STUDY OF SOME THERMODYNAMIC PROPERTIES OF 5f ELEMENTS[¶]

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INTRODUCTION

Nugent, Burnett, and Morss [L.Nugent, 1] have recently tabulated the enthalpy of sublimation for the 4f and 5f metals at 298.15K, $\Delta H_s^\circ(M)$, and the standard enthalpy of formation at 298.15K, $\Delta H_f^\circ\ (M_{aq}^{3+})$, for the tripositive aqueous metal ions for these two series. Values in this tabulation for the latter half of the 5f series were not obtained from experimental measurements, but from theoretical consideration and empirical correlations drawn from the trends in the 4f series. In the present work we use new experimental data for the 5f series to modify the empirical correlations, and tabulate new values for $\Delta H_f^\circ\ (M_{aq}^{3+})$ and $\Delta H_s^\circ(M)$ for the second half of the 5f series. In addition, values for $\Delta G_f^\circ\ (M_{aq}^{3+})$ $[\Delta G_f^\circ = -3FE^\circ\ (M_{aq}^{3+}/M) = \Delta H_f^\circ - T\Delta S_f^\circ$ for the reaction $M + 3H_{aq}^{+} = M_{aq}^{3+} + 3/2\ H_2]$ are given for the 5f series and the oxidation-reduction properties of the 5f elements are discussed.[*]

The method developed by NBM for the correlation of the thermodynamic data involved defining the function P(M) which connected the lowest energy level in the f^n configuration of the M^{3+} aqueous ion to the lowest energy level in the ground configuration $f^n s^2 d^1$ of the gaseous atom M(g); or if this configuration was not the lowest one in the gaseous atom then an additional promotional energy $\Delta E(M)$ was added from the lowest energy level of the gaseous atom ground state, M(g), to the lowest energy level of the excited configuration, $f^n s^2 d^1$ $M^*(g)$. From this definition, $P(M) = -\Delta H_f^\circ\ (M_{aq}^{3+}) + \Delta H_s^\circ(M)$ if the ground configuration of gaseous atom is $f^n s^2 d^1$; or $P(M) = -\Delta H_f^\circ\ (M_{aq}^{3+}) + \Delta H_s^\circ(M) + \Delta E(M)$, if the ground configuration of the gaseous atom is *not* $f^n s^2 d^1$. These definitions are illustrated in Fig. 1.

The function P(M) connects the ground state of the aqueous trivalent ion with the same number of f electrons, f^n, as in the gaseous atom M(g) or $M^*(g)$ $f^n s^2 d^1$. The energy difference between the initial state aqueous ion and the final state gaseous ion is the ionization energy necessary to remove the three outer electrons ΔH_{ion}° plus the energy of hydration needed to hydrate the trivalent gaseous ion in aqueous solution ΔH_{hyd}°. These two energy contributions should increase slowly as a function of Z, the atomic number, and form the basis for the correlation of the thermodynamic data discussed in ref. 1 and in this paper. We note one major difference between the 4f and 5f series. In the latter half of the 5f series the increase in the hydration energy is much less steep than in the 4f series, which

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[*] All values in this paper correspond to a temperature of 298.15°K and all electrode potentials are with respect to the normal hydrogen electrode (NHE).

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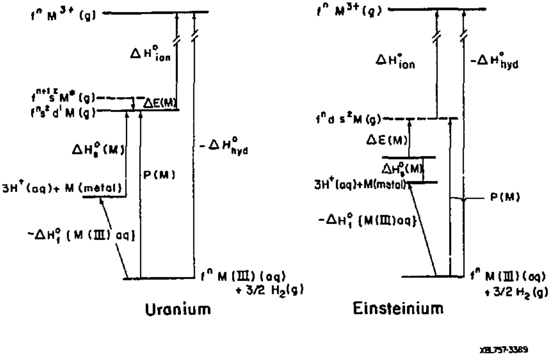

Fig. 1. Relations involving ΔH_f^o (M_{aq}^{3+}), ΔH_s^o (M), ΔE(M), P(M), ΔH_{ion}^o and ΔH_{hyd}^o for uranium and einsteinium as examples of 5f elements.

parallels the variation of the ionic radii of the trivalent ions in both series [F.David, 2]. L. Nugent et al have assumed a parallel trend in the two series for the function P(M). This difference between the series in the rate of increase of *the hydration energy causes the P(M) function we derive to vary in a linear* fashion with Z the atomic number, for the 5f series.

L. Nugent et al define a further quantity $\Delta H_s^*(M)$ which is equal to $\Delta H_s^o(M)$ if the $f^n s^2 d^1$ configuration is the lowest one in the gaseous atom or $\Delta H_s^*(M) = \Delta H_s^o(M) + \Delta E(M)$ if the $f^n s^2 d^1$ configuration is not the lowest configuration where $\Delta E(M)$ is as defined previously. This enthalpy of sublimation function $\Delta H_s^*(M)$ should exhibit a smooth variation with atomic number for those metals with the same number of valence electrons in the metallic state. An extrapolation of this type of function will allow estimated ΔH_s^o values for those elements for which no experimental data are available.

