TABLE VI

ESTIMATED ENTROPIES (IN GIBBS MOL^{-1}) FOR ACTINIDE MO_2^+(aq) IONS AT 25°

		S_{mag}		$\bar{S}°_{MO_2^+(aq)}$		
Element	Ground state	Spin only[a]	Spin–orbit[b]	Spin only[c]		Spin–orbit[d]
U	$^2F_{5/2}$	1.4	3.6	−7.0		−7.0
Np	$^2H_4$	2.2	4.4		−6.2	
Pu	$^4I_{9/2}$	2.8	4.6	−5.6		−6.0
Am	$^5I_4$	3.2	4.4	−5.2		−6.2

[a] $S_{mag} = R \ln (2S + 1)$. [b] $S_{mag} = R \ln (2J + 1)$. [c] $\bar{S}°_{NpO_2^+}$(exptl) − S_{mag,NpO_2^+}(spin only) + S_{mag,MO_2^+} (spin only). [d] $\bar{S}°_{NpO_2^+}$ (exptl) − S_{mag,NpO_2^+}(spin–orbit) + S_{mag,MO_2^+}(spin–orbit).

TABLE VII

ESTIMATED ENTROPIES (IN GIBBS MOL^{-1}) FOR ACTINIDE MO_2^{2+}(aq) IONS AT 25°

		S_{mag}		$\bar{S}°_{MO_2^{2+}(aq)}$		
Element	Ground state	Spin only[a]	Spin–orbit[b]	Spin only[c]		Spin–orbit[d]
U	$^1S_0$	0	0	−21.4		−23.6 (−20 (exptl)[4]
Np	$^2F_{5/2}$	1.4	3.6		−20 (exptl)	
Pu	$^3H_4$	2.2	4.4	−19.2		−19.2
Am	$^4I_{9/2}$	2.8	4.6	−18.6		−19.0

[a] $S_{mag} = R \ln (2S + 1)$. [b] $S_{mag} = R \ln (2J + 1)$. [c] $\bar{S}°_{NpO_2^{2+}(aq)}$ (exptl) − $S_{mag,NpO_2^{2+}}$(spin only) + $S_{mag,MO_2^{2+}}$(spin only). [d] $\bar{S}°_{NpO_2^{2+}(aq)}$(exptl) − $S_{mag,NpO_2^{2+}}$(spin–orbit) + $S_{mag,MO_2^{2+}}$ (spin–orbit).

provide better thermodynamic values for these interesting electrode reactions.

Entropies for Other Actinide Ions.—It is also possible to estimate the entropies for other actinide element oxycations from the value known previously for UO_2^{2+}(aq) and the experimental values determined in this research for NpO_2^+(aq) and NpO_2^{2+}(aq). The greatest uncertainty arises in estimation of the relative magnetic entropy. The effects of size and mass will be negligible only from uranium to americium. In Tables VI and VII, these estimates are summarized, using the separate methods for estimating the magnetic contribution. At the present time it is not possible to predict with certainty which of the two estimates is the more accurate.

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Standard-State Entropies for the Aqueous Trivalent Lanthanide and Yttrium Ions[1,2]

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The partial molal entropies of 13 trivalent rare earth and yttrium ions at 25° have been calculated from data in the literature and from this research on the heats and free energies of solution of the hydrated trivalent chlorides. These entropies are from 10 to 15 gibbs mol^{-1} more negative than previous estimates based on the old experimental value for Gd^{3+}(aq). The entropies of the lanthanide ions correlate well with the ionic radius if the internal electronic entropy is first subtracted. Consequently the present data do not demonstrate any effects on the entropy of the postulated change in hydration number occurring near the middle of the 4f group.

I. Introduction

The present estimated and tabulated values for the partial molal ionic entropies of all of the trivalent lanthanide and actinide ions are based upon the single value for Gd^{3+} calculated by Latimer[4,5] from solubility and calorimetric data on $Gd_2(SO_4)_3 \cdot 8H_2O$. The entropy obtained, −43 gibbs mol^{-1}, is subject to considerable error because of the inability to extrapolate the measured heats of solution of gadolinium sulfate to infinite dilution; others[6,7] using the same data have obtained −47 and −48 gibbs mol^{-1}.

