The entropies at 785°K. for the two hydrolysis reactions are found to be identical within ±0.12 e.u., as seems reasonable for reactions as closely similar as these, in which the corresponding solids have the same crystal structures, and nearly the same lattice parameters and atomic weights.

Since neither the trichlorides nor the oxychlorides are "magnetically dilute" compounds the magnetic entropy of a trichloride may be somewhat different from the magnetic entropy of the oxychloride of the same rare earth, but these effects probably would not be evident above our experimental errors.

The data presented here are in agreement with the observation reported previously[4] that the heats and free energies of reaction exhibit a steady trend toward more negative values with increasing atomic number of the metal cation.

The assumption that the rare earth trichlorides and oxychlorides are predominantly ionic compounds appears reasonable in view of their known physical and crystallographic properties. It seems plausible therefore to seek for a quantitative explanation of the variation in the heat of reaction in terms of the relative variation in coulombic interaction energy in the two solids as the metal cation undergoes contraction. The examination of our data from this point of view is in progress, and will be presented when the Madelung constant calculations for the solids have been completed.

An interesting empirical correlation, which is not obvious from detailed crystal energy considerations, is presented in Fig. 1, in which the heats of reaction are plotted as a function of the reciprocal of the cation radius. The radii are from Zachariasen[7] and are corrected to coördination number 9. The correlation is seen to be approximated rather closely by a straight line having a slope of $\sim -100$ kcal. per reciprocal ångström. It is clear, however, that the heats of reaction deviate significantly from the straight line curve. In view of the fact that it is meaningless to assign exact values to the radii of ions no special interpretation of these deviations seems warranted.

(7) W. H. Zachariasen, *Phys. Rev.*, **73**, 1104 (1948).

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[CONTRIBUTION NO. 288 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE][1]

# Thermochemistry of the Rare Earths. II. Lanthanum, Praseodymium, Samarium, Gadolinium, Erbium, Ytterbium and Yttrium

BY F. H. SPEDDING AND J. P. FLYNN

RECEIVED AUGUST 3, 1953

The integral heats of solution of the metals and anhydrous chlorides, in hydrochloric acid solutions, and the hydrated chlorides in water, have been measured at 25°. From these data the standard heats of formation of the anhydrous and hydrated chlorides have been calculated. In addition, estimates have been made of the free energies of formation of the same compounds.

## Introduction

The values tabulated by the Bureau of Standards[2] for the heats of formation of rare earth compounds are based upon the heat of solution data of Bommer and Hohmann.[3] A recent paper[4] from this Laboratory indicated that the accepted values in the case of cerium and neodymium may be too high by 8 to 10 kcal. Lohr and Cunningham[5] reported values for lanthanum and praseodymium which are also lower than those of Bommer and Hohmann.[3] In each case the heats of formation were calculated from heats of solution. The major contribution to the heat of formation came from the heat of solution of the metal in hydrochloric acid. It is in the latter value that the largest discrepancy occurs. The present paper extends the thermochemical work to include several other members of the rare earth group. Care was taken to use the best materials available for all measurements.

## Experimental

The calorimeter and the preparation of the anhydrous chlorides have been described.[6] The hydrated chloride samples were prepared by the method described earlier.[4] The hydrate, $PrCl_3 \cdot 6H_2O$, was prepared by desiccation of powdered $PrCl_3 \cdot 7H_2O$ over calcium chloride. The metals were prepared in tantalum containers by the method described by Spedding and Daane.[7] They were found, by spectrographic analysis, to be free of other rare earths and all common elements. Metal samples were prepared as fine lathe turnings in a dry helium atmosphere. In the case of metal experiments, only one sample was mounted in the calorimeter.

## Results

The heats of solution of rare earth metals obtained by other authors are given in Table I and the results of the present investigation in Table II. From these data and the heats of formation in solution of hydrogen chloride given by the National Bureau of Standards,[1] the heats of formation at 25° were calculated by the method set forth in the earlier paper.[4] The heats of reaction of the following reactions were used to calculate the heats of formation of the rare earth chlorides.

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, 1952.

(3) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 357 (1941).

(4) F. H. Spedding and Carl F. Miller, THIS JOURNAL, **74**, 4195 (1952).

