conditions than for the $PF_3$ reactions with $CO_2$ or $CS_2$. Previous workers[19] have shown that COS thermally decomposes via two independent simultaneous equilibria

$$2COS(g) \rightleftarrows CO_2(g) + CS_2(g)$$

$$COS(g) \rightleftarrows CO(g) + S(s)$$

It has been noted that these reactions were sensitive to the vessel used for reaction. For example, more decomposition was noted when "Jena" glass vessels were used or when silica was placed in a "Pyrex" vessel than for a clean Pyrex reaction. In this study no decomposition is noted at 500° and at 170, 270, or 4000 atm or for a mixture of COS and $CS_2$ at 500° (4000 atm).

Table III summarizes these most interesting experiments. If excess $PF_3$ is employed at the given conditions, complete reactions are observed. The reported experiments show the range of products which are obtained.

No reaction of any kind is observed below 260° (680 atm); however, at these conditions small amounts of CO and $SPF_3$ are recovered

$$PF_3(g) + COS(g) \rightarrow CO(g) + SPF_3(g)$$

The amount of reaction increases with more rigorous conditions until a 23% conversion is obtained at 300° (540 atm).

When the pressure is increased to 3000 atm at 300°, more than 50% of the $PF_3$ is consumed, with no apparent change in the amount of conversion at 4000 atm. When a large excess of $PF_3$ is not employed, the products include $SPF_3$, $OPF_3$, $CS_2$, CO, and carbon. At 500° and a minimum pressure of 340 atm the same products are obtained.

The products can all be rationalized by postulating an initial complex between the carbonyl sulfide and phosphorus trifluoride. There actually are two possible intermediates which fit the experimental data, $OCS{\cdot}PF_3$ and $SCO{\cdot}PF_3$. The complex decomposes forming CO and $SPF_3$ or CS and $OPF_3$. The former would appear to explain the reactions at lower temperatures and pressures. Both interactions may take place at increased pressure or temperature. The following reaction sequence may be postulated for the formation of $CS_2$

$$COS(g) + PF_3(g) \rightarrow SPF_3(g) + CO(g)$$

$$COS(g) + PF_3(g) \rightarrow OPF_3(g) + CS(g)$$

$$COS(g) + CS(g) \rightarrow CO(g) + CS_2(g)$$

The carbon can then be formed by the reaction

$$CO(g) + PF_3(g) \rightarrow OPF_3(g) + C(s)$$

The formation of a complex where $PF_3$ acts as a Lewis acid can be used to explain all of the observed initial reactions of $CO_2$, $CS_2$, and COS with $PF_3$. In this study the products at even the lowest set of physical conditions can be postulated as arising from the abstraction of a chalcogen atom by $PF_3$. Consider COS as a Lewis base

$$:\ddot{O}=C=\ddot{S}:$$

interacting with the expanded octet of $PF_3$, viz.

$$\underset{..}{\overset{..}{O}}=C=\underset{..}{\overset{..}{S}}\rightarrow PF_3$$

The complex will then decompose forming $SPF_3$ and CO.

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**Registry No.** $PF_3$, 7783-55-3; $CO_2$, 124-38-9; $CS_2$, 75-15-0; COS, 463-58-1; $OPF_3$, 13478-20-1; $SPF_3$, 2404-52-6.

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# Enthalpy of Formation of Neodymium Dichloride and Thulium Dichloride

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Well-characterized samples of $NdCl_{2.06}$ and $TmCl_2$ were allowed to react in a solution microcalorimeter with HCl(aq). From measured heats of solution and from related thermochemical data, the enthalpies of formation of $NdCl_2(c)$ and $TmCl_2(c)$ have been calculated to be $-706.9 \pm 4.2$ and $-709.1 \pm 4.2$ kJ $mol^{-1}$. The energetics of oxidation and hydration of all the dipositive lanthanide ions have been calculated and correlated; in particular, $\Delta H_f°(Nd^{2+}(aq))$ and $\Delta H_f°(Tm^{2+}(aq))$ are estimated to be $-402$ and $-442$ kJ $mol^{-1}$.