It was pointed out recently[7] that the requisite data exist to calculate new values for many of the trivalent lanthanides from thermal and free energy data on the hydrated rare earth chlorides. In using these values to obtain a more reliable set of entropies for all of the trivalent lanthanide ions, a good correlation of the rare earth ionic entropies with radius was observed if the internal electronic entropies were considered. To improve and extend the correlation to all of the lanthanide

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[2] Supported by the U. S. Atomic Energy Commission.

[3] Taken in part from the Ph.D. thesis of R. J. Hinchey, Purdue University, Jan 1967.

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[6] F. R. Rossini, D. W. Wagman, W. H. Evans, S. Levine, and I. Jaffe, "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C., 1952, Part I.

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ions, additional calorimetric and equilibrium data have been obtained.

II. Experimental Section

Reagents. Rare Earth Trichloride Hydrates.—Concentrated solutions of the various rare earth trichlorides (except cerium) were prepared by dissolving the appropriate 99.9% pure oxide[8] in excess 2 N HCl. The solutions were digested by boiling and were passed through an acid-washed Dowex 1X8 chloride-form anion-exchange column to remove traces of iron as indicated by a thiocyanate test. After further concentrating, the salts were allowed to crystallize from the acidic solution over a period of several weeks in a desiccator over Drierite. The crystals were separated by filtration and washed with small amounts of conductivity water. The corresponding cerium(III) salt was prepared from reagent grade cerous nitrate by fuming with concentrated HCl, followed by treatment with hydrogen peroxide in 2 N HCl, reduction in volume, and subsequent recrystallization. Analysis for rare earth content was made by precipitation of the oxalate and ignition to the oxide. The analysis indicated the crystals to be $\geq 99.9\%$ pure. Specimens of the various salts dissolved in water gave only slightly acidic pH values similar to the characteristic values observed for pure chloride solutions observed by others.[9]

Procedures.—The heats of solution of $EuCl_3 \cdot 6H_2O$ and $LuCl_3 \cdot 6H_2O$ were measured with laboratory calorimeters CS-1 and CS-2 whose details of construction and operation have been described elsewhere.[10,11]

Small samples of the hydrated rare earth salts were weighed in glass bulbs having a volume of about 1 cm³. The bulbs were evacuated and a constriction in the neck of the bulb was sealed with a microtorch. To prevent possible decomposition of the hydrated salt the sample was cooled with liquid nitrogen during the sealing operation. The procedure was checked by reweighing some samples.

The integral heats of solution of $EuCl_3 \cdot 6H_2O$ and $LuCl_3 \cdot 6H_2O$ were measured at four and five different concentrations (1.4×10^{-3}–2.6×10^{-3}) for each salt and extrapolated to infinite dilution by means of a ρ plot.[10] The standard heats of solution, $\Delta H_s°$, were found to be -8770 ± 30 and $-11{,}910 \pm 20$ cal mol^{-1} at 25° for $EuCl_3 \cdot 6H_2O$ and $LuCl_3 \cdot 6H_2O$, respectively.

Heat capacity measurements were made in a brass microcalorimeter[12] designed for measurements on actinide salts at 298°K. A glass-enclosed thermistor probe was fitted into a central well in the 7-cm³ calorimeter chamber. The vessel was sealed with a threaded cap and O ring. Heat conduction paths through the salt were provided by four brass washers which fitted tightly on the thermistor well. A manganin wire heater of about 100 ohms was wound noninductively on the outer surface of the calorimeter for electrical calibration. The heat capacity calorimeter was interchangeable with the solution microcalorimeter so that the temperature bath, bridge, amplifier, and recorder system were the same.[12] The calorimeter was calibrated and tested by measuring the heat capacities of water and several common salts including $GdCl_3 \cdot 6H_2O$. With care in selecting similar known salts for calibration specific heats could be measured with a precision of about 1%, which was sufficient for the purposes of this research. The heat capacities of $SmCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, and $GdCl_3 \cdot 6H_2O$ were found to be 86.4, 87.7, 81.6, and 83.0 gibbs mol^{-1}, respectively, at 25°, with errors of approximately ± 0.8 gibbs mol^{-1} in each case.

