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THERMOCHEMICAL REGULARITIES AMONG LANTHANIDE AND ACTINIDE OXIDES*

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Summary

This paper systematically treats the thermochemical properties of binary and complex oxides of the lanthanides and actinides, in terms of other well-characterized species and thermochemical cycles. Since the trivalent lanthanides provide a reference series against which the lanthanide and actinide sesquioxides can be compared, the trivalent-ion energetics are considered first. Recent interest in monoxides, prompted by high-pressure synthesis of lanthanide monoxides and interest in divalent actinide metals and oxides, has led us to include a treatment of the relative stabilities of monoxides and sesquioxides. The important tetravalent state is viewed from the perspective of the dioxides as well as the perovskites $BaMO_3$. Since there are no higher-valent lanthanides, systematic trends in pentavalent and hexavalent complex actinide oxides are not treated in this review.

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1. Introduction

Enthalpies of formation of the lanthanide sesquioxides were systematically determined by combustion and solution calorimetry between 1955 and 1973. Following the review of Holley, Huber, and Baker [1], only a few new experimental determinations have been made [e.g., 2]. Subsequent reviews [3-7] have included new measurements. Relatively few measurements have been made on the dioxides; for TbO_2, in particular, only an extrapolation from TbO_{2-x} enthalpies of solution is available [2,4]. The situation is even worse for the monoxides, where only a single reliable datum is available [3,4,8]. These data on binary lanthanide oxides will be discussed in subsequent sections. Only one measurement set is available on ternary lanthanide oxides, the perovskites $BaLnO_3$ [9] containing tetravalent lanthanides. Surprisingly, there are no thermodynamic data on the many complex Ln(III) oxides [3,7,10]. The behavior of complex oxides is important, for example, to model actinide behavior in geochemical, nuclear fuel, and nuclear waste environments.

The most stable set of actinide oxides is the dioxides. The oxides ThO_2 and UO_2-AmO_2 have been characterized thermochemically [11]. Thermodynamic data are known for all the oxides of uranium that are stable at 1 atm pressure [12,13] but for other actinide oxides only recently have measurements been reported for Pu_2O_3 [14,15] and Cm_2O_3 [16]. In contrast to the lack of data on ternary actinide(IV) oxides, there are many thermodynamic data for complex actinide oxides containing U(VI) and several measurements for those containing U(V) [3,11,17]. Clearly there are large gaps in thermodynamic characterization of f-element oxides, especially of monoxides, actinide sesquioxides, and complex oxides containing Ln(III) and An(IV), the two most important oxidation states.

Oxide thermodynamic data are necessary for preparative, geochemical, nuclear technology, and metallurgical purposes. They also serve an important role in the characterization and understanding of the energetics of ionic compounds [5,11]. It is this latter role that we shall emphasize in this review, comparing the lanthanide and actinide oxides in each oxidation state with gaseous atoms and other ionic species in order to explain and to predict the stability relationships among the oxides.

There have been some earlier treatments of this sort. Morss [5] and Johnson [18,19] have focussed on Born-Haber cycles that include ionization potentials and lattice energies of lanthanide oxides. Ackermann et al. [20,21] compared the sesquioxides and dioxides with gaseous atoms and aqueous ions, in ways that we will extend in later sections. Johansson [22,23] compared oxides and halides in various oxidation states to identify differences in stability of di-, tri-, and tetra-valent metals and to establish boundaries between these important oxidation states. Morss and Fuger [24] compared dioxides and aqueous tetravalent ions as a function of the size of these ions.

This paper begins with a systematic treatment of the lanthanide and actinide sesquioxides. These are the "normal" oxides for most of the lanthanides and are important for the actinides plutonium through einsteinium. Discrepancies in reported thermochemical properties, important needed measurements, and useful predictions are listed. Recent interest in monoxides justifies the inclusion of these compounds in this review, and the near-absence of experimental data is highlighted. The important tetravalent oxides MO_2 and $BaMO_3$ are highlighted since new experimental and theoretical papers have appeared on these oxides in recent years. Since there are no lanthanides of higher oxidation states, we exclude actinide(V) and (VI) complex oxides, although many new experimental measurements have been published in the past decade.

2. Sesquioxides

Inasmuch as the trivalent state is the most common for the lanthanides, the sesquioxides have been extremely well characterized [4,6,7]. Although trivalent ions exist for almost every actinide, actinide sesquioxides are relatively less common than their lanthanide counterparts because the tetravalent actinide ions and dioxides are so stable. The first conventional determination of a thermophysical actinide sesquioxide property (the specific heat of Pu_2O_3 [15]) and of a thermochemical property (the enthalpy of formation of Cm_2O_3 [16]) have only been made very recently, although these compounds have been known for almost four decades and their polymorphic transitions are well characterized [25-28].

Cubic sesquioxides are known for lanthanides and for actinides from plutonium through einsteinium [29]. In some cases, the cubic (low-temperature "C") sesquioxides are hyperstoichiometric, and thermodynamic measurements were made from monoclinic ("B") or hexagonal ("A") isomorphs, but since the enthalpy of transition among these isomorphs is small, it can if necessary be estimated. Given this series of isostructural compounds with $\underline{f}^n$ configurations, we can apply a powerful correlation first utilized by Nugent, Burnett, and Morss [30] to compare the metals, gaseous atoms, and aqueous ions. They explained why the sublimation enthalpies (Fig. 1, top) and $\Delta H_f^\circ(M^{3+},aq)$ (Fig. 1, bottom) vary as they do, especially for the divalent metals europium and ytterbium. They proposed the correlation function P(M), defined as shown in Figure 2. For a "normal" lanthanide such as gadolinium (Figure 2a), where both the metal and atomic vapor are trivalent, P(M) connects the trivalent vapor and the trivalent oxide. For most other lanthanides, in which the gaseous atoms are divalent (Figure 2b), a promotion energy ΔE from the ground state of M(g) must be included to permit P(M) to connect two trivaent states. The P(M) function therefore should change systematically through the 4f and 5f series; it is more useful than ionization energies or hydration enthalpies which are large in magnitude, and usually very difficult to calculate accurately (thus their differences have larger error limits).

Figure 3 (for which the relevant data are in Table 1) displays the P(M) function for aqueous ions as the condensed state (as was done earlier by Nugent et al. [30] and by David et al. [31]), for the sesquioxides as the condensed state (as was done by Ackermann [20,21]), and for trichlorides as the condensed state. Unlike the sesquioxides, the trichlorides show a sharp structural change after terbium, so that the heaviest lanthanide trichlorides are not directly comparable with the lighter trichlorides. It is evident that each of the three P(M) functions for the lanthanides falls onto a curve approximated by the two arms of the letter V. (The change in slope at f^7 was explained by Nugent et al. [30]). Deviations, especially among the heavier lanthanides, are parallel for all three sets of data. In part these deviations are due to possible errors in thermodynamic measurements (enthalpies of formation of aqueous ions and trichlorides, and in some cases of sesquioxides as well, depend upon the same heat-of-solution data on the metals), and in part they may be due to errors in selection of spectroscopic data for ΔE or to subtle ligand-field effects. If these P(M) values were plotted with estimated error limits, they all would be consistent with the P(M) lines in Figure 3.

Despite the paucity of experimental data on trivalent actinides, it is evident that P($AmCl_3$) and P(Am^{3+}) are grossly out of line. A discrepancy at Am had been noted earlier in correlations of this sort [30,32]; this discrepancy helped stimulate more careful redeterminations of ΔH(sublimation, Am) and $\Delta H_f^\circ(Am^{3+}, aq)$. Despite substantial revisions of both of these data, which are now very well established from reliable and repeated experiments, P(Am) is some 70 kJ mol^{-1} too positive. Clearly, $\Delta H_f^\circ(Am_2O_3,s)$ should be determined, although it will probably follow a P(M) behavior to the $AmCl_3$ and Am^{3+} points. Alternatively, the spectroscopic values of ΔE may be in error. Ward and Hill [33] have proposed that ΔH(sublimation, Am) is ~40 kJ mol^{-1} too large because of the large positive change in entropy upon vaporization. Nevertheless, such an effect might be compensated by an unusually small $\Delta H_f^\circ(Am^{3+},aq)$ and would thus disappear in P(Am)!

Another way to compare the sesquioxides with other trivalent species is to study the enthalpies of solution of trivaent compounds:

$$MCl_3(s) = M^{3+}(aq) + 3Cl^-(aq) \qquad (1)$$

$$1/2\ M_2O_3(s) + 3H^+(aq) = M^{3+}(aq) + 3/2\ H_2O\ (1)$$

In essence, this sort of comparison looks at the difference in slope between pairs of P(M) lines in Figure 2. Relevant data are given in Table 2 and are displayed in Figure 4. It is evident that the enthalpies of solution of lanthanide sesquioxides become less exothermic proceeding from the light to the heavy lanthanides (as molar volume decreases due to the lanthanide contraction), in contrast to the opposite behavior for the trichlorides. This behavior explains the different slopes of the P(M) lines for $MO_{1.5}$ and MCl_3, and can be interpreted as in Figure 5: In an isostructural series such as hexagonal MCl_3, lattice energies increase as interionic distances decrease (lighter to heavier lanthanides). Hydration enthalpies also increase [34]; since ΔH(solution) becomes more exothermic from $LaCl_3$ to $GdCl_3$, the more exothermic trend in ΔH(hydration) outweighs the increase in U_{pot}. The opposite slope for ΔH(soln) for $MO_{1.5}$ implies that the increase in U_{pot} outweighs that in ΔH(hyd). We note also that the heavy lanthanide sesquioxides, which are less basic than the lighter sesquioxides, also yield less exothermic ΔH(solution) because in this case ΔH(solution) is an acid-base reaction.

