutral An oxides. The gas-phase thermodynamics of neutral An oxides has been recently reviewed by Konings et al. [1] who present evaluated values of the enthalpies of formation of AnO for An = Th, U, Np, Pu, Cm and AnO$_2$ for An = Th, U, Np, Pu (see Table S8). The Th oxide gas-phase thermodynamic data in Konings et al. [1] are virtually identical to those in a very recent, comprehensive compilation of the thermochemistry of Th [18]. In the case of Pa, the sole experimental study by Kleinschmidt and Ward [19] which provided values for the enthalpies of formation of gaseous PaO and PaO$_2$ is cited (also included in Table S8). The value in ref. [1] for $\Delta_f H^o$[CmO,g] relies on a previous evaluation of the thermodynamic properties of Cm and its oxides by Konings [20]. (See Table S9 for a compilation of the previously available bond dissociation enthalpies of neutral An oxides.)

Konings et al. [1] also discuss and adjust the model put forward by Haire [21] for the D[An-O] in

which the energetics of the $6d^17s^1$ configurations of the An atoms were used to assess and estimate values along the An series. The D[An-O] values presented by Konings et al. in their Fig. 19.18 [1], following Haire's work, apparently parallel the D[Ln-O] values; among the adjustments to these dissociation energies is our recent new experimentally-derived value for D[Cm-O] [5f], which suggests that D[Gd-O] is comparable to, or somewhat higher than D[Cm-O]. Konings et al. [1] appropriately indicate that more recent work by one of us [7] has shown that a $6d^2$ configuration in the AnO (and also in the LnO) appears to be more consistent with the existing experimental data. This correlation of the D[An-O] with the electronic energetics of the An atoms was tested in the present assessment.

The thermodynamics for the more studied (for reasons of availability and technological relevance) oxides of Th, U, and Pu are to be the most reliable among the actinide oxides and were selected as key values in the present assessment. In our previous studies of Pa [5e] and Cm [5f] we have already addressed the existing values for these two An and suggested some changes which we retain in the present work. In the case of Np, we came across some inconsistencies in the data, including in those from our previous work [5a-c] and, therefore, we have particularly focused on evaluating the Np data in the present assessment.

Cationic An oxides. The energetics of cationic An oxides is less well established. For singly charged AnO and AnO_2 species, most of the available experimental ionization energy (IE) determinations of AnO and AnO_2 [2,3a] are based on electron-impact measurements whose reliability is known to be variable and unpredictable [22]. Highly reliable spectroscopic data for IEs are only available for ThO, UO, and UO_2 from recent determinations by Heaven and co-workers [4] and their IEs are considered key values in our assessment. (See Table S9 for a compilation of the previously available bond dissociation enthalpies of singly charged An oxides, and Table S10 for the previously available ionization energies of the neutral An oxides.)

In our previous experimental work, we have determined IE[AnO] values for Np [5b,c], Pu [5b,c], Am [5b,c], and Cm [5f], anchored on the IE[UO] value of Heaven and co-workers [4c-e], and these were also considered key values for the present evaluation. In the case of Pa, we have previously addressed the energetics of the PaO^+ ion [5e] and here we have retained the estimate of IE[PaO] made therein.

In the case of IE[AnO_2], we have no doubt as to the validity of the value of IE[UO_2] from Heaven and co-workers [4c,d,f] indicated above; we additionally consider that our experimental determinations of IE[AnO_2] for Np [5c], Pu[5a], and Am [5b] are valid to within the assigned uncertainties; furthermore, our estimate of IE[PaO_2] [5e] is also considered as reliable. It should be noted that our IE[PuO_2] = 7.03 ± 0.12 eV was lower by ca. 2.5-3 eV than the previous literature values [2,23]. The value for IE[PuO_2] previously reported by Capone et al. [23] (10.1 ± 0.1 eV) was recently redetermined by the same authors [24] (~6.6 eV); their revised value is in fair agreement with our value but this work [24] was the object of controversy related to the experimental approach [25]. A contribution from a theoretical study was very recently added [26], in which the experimental range ~6.6–7.0 eV for IE[PuO_2] is confirmed as compared to the previous range ~9–10 eV, although a value of 6.2 eV is considered the best computed estimate. The particular case of IE[PuO_2] illustrates the challenges associated with obtaining reliable thermodynamic data for transuranium actinides, and the need for both high-quality spectroscopic measurements and the development of reliable theoretical methodologies for transuranium actinide molecules. The commonly cited value of IE[ThO_2] [2,3a] was used as a starting point in the evaluation, with the caveat that it was derived from inherently suspect high-temperature electron impact experiments.

A complementary contribution to the energetics of singly charged An oxide ions came from the D[An^+-O] and D[OAn^+-O] estimated in our studies of the reactions of An^+ and AnO^+ with oxidants with a large spectrum of oxidizing abilities [5a,b,e,f] (see Table S11). In these type of studies, if the reactant ions are properly thermalized, the reactions that are observed are either

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exothermic or thermoneutral. Although the existence of kinetic barriers may prevent the observation of some exothermic reactions, in carefully analyzed cases the comparative rate constants can be used to improve the estimates of the bond dissociation enthalpies. The constraints imposed on the $D[An^+-O]$ and $D[OAn^+-O]$ by the experimental observations were taken into account throughout the present assessment (see Table S12); specifically, observation of an oxidation reaction establishes a lower limit for the actinide-oxygen bond energy.

While the energetics of singly charged An oxides may be considered to some extent established, albeit in many cases tentatively, from previous work, there was an almost complete lack of data on doubly charged An oxides before our experimental studies of these species [5d-f]. (See Table S9 for a compilation of the previously available bond dissociation enthalpies of doubly charged An oxides, and Table S10 for the previously available ionization energies of the singly charged An oxides.)

In the present work, for the doubly charged An monoxides we rely on our revised values of the $IE[An^+]$ described above (see Table 1), our estimates of the $D[An^{2+}-O]$ [5d-f] (see Tables S11 and S12), and our somewhat approximate estimates of the $IE[AnO^+]$ [5d-f], with the sole exception of $IE[CmO^+]$ which was the object of a more direct experimental determination [5f]. Our previous estimates for $IE[AnO^+]$, with the exception of $IE[CmO^+]$, were adjusted in this work.