The solubilities of $CeCl_3 \cdot 7H_2O$ and $LuCl_3 \cdot 6H_2O$ were measured at $25.00 \pm 0.05°$ by equilibrating a saturated solution of the salt in a constant-temperature bath. Equilibrium was approached from both above and below 25°. Duplicate samples were removed for analysis at 1-day intervals with a thin-walled glass capillary pipet and weighed, and the rare earth was precipitated as the oxalate. The oxalate was dried under a lamp and ignited to the oxide. The weight of salt was calculated and the weight of water was obtained by difference. The concentrations of saturated solutions of $CeCl_3 \cdot 7H_2O$ and $LuCl_3 \cdot 6H_2O$ from replicate determination were observed to be 3.748 ± 0.025 and 4.136 ± 0.002 m, respectively, at 25.0°.

III. Calculations

Most of the thermodynamic functions in this communication will refer to the solution reaction represented by

$$MCl_3 \cdot nH_2O(c) = M^{3+}(aq) + 3Cl^-(aq) + nH_2O \quad (1)$$

Entropies of the trivalent ions can be calculated from $\Delta S°$ values for eq 1 and the entropies of the solid salts, chloride ion, and water. The NBS[13] entropies for $Cl^-(aq)$ and $H_2O(l)$ of -13.5 and 16.71 gibbs mol^{-1}, respectively, are adopted for all calculations. The entropies of the solid salts have been calculated from low-temperature heat capacity measurements and will be discussed in section IIIC.

A. Free Energy of Solution.—The standard free energy of solution for eq 1 is given by

$$\Delta F° = -RT \ln 27m^4\gamma_\pm{}^4 a_{H_2O}{}^n \quad (2)$$

where m refers to the molality of the saturated solution in moles of MCl_3/1000 g of H_2O, $\gamma_\pm$ is the mean ionic activity coefficient of the solute in a saturated solution, and a_{H_2O} is the water activity in the saturated solution. The water activity can be obtained from the corresponding osmotic coefficient

$$\ln a_w = \frac{-\phi\nu m}{55.5} \quad (3)$$

where ϕ is the osmotic coefficient in a solution of concentration m of a salt containing ν ions/mole.

The osmotic and activity coefficients were obtained from the isopiestic data of Spedding and his coworkers. The solubilities of the various hydrates were obtained from a variety of sources, including this research; the free energy data are summarized in Table I.[14–24] The activity and osmotic coefficients for several rare earth salt solutions were estimated to provide a more complete set of entropy data for the whole series. This was easily carried out graphically from plots for each atomic

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TABLE I

STANDARD FREE ENERGY, ENTHALPY, AND ENTROPY OF SOLUTION (EQ 1)