David et al. [31] used electrochemical data to estimate P(M) for aqueous actinide ions Cf^{3+} through No^{3+}. They concluded that the actinide P(M) is a single straight line rather than a V-shaped line. The P(M) point plotted in Figure 3 for Bk^{3+}, representing experimental sublimation and calorimetric data not yet available when David et al. published their paper, is consistent with a nearly straight-line behavior for the actinide P(M). From the interpolated P(M) and ΔH(solution) for cubic sesquioxides, we have estimated ΔH_f° for Am_2O_3 and the resulting value is shown in Table 1.

There are as yet no thermodynamic data on any ternary oxides containing trivalent lanthanides or actinides. It is likely that some such oxides (perovskite aluminates, spinels, etc.) stabilize trivalent ion sites, usefully enhancing the stability of Ln^{3+} and An^{3+} ions [35].

3. Monoxides

The only well-characterized lanthanide monoxide is EuO [6,7]; there is a real doubt that any of the other lanthanide or actinide monoxides reported before 1970 are valid [6,36]. EuO is readily prepared from metal and sesquioxide in open or sealed tantalum vessels at 1780-1825°C [37]. The next most easily reduced lanthanide is ytterbium: YbO appears to be stable below about 800°C but it has not been prepared free of Yb_2O_3 [38,39]. Electrode-potential data for aqueous ions [5,40] indicate that the stability of M^{2+} ions with respect to the reaction

$$2M^{3+}(aq) + M(s) = 3M^{2+}(aq) \qquad (2)$$

decreases in the sequence ($\Delta G°$ in kJ mol^{-1} for reaction 2 in parentheses) Eu (-475), Yb (-344), Sm (-212), Dy (-38), Tm (-12), Nd (+87), and Pm (+108). Since the free-energy change for the corresponding solid-state oxide reaction (based upon thermodynamic measurements)

$$Eu_2O_3(s) + Eu(s) = 3EuO(s) \qquad (3)$$

is only -113 kJ mol^{-1}, we may estimate $\Delta G°$ for reaction (2) to be approximately $-344 + (-113 + 475) = +18$ kJ mol^{-1} for Yb and for Sm and other lanthanides to be even more unfavorable with respect to divalent monoxides $(M^{2+})(O^{2-})$. Thus it is not surprising that early claims of other monoxides as bulk or even as surface phases are now discounted as oxynitrides, oxycarbides, or hydrides.

Great interest has centered on recent synthesis [41] of "metallic" $(M^{3+})(O^{2-})(e^-)$ monoxides of La, Ce, Pr, Nd, and Sm. These monoxides have been prepared by stabilizing them at high pressure and are described as "trivalent" monoxides. Figure 6 shows stability relationships for "divalent" and "trivalent" Ln(II) compounds.

In view of the intense interest in these oxides, it is unfortunate that the only reliable thermodynamic data are those on EuO. An early pioneering study [42,43] showed the unusual instability of Eu^{3+}(aq) (now known to be caused by the divalency of Eu metal) but a misinterpretation of the reaction calorimetry stoichiometry (reduction of O_2 apparently proceeded mostly to H_2O_2 rather than to H_2O) led these authors to erroneous ΔH_f° values for Eu^{2+}(aq), Eu^{3+}(aq), and EuO(s). Suggestions by Burnett [43] and Cunningham [44] led Morss and Haug to a different cycle for Eu^{2+}(aq) and $EuCl_2$(s) [45]. Meanwhile, Huber and Holley [8,46] used Burnett's material (analyzed as $EuO_{1.02}$ gravimetrically by ignition to Eu_2O_3) to determine ΔH_f°(EuO,s) by combustion calorimetry. Huber and Holley's corrected datum stands as the single cornerstone of lanthanide monoxide thermodynamics. Now that the EuO-Eu_2O_3 phase diagram has been elucidated to show that stoichiometric EuO exists at 1780-1825°C [37], a new preparation of EuO and a redetermination of its thermodynamic properties is urgently needed.

A large number of complex oxides containing Eu(II) are known [36,47,48]. The simplest of these is Eu_3O_4, for which many properties have been measured. Among these are its high-pressure vaporization thermodynamics [49], from which one derives for the reaction

$$EuO(s) + Eu_2O_3(s) = Eu_3O_4(s) \qquad (4)$$

$\Delta H° = -17$ kJ mol^{-1} and $\Delta G° = -20$ kJ mol^{-1}. The free-energy relationships among europium oxides and gaseous reductants have been established [50]. Crystal-chemistry parameters that favor the formation of Eu(II) complex oxides have been summarized by Greedan and McCarthy [47]. The stabilization of Eu(II) in complex oxides is not parallel by Sm(II) or Yb(II) complex oxides, none of which are known, although combination of equations (3) and (4) leads to the prediction of

$$4Yb_2O_3(s) + Yb(s) = 3Yb_3O_4(s) \qquad (5)$$

$\Delta G° = 18 + 3(-20) = -42$ kJ mol^{-1}. Hence, synthesis of Yb(II) complex oxides should be investigated.

As mentioned above, bulk samples of some lighter lanthanide monoxides have been prepared from the sesquioxides and metals under high pressure. From a sample of NdO kindly supplied by Dr. J. M. Leger, its enthalpy of solution has been measured in 4.00 M hydrochloric acid. This sample showed a face-centered cubic X-ray diffraction pattern with $a_0 = 5.00$ Å; neither the diffraction film nor physical examination revealed any metallic inclusions. Three samples yielded ΔH(solution, 4M HCl) = -403 ± 12 kJ mol^{-1}. If the material were pure NdO, auxiliary thermochemical data and this value lead to $\Delta H_f°(NdO,s) = -577 \pm 13$ kJ mol^{-1}. For the reaction $Nd(s) + Nd_2O_3(s) = 3NdO(s)$, we calculate $\Delta H° = +78$ kJ mol^{-1}. Leger et al. [41] have calculated that the $P\Delta V$ stabilization of the above reaction is ca. 50 kJ mol^{-1} at 50 kbar pressure, so that solution calorimetry does not confirm the stabilization of NdO at that pressure. These results are of course independent of the electronic state of Nd in NdO. The presence of 7 mass percent of Nd metal in the NdO sample would have made the enthalpy of solution 28 kJ too exothermic, so that $\Delta H°$ for the above reaction for pure NdO would decrease from 78 to 50 kJ mol^{-1}, the estimated borderline to the stabilization of NdO under high pressure. Thermochemical studies of pure samples of NdO, SmO, and YbO should be undertaken.

Among the actinides, monoxides have been claimed for all elements from thorium through americium [51-53]. Just as early claims for some lanthanide monoxides have been refuted, it is now recognized that "PuO", for example, may really be an oxide carbide [54]. Despite an interesting preparative report of AmO [53], and despite the subsequent observations of Am(II) in dihalides [55,56], we argue in the following paragraph that AmO is an unstable product of Am metal oxidation.

Assuming that reactions (2) and (3) for actinide oxides parallel the corresponding lanthanides, we use $E°(Am^{3+}/Am^{2+}) = -2.3$ V [57] and derive $\Delta G(2) = +67$ kJ mol^{-1} and $\Delta G(3) = +429$ kJ mol^{-1}, placing Am near Nd in the instability of its divalent species. It is conceivable that "trivalent" AmO might be produced under high pressure from the reduction of Am_2O_3 with Am, but it is unlikely that it can be produced by controlled oxidation of Am metal unless there is a kinetic barrier to oxidation of AmO at moderate temperatures. Clearly Akimoto's experiment [53] should be repeated, however. Somewhat better prospects exist for synthesis of heavier actinide monoxides from the metal sesquioxide; e.g., for CfO, we use $E°(Cf^{3+}/Cf^{2+}) = -1.60$ V [57] to derive $\Delta G(2) = -112$ kJ mol^{-1} and $\Delta G(3) = +250$ kJ mol^{-1}. Only for Md and No would one calculate their monoxides to be stable with respect to reaction (3). Nevertheless, the prospects for "trivalent" monoxides are sufficiently attractive that high-pressure syntheses of AmO and CfO following reaction (3) have been proposed and ought to be attempted.

A very valuable spectroscopic interpretation of the stability of lanthanide monoxides has been presented by Brewer [58]. He has calculated the enthalpy change for $Ln(s) + 1/2\ O_2(g) = LnO(g)$, and he shows that the gaseous monoxides of the heavy lanthanides are significantly less stable than are those of the light lanthanides. The reason is that for the gaseous atoms ($\underline{f}^n\underline{s}^2$) to bond effectively to oxygen, promotion to a bonding (e.g., $\underline{f}^n\underline{sp}$) state must occur; such states are significantly more accessible in the light lanthanide atoms than in the heavy lanthanide atoms. The situation in the actinides is expected to be parallel although the spectroscopic data are not as extensive [59,60].

4. Tetravalent Oxides

In general, the oxide ion--electronegative, ionic, and a hard base--favors the stabilization of high oxidation states of metallic ions. Thus it is not surprising that the highest oxidation states of most metallic elements are achieved in binary or complex oxides. This generalization has long been applicable to the lanthanides (in which the tetravalent state is the highest known) and to the actinides, although some recent syntheses have added new examples that confirm the above generalization. In a few cases (Cs_3NdF_7, Cs_3DyF_7, for example) complex fluorides are especially stable, although in other cases (Np(VII) and Am(VI) compounds) there are complex oxides but no complex fluorides or oxyfluorides known.

Ackermann et al. [20,21] reviewed the thermodynamics of actinide dioxides from three perspectives: (1) high-temperature thermodynamic functions of the systems U-UO_2, Pu-PuO_2, and Am-AmO_2; (2) correlation of $H_f^\circ(MO_2,s)$ with $H_f^\circ(M^{4+},aq)$, and (3) P(M) correlation. The first of these approaches can be refined when high-temperature EMF properties of the AmO_{2-x} system are measured and when $H_f^\circ(Am_2O_3)$ is measured; the second and third are revised here.