## Introduction

The dihalides of samarium, europium, and ytterbium have been known since the beginning of this century. However, only in 1959 was it reported by Druding and Corbett that certain other lanthanide metals were sufficiently soluble in the corresponding molten trihalides that stoichiometric dihalides could be identified on phase diagrams and isolated from the solid solutions.[1] Many of these halides are saline, and the phase diagrams and physical properties of most dihalides were reviewed by Brown in 1968.[2] More recently, Corbett has published an extensive review of the preparation and stabilities of reduced rare earth halides.[3]

Although the reasons for the stability of lanthanide dihalides with respect to the disproportionation reaction

$$3MX_2(c) = 2MX_3(c) + M(c) \qquad (1)$$

are well known,[3-5] very few studies of the stability of the dipositive ions and their compounds have been carried out.

$NdCl_2$ was the first nonclassical dihalide to be prepared, and its enthalpy of formation was first determined by Polyachenok and Novikov.[6] They reported $\Delta H_f°(NdCl_2(c)) = -163.2 \pm 1.9$ kcal mol$^{-1}$ on a well-characterized sample, and they calculated $\Delta H°_{298}$ and $\Delta S°_{298}$ for reaction 1 to be −3.4 kcal and −15 cal K$^{-1}$, respectively. Their conclusion was that $NdCl_2(c)$ is barely stable with respect to disproportionation at room temperature. However, more recently a very careful determination of $\Delta H_f°_{298}(NdCl_3(c)) = -249.0$ kcal mol$^{-1}$ has been reported by Stuve.[7] Using Stuve's result, recalculated auxiliary thermochemical data, and Polyachenok and Novikov's thermochemical observations of the heats of solution of Nd metal and $NdCl_2$, $\Delta H°$ for reaction 1 now becomes $2(-249.0) - 3(-162.9) = -9.3$ kcal. With the authors' estimate that $\Delta S°_{298}$ for reaction 1 is +1 cal K$^{-1}$ (mol M)$^{-1}$, it is clear that Polyachenok and Novikov's enthalpy of formation is inconsistent with the observed stability of $NdCl_2$ with respect to disproportionation.

The only other thermochemical observations on nonclassical dipositive oxidation states are the ionization potentials derived from optical spectra[8-11] and oxidation potentials derived from correlation of electron transfer and f–d absorption spectra.[12] The paucity of good thermochemical data on species involving Nd(II), Dy(II), and Tm(II) led the authors to remeasure the enthalpy of formation of $NdCl_2$ and to measure the enthalpy of formation of one heavy lanthanide dichloride.

Fortunately, Professor J. D. Corbett of Iowa State University was able to provide us with ca. 1-g samples of "$NdCl_{2.06}$" and $TmCl_2$. These samples had been carefully characterized and proved to be ideal for calorimetric measurements.

## Experimental Section

Samples of $NdCl_{2.06}$ and $TmCl_2$ were received from Ames Laboratory, Iowa State University, in evacuated Pyrex tubes. The $NdCl_{2.06}$ had been carefully analyzed in Professor Corbett's laboratory, with 100.1% recovery. It was a two-component mixture of $NdCl_2$ and $NdCl_{\sim 2.27}$ with some globules of Nd metal still present. The shiny black crystals of ($NdCl_2$ + $NdCl_{\sim 2.27}$) could easily be separated from the metal globules. The $TmCl_2$ sample had been prepared from sublimed trichloride and high-purity metal. Although this sample had not been analyzed, it had been found to melt congruently by Professor Corbett and thus was expected to be stoichiometric $TmCl_2$; its appearance was a finely divided green-black powder.

A conventional fiberglass glove box was filled with dry $N_2$. Within the box itself was a 100 ft$^3$ min$^{-1}$ fan which forced the $N_2$ through a layer of molecular sieve (Davison Grade 513, 4-Å pore size, 4–8-mesh beads). The fan was operated continuously except while weighing samples. An open dish of $P_4O_{10}$ remained dry and free-flowing for at least 24-hr periods in the glove box; samples of $NdCl_2$ and $TmCl_2$ could be exposed to the box atmosphere for hours with no change in weight or appearance.

