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UNIVERSITY OF CALIFORNIA

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INTRODUCTION

Metallic europium and ytterbium differ markedly in melting point and heat of vaporization from the other rare earth metals as seen in Table I.[1] Since the metals are the reference states for thermochemical measurements, it would seem reasonable to suppose that heats and free energies of formation of ions and compounds of these elements might differ substantially from analogous substances formed by the other rare earths. However, the thermodynamic data tabulated in the literature for europium compounds have been obtained largely by interpolation from the plots of available data on the other rare earths; indeed, there seems to be no experimental heat or free energy of formation data for europium compounds in the literature.

The present paper reports a measurement of the heat of solution of europium metal in 0.1 N HCl, and the preparation of EuO (c) and a measurement of its heat of solution in 1.0 N HCl.

EXPERIMENTAL

Materials

A. Europium Metal.

Metal samples obtained commercially proved to be spectrographically quite pure with respect to cationic impurities but showed microscopic inclusions of a fine reddish-brown powder randomly scattered throughout the sample. The nature of this powder is unknown, but it rendered the metal unsuitable for calorimetry. A sample of satisfactory metal was kindly furnished by Professor Frank Spedding, the chemical purity data for which is given in Table II.

The samples were cut and cleaned in a dry nitrogen atmosphere produced by boiling liquid nitrogen and subsequently passing the gas through a trap at liquid nitrogen temperature to remove water and through a copper wool furnace at $600^{\circ}C$ to remove oxygen.

A pyrex capillary plugged with Apiezon W wax pierced with 1 mil W wire was inserted into the bulb along side a wax coated bead in the neck of the bulb. The bulb was sealed by heating the neck with a hot wire. When the bulb had cooled, the W wire was removed allowing gas to re-enter the bulb. The wire was stuck in the wax in the neck of the bulb to prevent its loss. Then the wax plug in the capillary was quickly resealed with a fine point hot wire; the resulting weight loss and uncertainty was 3.4 ± 0.3 µg. Weighings were done on a quartz fibre torsion balance (Rodder Model E Microtech Services Company, Berkeley, California) sensitive to −0.05 µg.

B. Europium Monoxide.

The method of preparing europium monoxide was essentially that given by Matthias et. al.,[2] except that the container was a tantalum crucible with a close fitting cap. The europium metal and europium sesquioxide, both 99.9%

pure, were combined in the crucible. About 5% stoichiometric excess of metal was used to allow for escape around the cap. The crucible and contents were carefully outgassed and then heated to ~1550°C for about four hours. Spectrographic, stoichiometric and X-ray analyses of this preparation are given in Table III. The lattice parameter of the monoxide is in reasonable agreement with literature values.[2,3]

C. Solutions.

Solutions of HCl were prepared from analytical grade reagents. The solutions used for the heat measurements on europium metal were 0.1 N HCl saturated with O_2 gas. Those for the heat measurements on $EuO_{1.02}$ were 1.0 N HCl and were also saturated with O_2 gas.

CALORIMETER

The calorimeter is essentially the same as has been described pre-viously,[4] except for a significant improvement in the calibration circuitry. The heat capacity is approximately 9 calories; and the temperature sensitivity about $1 \times 10^{-5}{}^{o}C$; the thermal leakage modulus is 5×10^{-5} min^{-1}. The calorimeter chamber was thermostated at $25.00^{o}C$ but due to stirring, power input to the bridge, etc., the steady state temperature was several tenths of a degree higher. The correction for the heat of breakage of the calorimeter bulbs was determined by breaking several bulbs containing a small amount of water, and was found to be $(6 \pm 3) \times 10^{-4}$ calories $bulb^{-1}$. This correction and the corrections for the heat of saturation by $H_2O_{(g)}$ of the dry gas in the bulb and the hydrogen evolved from the metal were applied where necessary. The heat evolution was always complete within three minutes.

A potential divider in the thermometer circuit permitted the temperature change in the calorimeter to be recorded during the reaction. Thus accurate corrections for thermal leakage could be computed. Calibrating heat inputs on the order of 0.3 to 0.4 calorie were reproducible to $\pm 0.1\%$.

Pure Mg metal in 1 N HCl gave a performance check. The results are given in Table IV; the average is in good agreement with the figure of -111.322 $\pm$ 0.041 Kcal/mole determined by Shomate and Huffman on a much bigger scale.[5]

UNITS, AUXILIARY THERMODYNAMIC DATA AND LIMITS OF ERROR

We have taken the calorie to be equal to 4.1840 absolute joules, and the experimental limits of error are for the 95% confidence interval.

Though our heat measurements were made at a few tenths of a degree above $298.16^{\circ}K$, they are the same as $298.16^{\circ}K$ values within experimental error.