A brief review of the thermochemistry of lanthanide and actinide dioxides was given by Morss and Fuger [24]. Their treatment paralleled that of Figure 4 and is reproduced, with additions, in Figure 7. Their objective was to use $H_f^\circ(AmO_2,s)$ to estimate $H_f^\circ(Am^{4+},aq)$: Figure 7 is a more meaningful correlation of $H_f^\circ(MO_2,s)$ vs. $M^{4+}(aq)$ than was that of Ackermann and Chandrasekharaiah [20] for the same reasons cited in Section 2 above.

It is seen from Figure 7 that the entry for Tb is significantly discordant from the other M^{4+} points. Although the experimental data upon which $H_f^\circ(TbO_2,s)$ are based appear reliable, they are measurements of TbO_{2-x} and the value for TbO_2 is an extrapolation [2,4]. It is possible to prepare stoichiometric TbO_2 [7] and its enthalpy of solution should be measured. There is no direct way to measure $H_f^\circ(Tb^{4+},aq)$ but Tb^{4+} has recently been prepared electrochemically by stabilization in aqueous carbonate solution [61]. Unfortunately, no quantitative data could be obtained on the Tb^{4+}/Tb^{3+} couple but the successful oxidation of Tb(III) to Tb(IV) is consistent with the $E^\circ = 3.1$ V calculated by Nugent et al. [57]. An alternative hypothesis is that the lanthanide(IV) species in Figure 7 may not follow the same functional relationships as the actinide(IV) species. More on this topic will be discussed below.

Another powerful systematic correlation arises from the P(M) function applied to the tetravalent configuration as shown in Figure 8 [62]. For this purpose we must have a consistent comparison between gaseous atoms in trivalent configurations (f^nds^2) and in tetravalent configurations ($f^{n-1}d^2s^2$). The compilations of Brewer [58,59] yield energy differences E from the ground state to the $f^{n-1}d^2s^2$ state for some of these transitions, and Johansson _et al_. [22,23] have estimated others by comparing the enthalpies of formation of "normal" dioxides (TiO_2, ZrO_2, HfO_2, ThO_2) formed from "tetravalent" metals with experimental enthalpies of formation of CeO_2, UO_2, PuO_2, etc. Having corrected his estimate for E(Am) and using the newly determined $H_f^\circ(AmO_2,s)$ [24], we show the data necessary for tetravalent P(M) correlation in Table 3 and the P(M) function in Figures 8 and 9. We observe an anomaly at Tb that implies $H_f^\circ(TbO_2)$ -1000 kJ mol^{-1}, a value that would make the Tb point of Figure 7 nearly coincident with the interpolated line; nevertheless, such a value would imply a stability for TbO_2 that is inconsistent with chemical evidence. Alternatively, the P(Pr) may be slightly high, which implies that ΔH_f° (PrO_2) -950 kJ mol^{-1}. Then the three lanthanide data of Figure 7 would fall on a straight line of smaller slope than the actinide points. With the new value of $H_f^\circ(AmO_2,s)$, the P(M) actinide points in Ref. 21, Figure 4, agree nicely with those of our Figure 9. Thus we have interpolated to estimate $H_f^\circ(PaO_2,s)$ = -1106 kJ mol^{-1} and have used Johansson's E estimates to predict $H_f^\circ(EsO_2,s)$ = -785 kJ mol^{-1}. Important data in need of measurement are $H_f^\circ(Bk^{4+},aq)$ by titration calorimetry, which will lead to $S^\circ(Bk^{4+},aq)$, as well as $H_f^\circ(BkO_2,s)$ and $H_f^\circ(CfO_2,s)$ in order to extend Figure 8. Additionally, it may be possible to determine $E^\circ(Cm^{4+}/Cm^{3+})$ and $E^\circ(Cf^{4+}/Cf^{3+})$ for complexed aqueous solution, data that will be important for the tetravalent P(M) correlation. Such data will establish whether it is thermodynamically possible to prepare Es(IV) compounds.

An independent comparison can be made as a result of recent studies of ternary tetravalent lanthanide and actinide oxides $BaMO_3$, all of which appear to have perovskite-based structures. In contrast with the dioxides, which have cubic (eightfold) coordination of M^{4+}, the perovskites have octahedral (sixfold) coordination. Large ions such as Th^{4+} are favorably sited in 8-coordinate ThO_2 but smaller ions like Tb^{4+} are well-stabilized in 6-coordinate $BaTbO_3$. The traditional crystal-chemistry (hard sphere) model for perovskite has an ABO_3 formula with $r(A^{2+}) \approx r(O^{2-})$ and B^{4+} in octahedral holes formed by six O^{2-} ions; the energetically ideal $r(B^{4+})$ is that which allows contact between the six O^{2-} ions and B^{4+}, i.e., when $r(B^{4+}) = (\overline{2} - 1) \times r(O^{2-})$. A more general criterion is Goldschmidt's t parameter [63].

$$t = \frac{r_A + r_O}{\overline{2}(r_B + r_O)} \qquad (6)$$

Table 4 shows data for all perovskites $BaMO_3$ for which thermodynamic data are known. Three stability criteria are shown: the tolerance factor t (equation (6), using oxide radius 1.40), the change in molar volume for the solid-state reaction $MO_2(s) + BaO(s) = BaMO_3(s)$, and the enthalpy change H(complex) for the same reaction. Also included in Table 4 are two other important perovskites, $BaThO_3$ and $BaPuO_3$, for which we have thermochemical measurements in progress.

Since the structural and thermodynamic data for $BaMO_3$ ternary oxides do not present a systematic picture, it is premature to extend the thermodynamic predictions for other actinide(IV) perovskites. Both better structural data (single-crystal or profile-analysis powder data that yield atomic positions) and thermodynamic data are needed on the actinide perovskites, especially since these tetravalent ions are the most prevalent long-lived radioactive components of nuclear waste. Nonetheless, it is worth noting that $BaPrO_3$ and $BaTbO_3$ are stoichiometric M(IV) compounds, much more easily synthesized than PrO_2 or TbO_2 [64]. Similarly $BaCmO_3$ and $BaCfO_3$ are known [65] although the corresponding Es(IV) compound has not been reported.

Brauer and Kristen [66] have reported the partial stabilization of Nd(IV) and Dy(IV) when these ions are in a dilute concentration in other perovskites. These ions are also found, surprisingly in certain rare-earth mixtures [67]. Thus Es(IV) may be stabilized as a dilute constituent of a perovskite such as $BaCeO_3$.

Many studies have been devoted to the thermodynamics of hypostoichiometric dioxides [68,69]. There are typically five categories of such studies. Physical measurements (thermogravimetry and oxygen partial pressure) have been carried out on CeO_{2-x}, PrO_{2-x}, TbO_{2-x} [6,7], ThO_{2-x} [70], UO_{2-x} [71], PuO_{2-x} [20,72], AmO_{2-x} [73], CmO_{2-x} [74], and BkO_{2-x} [75]. High-temperature EMF studies have been carried out with solid-state electrolytes on the $(Th\text{-}U\text{-}Pu)O_{2-x}$ systems [71,76]. Both of these techniques lead to relative partial molal enthalpies of solution of oxygen, and, by integration with respect to the nonstoichiometry parameter x, to molal thermodynamic properties of MO_{2-x}. Such data have been comprehensively reviewed by Ackermann et al. [20,21] and will not be treated here. The third category of measurements is high-temperature mass spectrometry, which leads principally to the thermodynamic properties of the gaseous oxides. Again, such measurements have been critically reviewed [20,21]. A fourth type of experiment is that of reaction calorimetry, either in solution at 298 K (e.g., PrO_{2-x} [77] or TbO_{2-x} [78]) or solid-gas reaction calorimetry at high temperatures (e.g., PuO_{2-x} at 1373 K

[14] and TbO_{2-x} at 986 K [79]). Lastly, there is a body of theoretical studies that develop statistical vacancy/defect/interstitial models which are beyond the scope of this review.

5. Conclusions

This paper has attempted to show the close interaction among the electronic structures of lanthanide and actinide metals, their gaseous atoms, and their compounds, in terms of thermodynamic properties (sublimation, hydration enthalpy, lattice energy, and enthalpy of formation). By understanding how these properties are interrelated, and by devising comparative schemes to shed light on apparent inconsistencies among these data, our systematic understanding of the bonding of these two sets of elements can be advanced and crucial experiments to resolve uncertainties can be proposed. It is hoped that thermodynamicists will undertake to resolve problems such as the solution calorimetry of SmO, TbO_2, PrO_2, Am_2O_3, and Bk^{4+}(aq), and the high-temperature equilibria of the Am(III)-Am(IV) and Cm(III)-Cm(IV) oxides. Practical problems, such as the effect of growing americium content in plutonium oxide fuels during burnup, should also be pressed.

A second emphasis of this paper has been to encourage the preparation of marginally-stable but interesting lanthanide and actinide oxides--interesting thermodynamically but also from many perspectives of solid-state science. Species such as Yb(II) in complex oxides, and Es(IV) doped into a complex oxide, are of great fundamental interest in the development of f-element chemistry.