The second ionization energies of the AnO_2 for the cases of PaO_2 [5e] and UO_2, NpO_2, and PuO_2 [5d] were experimentally determined by us, and in the case of AmO_2, an estimate was obtained in our previous work [5d]; we have used all of these values in the present assessment. The $IE[UO_2^+]$ had previously been the object of a rough experimental determination [27]. It should be highlighted that our experimental determination of $IE[PaO_2^+]$ was accompanyied by a theoretical study performed by R. M. Pitzer and R. Tyagi which, besides providing insights into the nature of the intriguing protactinyl species PaO_2^{2+}, provided remarkably good agreement with the experimental value of $IE[PaO_2^+]$ [5e]. For the doubly charged An dioxides we relied on our estimates of $D[OAn^{2+}-O]$ [5d,e] to carry out the evaluation (see Tables S11 and S12).

Evaluation of the energetics of actinide oxides

As stated in the section where we summarized our methodology, we have evaluated the selected key data by means of the equations (1) to (4), performed a trial-and-error adjustment of the less reliable values based on experimental restraints and on correlations with independent data, and made estimates of the uncertainties of the final values. In Tables 2 and 3 we present the results of this analysis for the An monoxides and dioxides as evaluated bond dissociation enthalpies (Table 2) and ionization energies (Table 3).

To clarify the procedure, we will now describe a few representative examples. In the simpler cases of U and Pu, for which $D[An-O]$ and $IE[AnO]$ were key values, the $D[An^+-O]$ were easily obtained from equation (1); as $D[OAn-O]$ and $IE[AnO_2]$ were also key values, the $D[OAn^+-O]$ were therefore obtained through equation (2); with the $D[An^+-O]$ and $D[OAn^+-O]$ from above, the $IE[An^+]$ from this work, and the key $IE[AnO_2^+]$, the $D[An^{2+}-O]$, $IE[AnO^+]$, and $D[OAn^{2+}-O]$ were adjusted using as starting points the estimates from previous work (see Tables S9 and S10) and the equations (3) and (4).

In the cases of Np and Am, the $IE[AnO]$ and $IE[AnO_2]$ were the key values and, therefore, the $D[An-O]$ and $D[An^+-O]$ were adjusted using equation (1) and the previously available $D[An^+-O]$ (see Table S9) as starting points, together with the $D[OAn-O]$ and $D[OAn^+-O]$ via equation (2) and the previously available values (see Table S9) as starting points; for the doubly charged species, the procedure was the same as described above for U and Pu.

Differences to the previously available values (Tables S9 and S10) of the adjusted D and IE values (Tables 2 and 3) were typically around or below 30 kJ mol^{-1}.

Correlations with external data were used to assess the evaluated D and IE values as described in the sections below. The correlations of the more straightforwardly evaluated bond dissociation enthalpies of neutral and cationic An monoxides with the electronic energetics of the atoms and

cations were only used as consistency checks. For the An dioxides, the correlations with condensed-phase data were also mainly used as consistency checks, although in the cases where less key data was available they were used in the adjustment of D and IE values.

In the cases of ThO_2^{2+}, CmO_2, CmO_2^{+}, and CmO_2^{2+}, for the sake of completeness, we have made rough estimates of the corresponding values, with accordingly large assigned uncertainties. For the estimates on the neutral and singly charged Cm dioxide we took as a reference available data on MO_2 [28] for M = Sc, Y, and La, that like Cm are trivalent metals. For the most reliable case of Y, the existing data lead to: D[OY-O] = 399 $\pm$ 21 kJ mol^{-1}, D[OY^{+}-O] = 170 $\pm$ 15 kJ mol^{-1}, and IE[YO$_2$] = 8.49 $\pm$ 0.16 eV, and these were used as a primary basis for estimating Cm values.

An monoxides. To assess the consistency of our assigned bond dissociation enthalpies of the An monoxides we have followed the recent evaluation of neutral AnO and singly charged AnO^{+} based on correlations with the electronic structures and energetics of the isolated metal atoms and ions [7], and have extended that analysis to the doubly charged AnO^{2+} in the present work. The correlations are presented in Figures 2, 3, and 4 for the D[An-O], D[An^{+}-O], and D[An^{2+}-O], respectively, and in all three cases the fits are quite good.

It should be pointed out that in the case of the An^{2+}, the promotion energies from the ground levels to 6d^2 and to 6d^{1}7s^1 configurations, besides displaying significant uncertainties (see Table S7), follow a parallel trend (see Figure S4), and therefore the validity of the specific pertinent electronic configuration—6d^2 or 6d^{1}7s^1— in the model for the An^{2+} cannot be ascertained. Nevertheless, in terms of verifying the D[An^{2+}-O] values proposed in this work there appears to be reasonable consistency regardless of which electronic configuration is employed. Also of note are the slight upward deviation of D[Th-O] and/or the slight downward deviation of D[Pa-O] from the fit in Figure 2, which may indicate that one or both of these values need to be adjusted slightly, though in each case likely by < 25 kJ mol^{-1} (i.e., < 3%).

An dioxides. To use a model equivalent to the one used for the An monoxides to test the consistency of the D[OAn-O], D[OAn^{+}-O], and D[OAn^{2+}-O] data would require knowledge of the electronic structures and energetics of the AnO, AnO^{+}, and AnO^{2+} species. Spectroscopic studies of gaseous An monoxides have been limited to neutral and singly charged Th and U monoxides [4]. A theoretical study of the electronic structure of PaO^{+} by R. M. Pitzer and co-workers is also available [28]. However, no generalized model can be tested with such a restricted set of data.

In the absence of the above test, we have first considered the mean bond enthalpies of the An dioxides which we present in Figure 5. There, not unexpectedly, the mean bond enthalpy for the AnO$_2^{+}$, formally An(V), peaks at Pa, while for the AnO$_2^{2+}$, formally An(VI), the peak is at U. Moreover, there are approximately linear decays for both the AnO$_2^{+}$ and AnO$_2^{2+}$ when moving from U onwards in the series. Interestingly, there is a plateau for Th and Pa in the case of the AnO$_2$, formally An(IV), with PaO$_2$ perhaps being slightly higher. This may not be unanticipated if we take into account the available corresponding data for Zr and Nb [30], which show clear similarities to the cases of Th and Pa, respectively: D[Zr-O] = 766 $\pm$ 11 kJ mol^{-1}, D[OZr-O] = 633 $\pm$ 28 kJ mol^{-1}, D[Nb-O] = 727 $\pm$ 11 kJ mol^{-1}, and D[ONb-O] = 724 $\pm$ 24 kJ mol^{-1}, leading to mean bond enthalpies of 700 $\pm$ 30 kJ mol^{-1} for ZrO$_2$ and 725 $\pm$ 26 kJ mol^{-1} for NbO$_2$. Another salient feature of the AnO$_2$ mean bond enthalpies is the levelling off at Am and Cm.