Because two phases were present in the $NdCl_{2.06}$, the material was inspected in a Mullite mortar, metal globules were removed, and the crystals were pulverized enough to ensure that the samples would be representative of the overall chemical analysis. Samples of each dichloride were then transferred into washed, annealed, preweighed Pyrex microcalorimeter bulbs; a glass funnel was used for transfer to ensure that no powder was deposited on the bulb walls or necks. The bulbs were flat-bottomed hemispheres with volumes of ca. 0.05 cm$^3$.

Sample masses were determined by weighing each bulb before and immediately after filling on a Cahn Gram electrobalance within the glove box. The balance was calibrated in situ before and after each series of runs. Repeated calibrations showed that the accuracy of sample weighings was better than 0.2%, so that the sample masses reported in Tables I and II are accurate to 0.2% or better. After weighing the filled bulbs, they were sealed with a small sphere of Apiezon W wax in their necks. After completion of all experiments, a sealed, unused calorimeter bulb containing $NdCl_{2.06}$ was opened in the glove box. An X-ray powder photograph of this sample was identical with that reported for $NdCl_{2.08}$.[13]

The sample bulbs were affixed to the bottom of the stirring shaft of a microcalorimeter which has been described.[14] The calorimeter vessel was protected from the HCl solution with several layers of epoxy paint (Du Pont Corlar). For each run, the vessel was loaded with 24 cm$^3$ of 4.00 *M* (4.36 *m*) HCl.

**Table I.** Heats of Solution of $NdCl_{2.06}$ (Gram Formula Weight 217.27) in 4.00 *M* HCl at 25.0°

| Mass/mg | Heat obsd/J[a] | $\Delta H_{soln}$/(kJ gfw$^{-1}$) |
|---|---|---|
| 13.680 | 18.441 | −292.90 |
| 6.487 | 8.759 | −293.33 |
| 17.998 | 24.687 | −298.01 |
| 19.218 | 26.078 | −294.83 |
| 14.576 | 19.394 | −289.07 |
| 13.040 | 17.689 | −294.73 |
| 16.374 | 21.896 | −290.54 |
| 50.39[b] | 67.86 | −292.58 |
| 45.33[b] | 60.37 | −289.38 |
| | Av | −292.82 ± 1.92 ($2\sigma_m$) |
| | Cor to $NdCl_{2.00}$ | −303.4 |

[a] Includes correction for heat absorbed by evaporation of solvent into $H_2$ gas evolved: 630 *J* (mol of $MCl_2$)$^{-1}$. [b] Reaction carried out in 875-cm$^3$ calorimeter.

**Table II.** Heats of Solution of $TmCl_2$ in 4.00 *M* HCl at 25.0°

| Mass/mg | Heat obsd/J[a] | $\Delta H_{soln}$/(kJ mol$^{-1}$) | Mass/mg | Heat obsd/J[a] | $\Delta H_{soln}$/(kJ mol$^{-1}$) |
|---|---|---|---|---|---|
| 10.786 | 13.834 | −307.63 | 12.212 | 15.531 | −305.03 |
| 19.286 | 24.792 | −308.32 | 41.34[b] | 52.50 | −304.58 |
| 12.388 | 15.623 | −302.47 | | Av | −305.61 ± 2.13 ($2\sigma_m$) |

[a] Includes correction for heat absorbed by evaporation of solvent into $H_2$ gas evolved. [b] Reaction carried out in 875-cm$^3$ calorimeter.

Because of the possibility that the dipositive lanthanide ions might be oxidized by dissolved oxygen rather than $H_3O^+$ during dissolution of the dichlorides,[15] some runs were done using HCl solutions thoroughly flushed with $H_2$ and with the entire calorimeter assembly blanketed by Ar. As a final check against reaction with oxygen, runs were conducted with somewhat larger samples in an 875-cm$^3$ dewar-flask calorimeter.[16] This vessel also contained $H_2$-flushed 4.00 *M* HCl and an Ar blanket.