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TABLE 1. Data for the Trivalent P(M) Correlations (kJ mol^{-1})[a]

				M^{3+}		MCl_3		C-$MO_{1.5}$
M	ΔH°_{subl}[b]	ΔE[c]	$\Delta H^\circ_f(M^{3+},aq)$[d]	P(M)	$\Delta H^\circ_f(MCl_3)$[e]	P(M)	$\Delta H^\circ_f(MO_{1.5})$[f]	P(M)
Y	421		-715	1136	-996	1417	-953	1374
La	431	-172	-709	1140	-1073	1504	-900	1331
Ce	420	- 57.0	-700	1120	-1058	1478	-898	1318
Pr	357	50	-706	1113	-1059	1466	-914	1321
Nd	327	80.9	-697	1105	-1042	1450	-904	1312
Pm	(318)	71	(-688)	(1077)				
Sm	207	185	-691	1083	-1026	1418	-914	1306
Eu	177	302	-606	1085	- 936	1415	-831	1310
Gd	398	-130	-687	1085	-1008	1406	-913	1311
Tb	389	3.4	-698	1090	-1007	1399	-933	1325
Dy	290	90.5	-696	1077	- 989	1369	-932	1312
Ho	301	88	-707	1096	- 995	1384	-940	1329
Er	312	85.9	-708	1106	- 994	1392	-949	1347
Tm	232	157.0	-705	1094	- 991	1380	-944	1333
Yb	156	277	-674	1107	- 960	1393	-907	1340
Lu	428		-703	1131	- 986	1414	-939	1367
Ac	(418)	-393						
Th	598	-251						
Pa	660	-141.1						
U	536	- 84.0	-489	1025	- 866	1402		
Np	465	- 42	-527	992	(-899)	1364		
Pu	342	75.5	-592	1010	-960	1378	-842	1260
Am	284	181	-617	1082	-978	1443	(-855)[g]	(1320)
Cm	387	- 14.5	-615	1002	-971	1358	-841	1228
Bk	310	88	-601	999	(-952)	(1350)		
Cf	196	202.3	(-603)	(1001)	(-924)	(1322)		
Es	128	231.7	(-596)	(956)				
Fm		243	(-592)					
Md		331	(-510)					
No		448	(-370)					

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a. Esimates in parentheses.

b. Ref. 3; F. L. Oetting, M. H. Rand, and R. J. Ackermann, "The Chemical Thermodynamics of Actinide Elements and Compounds", Part 1, IAEA, Vienna, 1976; and Chem. and Eng. News, Feb. 7 (1973) 7.

c. $f^{n+1}s^2$ configuration to f^nds^2 configuration. Refs. 30 and 31.

d. Refs. 3, 5, 31; J. Fuger and F. L. Oetting, "The Chemical Thermodynamics of Actinide Elements and Compounds", Part 2, IAEA, Vienna, 1976; and J. Fuger, R. G. Haire, and J. R. Peterson, J. Inorg. Nucl. Chem., 43 (1981) 3209.

e. Refs. 3, 5, 12, and calculations by the author.

f. Refs. 3, 4, 7, 14, and 16.

g. Estimated as $\Delta H^\circ_{sub} + \Delta E - P(Am)$.

TABLE 2. Terms in Calculation of $\Delta H(\text{soln})$ of $MO_{1.5}$ and MCl_3[a]
(all units kJ mol^{-1} or cm^3 mol^{-1})

M	$\Delta H_f^\circ(MO_{1.5})$[b]	$\Delta H^\circ(\text{soln}), MO_{1.5}$[c]	Molar Vol. $MO_{1.5}$[d]		$\Delta H^\circ(\text{soln}, MCl_3)$[e]	Molar Vol. MCl_3[f]	
Y	-953	-191	44.9	C	-225	74.7	M
La	-897	-241	49.6	H	-138	63.8	H
Ce	-898	-231	47.9	H	-144	62.4	H
Pr	-912	-221	46.7	H	-149	61.4	H
	-914	-223	52.2	C			
Nd	-904	-221	45.9	H	-156	60.6	H
Pm			44.9	H	(-162)	60.1	H
Sm	-912	-208	45.0	M	-167	59.2	H
	-914	-206	49.2	C			
Eu	-826	-209	44.0	M	-171	58.6	H
	-831	-203	48.4	C			
Gd	-908	-208	43.4	M	-181	58.1	H
	-913	-202	47.6	C			
Tb	-933	-194	46.5	C	-192	57.7	O
Dy	-932	-193	45.6	C	-207	74.3	M
Ho	-940	-195	44.9	C	-213	73.0	M
Er	-949	-189	44.1	C	-215	72.1	M
Tm	-944	-190	43.4	C	-216	71.3	M
Yb	-907	-196	42.8	C	-216	70.6	M
Lu	-939	-192	42.2	C	-218	70.3	M
Ac					(-105)	69	H
U					-125	62.4	H
Np					(-130)	61.5	H
Pu	-842	-179	45.6	H	-133	60.6	H
Am			45.0	H	-140	60.2	H
Cm	-841	-203	45.8	M	(-145)	59.4	H
Bk					(-150)	58.7	H
Cf					(-153)	58.3	H
Es					(-154)	58.2	H

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a. Other terms $[\Delta H_f^\circ(M^{3+},aq)$ and $\Delta H_f^\circ(MCl_3)]$ are found in Table 1. Estimated values in parentheses.

b. References 3, 4, 7, 14, and 16.

c. Calculated: $\Delta H(\text{soln}) = \Delta H_f^\circ(M^{3+},aq) + 1.5\Delta H_f^\circ(H_2O,\ell) - \Delta H_f^\circ(MO_{1.5},s)$.

d. References 7, 15, 29, 72, and Gmelin Handbuch, Transurane Vol. C. H = hexag. $MO_{1.5}$; M = monoclinic $MO_{1.5}$; C = cubic $MO_{1.5}$.

e. J. Burgess and J. Kijowski, Adv. Inorg. Chem. Radiochem., 24 (1981) 57, and Ref. 4, 5, and 13. Estimates in parentheses.

f. H = hexag. MCl_3; O = orthorhombic MCl_3; M = monoclinic MCl_3. References 3, 2; Gmelin Handbuch, Uran, Vol. C, and Transurane, Vol. C.

TABLE 3. Terms in Dioxide P(M) Correlation[a]
(all terms kJ mol^{-1})

M	Ground State	$\Delta E(f^{n-1}d^2s^2)$[b]	$\Delta H^\circ_f(M,g)$[f]	$WH^\circ_f(MO_2,s)$[g]	P(M)
Ce	fds^2	(360)	420	-1089	(1869)
Pr	f^3s^2	(552)	357	-958	(1867)
Tb	f^9s^2	(427)	389	-972(?)	(1788)
Hf	$f^{14}d^2s^2$	0	619	-1145	1764
Th	$f^0d^2s^2$	0	598	-1226	1824
Pa	f^2ds^2	23.7	660	(-1106)[c]	(1790)
U	f^3ds^2	137.6	536	-1085	1759
Np	f^4ds^2	(238)	465	-1074	(1777)
Pu	f^6s^2	431	342	-1056	1829
Am	f^7s^2	(615)	284	-932	(1831)
Cm	f^7ds^2	(515)	387	(-911)[d] (-896)	1831 (1798)
Bk	f^9s^2	(431)	310	(-1024)	(1765)
Cf	$f^{10}s^2$	(644)	196	(-887)[e]	(1727)
Es	$f^{11}s^2$	(787)	128	(-785)[c]	(1700)[a]

a. Estimates in parentheses.
b. References 22, 23, and 59; ground state to $f^{n-1}d^2s^2$ configuration.
c. Interpolated or extrapolated $\Delta H^\circ_f(MO_2)$ calculated as $\Delta H^\circ_f(M,g) + \Delta E - P'M)$.
d. Estimated from ΔH(solution) of CmO_2: L. Morss, J. Fuger, J. Goffart, and R. G. Haire, Lawrence Berkeley Laboratory Report LBL-12441, p. 263 (1981). Subsequent magnetic and analytical data indicate that this oxide is nearly $CmO_{1.9}$. The second ΔH°_f value assumes this composition, corrected to $\Delta H^\circ_f(CmO_2)$ by comparison with corresponding data for PrO_{2-x} and TbO_{2-x} [3,4].
e. Estimated from $\Delta H^\circ_f(M^{3+})$, $E^\circ(M^{4+}/M^{3+})$, and Figure 7.
f. Same references as in Table 1.
g. References 11 and 24.

TABLE 4. Perovskites: Structural and Thermodynamic Parameters[a]

			$MO_2(s) + BaO(s)$	$BaMO_3(s)$
	$IR(B^{4+})$		Δ(Molar Vol.)	ΔH(complex)
Compound	Å	t	cm^3/mol	kJ/mol
$BaTiO_3$	0.605	0.97	-5.8	-163
$BaMoO_3$	0.650	0.95	-5.4	-92[b]
$BaHfO_3$	0.71	0.92	-3.5	-134
$BaZrO_3$	0.72	0.92	-2.4	-126
$BaTbO_3$	0.76	0.90	+0.5	-88
$BaPrO_3$	0.85	0.864	+0.5	-147
$BaPuO_3$	0.86	0.860	+0.5	(-80)[c]
$BaCeO_3$	0.87	0.856	+1.7	-52
$BaUO_3$	0.89	0.849	+0.7	-57
$BaThO_3$	0.94	0.831	+2.3	(-20)[c]

[a] Data from C. W. Williams, L. R. Morss, and I. K. Choi, "Geochemical Behavior of disposed Radioactive Waste", American Chemical Society Symposium Series, in press.

[b] Unusually small ΔH(complex) since MoO_2 is stabilized by Mo-Mo bonds.

[c] Estimated.

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Figure Captions

1. Enthalpies of sublimation at 298 K (top) and enthalpies of formation of trivalent aquo-ions (bottom) for the lanthanides and actinides.

2. Energetics of lanthanide and actinide species showing trivalent oxide and P(M): (left) when M(g) configuration is $\underline{f}^n\underline{ds}^2$, (right) when M(g) configuration is $\underline{f}^{n+1}\underline{s}^2$.