All auxiliary thermodynamic data have been taken from "Selected values of Chemical Thermodynamic Properties" U.S. Bureau of Standards Circular 500 (1952).
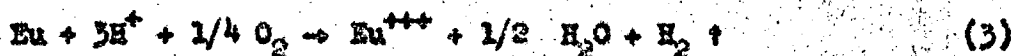
RESULTS AND DISCUSSION

The experimentally observed heats of solution of europium metal are tabulated in Table V.
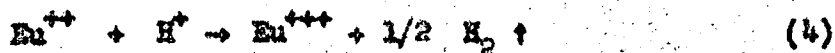
The calorimeter reactions involved where the solution is saturated with oxygen gas are considered to be:[6]

$$Eu + 2H^+ \rightarrow Eu^{++} + H_2 \uparrow \tag{1}$$

$$Eu^{++} + H^+ + 1/4 \; O_2 \rightarrow Eu^{+++} + 1/2 \; H_2O \tag{2}$$
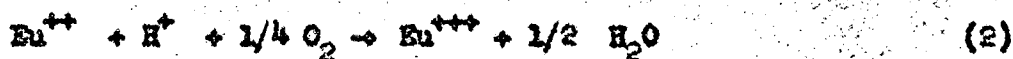
or, for the total reaction:

$$Eu + 3H^+ + 1/4 \; O_2 \rightarrow Eu^{+++} + 1/2 \; H_2O + H_2 \uparrow \tag{3}$$

There is also the competing reaction for the oxidation of Eu^{++}:[6]

$$Eu^{++} + H^+ \rightarrow Eu^{+++} + 1/2 \; H_2 \uparrow \tag{4}$$

But in considering the relative reaction rates, we have found that the former reaction is much faster than the latter. Samples of metal dissolved in argon flushed media show strong absorption in the ultraviolet, while similar samples in an oxygen flushed media show no such absorption. Depending on the degree of argon flushing, the absorption has persisted to a measurable extent for approximately two hours, while the heat evolution in the calorimetric measurements was complete in about 1-1/2 minutes.

In addition, the H_2 gas evolutions from oxygen saturated 0.1 N HCl solutions using La and Eu metals gave mole ratios of 1.53 and   respectively. Thus the calorimeter reaction is best defined by Eq. (3).

If we neglect the slight change in the composition of the HCl solution
due to consumption of HCl in the dissolution of the metal, and approximate the
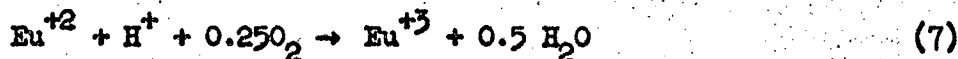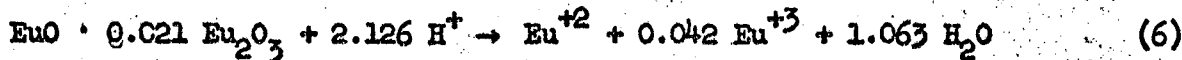state of infinite dilution by 0.1 N HCl, we calculate for

$$Eu^{+3}(aq) \quad \Delta H^o_{f_{Eu^{+3}(aq)}} = -130.4 \pm 1.0 \text{ kcal/mole}. \tag{5}$$

With entropy estimates from Montgomery,[7] the value for the $Eu^{+2} - Eu^{+3}$
potential,[8] and our value for the heat of formation of $Eu^{+3}(aq)$, we calculate
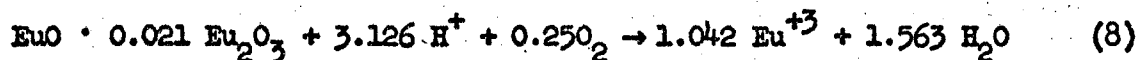$$\Delta H_{f_{Eu^{+2}(aq)}} = -115.7 \text{ kcal/mole}.$$
The experimentally observed heats of solution of $EuO_{1.02}$ are tabulated
in Table VI.