Salt	Soly, mol/1000 g of H_2O	$\gamma_{\pm}{}^a$ (satd)	ϕ^a (satd)	$-\Delta F^\circ_{298}$, cal mol^{-1}	$-\Delta H^\circ_{298}$, cal mol^{-1}	$-\Delta S^\circ_{298}$, gibbs mol^{-1}
$LaCl_3 \cdot 7H_2O$	3.8944[b]	4.767[b]	2.6563[b]	5783	7373[g,h]	5.34
$CeCl_3 \cdot 7H_2O$	3.748[k]	(4.60)	(2.66)	5714	6898[j,h]	3.97
$PrCl_3 \cdot 7H_2O$	3.975[e]	(5.50)	(2.81)	5969	7041[g,i]	3.60
$NdCl_3 \cdot 6H_2O$	3.9307[b]	6.206[b]	2.8383[b]	6665	9103[h]	8.18
$SmCl_3 \cdot 6H_2O$	3.6414[b]	5.132[b]	2.7370[b]	6337	9029[g,i]	9.03
$EuCl_3 \cdot 6H_2O$	3.619[f]	(5.48)	(2.77)	6471	8770[l]	7.42
$GdCl_3 \cdot 6H_2O$	3.5898[b]	5.833[b]	2.7967[b]	6566	8423[g,i]	6.23
$TbCl_3 \cdot 6H_2O$	3.5795[f]	(6.22)	(2.84)	6703	9556[k]	9.57
$DyCl_3 \cdot 6H_2O$	3.6302[c]	7.011[c]	2.9116[c]	6915	10067[c]	10.58
$HoCl_3 \cdot 6H_2O$	3.739[f]	(8.50)	(3.01)	7266	10325[k]	10.26
$ErCl_3 \cdot 6H_2O$	3.7840[d]	9.769[d]	3.0902[d]	7510	11314[g,h]	12.76
$YbCl_3 \cdot 6H_2O$	4.0028[b]	(12.65)	(3.32)	7848	10798[g,h]	9.93
$LuCl_3 \cdot 6H_2O$	4.136[l]	(14.25)	(3.52)	7873	11910[l]	13.55
$YCl_3 \cdot 6H_2O$	3.948[d]	12.307[d]	3.2051[d]	7914	11052[g,h]	10.53

[a] Values in parentheses are estimates (see text). [b] Reference 20. [c] Reference 21. [d] Reference 22. [e] Reference 23. [f] Reference 24. [g] Reference 14. [h] Reference 16. [i] Reference 18. [j] Reference 15. [k] Reference 19. [l] This work.

number of the measured coefficients against molality which produce a family of similar curves. It is estimated that the errors thus introduced in the free energies of solution for $CeCl_3 \cdot 7H_2O$, $PrCl_3 \cdot 7H_2O$, $EuCl_3 \cdot 6H_2O$, $TbCl_3 \cdot 6H_2O$, $HoCl_3 \cdot 6H_2O$, $YbCl_3 \cdot 6H_2O$, and $LuCl_3 \cdot 6H_2O$ are no more than ±150 cal mol^{-1}.

B. Heats of Solution.—The heats of solution of the salts $MCl_3 \cdot nH_2O$ at infinite dilution are summarized in Table I. The data for $EuCl_3 \cdot 6H_2O$ and $LuCl_3 \cdot 6H_2O$ as determined in this research were for such low dilutions that extrapolation to infinite dilution was no problem. The heats of solution at finite concentrations for the other rare earth salts are taken from the data of Spedding and coworkers[14-17] and were corrected to infinite dilution using recent values for the heats of dilution.[16,18] The heats of dilution for $CeCl_3(aq)$ and $YCl_3(aq)$ were estimated from the corresponding data for $LaCl_3(aq)$ and $ErCl_3(aq)$.[16] Such a procedure probably introduces an error of no more than ±100 cal.

C. Entropies of Solution.—The standard entropies of solution for the 13 lanthanides and yttrium trihalide hydrates have been calculated for eq 1 from the free energy and heat data and are summarized in the last column of Table I.

D. Heat Capacities and Entropies of the Solid Hydrates.—Pfeffer and his coworkers[25-28] have measured the heat capacities of several of the hydrated rare earth chlorides from a few degrees up to 250°K. Above 120°K, the function C_p/T which is nearly linear for these salts can be extrapolated up to 298°K, and the entropies can be calculated by integration to within ±0.5 gibbs mol^{-1}. The extrapolation procedure was checked up to 298°K by experimentally measuring C_p at this temperature for $GdCl_3 \cdot 6H_2O$. Some preliminary values of these entropies were published elsewhere.[7]

Karapet'yants[29] observed that the entropies of many similar compounds at 25° were linearly related to their heat capacities at the same temperature. However, for compounds containing species in electronically degenerate states the relationship is more complicated. In the rare earth ions, the 4f electrons are shielded from the effects of neighboring electric fields so that the orbital angular momentum is not quenched and the quantum number, J, for the total electronic angular momentum remains valid. In this case the degeneracy of the electronic states for the rare earth ions retains the free ion value of $(2J + 1)$, and the electronic contribution to the entropy is $S_e = R \ln (2J + 1)$. Consequently, if the heat capacities for the salts have been measured to low enough temperatures (as in the present case), the entropy at room temperature contains the $R \ln (2J + 1)$ "magnetic" entropy. However, the heat capacity at room temperature is usually only made up of the lattice contributions.

