Table V. Effect of Aging[a]

Aging time, min	Moles of Ce(IV) × 10^4	Moles of $CH_3N_2H_3$ × 10^4	Ce(IV): $CH_3N_2H_3$	Moles of N_2 × 10^4
9	9.00	55.5	1:6.15	1.90
33	9.00	55.5	1:6.15	1.49
63	9.00	55.5	1:6.15	1.26
91	9.00	55.5	1:6.15	0.981
153	9.00	55.5	1:6.15	0.859
221	9.00	55.5	1:6.15	0.783
266	9.00	55.5	1:6.15	0.719

[a] In all runs the acidity was adjusted to $[HClO_4] = 1.00$ M after aging.

In accordance with the stoichiometric and kinetic results, the $CH_3N_2H_3\cdot^+$ free radical produced in the rate-determining step may be rapidly consumed in two ways. First

$$2CH_3N_2H_3\cdot^+ \rightarrow CH_3N_2H_4^+ + CH_3N_2H\colon + H^+ \qquad (6)$$

followed by

$$2CH_3N_2H\colon \rightarrow (CH_3)_2N_2H_2 + N_2 \qquad (7)$$

or second

$$CH_3N_2H_3\cdot^+ + H_2O \rightarrow CH_3OH + N_2 + 4H^+ \qquad (8)$$

where reaction 8 may be a combination of several reactions. The first mechanism yields the overall equation

$$4Ce^{IV} + 2CH_3N_2H_3 \rightarrow 4Ce^{III} + (CH_3)_2N_2H_2 + N_2 + 4H^+ \qquad (9)$$

while the second mechanism yields

$$4Ce^{IV} + CH_3N_2H_3 + H_2O \rightarrow 4Ce^{III} + CH_3OH + N_2 + 4H^+ \qquad (10)$$

Both mechanisms result in the observed N_2:Ce(IV) mole ratio of 1:4. We were not able, however, to further distinguish between the two net reactions.

Effect of Aging. When Ce(IV) was added to water and allowed to age prior to its acidification the amount of N_2 liberated in the reaction was found to decrease severely. For example, after 266 min of aging the N_2 evolution fell to 37% of what was evolved using a freshly prepared acidified Ce(IV) solution. This observation suggests that in an unacidified solution the Ce(IV) undergoes polynuclear complex formation resulting in a different mechanistic pathway. The conditions used in the aging experiments are given in Table V.

Registry No. Ce(IV), 16065-90-0; $CH_3N_2H_3$, 51891-74-8.

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Reduction Potentials of Rare Earth Couples in Liquid Ammonia

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Earlier work revealed the chemical generation of the ammoniated electron via reduction by Yb(II) or Eu(II) in liquid ammonia. Partly to explore this phenomenon further, formal reduction potentials of the Eu(III)/Eu(II) and Yb(III)/Yb(II) couples were determined. This was done by means of potentiometric titrations with AgI or CuI in liquid ammonia at room temperature. An apparatus for high-pressure titration in liquid ammonia at room temperature was developed. The formal reduction potentials for the Eu and Yb couples were found to be 0.063 ± 0.010 and −0.662 ± 0.013 V, respectively. By employing auxiliary data, $\Delta G°$ for $Yb^{2+} + 3NH_2^- \rightarrow Yb(NH_2)_3 + e_{am}^-$ was calculated and found to be approximately −71 kJ mol^{-1}. Finally, reduction potentials based on ionic radii and solvation thermodynamics were computed, and these were in satisfactory agreement with the observed values for aqueous systems, but less so for liquid ammonia systems.

Introduction

A principal motivation for the present study was a remarkable reaction observed a few years ago in this laboratory, namely, the production of substantial concentrations of the ammoniated electron by inducing the oxidation of dipositive rare earth ions in liquid ammonia solution.[1] This reaction, $Yb^{2+} + 3NH_2^- \rightarrow Yb(NH_2)_3 + e_{am}^-$, permits preparation of active metals such as potassium by evaporation of the solvent. A similar reaction was observed earlier by Allbut and Fowles,[2] using zirconium(III) salts. In that thermodynamic information on redox reactions can be derived readily from electrometric studies, we undertook the measurement of reduction potentials for the Eu^{3+}/Eu^{2+} and Yb^{3+}/Yb^{2+} couples in liquid ammonia.