## Results

Observed heats of solution of $NdCl_{2.06}$ and $TmCl_2$ are shown in Tables I and II. All samples were observed to react as rapidly as the calorimeter could respond to the generated heat (implying a reaction time of 15 sec or less). No undissolved material was observed after any experiment. All reactions were carried out at 25.0 ± 0.1°.

Before converting these observed heats of solution to heats of formation, it is appropriate to correct the $\Delta H_{soln}(NdCl_{2.06})$ to $\Delta H_{soln}(NdCl_{2.00})$. As mentioned above, Corbett observed this preparation to be a heterogeneous mixture of $NdCl_2$ + $NdCl_{\sim 2.27}$. The latter phase is only slightly stable with respect to disproportionation into $NdCl_2$ and $NdCl_3$, so it is reasonable to interpret $NdCl_{2.06}$ as a mixture of $NdCl_2$ and $NdCl_3$. One gram-formula weight of $NdCl_{2.06}$ (217.27 g) contains 0.94 mol of $NdCl_2$ and 0.06 mol of $NdCl_3$. The enthalpy of solution of $NdCl_3(c)$ in 4.00 *M* HCl is −127.28 kJ mol$^{-1}$.[7] The enthalpy of reaction of Table I, corrected to pure $NdCl_2$, becomes −303.4 kJ mol$^{-1}$.

Enthalpies of formation of $NdCl_2(c)$ and $TmCl_2(c)$ are calculated directly from the thermochemical equations

$$M(c) + 3HCl\ (4.0\ M) \rightarrow MCl_3\ (\text{in } 4.0\ M\ HCl) + {}^3/_2 H_2(g) \qquad \Delta H_1$$

$$MCl_2(c) + HCl\ (4.0\ M) \rightarrow MCl_3\ (\text{in } 4.0\ M\ HCl) + {}^1/_2 H_2(g) \qquad \Delta H_2$$

$$H_2(g) + Cl_2(g) \rightarrow 2HCl\ (4.0\ M) \qquad \Delta H_3$$

$$\Delta H_f(MCl_2(c)) = \Delta H_1 - \Delta H_2 + \Delta H_3$$

**Table III.** Heats of Solution of $MCl_2$ in Water at 25°

| M | $r_{M^{2+}}$/Å[a] | $\Delta H_{soln}$/kJ mol$^{-1}$ | M | $r_{M^{2+}}$/Å[a] | $\Delta H_{soln}$/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| Ba | 1.36 | −13.4 | Dy | 1.09 | (−59) |
| Nd | 1.22 | (−29) | Tm | 1.04 | (−67) |
| Sm | 1.18 | (−36) | Yb | 1.03 | (−71) |
| Eu | 1.17 | −37.7 | Ca | 1.00 | −81.2 |
| Sr | 1.13 | −51.0 | | | |

[a] Reference 25 for $Ba^{2+}$, $Eu^{2+}$, $Sr^{2+}$, and $Ca^{2+}$ (coordination number 6). Other radii from interionic distance differences in $MCl_2$.

$\Delta H_1$ has been measured by Stuve.[7,17] $\Delta H_2$ is reported in Tables I and II. $\Delta H_3$ is twice the partial molal enthalpy of formation of HCl in its 4.00 *M* aqueous solution, calculated from the apparent molal enthalpies of formation given by the National Bureau of Standards.[18] The results are

$$\Delta H_f°(NdCl_2(c)) = -693.6 - (-303.4) - 316.7 = -706.9 \pm 4.2 \text{ kJ mol}^{-1}$$

$$\Delta H_f°(TmCl_2(c)) = -698.0 - (-305.6) - 316.7 = -709.1 \pm 4.2 \text{ kJ mol}^{-1}$$

where error limits represent estimated 95% confidence.