3. Trivalent P(M) for trichlorides, sesquioxides, and aqueous ions.

4. Enthalpy of solution of $MO_{1.5}$ and MCl_3 as a function of molar volume.

5. Energy-level diagram for cycles involving enthalpy of solution of MCl_3 and $MO_{1.5}$.

6. Energetics of lanthanide monoxides: divalent ($M^{2+}O^{2-}$) and "trivalent" ($M^{3+}O^{2-}e^-$).

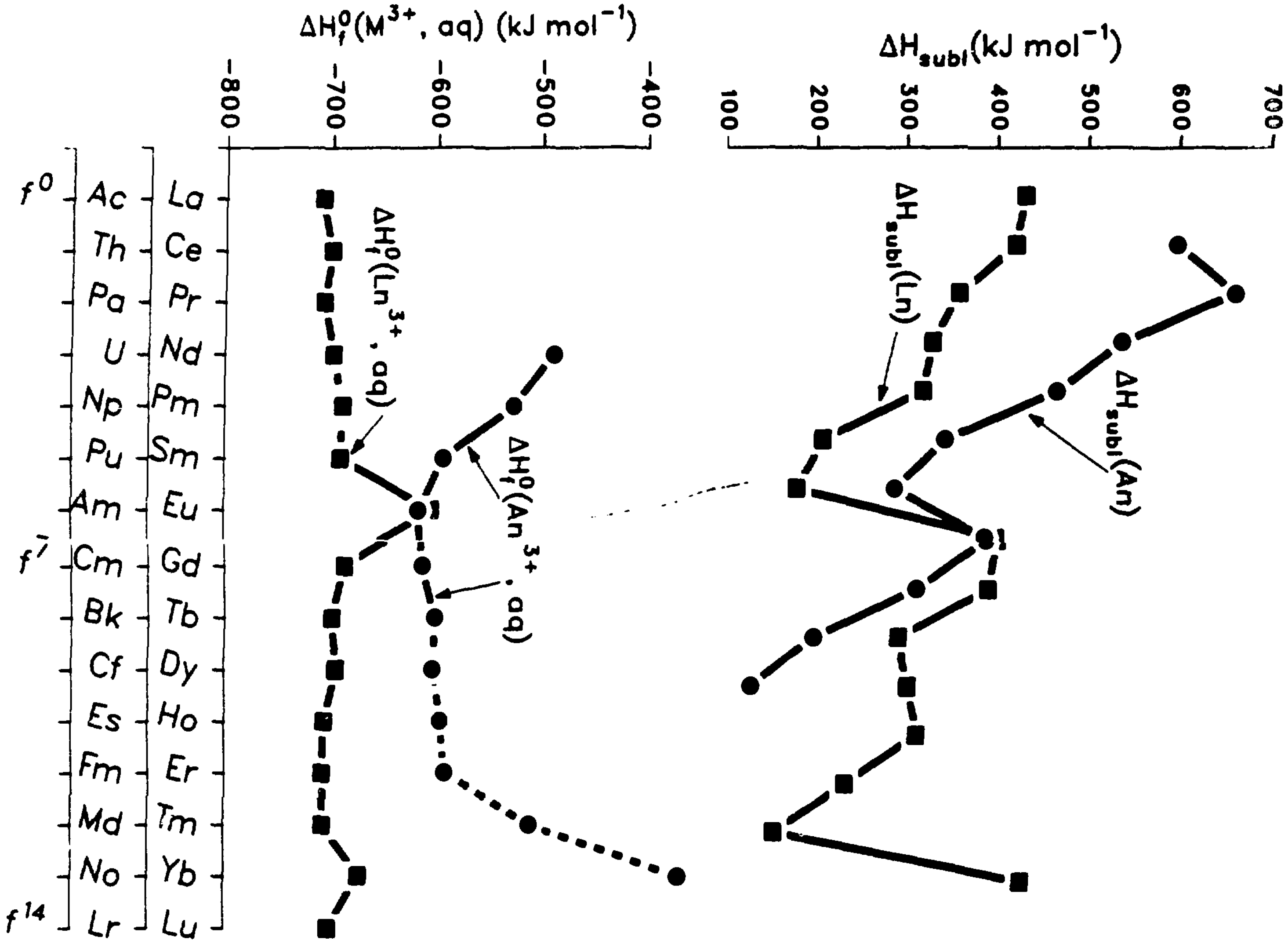
7. Enthalpy of solution of MO_2 as a function of molar volume.