(5) H. R. Lohr and B. B. Cunningham, *ibid.*, **73**, 2025 (1951).

(6) F. H. Spedding and Carl F. Miller, *ibid.*, **74**, 3158 (1952).

(7) F. H. Spedding and A. H. Daane, *ibid.*, **74**, 2783 (1952).

TABLE I

HEATS OF SOLUTION OF RARE EARTH METALS IN HYDROCHLORIC ACID BY OTHER INVESTIGATORS

| Metal | Investigators | HCl concn. | $t$, °C. | $-\Delta H^a$ |
|---|---|---|---|---|
| Y | Bommer and Hohmann[3] | 0.12 $N$ | 20 | 168.3 ± 0.7 |
| La | Sieverts and Gotta[8] | 1 $N$ | 20 | 164.27 |
| | Sieverts and Gotta | 1 $N$ | 17 | 164.72 |
| | Neumann, Kröger and Kunz[9] | 2.8 $N$ | | 167.72 ± 0.31 |
| | Bommer and Hohmann | 0.12 $N$ | 20 | 176.5 ± 0.7 |
| | Lohr and Cunningham[5] | 1.5 $N$ | 25 | 167.0 ± 1.4 |
| Pr | Bommer and Hohmann | 0.12 $N$ | 20 | 172.9 ± 0.7 |
| | Lohr and Cunningham | 1.5 $N$ | 25 | 165.3 ± 0.9 |
| | Sieverts and Gotta | 2 $N$ | 18 | 168.87 |
| Gd | Bommer and Hohmann | 0.12 $N$ | 20 | 168.8 ± 0.7 |
| Er | Bommer and Hohmann | 0.12 $N$ | 20 | 162.6 ± 0.7 |

[a] $\Delta H$ is in kcal./mole; $t$, °C. is the temperature of the measurements.

TABLE II

HEATS OF SOLUTION OF RARE EARTH METALS AND CHLORIDES IN HYDROCHLORIC ACID AT 25°

| Materials | $m^{1/2}$ | $m_F^{1/2}$(HCl) | $m_B^{1/2}$(HCl) | $-\Delta H^a$ |
|---|---|---|---|---|
| La | 0.05282 | 0.5196 | 0.5115 | 168.62 |
| | .04743 | .5196 | .5131 | 168.72 |
| $LaCl_3$ | .1213 | .5014 | .5014 | 31.277 |
| | .1767 | .5014 | .5014 | 30.994 |
| Pr | .04229 | .5196 | .5145 | 168.28 |
| | .05083 | 1.2122 | 1.2090 | 165.59 |
| $PrCl_3$ | .1005 | 0.5014 | 0.5014 | 34.130 |
| | .1611 | 0.5014 | 0.5014 | 33.855 |
| | .1074 | 1.2122 | 1.2122 | 30.209 |
| | .1704 | 1.2122 | 1.2122 | 29.804 |
| Gd | .04748 | 0.5196 | 0.5131 | 163.69 |
| | .05103 | .5196 | .5121 | 163.08 |
| $GdCl_3$ | .07905 | .5014 | .5014 | 41.719 |
| | .1232 | .5014 | .5014 | 41.641 |
| | .1522 | .5014 | .5014 | 41.451 |
| Er | .06251 | 1.2114 | 1.2065 | 157.97 |
| | .05469 | 1.2134 | 1.2097 | 157.99 |
| | .05459 | 1.2134 | 1.2097 | 158.29 |
| $ErCl_3$ | .09173 | 1.2134 | 1.2134 | 46.301 |
| | .1316 | 1.2134 | 1.2134 | 46.118 |
| Y | .07223 | 1.2103 | 1.2038 | 161.97 |
| | .09106 | 1.2100 | 1.1997 | 162.15 |
| $YCl_3$ | .09057 | 1.2134 | 1.2134 | 46.777 |
| | .1359 | 1.2134 | 1.2134 | 46.827 |
| | .1791 | 1.2134 | 1.2134 | 46.244 |

[a] $\Delta H$ is in kcal./mole; $m_D$ and $m_F$ are the initial and final hydrochloric acid molalities.