## Discussion

The previous determination of the enthalpy of formation of $NdCl_2$, −163.2 ± 1.9 kcal mol$^{-1}$, has been recalculated using Polyachenok and Novikov's thermochemical observations[6] and more recent auxiliary thermochemical data[18] to be −162.9 kcal mol$^{-1}$ or −681.6 kJ mol$^{-1}$. The discrepancy between their result and that reported here could have been caused if dissolved $O_2$ had acted as the oxidant in place of some $H^+(aq)$ in the Russian experiments. This phenomenon was observed by Baker et al.[15] However, there is no significant difference between observed heats (Tables I and II) using the microcalorimeter and the large calorimeter which was kept scrupulously oxygen free. The only other conclusion is that, despite good elemental analyses, the Russian $NdCl_2$ was not stoichiometric. This possibility is plausible because the $NdCl_2$ and $NdCl_2$–$NdCl_3$ eutectic melting points of Polyachenok and Novikov are 6 and 9°, respectively, below those reported by Corbett and coworkers.[19,20]

Using Stuve's results[7,17] for the enthalpies of formation of $NdCl_3(c)$ and $TmCl_3(c)$, $\Delta H$ values for the disproportionation reaction (eq 1) are found to be 2(−1041.8) − 3(−706.9) = 37.1 kJ for Nd and 2(−986.6) − 3(−709.1) = 154.1 kJ for Tm. As expected by classical considerations (the parallel between $Sm^{2+}$ and $Tm^{2+}$), spectrochemical interpretations,[12] and thermodynamic arguments,[3-5] the disproportionation of $TmCl_2$ is much more endothermic than is that of $NdCl_2$. Since $\Delta S$ for reaction 1 is estimated to be nearly zero, $TmCl_2$ is much more stable with respect to disproportionation than is $NdCl_2$.

It is also of considerable interest to compare thermochemical measurements with the estimated M(III–II) reduction potentials of Nugent et al.[12] in particular because these authors report a "measured" $E°[\text{Tm(III–II)}] = -2.3 \pm 0.2$ V, which was derived from the measured first electron-transfer bands of $TmBr_6^{3-}$ and $TmCl_6^{3-}$ in acetonitrile and correlated with spectroscopic and electrometric measurements for corresponding Sm, Eu, and Yb species. In order to make this comparison, using experimental calorimetric information, it is necessary to estimate $\Delta H_f°(M^{2+}(aq))$ and $\bar{S}°(M^{2+}(aq))$ for elements whose dipositive ions reduce water instantaneously. To estimate $\Delta H_f°(M^{2+}(aq))$, it is necessary to estimate the heat of solution of the dichlorides in water; to estimate $\bar{S}°(M^{2+}(aq))$, it is necessary to compare the properties of the ions with similar properties of similarly hydrated ions.

Fortunately, heats of solution of several dichlorides, with metal ion radii bracketing the dipositive lanthanide ion radii, are known. Table III shows the data used for estimating enthalpies of solution of the dichlorides of Nd, Sm, Dy, Tm, and Yb. Since the heat of solution is the difference between lattice enthalpy and hydration enthalpy, one might calculate these two quantities and take their difference. However, the uncertainties in these two calculations, for different crystal structures and different hydrated ions, certainly involve errors which might be larger than the resulting calculated heat of solution. Therefore, heats of solution of the dichlorides which are unstable in water were estimated by plotting ionic radii (estimated from crystallographic unit cell parameters in the dichlorides) against heats of solution. The results are given in parentheses in the right-hand column of Table III. From these enthalpies of solution, $\Delta H_f°(M^{2+}(aq))$ may be calculated as shown. The results of these calculations, using appropriate

$$\begin{array}{ll}
M(c) + Cl_2(g) = MCl_2(c) & \Delta H_f°(MCl_2(c)) \\
MCl_2(c) = M^{2+}(aq) + 2Cl^-(aq) & \Delta H_{soln}°(MCl_2) \\
2H^+(aq) + 2Cl^-(aq) = H_2(g) + Cl_2(g) & -2\Delta H_f°(HCl(aq)) \\
\hline
M(c) + 2H^+(aq) = M^{2+}(aq) + H_2(g) & \Delta H_f°(M^{2+}(aq))
\end{array}$$

data from this research from Table III and from the literature,[21-23] are listed in Table IV.