Samples of $EuO_{1.02}$ were single chunks of approximately 500 μg mass.
We have treated $EuO_{1.02}$ as an ideal solid solution of Eu_2O_3 in EuO, although
this almost certainly is not correct. The solvent was 1.0 N HCl since the
dissolution was faster than in 0.1 N HCl. The reactions involved are:

$$EuO \cdot 0.021 \text{ } Eu_2O_3 + 2.126 \text{ } H^+ \rightarrow Eu^{+2} + 0.042 \text{ } Eu^{+3} + 1.063 \text{ } H_2O \tag{6}$$

$$Eu^{+2} + H^+ + 0.25O_2 \rightarrow Eu^{+3} + 0.5 \text{ } H_2O \tag{7}$$

and for the total reaction:

$$EuO \cdot 0.021 \text{ } Eu_2O_3 + 3.126 \text{ } H^+ + 0.25O_2 \rightarrow 1.042 \text{ } Eu^{+3} + 1.563 \text{ } H_2O \tag{8}$$

The correction to the infinitely dilute state can be approximated from
the data on the heat of solution of $PuCl_3$ obtained by Westrum and Robinson.[9]
Extrapolating their data gives a difference of -1.5 Kcal/mole between 1.00 N HCl
and infinite dilution. Applying this to our data and calculating as before,
we find:

$$\Delta H^o_{f_{EuO} \cdot 0.021 Eu_2O_{3(c)}} = -153.5 \text{ Kcal/mole} \tag{9}$$

The heat of formation of EuO is then the heat of formation of EuO · 0.021 Eu_2O_3 minus 0.021 times the heat of formation of Eu_2O_3.[10] Thus:

$$\Delta H^o_{f_{EuO(c)}} = -153.5 + 0.021 \times 394.4$$

$$= -145.2 \text{ Kcal/mole} \,. \tag{10}$$

The heat of formation of $Eu^{+3}(aq)$ is some 30 Kcal. more positive than the heats of formation of the adjacent elements Sm^{+3} and Gd^{+3}.

The atomic valence of the metal is similar to that of Ba, rather than Sm or Gd and its magnetic moment is Ca 7.12 B.M., corresponding to the $4f^7$ configuration in the metal lattice.

For the majority of the rare earths, the heats of formation of the tripositive ions decrease linearly by about 0.8 Kcal per atomic number. For each of these elements the terms in the Born-Haber cycle:

$$M(c) \xrightarrow{(1)} M(g) \xrightarrow{(2)} M^{+3}(g) + 3e^- \xrightarrow[\quad]{+3H^+(aq)} M^{+3}(aq) + 3/2\, H_2 \tag{11}$$

must sum to nearly the same value. But reaction (1) for Eu is some 41 Kcal less positive than the average heats of sublimation for the other "typical" rare earths, and the sum of the three reaction heats is some 33 Kcals more positive. Hence, the sum of the first three ionization potentials for Eu must be about 74 Kcal or 3.36 e.v. more positive than the average for the typical rare earths.

ACKNOWLEDGMENTS

FOOTNOTE AND REFERENCES

[a] Work performed under the auspices of the U. S. Atomic Energy Commission.

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10. Charles E. Holley, Jr., Private Communication.

Table I.

	Sm	Eu	Gd		Tm	Yb	Lu
Met. Valence	2.9	2.1	3		3	2	3
M.P. ^{o}C	1072	826	1312		1545	824	1652
B.P. ^{o}C	1670	1430	2800		1720	1320	3000
ΔH_{sub} Kcal/mole	50.6	42.2	81.3		58.4	41.3	94.0
ρ g/cc	7.50	5.30	7.95		9.27	7.02	9.81
Met. Rad. $\overset{o}{A}$	1.81	2.04	1.81		1.75	1.95	1.73
At. Vol. cc/mole	20	29	20		18	26	18

Table II. Analysis of Europium Metal
(results expressed as %)

Al < 0.01	Gd < 0.05	Sc < 0.01
Ba < 0.01	Ho < 0.05	Si < 0.01
Ca < 0.01	La < 0.01	Ta < 0.1
Nb < 0.01	Lu < 0.05	Tb < 0.5
Ce < 0.1	Mg < 0.01	Tm < 0.05
Dy < 0.05	Na < 1	Yb < 0.01
Er < 0.05	Nd < 0.1	Y < 0.01
Fe < 0.01	Pr < 0.5	Zr < 0.01

Note: The numbers following "<" are limits of detection

Table III. Analysis on $EuO_{1.02}$

(results expressed as %)

Al < 0.01	Gd < 0.05	Mn < 0.01	Si < 0.01	W < 0.1
Ca < 0.01	La < 0.01	Na < 1	Sm < 0.01	Yb < 0.01
Fe < 0.01	Mg < 0.01	Nd < 0.1	Th < 0.05	Y < 0.01