The scant information available on electrode potentials in liquid ammonia has been discussed by Jolly[3] and by Jander et al.[4] The known standard reduction potentials are the result of thermodynamic calculations, since a reference electrode of known potential vs. the standard hydrogen electrode has not been available until recently.[5] In no case has the potential of a rare earth couple in liquid ammonia been recorded. The reduction potential of nitrogen ($^1/_2N_2 + 3NH_4^+ + 3e^- \rightarrow 4NH_3$) is very low, only 0.04 V, but fortunately a high overvoltage exists, and a span of approximately 2 V is actually available. Since electrode potentials can be obtained expeditiously from an analysis of titration curves, we devised a pressurized apparatus for carrying out titrations at 25 °C in liquid ammonia medium. Silver or cuprous iodide served as the oxidant. In all earlier apparatus[6] the solutions were cooled to the boiling point of ammonia or below in order to maintain a pressure of 1 atm. Our room-temperature apparatus proved to be simpler and more convenient than the low-temperature assemblies. In the case of the Yb^{3+}/Yb^{2+} couple, an alternative means of constantly varying the ratio of the two ion concentrations was afforded by the known slow oxidation of Yb(II) by NH_4^+.[7]

Experimental Section

Titration Assembly. The apparatus shown in Figure 1 was of stainless steel, except for the buret and rinse-receiving bulb, which

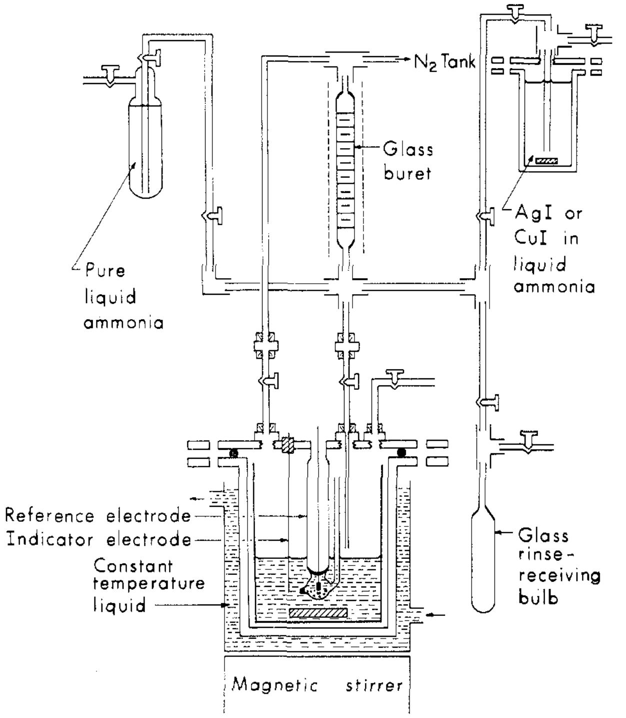

Figure 1. Apparatus for titration using liquid ammonia solutions at room temperature.

were of glass and were attached with Kovar seals. Heavy plastic tubing surrounded the buret in case of rupture. All connections were of the Swagelok type (Crawford Fitting Co., Solon, Ohio). The needle valves and tubing were $^1/_8$-in. size. The glass reference electrode was connected to the lid of the cell by a Kovar seal, and the platinum indicator electrode was attached using a porcelain pass-through. The glass-enclosed magnetic stirring bar could be activated through the stainless steel cell, which held a glass liner.

The cell was thermostated at 25.0 ± 0.1 °C by water circulated from a constant-temperature bath. It was found that very slight temperature differences in the vicinity of the buret caused the liquid ammonia inside to boil, preventing accurate volume readings. This phenomenon arises from the high temperature coefficient of vapor pressure for liquid ammonia, dP/dT, which is 231 Torr deg^{-1} at 25 °C. This boiling was avoided by employing a nitrogen overpressure of 1 atm from a 0–1500 psig pressure regulator; any oxygen was removed by activated copper.

In operation, the cell was charged with europium or ytterbium metal and the stoichiometric amount of ammonium iodide. After evacuation, ammonia gas was admitted, and the inner part of the reference electrode chilled by passing precooled gas into it. This ensured condensation of ammonia inside the reference electrode, forming the AgCl–KCl electrolyte. After admitting 50 ml of liquid ammonia from the reservoir, the mixture was stirred at 25 °C until the rare earth diiodide was formed. The hydrogen released was monitored by expelling it into a gas buret holding 6 M H_2SO_4. A few milliliters of titrant was drawn into the buret, and this was flushed into the rinse-receiving bulb, which was chilled. After filling of the buret and application of the nitrogen overpressure, the titration was carried out, after which the buret was rinsed several times with pure liquid ammonia. Both neutralization (NH_4I with KNH_2) and redox (AgI or CuI with EuI_2 or YbI_2) titrations were carried out.