To estimate aquo ion entropies, eq 2 was used,[24] where $R$

$$\bar{S}°(M^{z+}(aq)) = \frac{3}{2}R \ln (\text{at. wt}) + R \ln (2J + 1) + 257.8 - 33.00\frac{(z + 3)^2}{r + 1.20} \qquad (2)$$

$= 8.314$ J K$^{-1}$ mol$^{-1}$, $J$ is the total angular momentum quantum number of the ion $M^{z+}$, $z$ is the ionic charge, and $r$ is the ionic radius for coordination number 6 consistent with the tabulation of Shannon and Prewitt[25] (Table III). Values of $\bar{S}°$ calculated by eq 2 have units J K$^{-1}$ mol$^{-1}$ and are consistent with the definition $\bar{S}°(H^+(aq)) = 0$. Entropies for ions $M^{2+}(aq)$, calculated from eq 2, were combined with experimental entropies[18,26] for ions $M^{3+}(aq)$ and $H_2(g)$ to derive $\Delta S$ for the reaction

$$M^{3+}(aq) + {}^1/_2H_2(g) = M^{2+}(aq) + H^+(aq) \qquad (3)$$

and the results are listed in Table IV.

Enthalpy changes of reaction 3 are the difference between $\Delta H_f°(M^{2+}(aq))$ and $\Delta H_f°(M^{3+}(aq))$ as shown in Table IV. From $\Delta H$ and $\Delta S$ for reaction 3, $E°(M^{3+}–M^{2+})$ is $-(\Delta H -$

**Table IV.** Thermodynamic Properties of Lanthanide(II) and -(III) Aquo Ions at 25°

| M | $\Delta H°_f(M^{2+}(aq))$/(kJ mol$^{-1}$)[a] | $\bar{S}°(M^{2+}(aq))$/(J mol$^{-1}$ K$^{-1}$)[b] | $\Delta H_3$/kJ mol$^{-1}$ [c] | $\Delta S_3$/(J mol$^{-1}$ K$^{-1}$)[c] | $E°$/V[d] | $E°$(lit.)/V[e] |
|---|---|---|---|---|---|---|
| Nd | −402 | −3 | 294 | 139 | −2.62 | −2.62 |
| Sm | −521 | −26 | 171 | 120 | −1.40 | −1.55 |
| Eu | −528[f] | −10[f] | 77 | 147 | −0.34 | −0.35 |
| Dy | (−407)[g] | −16 | 292 | 150 | −2.56 | −2.6 |
| Tm | −442 | −23 | 260 | 155 | −2.22 | −2.3 |
| Yb | −537 | −48 | 138 | 125 | −1.04 | −1.15 |

[a] Calculated as described in text. [b] Calculated from eq 2. [c] $\Delta H_3$ and $\Delta S_3$ refer to reaction 3. [d] $E°(M^{3+}–M^{2+}) = -(\Delta H - T\Delta S)/96487$. [e] Reference 12. [f] Reference 23. [g] Estimated from the hydration cycle (Table V).