Entropy of Formation

The entropy of formation of the aqueous ion M_{aq}^{3+}, ΔS_f^o, is given by the relation:

$$\Delta S_f^o = S_{M_{aq}^{3+}}^o + 3/2\, S_{H_2} - S_M^o \ .$$

The data tabulated in Table 1, column 1, are obtained by the estimation of the entropy of the aqueous ions $S_{M_{aq}^{3+}}^o$ using the method of Hinchey and Cobble for estimations on the aqueous actinide ions Ac_{aq}^{3+} through Am_{aq}^{3+} [R. Hinchey, 3] and the entropy of the metal S_M^o are those listed by Krestov [4].

Enthalpies of Formation and Sublimation

The experimental data of the enthalpies of formation, ΔH°_f, and of sublimation ΔH°_S are listed in Table 1, column 2 and 3.

According to the redox potentials of the couple M^{3+}/M^{2+} in the case of Fm, Md and No, we assume that these three elements are divalent in the metallic state. Then an estimation of the sublimation energy is obtained through a correlation of divalent metals of the sixth and seventh periods drawing a parallel with the curve obtained with Ba, Eu and Yb from the point of radium which is 7 kcal mol^{-1} lower than that of barium. We correct the estimation of ΔH°_S(Fm), ΔH°_S(Md) and ΔH°_S(No) by taking into account the fact that the difference in the radii: R^{2+}(Ba) - R^{2+}(Yb) = 0.45 Å is not the same difference found for R^{2+}(Ra) - R^{2+}(No) ≃ 0.39 Å [R.Silva,

TABLE 1. Values of various thermodynamic quantities for the actinide series. Numbers in parentheses are estimated errors.

1	2	3	4	5	6
M	$-\Delta S^\circ_f$ eu	$-\Delta H^\circ_f$ kcal mol^{-1}	ΔH°_s kcal mol^{-1}	P(M) kcal mol^{-1}	$-E^\circ(M^{3+}/M)$ V/NHE
Ra		126[a]	57(1)[g]		
Ac	11.5	157(5)[b]	105(2)[b]	262[b]	2.22(.09)[b]
Th	6.9	90(4)[b]	142.6(1)[h]	255[b]	1.27(.07)[b]
Pa	6.9	111.5(8)[b]	141.5(5)[i]	253[b]	1.58(.13)[b]
U	7.3	122.6[c]	128(2)[a]	250.5[b] 250.6	1.74(.03)[c]
Np	8.6	126.2[c] 138(5)[b]	110(2)[j]	248[b] 236.2	1.96(.09)[b]
Pu	11.2	141.7[c]	83.3[h]	245.5[b] 243	1.99(.03)[c]
Am	16.9	147.4[d]	57.5(2.5)[h]	243[b] 248	2.06(.03)[d]
Cm	14.2	147.1[e]	94(2)[k]	241[b] 241	2.07(.03)[e]
Bk	15.2	138(6)[f] 141(5)[b]	76(2)[b]	238[b] 235	1.97(.09)[b]
Cf	15.5	140(5)[b]	47(2)[b]	235.5[b]	1.95(.09)[b]
Es	15.8	139.5(5)[b]	38(2)[b]	233[b]	1.95(.09)[b]
Fm	15.8	139.5(5)[b]	33(2)[b]	230.5[b]	1.95(.09)[b]
Md	16.0	117(9)[b]	32(2)[b]	228[b]	1.62(.09)[b]
No	15.0	86.5(9)[b]	31(2)[b]	225.5[b]	1.19(.09)[b]
Lr	16.2	144(5)[b]	83(2)[b]	227[b]	2.01(.09)[b]

[a] Reported in ref. 1
[b] This work
[c] Ref. 12
[d] Ref. 16
[e] Ref. 17
[f] Ref. 18
[g] *Ref. 19 and 20*
[h] Ref. 21
[i] Ref. 22
[j] Ref. 23
[k] Ref. 24

5]. Therefore $\Delta H_s^\circ(M)$ was estimated with the relation

$$\Delta H_s^\circ(M) \;=\; \Delta H_s^\circ(Ra) - 7 \times \frac{0.39}{0.45} \times \frac{Z(M) - 95}{6} \quad ,$$

and the data are listed in Table 1, column 3.