In the overview of An thermodynamics by Konings et al. [1], there are significant amounts of thermodynamic data for the solid An compounds and also for cationic An and An oxide species in aqueous solution. These condensed-phase data show remarkable correlations with each other, of which clear examples are summarized by the authors in their Fig. 19.21 [1], where parallel trends in the enthalpies of formation of several solid An(IV) species and also of aqueous An^{4+} can be seen along the An series (see Figure S5 for a partial reconstruction of Fig. 19.21 from ref. 1).

In order to try the same type of correlation with equivalent condensed-phase data, we have

calculated the enthalpies of formation of the gaseous neutral and ionic An dioxides. These can be derived from the bond dissociation enthalpy values in Table 2 and the enthalpies of formation of the gaseous neutral and cationic An (see Table S2) via equations (5) and (6).

$$\Delta_f H^o[AnO_2^{0/+/2+},g] = \Delta_f H^o[AnO^{0/+/2+},g] + \Delta_f H^o[O,g] - D[OAn^{0/+/2+}\text{-}O] \qquad (5)$$
$$\Delta_f H^o[AnO^{0/+/2+},g] = \Delta_f H^o[An^{0/+/2+},g] + \Delta_f H^o[O,g] - D[An^{0/+/2+}\text{-}O] \qquad (6)$$

In Table 4 we present the calculated enthalpies of formation of the gaseous dioxides, as well as those of the gaseous monoxides.

In terms of relative stabilities for each oxidation state along the An series, relative to the metallic element, we can see from the values in Table 4 that PaO_2^+ is the most stable An(V) species, while UO_2^{2+} is the most stable An(VI) species, with the stabilities of both oxidation states decreasing upon advancing across the series. Another issue that can be evaluated from the $\Delta_f H^o$ values for the gaseous actinyls AnO_2^{2+} is their stability relative to "Coulombic explosion" [31], that is, to their dissociation to two monopositive ions, $AnO^+ + O^+$ or $An^+ + O_2^+$. We have previously addressed this issue for the cases of Pa [5e], and U, Np, Pu and Am [5d], concluding that the corresponding actinyls are all stable towards Coulombic explosion, although this conclusion is somewhat doubtful in the case of Am because of uncertainties in the enthalpy of formation and potential entropic factors [5d]. The same conclusions still hold with the slightly modified $\Delta_f H^o[AnO_2^{2+},g]$ values obtained in the present work. The cases of ThO_2^{2+} and CmO_2^{2+}, not evaluated previously, are disparate: while "CmO_2^{2+}", if formed, would be unstable and would exothermically dissociate to $CmO^+ + O^+$ and $Cm^+ + O_2^+$, "ThO_2^{2+}", if formed, would most probably be stable towards Coulombic explosion, but might spontaneously dissociate to $ThO^{2+} + O$, as indicated by our estimated $D[OTh^{2+}\text{-}O] \approx 0$ (see Table S13 for an analysis of Coulombic explosion of AnO_2^{2+}).

With the $\Delta_f H^o$ for the An dioxides from Table 4, we obtained the correlations with condensed phase thermochemistry that we present in Figures 6, 7, and 8, in which we can see reasonable correlations of the $\Delta_f H^o[AnO_2,g]$ with $\Delta_f H^o[An^{4+},aq]$, $\Delta_f H^o[AnO_2^+,g]$ with $\Delta_f H^o[AnO_2^+,aq]$, and $\Delta_f H^o[AnO_2^{2+},g]$ with $\Delta_f H^o[AnO_2^{2+},aq]$, respectively (see Table S12 for $\Delta_f H^o$ values from condensed phases). Although not covering all the gas-phase data from Th to Cm, we used these relationships to adjust our evaluated D and IE values. A fair correlation was also obtained between $\Delta_f H^o[AnO_2,g]$ and $\Delta_f H^o[AnO_2,c]$, which could be expected because, as indicated above, $\Delta_f H^o[An^{4+},aq]$ and $\Delta_f H^o[AnO_2,c]$ show a good correlation [1]. Intriguingly, the $\Delta_f H^o[ThO_2,g]$, which we retained from Konings et al. [1] although with a larger assigned uncertainty, is clearly out of the fit in Figure 6 (this data point at $\Delta_f H^o[ThO_2,g]$ = -456 kJ mol^{-1}, $\Delta_f H^o[Th^{4+},aq$] = -769 kJ mol^{-1} does not appear in Figure 6). The remarkably high stability of condensed-phase Th(IV) species, which is evidently a special case in condensed-phase actinide chemistry, is also clearly seen in other correlations, such as is evident in Figure 19.21 of reference [1] (see Figure S5). If the formation enthalpy for ThO$_2$,g is valid, it would appear that effects which result in an unusual stability of Th(IV) species in the condensed phase—specifically in ionic solids and as an ion in aqueous solutions—are not similarly manifested in the thorium dioxide molecule, which presumably exhibits more covalent character. It should be noted that in Figure 7 the Pa point corresponds not to PaO_2^+,aq but rather to the Pa(V) species that is stable in aqueous solution, $PaOOH^{2+}$ [1].

Other correlations of the data obtained for the An dioxides in the present assessment were attempted with fair results, namely $D[OAn^+\text{-}O]$ vs. $D[OAn\text{-}O]$ and $D[OAn^+\text{-}O]$ vs. $IE[AnO_2]$ (see Figures S6 and S7). The correlation between $D[OAn^+\text{-}O]$ and $IE[AnO_2]$ may reflect the relative stabilities of the An(V). The significance of the correlation between $D[OAn^+\text{-}O]$ and $D[OAn\text{-}O]$ is not clear but it was also helpful in estimating the thermodynamic properties of curium dioxide (incidentally, a good correlation also exists between $D[An^+\text{-}O]$ and $D[An\text{-}O]$, see Figure S8). A fairly good correlation was also found between $D[OAn\text{-}O]$ and the promotion energy from the

ground level to a 6d^2 configuration of the An^{2+} atomic ions from Pa to Am (see Figure S9). This correlation suggests that the An in AnO can be considered approximately as an An^{2+} ion, and the bonding to the second O atom in OAn-O involves a 6d^2 configuration at the An metal center. The several correlations we have identified evidently reflect a generalized gradual variation of the intrinsic properties of the An(IV) to An(VI) from Pa to Cm; Th is clearly an outlier.