**Scheme I**

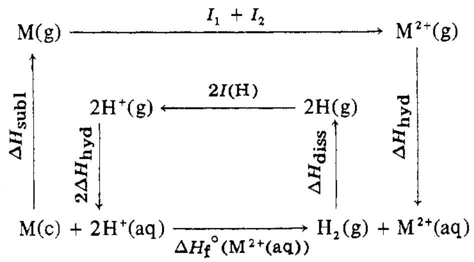

**Table V.** Absolute Enthalpies of Hydration of Dipositive Lanthanide Ions (kJ $mol^{-1}$)

| M | $\Delta H_{hyd}°$ ($M^{2+}$) | $-I_1 - I_2$[a] | $-\Delta H_{subl}$[b] | $\Delta H_f°$ ($M^{2+}$(aq))[c] | $\Delta H$ terms[d] |
|---|---|---|---|---|---|
| Nd | −1416 | −1564 | −328 | −402 | 878 |
| Sm | −1461 | −1611 | −207 | −521 | 878 |
| Eu | −1458 | −1633 | −175 | −528 | 878 |
| Dy | −1517[e] | −1698 | −290 | (−407) | 878 |
| Tm | −1555 | −1759 | −232 | −442 | 878 |
| Yb | −1589 | −1778 | −152 | −537 | 878 |

[a] References 8–10. [b] Reference 26. [c] From Table IV, except that the entry for Dy was calculated from other terms and then entered into Table IV. [d] $\Delta H_{dissoc}(H_2) + 2I(H) + 2\Delta H_{hyd}(H^+$, absolute)). [e] Estimated from a plot of other $\Delta H_{hyd}°(M^{2+})$ vs. ionic radii.

$T\Delta S)/96487$ V. These thermochemical $E°$ values may be compared with electrometric or spectroscopic $E°$ values, as shown in the last two columns of Table IV. The agreement between thermochemical and spectroscopic $E°$ values is excellent, considering that the error limits on the thermochemical values are ±0.05 V and that the estimated uncertainties on the spectroscopic values are ±0.2 V.[12] There is also good agreement with thermochemical $E°$ values calculated recently by Johnson by a different method.[27] It is interesting to note that the greatest discrepancy lies in the values for Sm. Another thermochemical correlation also shows a large discrepancy for Sm.[28] The thermochemistries of $Sm^{II}$(aq) and $Sm^{III}$(aq) are both being reinvestigated by the senior author.

Finally, it is appropriate to estimate the enthalpies of hydration of the divalent lanthanide ions for which saline dichlorides are known. An appropriate enthalpy cycle is shown in Scheme I. (The two electrons released and recombined in this cycle have been omitted; the enthalpies involved cancel.) Thus $\Delta H_{hyd}(M^{2+}) = -(I_1 + I_2) - \Delta H_{subl} + \Delta H_f°(M^{2+}(aq)) + \Delta H_{dissoc}(H_2) + 2I(H) + 2\Delta H_{hyd}(H^+)$. In order to derive "absolute" enthalpies of hydration, the corresponding "absolute" enthalpy of hydration of the proton[29] has been used; the last three terms sum to 435.9 + 2(1312.0) + 2(−1090.8) = 878.3 kJ. All the terms in this cycle and the calculated hydration enthalpies are shown in Table V. Since experimental information for Dy is lacking, its hydration enthalpy was estimated from a plot of ionic radii vs. hydration enthalpies of the other divalent lanthanides; the resulting $\Delta H_f°(Dy^{2+}(aq))$ was then entered into Table IV. From Table V, it is evident that the variation in stability of the dipositive aquo ions (with respect to the metals) is due to the variation in enthalpy of sublimation of the metals. This observation is entirely consistent with the conclusions of Corbett[3] and of Johnson[5] with respect to the relative stability of lanthanide dihalides. Both sublimation enthalpies[28] (which are responsible for variations in enthalpies of formation of $LnX_2$ and $Ln^{2+}$(aq)) and *third* ionization potentials[11] (which enter into enthalpies of formation of $LnX_3$ and $Ln^{3+}$(aq)) vary in a manner dictated by the energy differences between $4f^{n+1}s^2$ ("divalent") and $4f^nds^2$ ("trivalent") configurations.

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**Registry No.** $NdCl_2$, 25469-93-6; $TmCl_2$, 22852-11-5; HCl, 7647-01-0; $Nd^{2+}$, 16727-26-7; $Sm^{2+}$, 16396-66-0; $Eu^{2+}$, 16910-54-6; $Dy^{2+}$, 14701-44-1; $Tm^{2+}$, 16910-52-4; $Yb^{2+}$, 22541-96-4.

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