Reference Electrode. The silver–silver chloride electrode developed earlier[5] was employed. Its potential at 25 °C vs. the standard hydrogen electrode was 0.622 ± 0.003 V. Potential measurements were made to ±1 mV using a specially constructed digital voltmeter which drew less than 10^{-12} A.

Reagents. Europium and ytterbium metals from Research Chemicals Co., Phoenix, Ariz., were used. Spectrochemical analysis revealed a total of 0.035% impurities (Mg, Ca, Mn, Fe) in the europium and a total of 0.094% impurities (Mg, Ca, Al, Si, Cu) in the ytterbium. Freshly precipitated AgI or CuI, after washing and drying, was weighed into a stainless steel reservoir holding a magnetic stirrer. Ammonia was introduced, the amount being determined by weighing the entire reservoir. This permitted calculation of the molality. The molar concentration as well was determined by withdrawing known volumes using the buret, evaporating the solvent, and weighing. Potassium amide solutions were prepared using vacuum-melted metal in glass and allowing the system to stand several days in liquid ammonia. Periodic tests for hydrogen showed when reaction was complete. The molar concentration was determined acidimetrically. Potassium amide solutions were found to attack stainless steel slowly and thus to become contaminated with heavy metals, presumably as amide complexes.

Solubility Measurements. The solubilities of EuI_2 and YbI_2 in liquid ammonia at 25 °C were determined gravimetrically using pressurized glass apparatus. When saturated solutions of $Ca(NH_2)_2$ were prepared by the decomposition of calcium metal in liquid ammonia, the filtrates were always turbid; this problem was remedied by addition of dehydrated colloidal silica (Cab-O-Sil, Cabot Co., Boston, Mass.). Evaporation of the solvent and hydrolysis gave $Ca(OH)_2$, which was titrated with 0.01 M HCl.

Analysis for Silver. At the end of most titrations with AgI solutions, the amount of metallic silver as determined. This was accomplished by collecting the Ag and AgI in a sintered-glass crucible, removing the AgI with KCN solution under nitrogen, and weighing the remaining silver metal.

Alternative Measurement of the Yb^{3+}/Yb^{2+} Potential. Since ytterbium(II) is slowly oxidized by ammonium ion in liquid ammonia, the cell with the electrodes was charged with ytterbium metal and ammonium iodide in the exact molar ratio of 1:2.5. Addition of liquid ammonia resulted in the rapid (5 min) formation of YbI_2, followed by slow (2 h) further oxidation by the remaining NH_4^+. The hydrogen evolution and potential were measured periodically.

The alternative determination of the potential of the Yb(III)/Yb(II) couple, by following the potential changes during the course of oxidation of Yb(II) by NH_4^+, extended over a Yb(III):Yb(II) concentration ratio from 0.011 to 5.85.

Titrations with Potassium Amide Solutions. Potentiometric titrations of ammonium iodide with potassium amide solutions invariably gave double inflections. This was traced to the presence of heavy metals in the solutions, arising, as noted earlier, from the attack of stainless steel by amide ion. Attempted titrations of europium and ytterbium diiodides with KNH_2, producing the ammoniated electron, were erratic and irreproducible. This was ascribed to precipitation of elemental iron, manganese, and other metals under the strong reducing conditions, accompanied by their catalytic decomposition of the ammoniated electron.

Other Reactions of Ytterbium(II). In attempts to find other suitable reactions similar to the principal one of interest ($Yb^{2+} + 3NH_2^- \rightarrow Yb(NH_2)_3 + e_{am}^-$), tests in pressurized glass vessels were carried out. When ytterbium(II) thiocyanate instead of the iodide was used, the blue color of the ammoniated electron was produced as briefly noted earlier,[1] but the solutions bleached rapidly. Acidification of the residues produced hydrogen sulfide. It was thought that the cyclopentadienide ion might function in the same way as the amide ion. Experiments showed, however, that YbI_2 and KC_5H_5 in liquid ammonia at room temperature produced no blue color. Since no hydrogen was produced either, the ytterbium was not oxidized to Yb(III).