Comparisons with theoretical calculations. As a final part of this section, we should mention that several recent theoretical calculations have examined the thermodynamics of a few An oxide species. As a first example of note, agreement of our values for the $\Delta_f H^o$[AnO$_2$$^{2+}$,g] in the cases of U and Pu with the calculated ones [32], $\Delta_f H^o_0$[UO$_2$$^{2+}$,g] = 1527 ± 42 kJ mol^{-1} and $\Delta_f H^o_0$[PuO$_2$$^{2+}$,g] = 1749 ± 63 kJ mol^{-1}, is evident. Recent theoretical studies of the solvation of actinyls by water [33] have also showed a fair agreement between calculated free energies of hydration and the ones that can be derived from the enthalpies of formation for the gaseous actinyl ions from the present work (Table 4), in conjunction with the known enthalpies of formation of these species in aqueous phase (see Table S14), as performed in our previous work [5d]. Other recent theoretical studies have led to disparate values for several An oxide bond dissociation enthalpies and ionization energies [12a,26,34], some of them showing reasonable agreement with the data evaluated in the present work.

Conclusions

We have performed an assessment of the gas-phase energetics of neutral and singly and doubly charged cationic actinide monoxides and dioxides from thorium to curium based on experimental data and on correlations with the electronic energetics of the atoms or cations and with condensed-phase thermochemistry, and provide a consistent set of new or revised values of metal-oxygen bond dissociation enthalpies, ionization energies, and enthalpies of formation for these species. The assessment highlights the need for additional high-accuracy experimental measurements for elementary actinide molecules and even atoms, particularly for the transuranium actinides, and the development of advanced theoretical approaches to more reliably compute key thermodynamic properties of actinide molecules.

Supporting Information Available: Tables S1-S14 and Figures S1-S9 provide thermodynamic data and correlations of data supplementary to the data in the manuscript. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Second ionization energies of An elements [a]

An	IE[An$^+$]
Th	11.65 ± 0.3
Pa	11.6 ± 0.3
U	11.7 ± 0.3
Np	11.55 ± 0.3
Pu	11.8 ± 0.3
Am	12.0 ± 0.3
Cm	12.4 ± 0.3

[a] This work; in eV.

Table 2. Bond dissociation enthalpies of An oxides [a]

An	D[An-O]	D[An$^+$-O]	D[An^{2+}-O]	D[OAn-O]	D[OAn$^+$-O]	D[OAn^{2+}-O]
Th	872 ± 25	843 ± 25	829 ± 80	684 ± 14	462 ± 36	0 ± 170 [b]
Pa	801 ± 59	800 ± 50	781 ± 30	780 ± 48	780 ± 29	317 ± 110
U	758 ± 13	774 ± 13	706 ± 45	750 ± 14	741 ± 14	529 ± 31
Np	744 ± 21	760 ± 10	524 ± 26	632 ± 43	610 ± 22	504 ± 10
Pu	658 ± 10	651 ± 19	439 ± 49	599 ± 22	509 ± 38	403 ± 95
Am	582 ± 34	560 ± 28	367 ± 13	509 ± 65	410 ± 56	256 ± 129
Cm	709 ± 43	670 ± 38	342 ± 12	405 ± 70	202 ± 60	0 ± 150 [b]

[a] The values are from the evaluation in this work; 298.15 K, in kJ mol^{-1}. See Table S9 for previously available values and references. [b] Rough estimate.

Table 3. Ionization energies of An oxides [a]

An	IE[AnO]	IE[AnO$^+$]	IE[AnO$_2$]	IE[AnO$_2^+$]
Th	6.60242 ± 0.00002	11.8 ± 0.7	8.9 ± 0.4	16.6 ± 1 [b]
Pa	5.9 ± 0.2	11.8 ± 0.7	5.9 ± 0.2	16.6 ± 0.4
U	6.0313 ± 0.0006	12.4 ± 0.6	6.128 ± 0.003	14.6 ± 0.4
Np	6.1 ± 0.2	14.0 ± 0.6	6.33 ± 0.18	15.1 ± 0.4
Pu	6.1 ± 0.2	14.0 ± 0.6	7.03 ± 0.12	15.1 ± 0.4
Am	6.2 ± 0.2	14.0 ± 0.6	7.23 ± 0.15	15.7 ± 0.6
Cm	6.4 ± 0.2	15.8 ± 0.4	8.5 ± 1	17.9 ± 1 [b]

[a] The values are from the evaluation in this work; in eV. See Table S10 for previously available values and references. [b] Rough estimate.

Table 4. Enthalpies of formation of gaseous An oxides [a]

An	$\Delta_f H^o[\text{AnO,g}]$	$\Delta_f H^o[\text{AnO}^+,\text{g}]$	$\Delta_f H^o[\text{AnO}^{2+},\text{g}]$	$\Delta_f H^o[\text{AnO}_2,\text{g}]$	$\Delta_f H^o[\text{AnO}_2^+,\text{g}]$	$\Delta_f H^o[\text{AnO}_2^{2+},\text{g}]$
Th	-21 ± 26	617 ± 26	1775 ± 85	-456 ± 19	404 ± 38	2004 ± 190
Pa	18 ± 60	587 ± 52	1726 ± 44	-513 ± 77	57 ± 60	1658 ± 119
U	24 ± 15	606 ± 15	1803 ± 54	-477 ± 21	114 ± 21	1523 ± 62
Np	-30 ± 21	559 ± 10	1909 ± 39	-413 ± 48	198 ± 24	1654 ± 40
Pu	-60 ± 10	529 ± 19	1879 ± 57	-410 ± 24	269 ± 43	1725 ± 111
Am	-49 ± 34	549 ± 28	1900 ± 32	-309 ± 73	389 ± 63	1903 ± 133
Cm	-76 ± 44	541 ± 39	2066 ± 33	-232 ± 83	588 ± 72	2315 ± 154