In an analysis similar to that which Westrum[30] carried out on rare earth oxides, it is possible to demonstrate[7] that the lattice or net entropy of a hydrated rare earth chloride (the total entropy less $R \ln (2J + 1)$ is very simply related to the heat capacity at 298°K. Table II is a summary of the heat capacity and entropy data. It can be seen in the last column of this table that the ratio of the net or lattice entropy and heat capacity (S_n/C_p) is a constant of 1.09–1.10 for all of the hexahydrates and has a value of 1.07 for the two heptahydrates.

TABLE II

ENTROPIES AND HEAT CAPACITIES OF LANTHANIDE SALTS

Salt	C_{p298}, gibbs mol^{-1}	S_{298}, gibbs mol^{-1}	Ionic state	S_e, gibbs mol^{-1}	S_n,[a] gibbs mol^{-1}	$(S_n/C_p)_{298}$
$LaCl_3 \cdot 7H_2O$	103.0[b]	110.6[b]	$^1S_0$	0.00	110.6	1.07
$CeCl_3 \cdot 7H_2O$		(112.3)	$^2F_{5/2}$	3.56	(108.7)	
$PrCl_3 \cdot 7H_2O$	100.2[b]	111.2[b]	$^3H_4$	4.37	106.8	1.07
$NdCl_3 \cdot 6H_2O$	86.2[b]	99.4[b]	$^4I_{9/2}$	4.58	94.8	1.10
$SmCl_3 \cdot 6H_2O$	86.4[c,d]	(98.2)	$^6H_{5/2}$	3.64[e]	(94.6)	(1.10)
$EuCl_3 \cdot 6H_2O$	87.7[c,d]	(95.5)[c]	$^7F_0$	2.23[e]	(93.3)	(1.09)
$GdCl_3 \cdot 6H_2O$	81.9[b] 83.0[c]	93.6[b]	$^8S_{7/2}$	4.13	89.5	1.09
$TbCl_3 \cdot 6H_2O$		(95.1)	$^7F_6$	5.10	(90.0)	
$DyCl_3 \cdot 6H_2O$	81.9[b]	96.0[b]	$^6H_{15/2}$	5.51	90.5	1.10
$HoCl_3 \cdot 6H_2O$	83.0[b]	97.0[b]	$^5I_8$	5.63	91.4	1.10
$ErCl_3 \cdot 6H_2O$	82.6[b]	95.4[b]	$^4I_{15/2}$	5.51	89.9	1.09
$TmCl_3 \cdot 6H_2O$			$^3H_6$	5.10		
$YbCl_3 \cdot 6H_2O$	81.6[c]	(93.9)[c]	$^2F_{7/2}$	4.13	(89.8)	(1.10)
$LuCl_3 \cdot 6H_2O$	81.9[b]	90.09[b]	$^1S_0$	0.00	90.1	1.10
$YCl_3 \cdot 6H_2O$		(88.0)	$^1S_0$	0.00	(88.0)	

[a] S_n, the net or lattice entropy, is the difference between the measured entropy and the electronic entropy, S_e. [b] Extrapolated from the data of Pfeffer, *et al.*[25-28] [c] This work. [d] See text regarding electronic effects on the heat capacity of these salts. [e] Contains contribution from thermally populated higher electronic states (see text).

In principle it should be possible to estimate the net structural entropy and the total entropy for $SmCl_3 \cdot 6H_2O$, $EuCl_3 \cdot 6H_2O$, and $YbCl_3 \cdot 6H_2O$ assuming that the ratio (S_n/C_p) has the same value as the other

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adjacent rare earths. At 25°, however, more than one electronic state of Sm^{3+} and Eu^{3+} is populated so that there is a small electronic heat capacity contribution estimated as 0.41 and 2.09 gibbs mol^{-1} for Sm^{3+} and Eu^{3+}, respectively.[31] Consequently for these ions the structural or net heat capacity (the measured value less the electronic value) was used to estimate the structual or net entropy, S_n, given in Table II.