Solubility Studies. The solubilities of EuI_2 and YbI_2 in liquid ammonia at 25 °C were found to be 0.0042 and 0.011 M, respectively, accurate to ±5%. The solubility of $Ca(NH_2)_2$ was established at 2.5×10^{-4} M. Liquid ammonia, saturated with both AgCl and KCl, was found to contain 2.23 mg of AgCl and 0.55 mg of KCl per milliliter of solution at 25 °C.

Results and Treatment of Data

Potentials of Europium and Ytterbium Couples. Typical titration data for the oxidation of EuI_2 and YbI_2 by AgI in liquid ammonia are plotted in Figures 2 and 3. The corresponding curves using CuI are shown in Figure 4. Potentials at the half-equivalent points represent the situation at which the concentrations of the dipositive and tripositive ions are equal and are expected to be independent of the nature of the oxidant. This permitted calculation of standard formal reduction potentials, E'.

In the case of ytterbium(II) titrations, the half-equivalence point did not truly represent equal Yb(III) and Yb(II) concentrations. This was because Yb(III) resulted not only

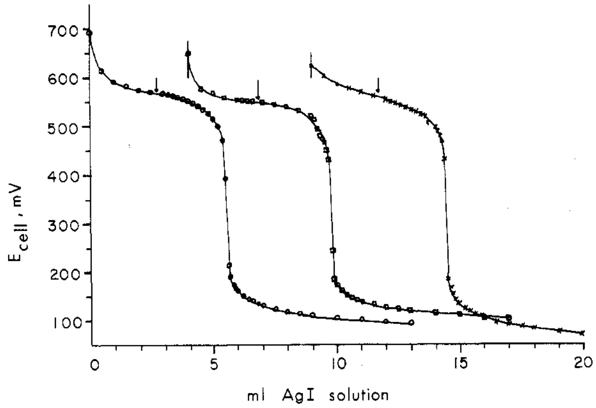

Figure 2. Titration of EuI_2 with AgI in liquid ammonia.

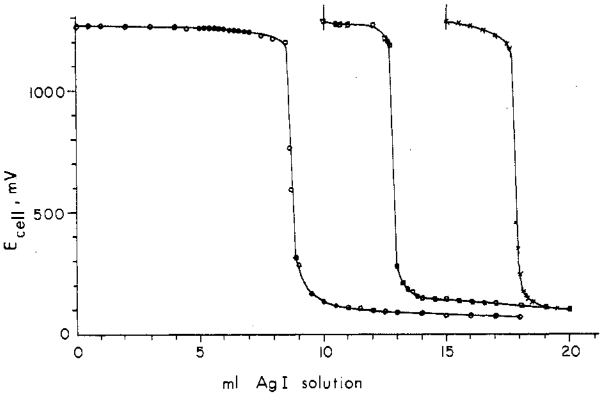

Figure 3. Titration of YbI_2 with AgI in liquid ammonia.

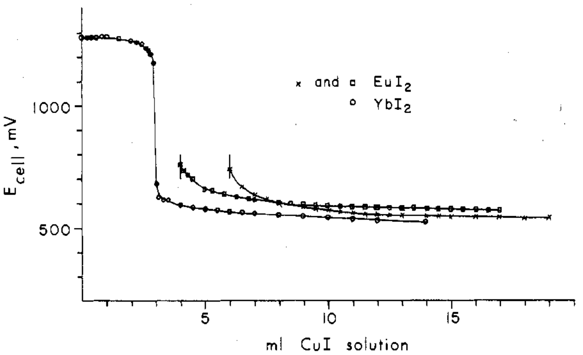

Figure 4. Titration of EuI_2 and YbI_2 with CuI in liquid ammonia.

from oxidation by Ag(I) or Cu(I) but also from oxidation of this powerful reducing agent by the solvent, as revealed by increased amounts of hydrogen liberated and decreased amounts of silver precipitated. The formal potentials are summarized in Table I.

Discussion

Potentials of the Rare Earth Couples. The formal reduction potentials for the Yb(III)/Yb(II) couple is readily computed from the cell potential at the half-equivalence point for both titration with AgI and titration with CuI. The two values agree within 3 mV. The potential from the alternative method, based on continuous oxidation of Yb(II) to Yb(III) by NH_4^+, was −0.650 V, 12 mV more positive than that from the AgI titrations. We take the most reliable value at 25 °C as −0.662 ± 0.013 V.