$$R(s) + HCl\ (aq., m_B) = 3/2H_2(g) + RCl_3\ (aq., m)\cdot HCl\ (aq., m_F) \quad (1)$$

$$RCl_3(s) + HCl\ (aq., m_F) = RCl_3\ (aq., m)\cdot HCl\ (aq., m_F) \quad (2)$$

$$3/2H_2(g) + 3/2Cl_2(g) = 3HCl(g) \quad (3)$$

$$3HCl(g) + HCl\ (aq., m_F) = HCl\ (aq.\ m_B) \quad (4)$$

These reactions were combined to obtain

$$R(s) + 3/2Cl_2(g) = RCl_3(s) \quad (5)$$

The heat of reaction of reaction 1 was measured directly. The heat of reaction of reaction 2 was obtained from the heat of solution of rare earth chlorides in water. In another paper,[10] the heats of solution are reported at several concentrations. From these data a least squares relationship was developed to represent the heat of solution as a function of concentration. The lowering effect of HCl on the heats of solution of rare earth chlorides was determined by conducting a series of experiments in acid solution. The observed heats of solution in acid were compared to the values calculated from the least squares formula for pure water. The heat of reaction of reaction 2 was taken to be the calculated heat of solution for water minus the lowering effect of HCl. The thermal data for reactions 3 and 4 were taken from the National Bureau of Standards Circular 500.[2] The heats of formation of the anhydrous chlorides are given in Table III.

TABLE III

HEATS OF FORMATION, ESTIMATED ENTROPIES, AND FREE ENERGIES OF FORMATION OF RARE EARTH CHLORIDES AT 25°, HEATS OF FORMATION OF RARE EARTH IONS AT 25°

| Substance | $-\Delta H°^a$ | $-\Delta F°$ | $S°$ |
|---|---|---|---|
| La | 0.0 | 0.0 | 13.7 |
| Pr | .0 | .0 | 13.7 |
| Gd | .0 | .0 | 14.0 |
| Er | .0 | .0 | 14.3 |
| Y | .0 | .0 | 11.3 |
| $LaCl_3$ | 255.91 | 238.3 | 34.5 |
| $PrCl_3$ | 252.09 | 234.5 | 34.5 |
| $GdCl_3$ | 240.09 | 222.5 | 34.9 |
| $ErCl_3$ | 229.07 | 211.4 | 35.1 |
| $YCl_3$ | 232.69 | 215.2 | 32.7 |
| $La^{+++}$ | 168.77 | ... | ... |
| $Pr^{+++}$ | 167.69 | ... | ... |
| $Gd^{+++}$ | 163.01 | ... | ... |
| $Er^{+++}$ | 158.79 | ... | ... |
| $Y^{+++}$ | 161.31 | ... | ... |

[a] $\Delta H°$ and $\Delta F°$ are in kcal./mole; $S°$ is in entropy units. The $\Delta H°$'s calculated from different determinations agreed within 0.20 kcal.

TABLE IV

HEATS OF SOLUTION OF HYDRATED RARE EARTH CHLORIDES IN WATER AT 25°

| Hydrate | $m^{1/2}$ | $-\Delta H$, cal./mole | Hydrate | $m^{1/2}$ | $-\Delta H$, cal./mole |
|---|---|---|---|---|---|
| $LaCl_3\cdot 7H_2O$ | 0.1277 | 6596 | $GdCl_3\cdot 6H_2O$ | 0.1211 | 7701 |
| | .1703 | 6566 | | .1737 | 7672 |
| | .2067 | 6520 | $YCl_3\cdot 6H_2O$ | .1371 | 10434 |
| $PrCl_3\cdot 7H_2O$ | .1267 | 6374 | | .2004 | 10244 |
| | .1731 | 6256 | | .2408 | 10160 |
| $PrCl_3\cdot 6H_2O$ | .1078 | 9097 | $ErCl_3\cdot 6H_2O$ | .1703 | 10574 |
| | .1582 | 8912 | | .2203 | 10484 |
| | .1968 | 8821 | $YbCl_3\cdot 6H_2O$ | .1285 | 10161 |
| $SmCl_3\cdot 6H_2O$ | .1277 | 8656 | | .1789 | 9909 |
| | .1782 | 8123 | | | |
| | .2188 | 7862 | | | |

Only Matignon[11] has reported the heats of solution of hydrated rare earth chlorides. He gave the value of −5.3 kcal./mole for $PrCl_3\cdot 7H_2O$. The heats of solution obtained in the present work are given in Table IV. From these data and the heats of solution given in another paper,[10] the heats of hydration were calculated from the equations

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(8) A. Sieverts and A. Gotta, *Z. anorg. allgem. Chem.*, **172**, 1 (1928).