Also, in the case of Sm^{3+} and Eu^{3+}, the entropy contribution from the thermally populated higher electronic states can be calculated from the known energy levels.[32] Such calculations give an additional electronic contribution of 0.08 and 2.23 gibbs mol^{-1} for Sm^{3+} and Eu^{3+}, respectively. In the case of $CeCl_3 \cdot 7H_2O$, the direct interpolation of the net entropy at 298°K, S_n, between $LaCl_3 \cdot 7H_2O$ and $PrCl_3 \cdot 7H_2O$ seemed valid without resorting to measurement of the heat capacity. A similar situation exists for $TbCl_3 \cdot 6H_2O$. The total entropies were then obtained by addition of the $R \ln (2J + 1)$ "magnetic" entropy as indicated in Table II.

The entropy for $YCl_3 \cdot 6H_2O$ was based upon the net lattice entropy for $ErCl_3 \cdot 6H_2O$, with a correction term[33] subtracted for the mass differences of the two ions, which also have nearly the same ionic radii.

E. Ionic Entropies of the Lanthanides.—Entropies of the individual aqueous trivalent lanthanide ions and $Y^{3+}(aq)$ can be calculated at 25° from the data of Tables I and II and the known entropy of chloride ion; these values have been summarized in Table III.

Table III
Entropies of the Aqueous Trivalent Lanthanides and $Y^{3+}(aq)$

M^{3+}-(aq)	r_c,[a] Å	Ionic state	S_e, gibbs mol^{-1}	$-\bar{S}°_{25}$, gibbs mol^{-1}	$-\bar{S}°_{adj}$, gibbs mol^{-1}
La	1.061	$^1S_0$	0.00	52.21 ± 0.7	52.21
Ce	1.034	$^2F_{5/2}$	3.56	49.14 ± 1.4	52.70
Pr	1.013	$^3H_4$	4.37	49.87 ± 0.7	54.24
Nd	0.995	$^4I_{9/2}$	4.58	49.44 ± 0.6	54.02
Pm	0.979	$^5I_4$	4.37	(51)	(55)
Sm	0.964	$^6H_{5/2}$	3.64	52.42 ± 1.5	56.06
Eu	0.950	$^7F_0$	2.23	52.68 ± 1.3	54.91
Gd	0.938	$^8S_{7/2}$	4.13	53.39 ± 0.8	57.52
Tb	0.923	$^7F_6$	5.10	55.23 ± 1	60.33
Dy	0.908	$^6H_{15/2}$	5.51	55.34 ± 0.6	60.85
Ho	0.894	$^5I_8$	5.63	54.42 ± 0.5	60.05
Er	0.881	$^4I_{15/2}$	5.51	58.12 ± 0.6	63.73
Tm	0.869	$^3H_6$	5.10	(58)	(63)
Yb	0.858	$^2F_{7/2}$	4.13	56.79 ± 1	60.92
Lu	0.848	$^1S_0$	0.00	63.36 ± 0.5	63.36
Y	0.88	$^1S_0$	0.00	63.37 ± 1	63.37

[a] Crystal radii from ref 32 and 33.

It will be instructive to correlate the entropies with the ionic size and for this purpose the crystal radii of Templeton and Dauben[34] have also been included in Table III. The crystal radius of Y^{3+} is from the compilation of Zachariasen,[35] whose values for the rare earth ions seem most consistent with those of Templeton and Dauben. The errors indicated in the observed ionic entropies in Table III are dependent upon the probable errors in the heats and free energies of solution, which may run as high as 100–150 cal. Fortunately the errors in those rare earth ions which depend upon estimated activity and osmotic coefficients are not very large since there is some tendency for these errors to cancel each other in the resulting free energy of solution. The errors in the entropies of the solid salts, including estimated values, are not thought to be greater than ±0.5 to ±1.0 gibbs mol^{-1}. There is a possibility that the heats of solution of $ErCl_3 \cdot 6H_2O$ or $YbCl_3 \cdot 6H_2O$, or both, are in error by more than the probable error of ±100–150 cal mol^{-1}, as can be seen from the apparent reversal in trend of the heats with atomic number in Table I.