8. Energetics of tetravalent P(M) correlation.

9. Tetravalent P(M) for lanthanide and actinide dioxides.

10. Enthalpies of formation of UO_x and $BaUO_{3+x}$.

6/15/83-jmb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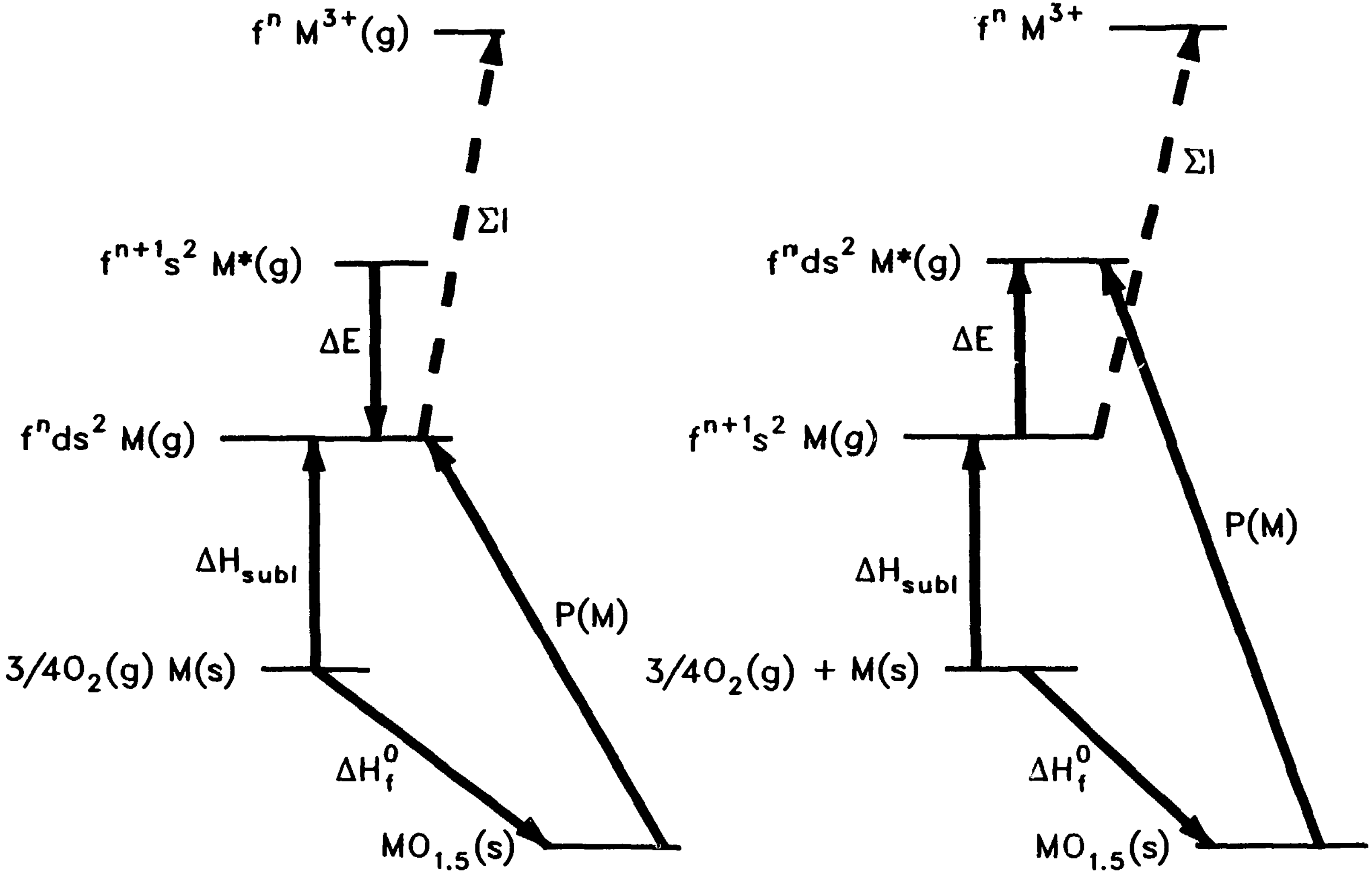
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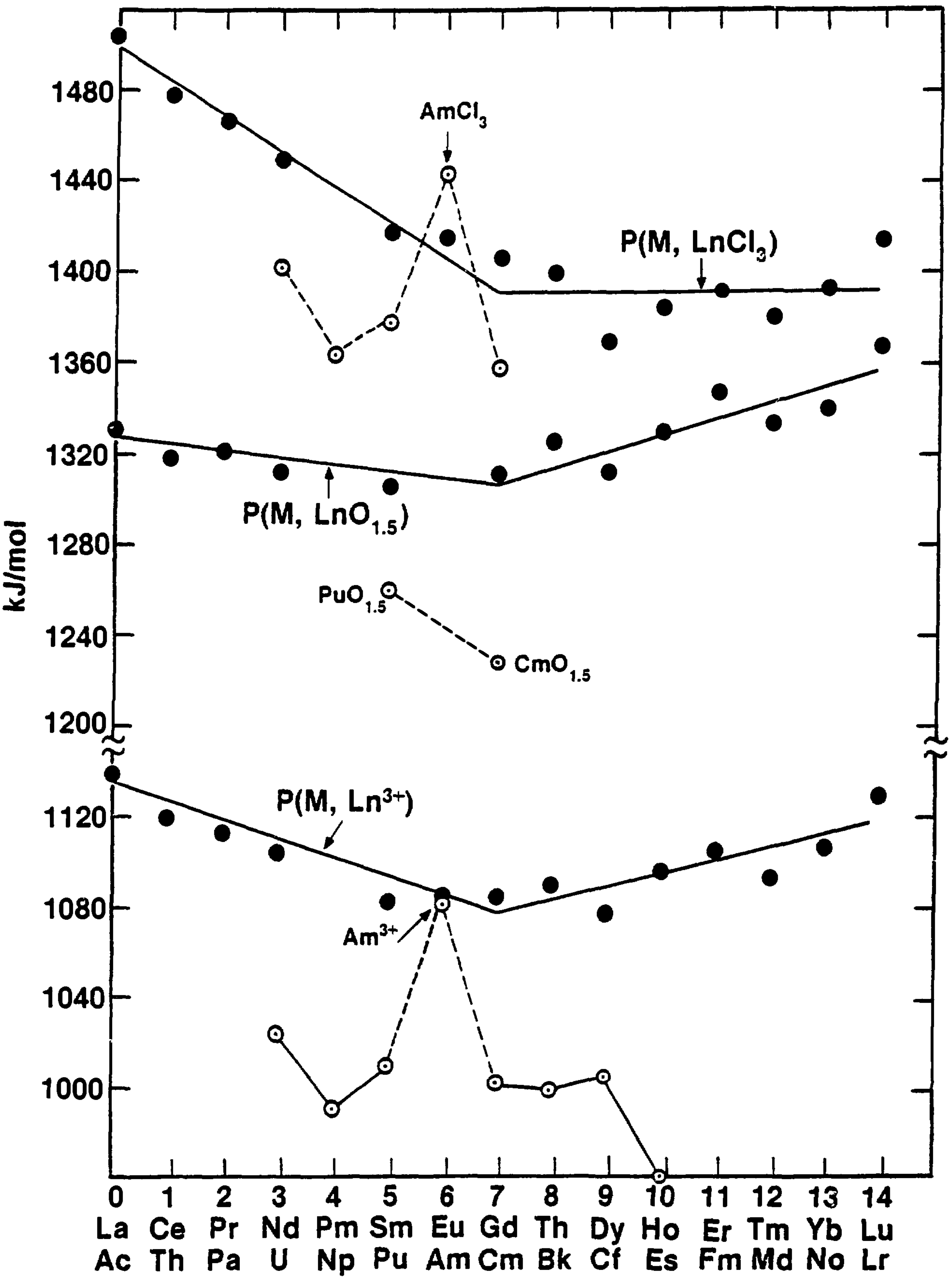kJ/mol
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P(M, LnO$_{1.5}$)