[a] The values are derived from the bond dissociation enthalpies evaluated in this work; 298.15 K, in kJ mol^{-1}.
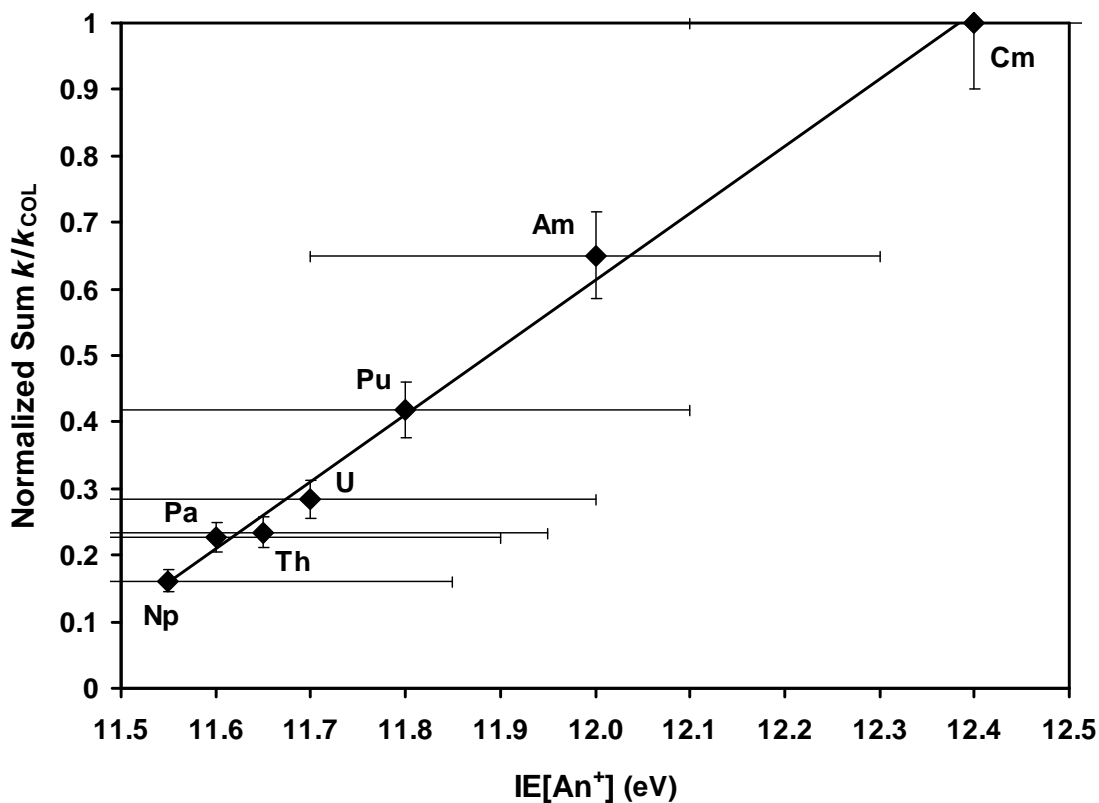
Figure 1. Plot of the normalized sum of the fraction of the reaction efficiency (k/k_{COL}) corresponding to electron transfer in reactions of An^{2+} with hydrocarbons [15], as a function of the $IE[An^+]$ estimated in this work (sum normalized to Cm^{2+} which had the greatest electron-transfer efficiency [15]; for details of the procedure as applied to the case of the lanthanides see [14]). (The linear fit has $R^2 = 0.994$.)