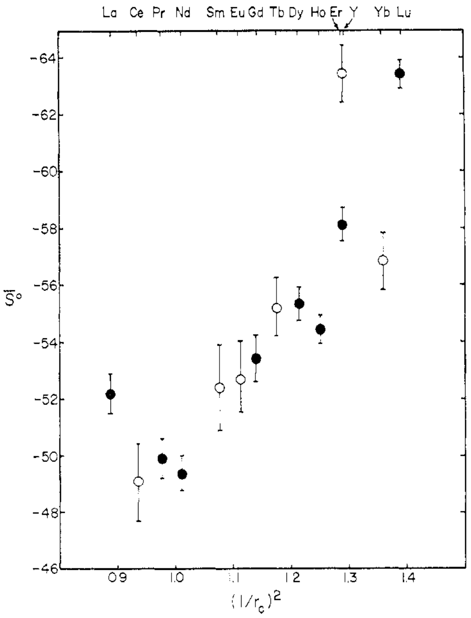

Figure 1.—The experimental ionic entropies of the trivalent lanthanide and $Y^{3+}(aq)$ ions plotted against $(1/r_c)^2$, where r_c is the ionic crystal radius. Closed circles are based upon low-temperature heat capacity data.

IV. Discussion

The ionic entropies for the trivalent lanthanides and $Y^{3+}(aq)$ are plotted against $(1/r_c)^2$ in Figure 1, where r_c is the ionic crystal radius. This type of radius function is one that Powell and Latimer[36,37] found satisfactory in their correlation of ionic entropies. While this radius function predicts the correct trend of entropy with radius, the general scatter of the data, particularly at the beginning and end of the series, seems greater than might have been expected.

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[31] D. H. Dennison and K. A. Gschneidner, U.S. Atomic Energy Commission Unclassified Report IS-1156, Ames Laboratory, Ames, Iowa, 1965.

[32] W. I. Carnall, D. M. Gruen, and R. L. Beth, *J. Phys. Chem.*, **66**, 2159 (1962); **67**, 1206 (1963).

[33] G. N. Lewis and M. Randall, "Thermodynamics," 2nd ed, revised by K. S. Pitzer and L. Brewer, McGraw-Hill Publications, New York, N. Y., 1961, p 517.

[34] D. H. Templeton and C. H. Dauben, *J. Amer. Chem. Soc.*, **76**, 5237 (1954).

[35] W. H. Zachariasen in "The Actinide Elements," G. T. Seaborg and J. J. Katz, Ed., McGraw-Hill Publications, New York, N. Y., 1954, p 775.

[36] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

[37] In actual fact these authors used an adjusted ionic radius, $1/(r_c + c)^2$, where c is a constant. In the present analysis it makes little difference if the constant term is introduced since the total spread in the radii of the ions involved is only 0.21 Å.

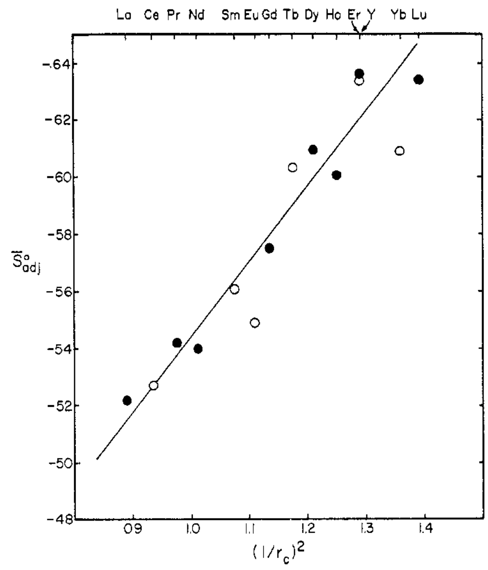

Figure 2.—Adjusted ionic entropies plotted against $(1/r_c)^2$. Adjusted entropies are the experimental entropies from which the internal electronic contribution has been subtracted (see text). Closed circles are based upon low-temperature heat capacity data.