(9) B. Neumann, C. Kröger and H. Kunz, *ibid.*, **207**, 133 (1932).

(10) F. H. Spedding and J. P. Flynn, THIS JOURNAL, **76**, 1477 (1954).

(11) C. A. Matignon, *Ann. chim. phys.*, **8**, 426 (1906).

$$RCl_3(s) + XH_2O = RCl_3(m_F) + \Delta H_1 \quad (6)$$

$$RCl_3 \cdot YH_2O(s) + (X - Y)H_2O = RCl_3(m_F) + \Delta H_2 \quad (7)$$

where $m_F$ is the same final molal concentration in each case and R is a rare earth. Subtraction of equation 7 from equation 6 gives the heat of hydration. From the heats of formation of the anhydrous chlorides and the heats of hydration, the heats of formation of the hydrated chlorides were calculated. The value −68,317 cal./mole as given by Bichowsky and Rossini[12] was used as the heat of formation of liquid water. The results of these calculations are given in Table V.

TABLE V

HEATS OF HYDRATION, HEATS OF FORMATION, ESTIMATED ENTROPIES, AND FREE ENERGIES OF FORMATION OF HYDRATED RARE EARTH CHLORIDES AT 25°

| Hydrate | $-\Delta H$ (hyd.)[a] | $-\Delta H°$ | $S°$ | $-\Delta F°$ |
|---|---|---|---|---|
| $LaCl_3 \cdot 7H_2O$ | 25.37 | 759.50 | 100.3 | 645.0 |
| $PrCl_3 \cdot 7H_2O$ | 28.45 | 758.76 | 100.3 | 645.4 |
| $PrCl_3 \cdot 6H_2O$ | 25.81 | 687.80 | 90.9 | 588.2 |
| $SmCl_3 \cdot 6H_2O$ | 30.79 | . . . | 91.1 | . . . |
| $GdCl_3 \cdot 6H_2O$ | 34.38 | 684.37 | 91.3 | 583.7 |
| $ErCl_3 \cdot 6H_2O$ | 38.22 | 677.19 | 91.5 | 578.6 |
| $YbCl_3 \cdot 6H_2O$ | 40.67 | . . . | 91.6 | . . . |
| $YCl_3 \cdot 6H_2O$ | 37.28 | 679.87 | 89.1 | 581.1 |

[a] $\Delta H$(hyd.), $\Delta H°$ and $\Delta F°$ are in kcal./mole and $S°$ is in entropy units.

From estimates of the entropies of the elements and compounds by the method of Latimer[13] the entropies of formation at 25° of the anhydrous and hydrated chlorides were approximated. Using the entropies and heats of formation, the free energies of formation were calculated. These results are included in Tables III and IV.

## Discussion

The data presented here on the heats of solution of the rare earth metals in hydrochloric acid solution are in better agreement with the results of Lohr and Cunningham,[5] Neumann, Kröger and Kunz,[9] and Sieverts and Gotta,[8] than with those of Bommer and Hohmann.[3] Bommer and Hohmann[3] prepared their metal samples by reduction of the anhydrous chlorides with potassium *in vacuo*. The resultant slag and metal were placed in a calorimeter and after the potassium chloride slag had dissolved, hydrochloric acid was added from a buret to dissolve the metal. Complete reduction of rare earths was assumed in the calculations. It