PuO$_{1.5}$
CmO$_{1.5}$
P(M, Ln^{3+})
Am^{3+}
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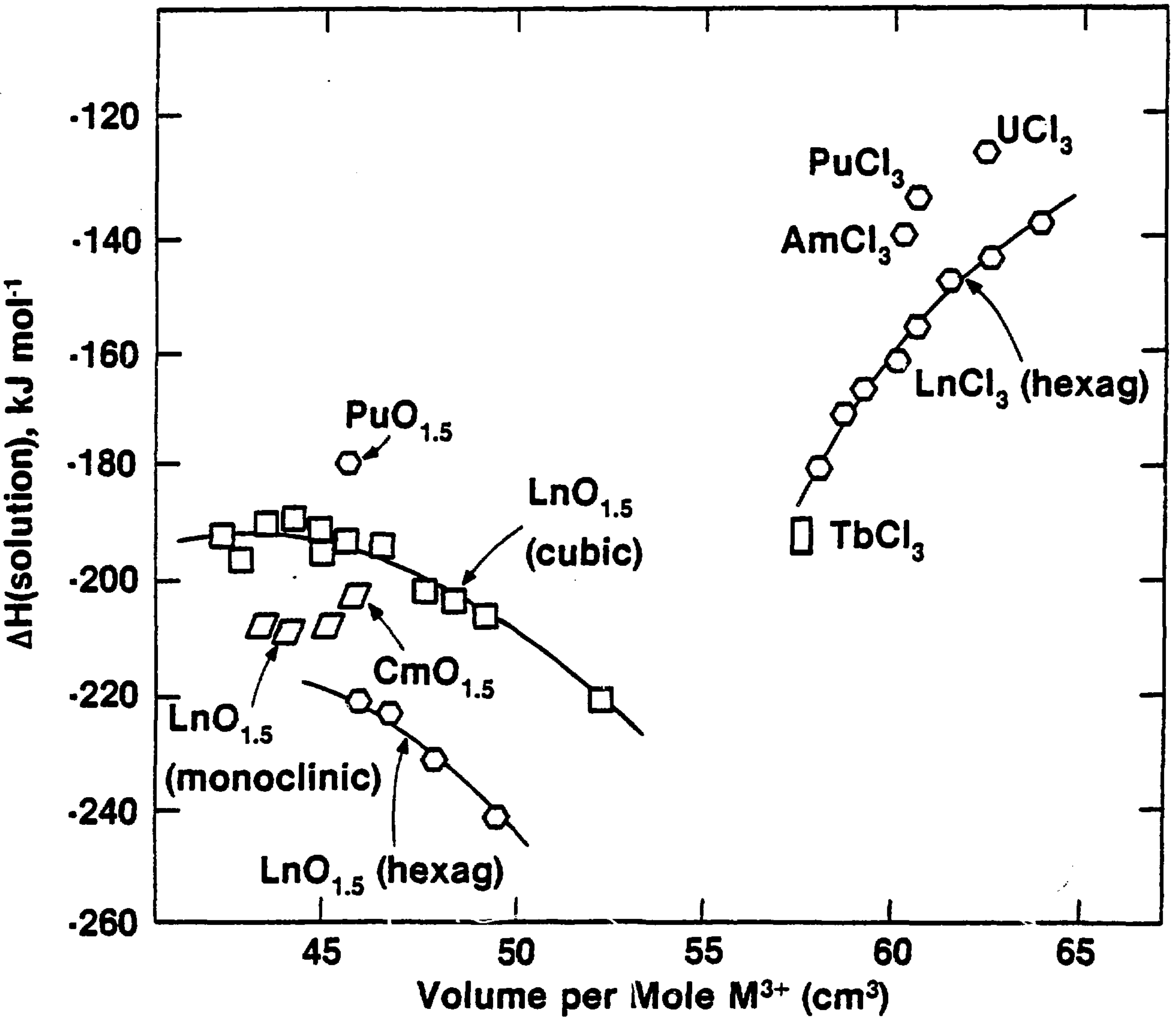
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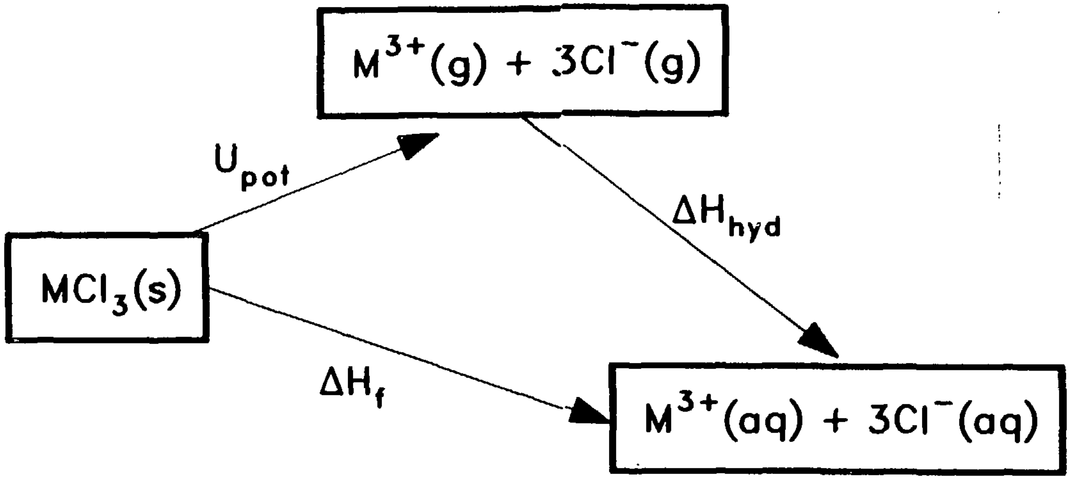
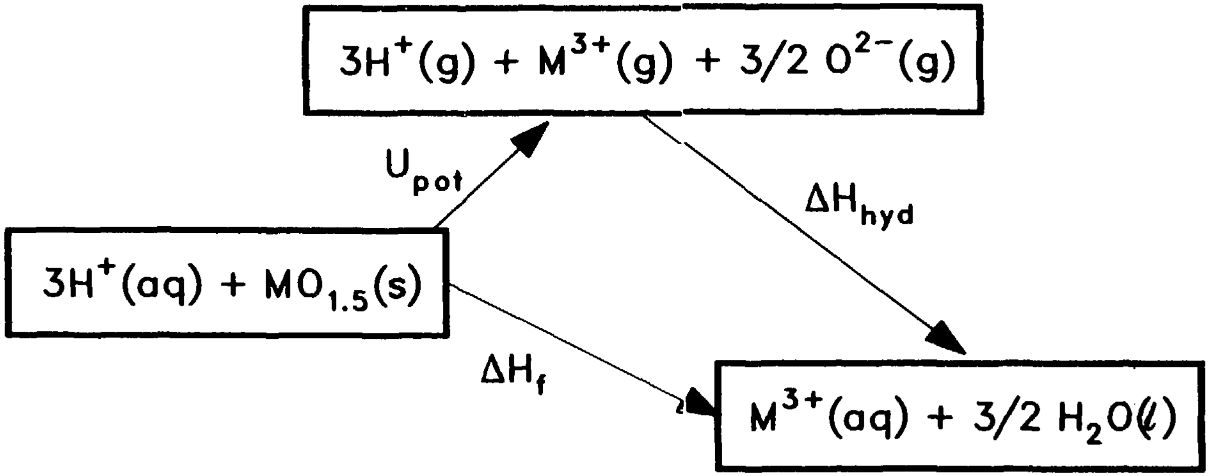
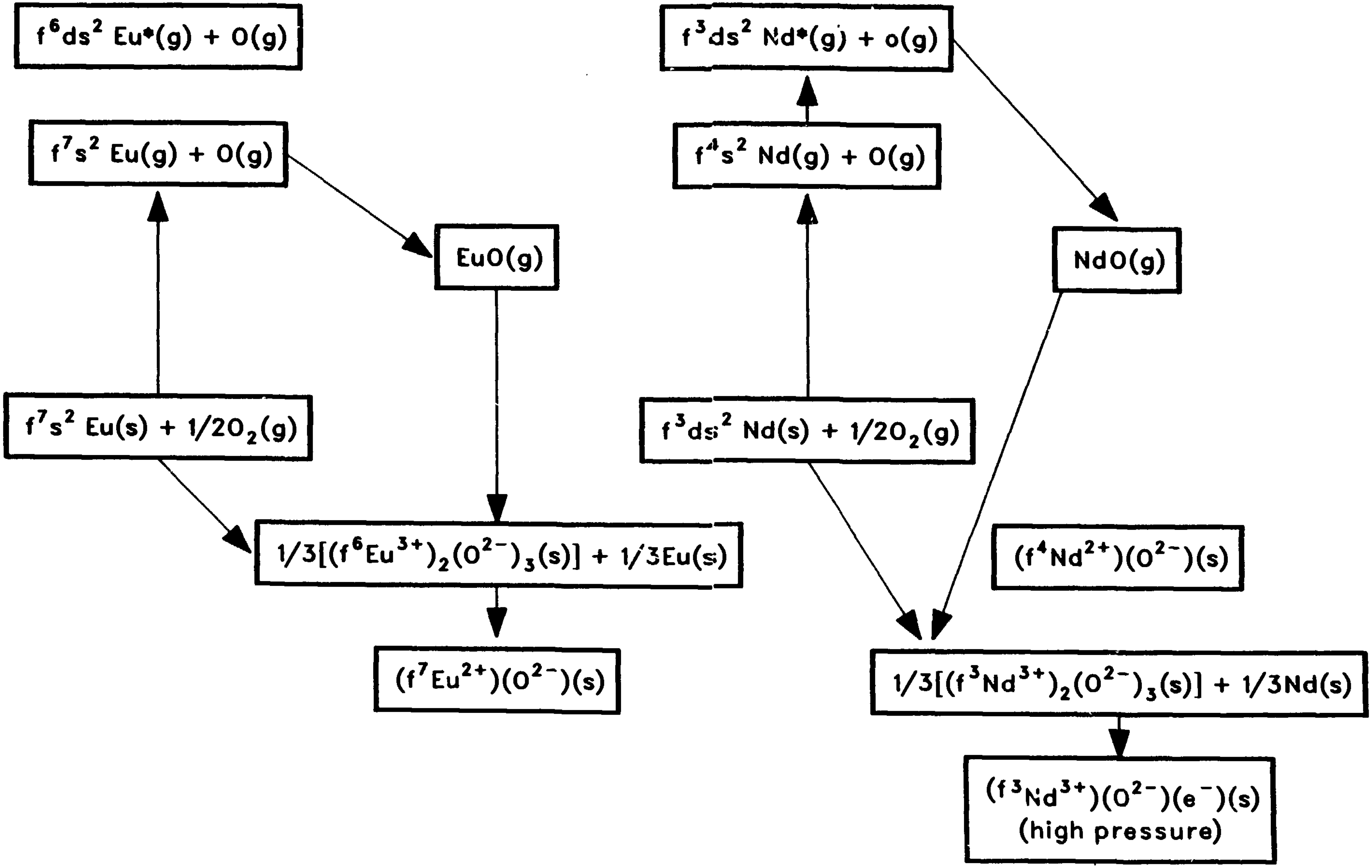
CmO1.5
LnO1.5 (monoclinic)
LnO1.5 (hexag)
UCl3
PuCl3
AmCl3
LnCl3 (hexag)
TbCl3