In Figure 2, the entropies have been corrected by removing the internal electronic entropy; these adjusted entropies, from the last column of Table III, are plotted in Figure 2 against $(1/r_c^2)$. The linear correlation now seems quite satisfactory; the average deviation of the points from the indicated straight line is about ±1 gibbs mol^{-1}, only slightly larger than the average error of the data. Further, as stated earlier in this communication, the heat data for Er^{3+} and/or Yb^{3+} may be in error by more than estimated. At present we have no explanation for what also appears to be a rather large deviation for Eu^{3+}, except to note that low-temperature heat capacity data for $EuCl_3 \cdot 6H_2O$ are missing, and estimations were required for the entropy of this salt. Finally, it must also be noted that some of the degeneracy of the ground state may be lifted in the rare earths of highest atomic number and that the adjusted entropies for these species may have been overcorrected.

The present data do not confirm the old entropy value for $Gd^{3+}(aq)$ of -43 gibbs mol^{-1}, nor any of the estimates of the entropies of lanthanides or actinides based upon it. Further, while the present data confirm the functional dependence of the Powell and Latimer correlation[36] of the ionic entropies with radius, they do not confirm the absolute values of their equation. This is not surprising since this equation was heavily based upon the old entropy value for Gd^{3+} and the trivalent and tervalent actinide elements. However, the actinide entropies themselves were also based on Gd^{3+} and cannot be considered as independent values. Further, the actinide values were for 1 *M* acid solutions. The present analysis suggests that the Powell and Latimer equation will now have to be revised.

Inasmuch as the present research confirms the same type of correlation between entropy and radius for the lanthanide ions as is observed for all of the monatomic cations in the periodic table, we find no evidence of a change in hydration number from the entropy data. Such an entropy effect has been proposed by Bertha and Choppin[38] from less complete information than the present on the entropies of the lanthanide ions. These workers measured the entropies of solution of the rare earth iodates but were required to estimate the entropies of the solid salts to obtain the entropies of the aqueous species. This was done by fixing the entropy of $Gd(IO_3)_3(c)$ from the older value for the entropy of $Gd^{3+}(aq)$, which, unfortunately, has now been demonstrated to be in error by 10 gibbs mol^{-1}. Further, it can be seen from Table II that even the lattice entropy of the solid rare earth salts varies across the series. Consequently it is believed that Bertha and Choppin's conclusions regarding change in hydration as being reflected by the ionic entropies was an artifact of their treatment of the data, with perhaps additional uncertainties arising from their admittedly difficult heat of precipitation measurements.

A number of the thermodynamic functions of both actinide and lanthanide ions and compounds which have been based upon the older value for the entropy of $Gd^{3+}(aq)$ should now be revised in view of the results presented in this communication.

In conclusion, it is worth noting that although the aqueous lanthanide ions appear to retain all or nearly all of their magnetic entropy in solution, an important contribution to the free energy of complexation reactions would result if the degeneracy of the electronic ground states were removed as a result of complex formation. For example, if this happened for Er^{3+} in a given complex, the ΔS of complex formation would be decreased by 5.5 gibbs mol^{-1}, resulting in a free energy of complex formation at 25° which would be nearly 1.6 kcal more positive than would be observed if the magnetic entropy were not removed. The apparent nomadic behavior of the stability of Y^{3+} [39] complexes with respect to corresponding rare earth complexes with the same ligand might be due to some extent to such a varying entropy-reducing effect by ligands on the rare earth species. Unfortunately other ligand effects could also be expected on the enthalpy of such reactions so that the unraveling of different contributions is not simple.

(38) S. L. Bertha and G. R. Choppin, *Inorg. Chem.*, **8**, 613 (1969).
(39) P. Krumholz, *Progr. Sci. Technol. Rare Earths*, 129 (1964).