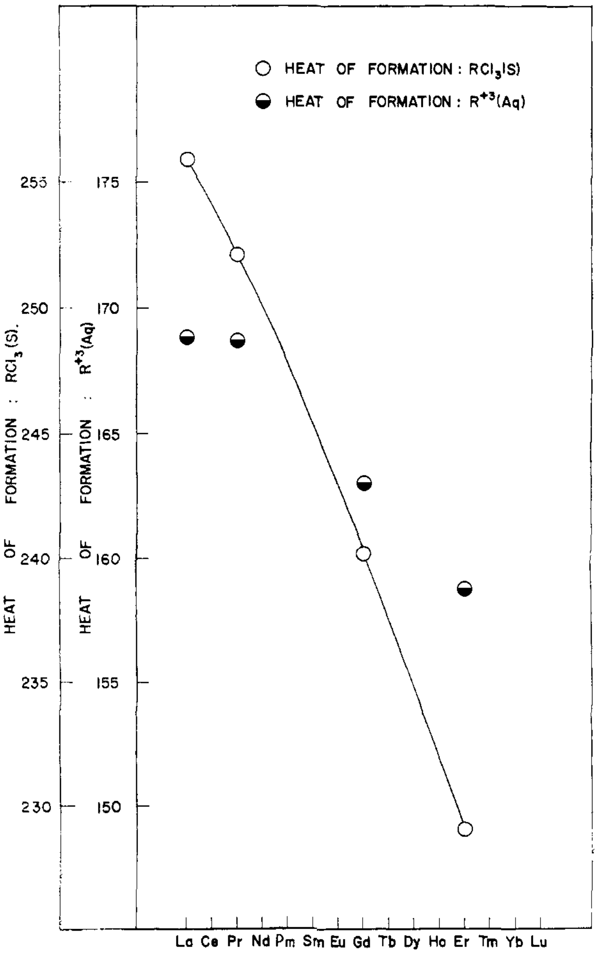

Fig. 1.—Heats of formation of rare earth trichlorides and rare earth ions in kcal./mole.

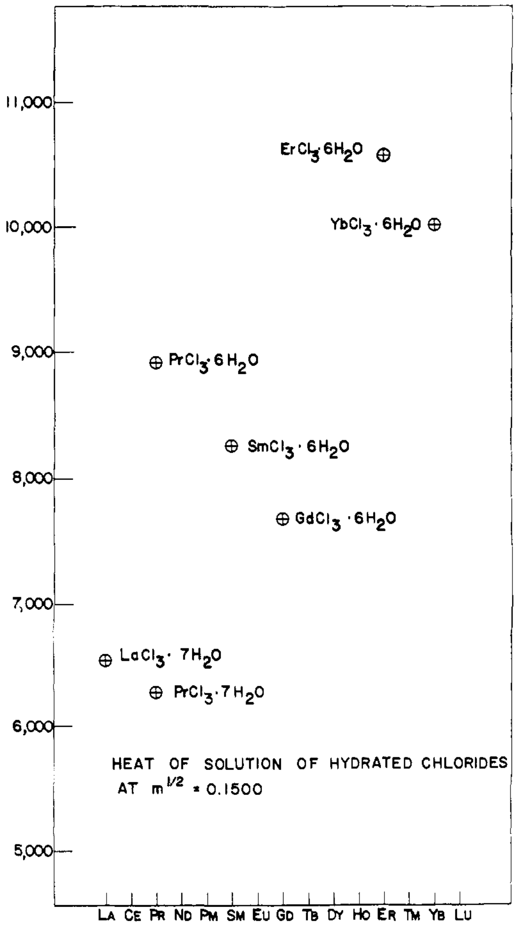

Fig. 2.—Integral heats of solution of the hydrated rare earth trichloride at $m^{1/2}$ = 0.1500 in cal./mole.

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[12] F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publ. Corp., New York, N. Y., 1948 (second printing).

[13] W. M. Latimer, THIS JOURNAL, **73**, 1480 (1951).

would seem that such a technique would reduce the accuracy of the heat leak corrections; furthermore, potassium dissolved or occluded by the rare earth metals would lead to high results. The presence of varying amounts of oxides in the metals used by the other authors would explain the differences in their results; the lanthanum metal used by Sieverts and Gotta[8] was only 84% pure. The metals used in the present work were prepared by reducing the anhydrous fluorides with calcium; the reductions were made in tantalum containers in an inert atmosphere. Unfortunately, a reliable method for the determination of oxygen in rare earth metals is not presently available. Since precautions were taken to keep oxygen out of the reactant materials and away from the reduction reaction, it is believed the metals contained a minimum of this element. Oxide impurities would produce lower results in the data reported here.