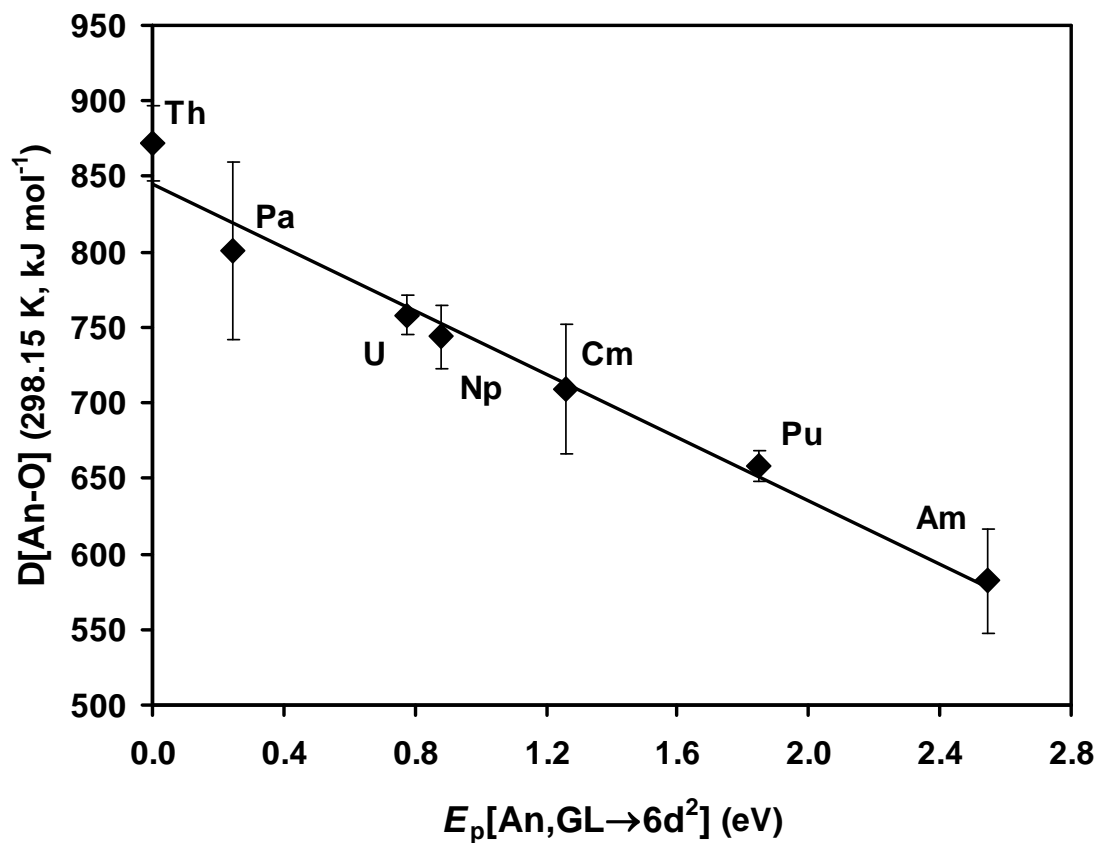
Figure 2. Plot of the D[An-O] obtained in this work (Table 2) as a function of the promotion energy (E_p) of the An atoms from the ground level to the lowest $6d^2$ configuration (Table S3). (The linear fit has $R^2 = 0.977$.)
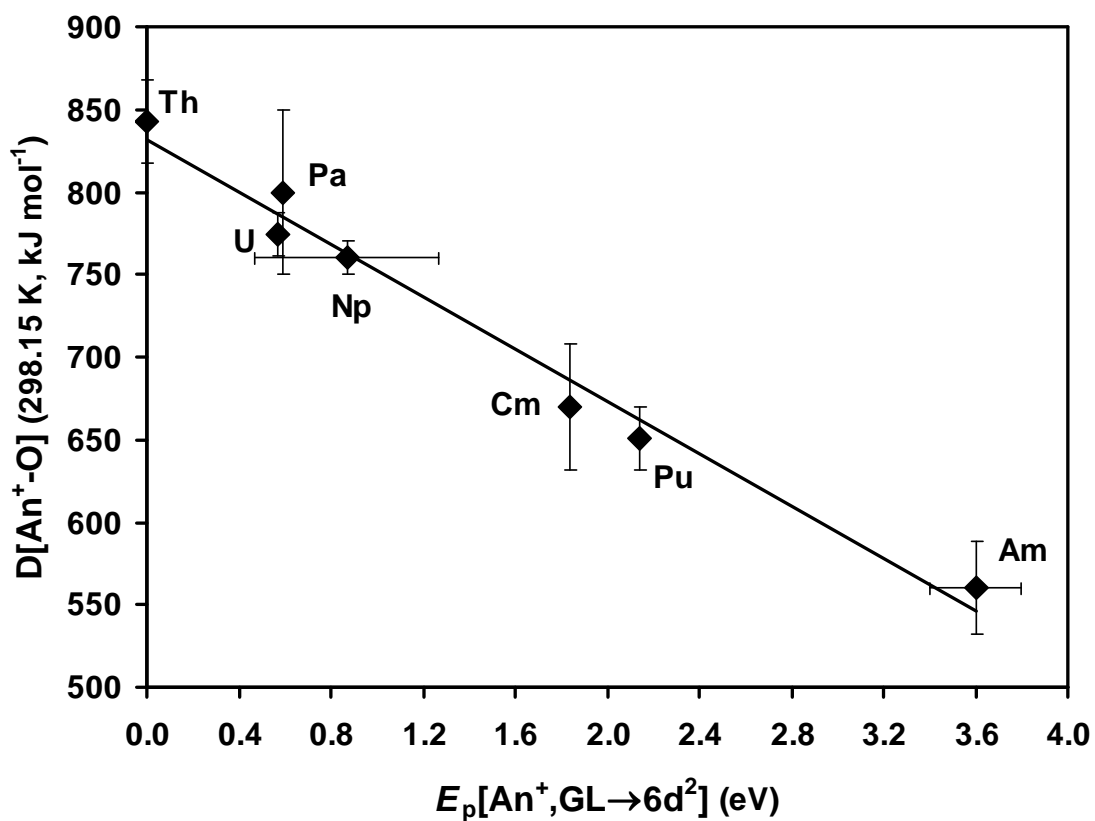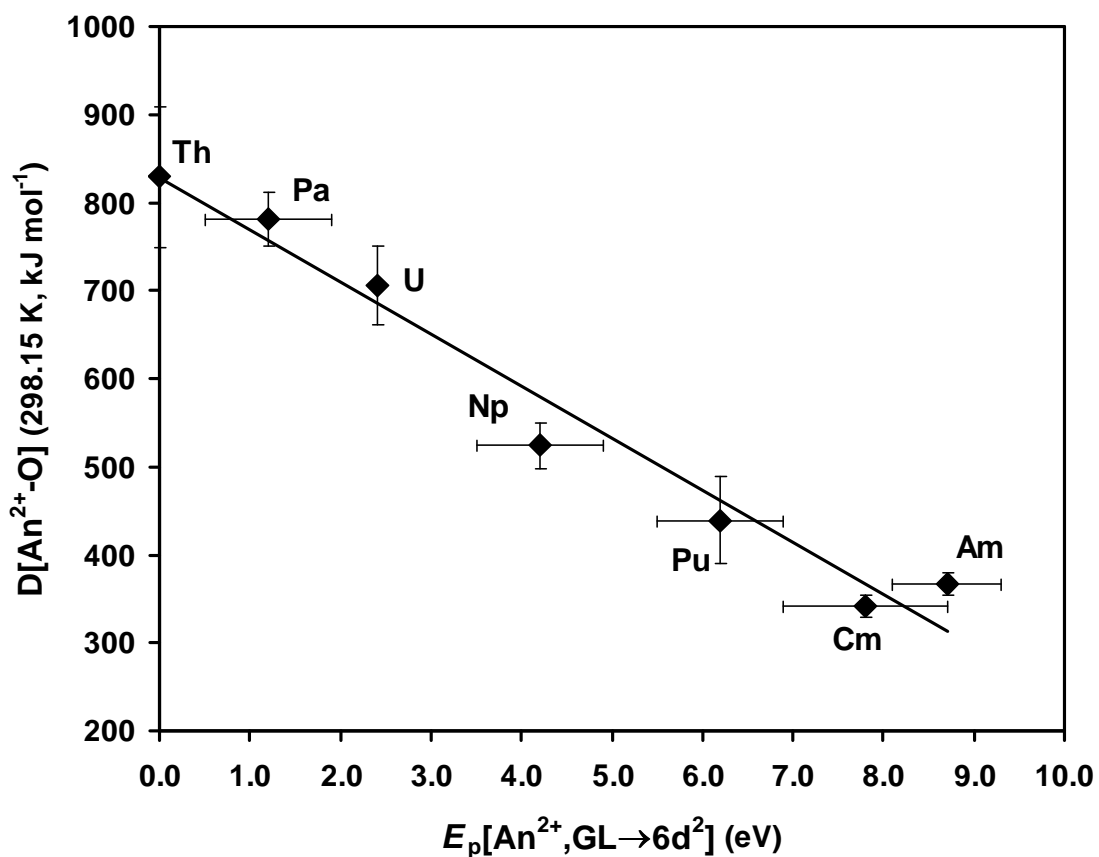
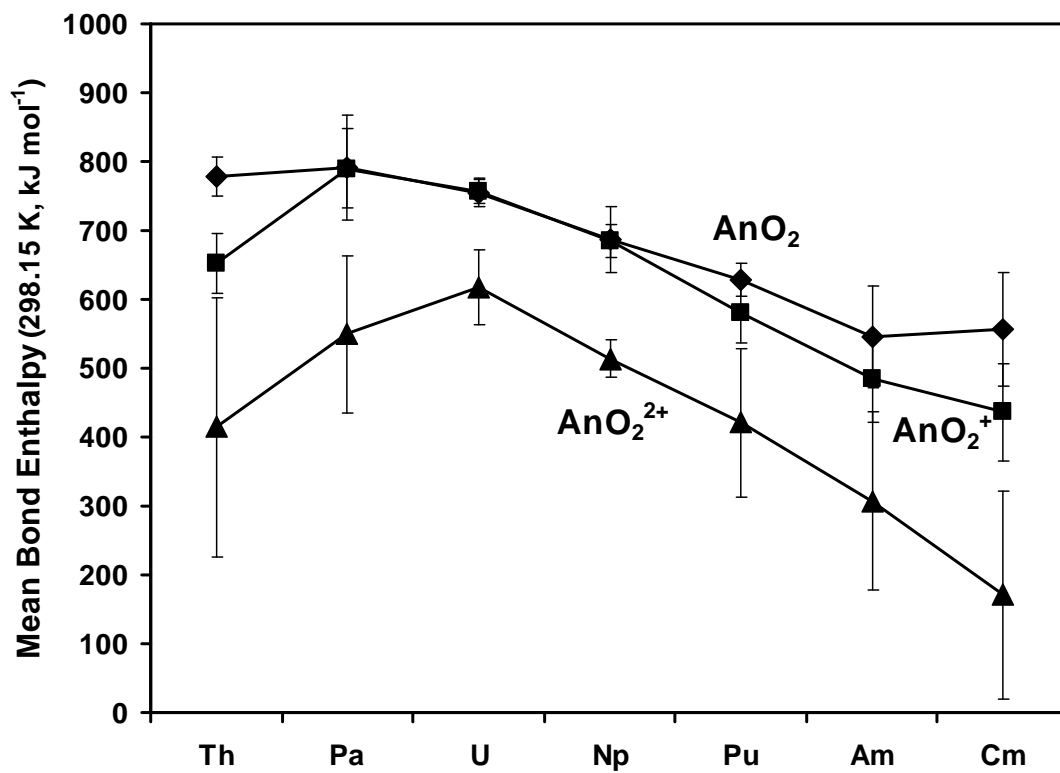**Figure 3.** Plot of the D[An$^+$-O] obtained in this work (Table 2) as a function of the promotion energy (E_p) of the An$^+$ cations from the ground level to the lowest 6d^2 configuration (Table S4). (The linear fit has R^2 = 0.982.)