Similarly the most reliable formal potential for the Eu(III)/Eu(II) couple, based on the AgI titrations, was 0.063 ± 0.010 V. Figure 4 shows that the equivalence point in the titration of EuI_2 with CuI was barely detectable, and thus the potential of the Cu(I)/Cu(0) couple, 0.36 V,[3] must be slightly more positive than that of the europium system. No estimate of the potential of the Eu(III)/Eu(II) couple was made from the CuI titrations. Analysis of the cell contents at the end of the reaction disclosed much metallic copper, so the bulk of the Eu(II) was oxidized.

Table I. Formal Reduction Potentials of Eu(III)/Eu(II) and Yb(III)/Yb(II) Couples in Liquid Ammonia at 25 °C

Couple	Oxidant	Potential at half-equivalence point, V	E', V	Av E', V
Eu(III)/Eu(II)	AgI	0.568	+0.054	+0.063 ± 0.010
		0.560	+0.062	
		0.548	+0.074	
Yb(III)/Yb(II)	AgI	1.268	−0.646	−0.662 ± 0.013
		1.289	−0.667	
		1.294	−0.672	
Yb(III)/Yb(II)	CuI	1.280	−0.658	−0.659 ± 0.010
		1.282	−0.660	

Formal reduction potentials differ from standard potentials only in that the latter contain the term $(-RT/nF)\ln(\gamma_{red}/\gamma_{ox})$. Even if the activity coefficient ratio is as large as 2, the standard potentials would be only 18 mV more positive than the formal potential.

Chemical Generation of the Ammoniated Electron. One way of viewing the reaction

$$Yb^{2+} + 3NH_2^- \rightarrow Yb(NH_2)_3 + e_{am}^- \quad (1)$$

is as the sum of the following three

$$Yb(NH_2)_2 + NH_2^- \rightarrow Yb(NH_2)_3 + e^- \quad (2)$$

$$e^- \rightarrow e_{am}^- \quad (3)$$

$$Yb^{2+} + 2NH_2^- \rightarrow Yb(NH_2)_2 \quad (4)$$

Earlier work[8] yielded a potential of approximately 2.10 V for reaction 2. Jolly[9] computed a potential of −1.95 V at 25 °C for reaction 3. Since the ionic radii of Yb^{2+} and Ca^{2+} (0.103 and 0.099 nm, respectively) are fairly close, the equilibrium constant of reaction 4 can be estimated from the formation constant of $Ca(NH_2)_2$, which was calculated from its solubility and found to be 1.6×10^{10} $mol^{-3}\ l.^3$. Summarizing the free energies ($\Delta G° = -nF\Delta E° = -RT \ln K$) gives for reaction 1 a $\Delta G°$ value of approximately −71 kJ mol^{-1} and an equilibrium constant of approximately 6×10^{12} $mol^{-3}\ l.^3$.

As the reduction potential for the Yb^{3+}/Yb^{2+} couple is known (Table I), its value can be combined with the data corresponding to reactions 2 and 4 to yield a rough value (197 kJ mol^{-1}) for the free energy change of reaction 5. From this,

$$Yb(NH_2)_3 \rightarrow Yb^{3+} + 3NH_2^- \quad (5)$$

the solubility product of ytterbium(III) amide in liquid ammonia can be estimated at 10^{-35} $mol^4\ l.^{-4}$, probably correct within 1 or 2 orders of magnitude. There is little doubt that the extreme insolubility of $Yb(NH_2)_3$ is the factor which lowers the free energy change of reaction 1 sufficiently so that the already great reducing power of Yb^{2+} in basic solution exceeds that of the ammoniated electron.

Computation of Reduction Potentials from Solvation Thermodynamics. Two general methods for estimating reduction potentials of R^{3+}/R^{2+} couples (R is a rare earth metal) have been used;[10] the first is based on spectral data and the second is based on the thermodynamic calculations of solvation energies. The second method is followed here. Reduction potentials for the rare earth couples of interest, against the standard hydrogen electrode set at zero, may be estimated from

Table II. Solvation Thermodynamic Data for $R^{3+} + e^- = R^{2+}$ in Water

R^{n+}	r, nm	$-\Delta G^\circ_{con}/z$, kJ mol^{-1}	$-\Delta G^\circ_{aq}$, kJ mol^{-1}	ΔG°, kJ mol^{-1}	E°(calcd), V	E°(lit.), V
Eu^{3+}	0.103	1591	3537	39 ± 36	−0.40 ± 0.37	−0.37[a]
Eu^{2+}	0.112	1165	1504			
Yb^{3+}	0.094	1646	3697	118 ± 72	−1.23 ± 0.74	−1.15[b]
Yb^{2+}	0.103	1198	1572			
Sm^{3+}	0.104	1585	3518	146 ± 36	−1.51 ± 0.37	−1.55[b]
Sm^{2+}	0.113	1161	1497			

[a] Average of two recent determinations: L. R. Morss and H. O. Haug, *J. Chem. Thermodyn.*, **5**, 513 (1973); G. Biedermann and H. B. Silber, *Acta Chem. Scand.*, **27**, 3761 (1973). [b] L. J. Nugent, R. D. Baybarz, and J. L. Burnett, *J. Phys. Chem.*, **73**, 1178 (1969).