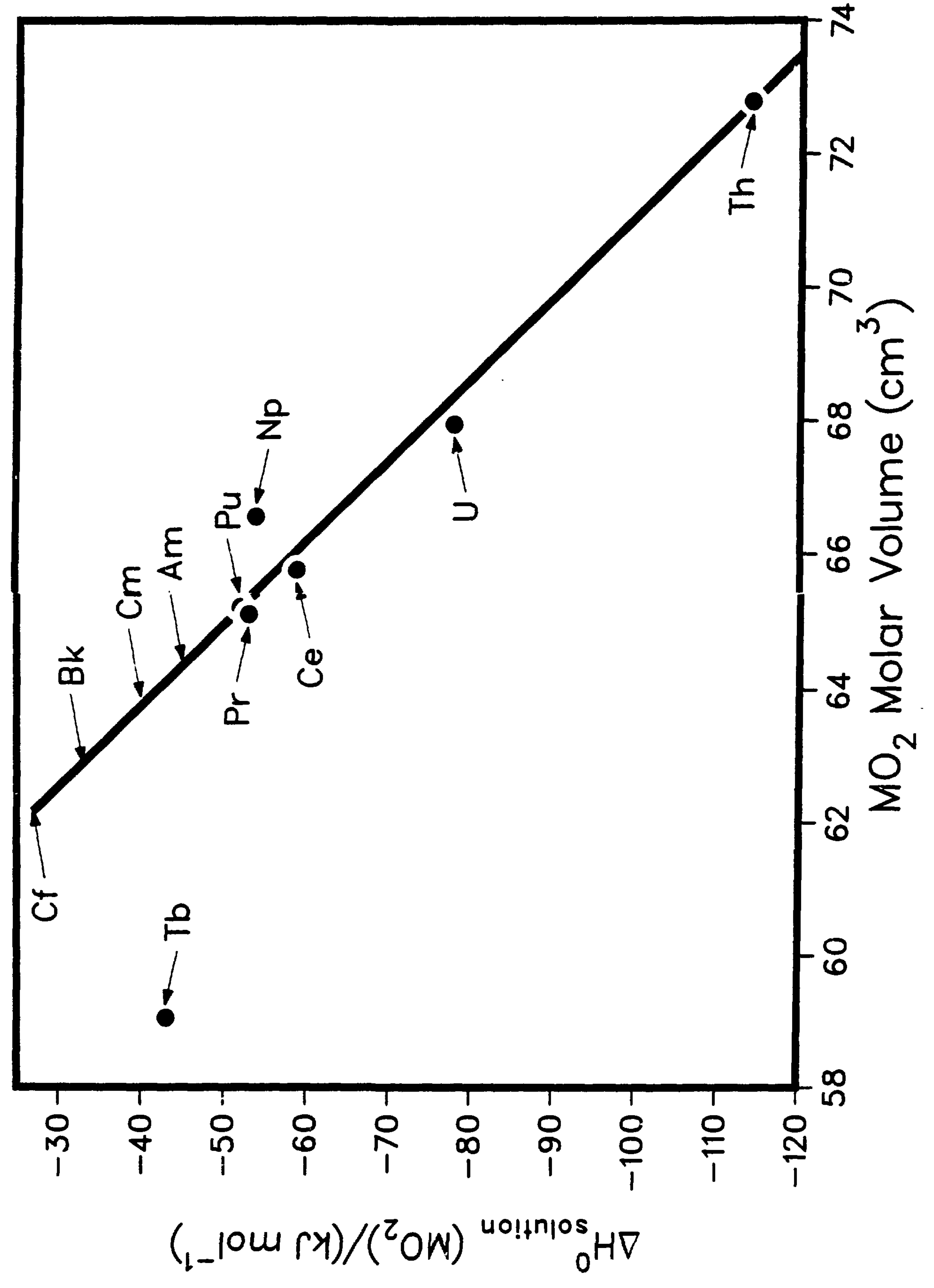


Trichlorides

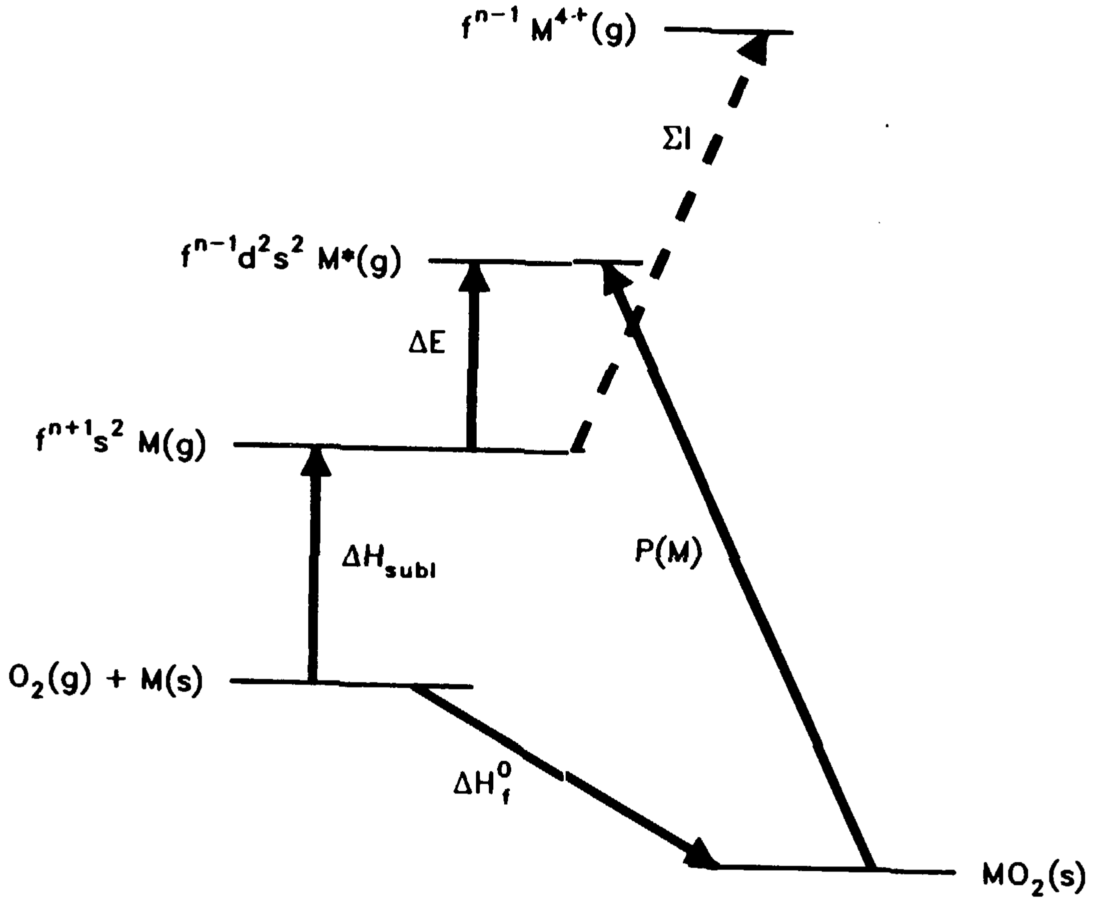


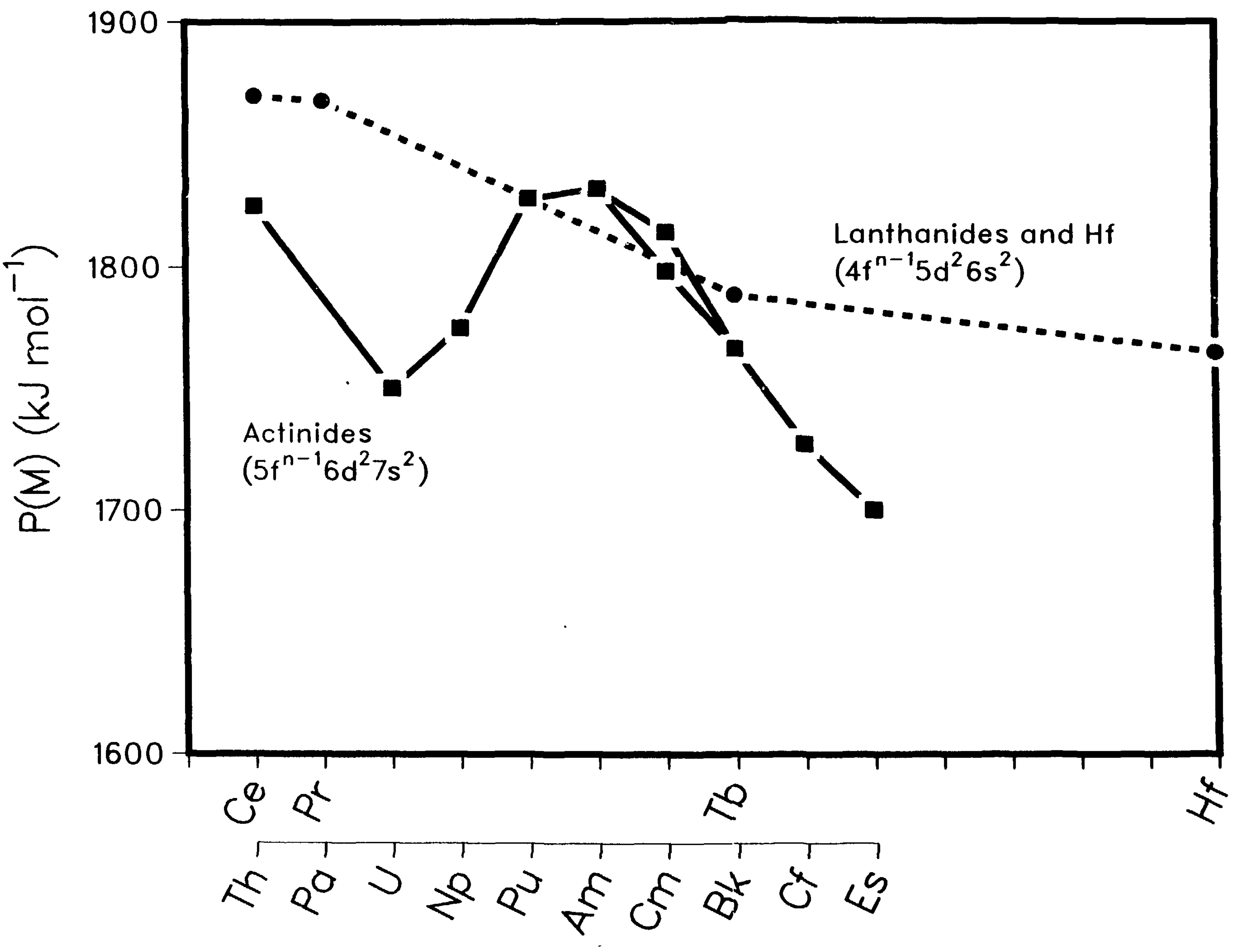
Sesquioxides

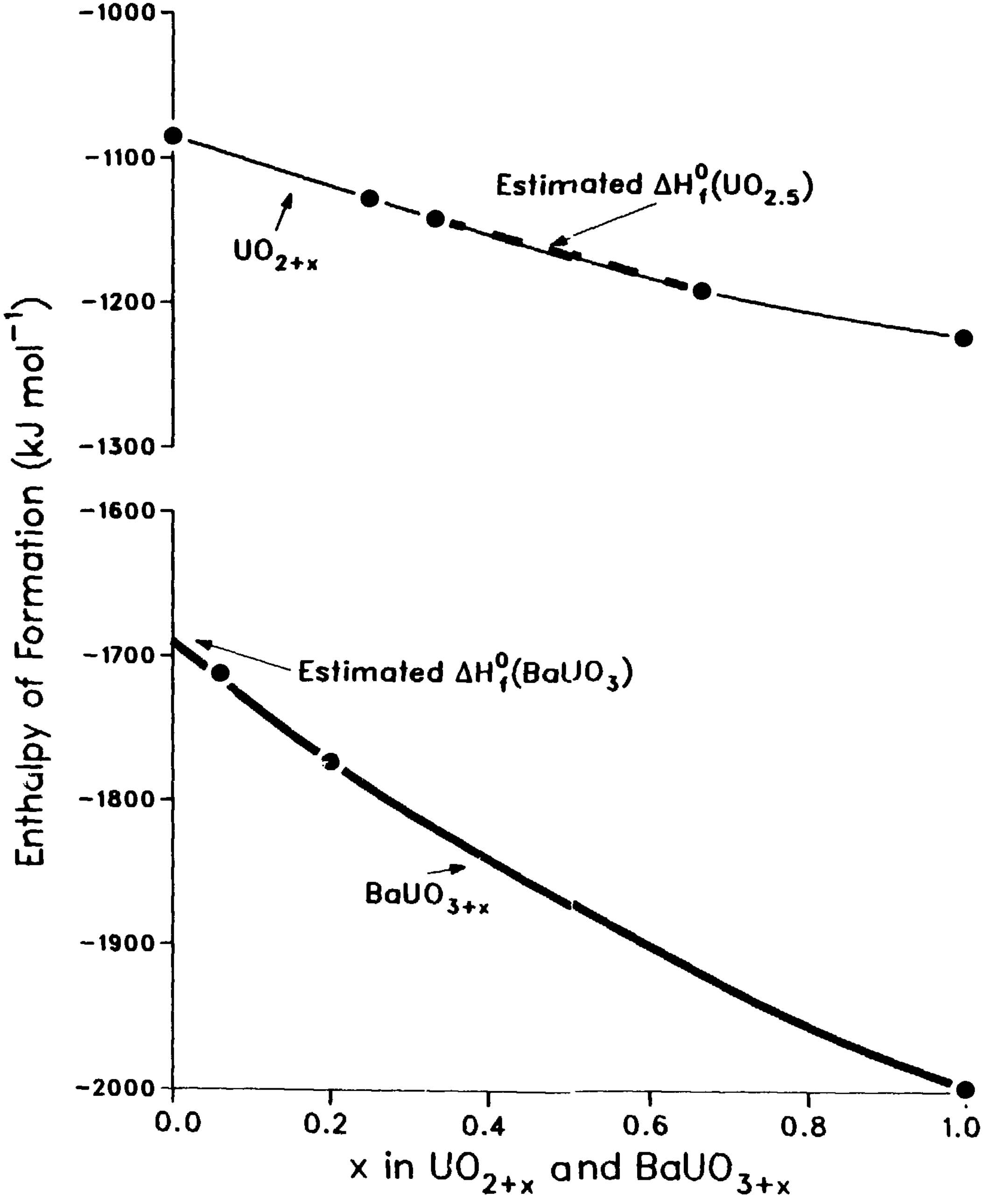

f^6ds^2 Eu*(g) + O(g)
f^7s^2 Eu(g) + O(g)
EuO(g)
f^7s^2 Eu(s) + $1/2O_2$(g)
$1/3[(f^6Eu^{3+})_2(O^{2-})_3(s)] + 1/3Eu(s)$
$(f^7Eu^{2+})(O^{2-})(s)$
f^3ds^2 Nd*(g) + o(g)
f^4s^2 Nd(g) + O(g)
NdO(g)
f^3ds^2 Nd(s) + $1/2O_2$(g)
$(f^4Nd^{2+})(O^{2-})(s)$
$1/3[(f^3Nd^{3+})_2(O^{2-})_3(s)] + 1/3Nd(s)$
$(f^3Nd^{3+})(O^{2-})(e^-)(s)$
(high pressure)



$\Delta H^0_{solution}(MO_2)/(kJ\ mol^{-1})$
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
MO_2 Molar Volume (cm^3)
58
60
62
64
66
68
70
72
74
Tb
Cf
Bk
Cm
Am
Pu
Pr
Ce
Np
U
Th

$f^{n-1}M^{4+}(g)$
ΣI
$f^{n-1}d^2s^2\ M^*(g)$
ΔE
$f^{n+1}s^2\ M(g)$
ΔH_{subl}
P(M)
$O_2(g) + M(s)$
ΔH_f^0
$MO_2(s)$


1900
1800
1700
1600
P(M) (kJ mol^{-1})
Lanthanides and Hf
(4f^{n-1}5d^{2}6s^2)
Actinides
(5f^{n-1}6d^{2}7s^2)
Ce
Pr
Tb
Hf
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es


Enthalpy of Formation (kJ mol^{-1})
−1000
−1100
−1200
−1300
−1600
−1700
−1800
−1900
−2000
Estimated $\Delta H_f^0(UO_{2.5})$
UO_{2+x}
Estimated $\Delta H_f^0(BaUO_3)$
$BaUO_{3+x}$
0.0
0.2
0.4
0.6
0.8
1.0
x in UO_{2+x} and $BaUO_{3+x}$