Figure 4. Plot of the D[An^{2+}-O] obtained in this work (Table 2) as a function of the promotion energy (E_{p}) of the An^{2+} cations from the ground level to the lowest 6d^2 configuration (Table S5). (The linear fit has R^2 = 0.967.)

Figure 5. Mean bond enthalpy of neutral and cationic An dioxides (calculated from data in Table 2).
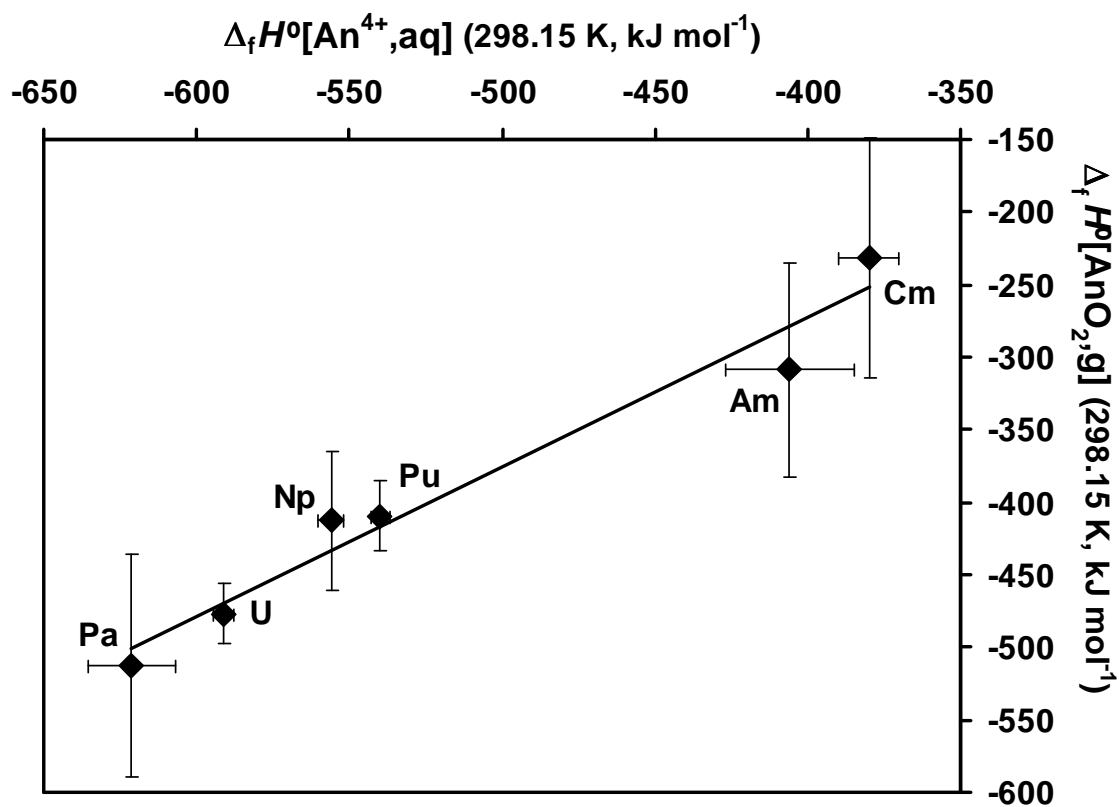
Figure 6. Plot of the $\Delta_f H^o[AnO_2,g]$ obtained in this work (Table 4) as a function of the $\Delta_f H^o[An^{4+},aq]$ (Table S12). (The linear fit has $R^2 = 0.964$; the point for $ThO_2,g/Th^{4+}$,aq is not included in the plot, as discussed in the text.)
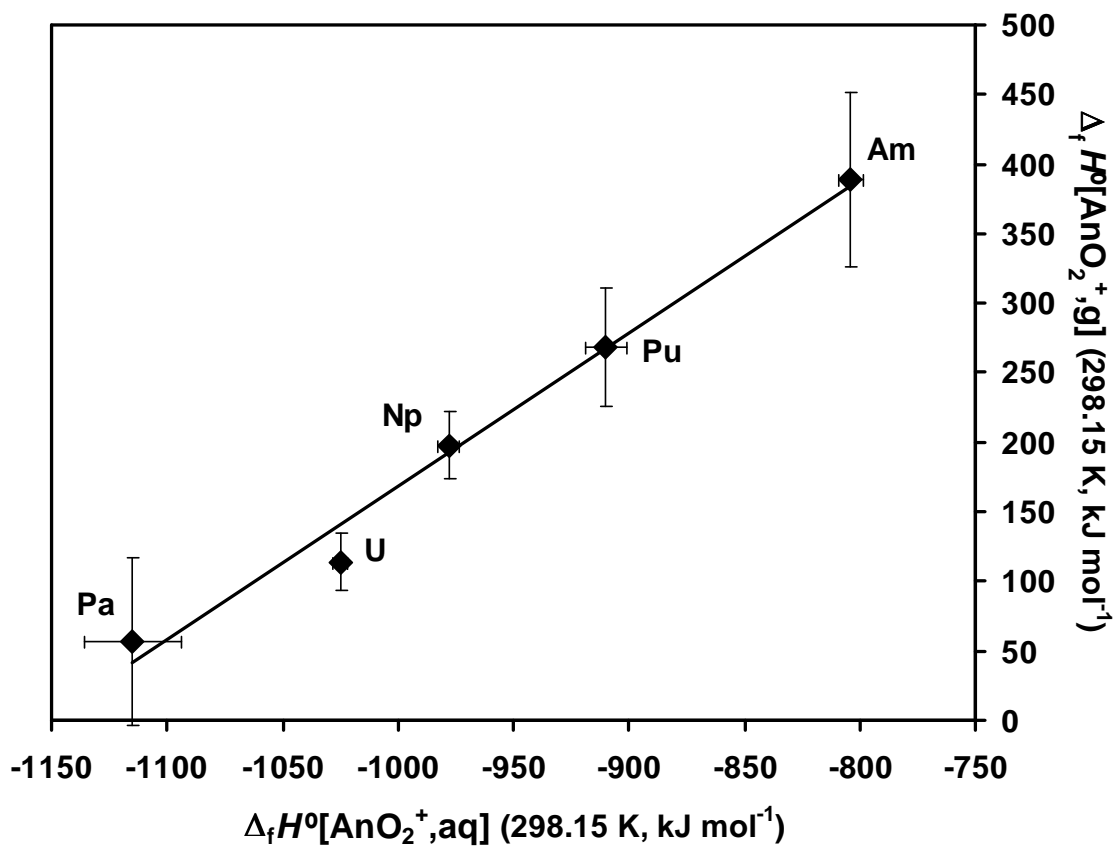
Figure 7. Plot of the $\Delta_f H^o[AnO_2^+,g]$ obtained in this work (Table 4) as a function of the $\Delta_f H^o[AnO_2^+,aq]$ (Table S12). (The linear fit has $R^2 = 0.985$; the Pa point corresponds not to PaO_2^+,aq but rather to the Pa(V) species that is stable in aqueous solution, $PaOOH^{2+}$.)