Table III. Solvation Thermodynamic Data for $R^{3+} + e^- = R^{2+}$ in Ammonia

R^{n+}	r, nm	$-\Delta G^\circ_{con}/z$, kJ mol^{-1}	$-\Delta G^\circ_{am}$, kJ mol^{-1}	ΔG°, kJ mol^{-1}	E°(calcd), V	E°(lit.), V
Eu^{3+}	0.103	1558	3669	43 ± 36	−0.45 ± 0.37	+0.063[a]
Eu^{2+}	0.112	1113	1556			
Yb^{3+}	0.094	1659	3848	132 ± 72	−1.37 ± 0.74	−0.662[a]
Yb^{2+}	0.103	1150	1631			
Sm^{3+}	0.104	1551	3651	149 ± 36	−1.54 ± 0.37	−1.390[b]
Sm^{2+}	0.113	1109	1548			

[a] This work. [b] Estimated by using the $(\Delta G^\circ_{am-Eu^{3+}} - \Delta G^\circ_{am-Eu^{2+}})$ value for $(\Delta G^\circ_{am-Sm^{3+}} - \Delta G^\circ_{am-Sm^{2+}})$ in calculating ΔG°_{am} for the Sm^{3+}/Sm^{2+} couple. This is valid because the radius values of Sm^{3+} and Sm^{2+} are only 0.001 nm larger than corresponding Eu^{3+} and Eu^{2+} radii.

free energy changes in reaction 6. The solvent can be either

$$R^{3+} + {}^1/_2H_2 \rightarrow R^{2+} + H^+ \qquad (6)$$

water or ammonia. A free energy cycle is set up based on the above reaction. The quantities necessary to find the corresponding net free energy, ΔG°, are the dissociation energy of H_2, the ionization energy of H, the solvation energy of H^+, the third ionization potentials of the rare earth elements, and the solvation energies of R^{3+} and R^{2+}. All except the last two are known quantities. Noyes[11] and Plambeck[12] have developed procedures for computing the free energies of solvation of ions. Noyes[13] has summarized the conventions which must be followed consistently in the treatment of these processes.

It is recognized that reduction potentials cannot be computed accurately from solvation thermodynamics, especially when the species are di- and tripositive ions. This is because the desired term is the difference between two large terms. Nevertheless, it develops that moderately satisfactory computations can be made and general trends detected if a self-consistent set of thermodynamic data and ionic radii are used.

Following the procedure of Plambeck, who employed the ionic radii of Pauling, free energies of hydration and ammoniation of di- and tripositive ions of europium, ytterbium, and samarium were computed. This gave ΔG° and thus E° for reaction 6 in both water and ammonia.

The ionic radius of Yb^{2+} given by Pauling[14] is in error, and the corrected value of 0.103 nm was obtained by assuming that it is larger than that of Yb^{3+} by the same amount as in the europium case. A similar procedure was used for Sm^{2+}. The third ionization energies of the rare earth elements have been computed recently by Johnson,[15] by Faktor and Hanks,[16] and by Morss.[17] The results of Johnson, which were documented in most detail, were employed in this work, despite their larger error limits.

The results of these thermodynamic derivations are summarized in Tables II and III. While the agreement of calculated reduction potentials for aqueous systems is in fair agreement with accepted literature values, those computed for liquid ammonia tend to be 0.2–0.7 V more negative than the values observed in this study. The origin of these discrepancies is not known.

Acknowledgment. Acknowledgment is made to the National Science Foundation for support of part of this work under Grant GP 19882.

Registry No. Eu^{3+}, 22541-18-0; Eu^{2+}, 16910-54-6; Yb^{3+}, 18923-27-8; Yb^{2+}, 22541-96-4; Sm^{3+}, 22541-17-9; Sm^{2+}, 16396-66-0; $Yb(NH_2)_3$, 19357-82-5; ammonia, 7664-41-7.

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