We now have for the actinide elements U, Np, Pu, Am and Cm, enough experimental information, plus the data in Table 1, and the excitation energies ΔE taken from ref. 1 to calculate the function defined previously P(M). This function is evaluated in Table 1, column 4. We note, as L. Nugent et al did previously, that the value of P(Np) appears about 10 kcal mol^{-1} lower than expected and we agree with their suggestion that the experimental value of $\Delta H_f^\circ(Np)$ is probably erroneous.

Recently a number of electrochemical measurements have been performed on tracer quantities of the heavier actinide ions. We will use this information to obtain values for ΔH_f° of these ions and thereby estimate the quantity P(M) for this part of the 5f series.

The half wave potential of Fm has recently been measured in a non-complexing medium as -1.47 ± 0.01 V [K.Samhoun, 6]. We estimate the amalgamation energy to be -0.90 ± 0.09 V by comparison with other divalent ions [F.David, 2] and obtain the value -2.37 ± 0.1 V for the Fm^{2+}/Fm standard potential. Finally, with the value of Fm^{3+}/Fm^{2+} potential of -1.1 ± 0.2 V [L.Nugent, 7] we find $E^\circ(Fm^{3+}/Fm) = -1.95 \pm 0.13$ V, $\Delta G_f^\circ = -135 \pm 9$ kcal mol^{-1}. With these values P(Fm) = 231 ± 16 kcal mol^{-1} and is tabulated in Table 1, column 4.

The half wave potential for the reaction $No^{2+} \rightarrow No$ has been determined as -1.60 ± 0.05 V [R.Meyer, 8] which is slightly more negative than for the corresponding Fm couple. Fm, Md and No are known to be amalgamated under the same conditions with comparable yields and faster than all other actinides [J.Maly, 9,10]. Therefore we estimate the $Md^{2+} \rightarrow Md$ half wave potential as $E\,1/2 = -1.52 \pm 0.08$ V. From this data and earlier measurements of the M^{3+}/M^{2+} potential we calculate $\Delta H_f^\circ(No_{aq}^{3+}) = -86.5 \pm 9$ kcal mol^{-1} and $\Delta H_f^\circ(Md_{aq}^{3+}) = -117 \pm 9$ kcal mol^{-1}. We then find P(Md) = 228 ± 17 kcal mol^{-1}, and P(No) = 224.5 ± 20 kcal mol^{-1}. These values are not in agreement with those derived by L. Nugent et al.

We find a linear function fits the derived P(M) values with a standard deviation of 2 kcal mol^{-1} for the elements U, Pu, Am, Cm, Fm, Md and No. We shall assume ΔH_s^* is also linear with Z and the slope of this line can be obtained from the following ratios

$$\frac{\text{slope } P(M)_{4f}}{\text{slope } P(M)_{5f}} \;=\; \frac{\text{slope } \Delta H^*_{s(4f)}}{\text{slope } \Delta H^*_{s(5f)}}$$

where the slope $P(M)_{4f}$ is obtained only from the first half of the 4f series. With this assumption we get ΔH_s° for Ac, Bk, Cf, Es and Lr and the data are included in Table 1, column 3. A correction of 4 kcal mol^{-1} has been applied to those new values so as to normalize the equation

$$\Delta H_s^\circ \;=\; \Delta H_s^* - \Delta E(M)$$

with the experimental data on Am. Note this method confirms our earlier estimate of ΔH_s° for Fm; it appears very similar to $\Delta H_s^\circ(Yb) = 36$ kcal mol^{-1} and seems more consistent than the value of 46 kcal mol^{-1} obtained previously by L. Nugent et al. The low values (similar to Eu) deduced by this procedure for Md and No confirm these metals as divalent. We can now obtain P(Bk) ≈ 235 kcal mol^{-1} and the point is in good agreement with that determined from the P(M) line. We also include in this tabulation values for Lr and Ac where we have added 4 kcal mol^{-1} for these elements as discussed by L. Nugent et al.

The original values used to fix our P(M) function (Table 1, column 4) contained numbers with large errors. Therefore we consider the data obtained on the straight line (Fig. 2, Table 1, column 4) as the best values of P(M).

We are now able to estimate ΔH_f° for Ac, Th, Pa, Bk, Cf, Es, Fm, Md, No and Lr by use of the P(M) function, ΔH_s°, and ΔE as described earlier. Our values are given in Table 1, column 2. We also include a new value for Np where the experimental data appears low.

Redox Potentials $E^\circ(M^{3+}_{aq}/M)$ and the Redox Properties of the 5f Elements

We now calculate ΔG_f° and $E^\circ(M^{3+}_{aq}/M)$ for the 5f series from the values of ΔH_f° and ΔS_f° we have obtained earlier. These last data are tabulated in Table 1, column 5. From this tabulation and data or estimates reported previously [F.David, 11] in the literature we can calculate $E^\circ(M(X)/M)$ for 1M $HClO_4$ at 25°C, and where X stands for the oxidation number. We can then compare the relative stability of each oxidation state ($X = 2$ to 6) plotting $-X$ times $E^\circ(M(X)/M)$ as a function of Z. These data are shown in Fig. 3. The estimated values of Nugent et al were used for $X = 4$ [Nugent,7].