In general, the heats of formation of the rare earth chlorides and ions studied in this work decrease with increasing atomic number of the rare earth. The heat formation of the aqueous praseodymium ion is nearly equal to that of lanthanum, making a sharp break in the plot in Fig. 1. This break is not as sharply manifested when the heats of formation of the chlorides (Fig.1) are considered; the reason for this is that the heat of solution of the anhydrous chloride, which enters into the calculations, is greater for praseodymium chloride than it is for lanthanum chloride. The heats of formation presented here do not agree with those given in the tabulations of the National Bureau of Standards[2] since the values reported there are based upon the heat of solution data of Bommer and Hohmann.[3]

The free energies of formation of the compounds given in Tables III and V are based upon estimates of the entropies of the compounds. These values are subject to revision as more accurate entropy values for the compounds become available.

The plot in Fig. 2 of the heats of solution of the hydrates shows some interesting features of these compounds. Praseodymium chloride forms the most stable seven-hydrate and gadolinium chloride the most stable six-hydrate under ordinary laboratory conditions. There is a regular decrease in $\Delta H$ with atomic number in the case of $PrCl_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$ and $GdCl_3 \cdot 6H_2O$. That $ErCl_3 \cdot 6H_2O$ and $YbCl_3 \cdot 6H_2O$ were observed to have higher heats of solution than expected indicates a possible structural change. Such a change could probably be brought about by changes in packing due to the smaller erbium ion. An X-ray study of the structures of the hydrated chlorides of the rare earths is presently under way at this Laboratory; when completed, the anomalous behavior in the thermal data reported here may be resolved.

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AMES, IOWA

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[CONTRIBUTION NO. 289 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE[1]]

# Integral Heats of Solution of Some Rare Earth Trichlorides

BY F. H. SPEDDING AND J. P. FLYNN

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The integral heats of solution of the trichlorides of lanthanum, praseodymium, samarium, gadolinium, erbium, ytterbium and yttrium have been measured in water at 25°. Using the limiting slope given by the Debye–Hückel theory, the data have been extrapolated to infinite dilution.

## Introduction

Recent work[2] on the heats of solution of the anhydrous chlorides of cerium and neodymium gave results one to two kcal. per mole higher than those reported elsewhere.[3,4] It therefore seemed advisable to extend the work on the heats of solution of the rare earth trichlorides. The present paper presents the results obtained for the trichlorides of lanthanum, praseodymium, samarium, gadolinium, erbium, ytterbium and yttrium.

## Experimental

The source materials were in the form of spectrographically pure oxides. The preparation of the anhydrous chlorides has been described.[5] The apparatus and general experimental procedure were discussed in the paper[2] on cerium and neodymium. However, several changes in the isothermal solution calorimeter were made. The single large tube leading from the calorimeter in the bath to the outside was replaced by a number of small tubes to house the stirrer shaft, electrical leads and breaker assembly. As a result, each element had better thermal contact with the constant temperature bath, and much of the dead air space was eliminated. The calibrating heater was made separately rather than winding it on the same tube as the thermometer coils. A new thermometer was constructed of nickel and manganin rather than the copper manganin used previously. Nickel wire was chosen in place of copper because of its larger temperature coefficient of resistance and its larger specific resistance. The thermometer had a sensitivity of $2 \times 10^{-4}$ degree per microvolt and was calibrated *versus* a platinum resistance thermometer in the region of 25°. An electronic timer built at this Laboratory was used to measure the total time of electrical energy inputs during calibrations. The frequency of the oscillator used in the timer was calibrated against the Bureau of Standards

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(1) Work was performed in the Ames Laboratory of the Atomic Energy Commission.

(2) F. H. Spedding and Carl F. Miller, THIS JOURNAL, **74**, 3158 (1952).

(3) H. Bommer and E. Hohmann, *Z. anorg. allgem. Chem.*, **248**, 357 (1941).

(4) C. A. Matignon, *Compt. rend.*, **141**, 53 (1905).

(5) F. H. Spedding, P. E. Porter and J. M. Wright, THIS JOURNAL, **74**, 2055 (1952).