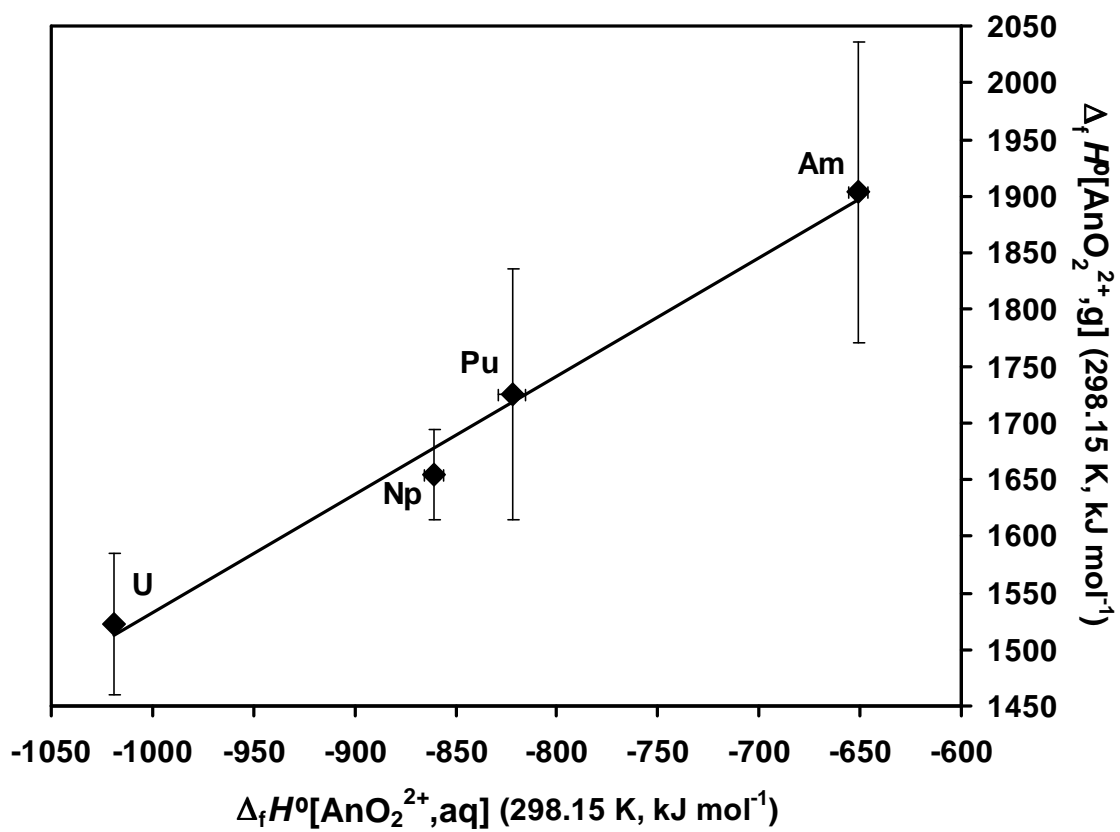**Figure 8.** Plot of the $\Delta_f H^o[AnO_2^{2+},g]$ obtained in this work (Table 4) as a function of the $\Delta_f H^o[AnO_2^{2+},aq]$ (Table S12). (The linear fit has $R^2 = 0.990$.)