This figure shows the stability of the trivalent state from Pu to Md, the progressive stability of the divalent state for the heavy elements, and the instability of

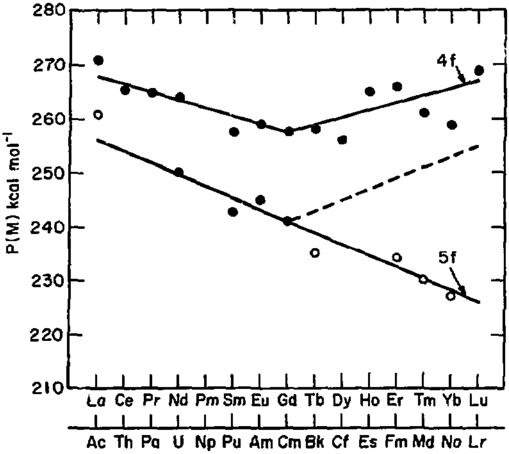

Fig. 2. Plot of P(M) against atomic number Z for the lanthanide and actinide series.

the oxidation states greater than three as Z increases, except for Bk(IV) which has increased stability due to the half filled shell configuration, $5f^7$.
There are two interesting values which we shall estimate, the standard potentials of the couples $Th^{4+}_{aq}/Th^{3+}_{aq}$, and $Pa^{4+}_{aq}/Pa^{3+}_{aq}$. For Th, we use the value $\Delta H^\circ_f(Th^{4+}_{aq})$ = -184.0 ± 1 kcal mol^{-1} [J.Fuger, 12]. $S^\circ_{Th^{4+}_{aq}}$ = -77 eu [A.Jones, 13], and S°_{Th} = 12.76 eu [G.Krestov, 4], then $E^\circ(Th^{4+}_{aq}/Th^{3+}_{aq})$ = -1.90 ± 0.03 V. Since $E^\circ(Th^{3+}_{aq}/Th)$ = -1.27 ± 0.07 V, we deduce $E^\circ(Th^{4+}_{aq}/Th^{3+}_{aq})$ = -3.81 ± 0.33 V, which is in good agreement with an earlier estimate [L.Nugent, 7].

For Pa, E°(Pa(V)/Pa(IV)) is determined at -0.25 V [M.Haissinsky, 14]. With the data from Table 1 and E°(Pa(V)/Pa) = -1.35 V [F.David, 11], we find E°(Pa(IV)/Pa(III)) = -1.8 V which again agrees with the earlier estimate [L.Nugent, 7].

The function -XE°(M(X)/M) = f(Z) appears to be almost linear for X = 4,5,6 except for the half filled shell configuration, $5f^7$. We extrapolate the straight line for X = 5 (dashed line, Fig. 3) except we use the half filled shell effect for $5f^7$ as observed for X = 4. Then we estimate 5E°(Cm(V)/Cm) = -1.8 V, 5E°(Bk(V)/Bk) = -0.8 V and 5E°(Cf(V)/Cf) = -1.9 V. Nugent et al estimated E°(Cm(IV)/Cm(III)) as 3.1 V [L.Nugent, 7] so we obtain E°(Cm(V)/Cm(IV)) = 1.3 V. Similarly we find E°(Bk(V)/Bk(IV)) = 3.5 V and E°(Cf(V)/Cf(IV)) = 0.8 V. Therefore our estimates suggest Bk(V) will be very unstable in aqueous solution but it appears that Cm(V) and Cf(V) could exist in solution even if our estimates are slightly low. We suggest these oxidation states could be prepared with the same strong oxidizing conditions as used to prepare Am(VI) [L.Asprey, 15].

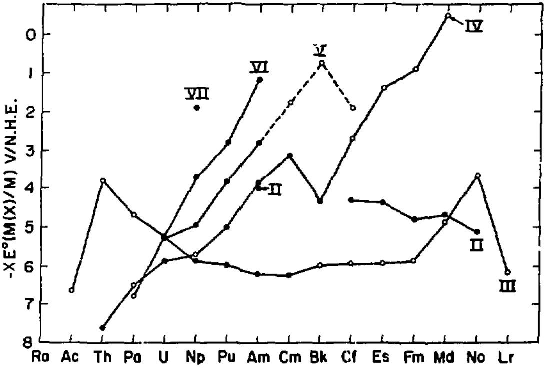

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Fig. 3. Variations of -XE°(M(X)/M) with Z for the oxidation state X = 2 to 6 for 5f elements.
- ● Values deduced from experimental data from the literature.
- ○ Estimated data.

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FOOTNOTES AND REFERENCES

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