Stoichiometric Analysis

O/Eu = 1.022
1.020
1.022   Ave 1.021 ± 0.002
1.019

X-Ray analysis: NaCl structure type $a = 5.145$ Å

Table IV. Heat of Solution of Mg Metal in 1 N HCl

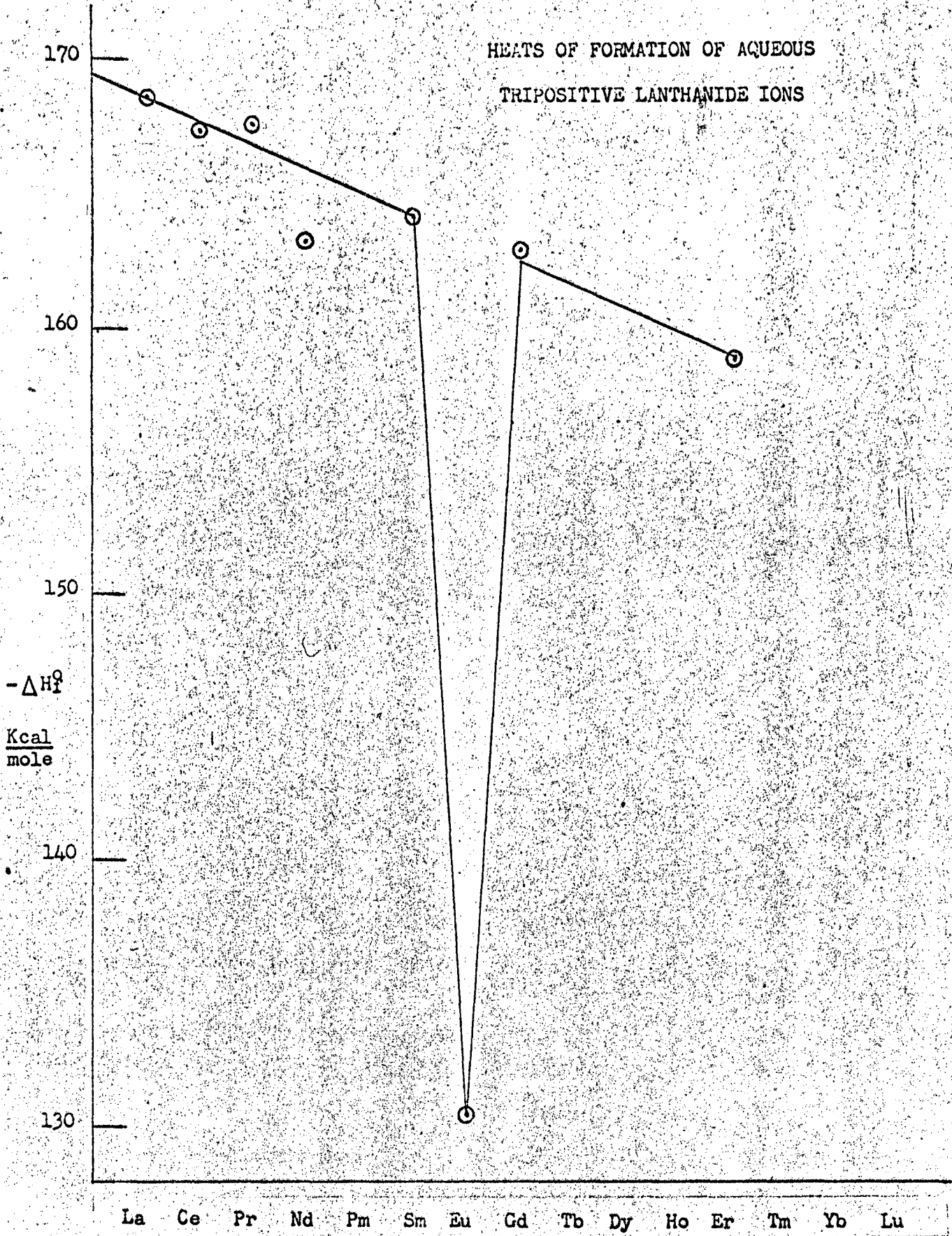|	Sample Weight (μg)	Heat Evolved (calories)	Δ H$_{298.5}$ (Kcal mole^{-1})
1	51.97	0.2377	-111.20
2	65.85	0.3023	-111.61
3	84.17	0.3846	-111.10
		Average	-111.30 ± 0.36

Table IV. Heat of Solution of Europium Metal in 0.1 N HCl

Medium	Sample Weight (µg)	Eu^{+3} Molarity	Heat Evolved (cal)	$\Delta H_{298.2}$ Kcal/mole
HCl 0.1 N				
Sat. with O$_2$	405.4	3.318×10^{-4}	0.4376	-164.85 ± 0.6
"	400.5	3.294×10^{-4}	0.4347	-164.94 ± 0.6
"	462.4	3.802×10^{-4}	0.4937	-163.91 ± 1.0
			Average	-164.57 ± 0.7

Table VI.   Heat of Solution of EuO · 0.021 Eu$_2$O$_3$ in 1 N HCl

Medium	Sample Weight (µg)	Eu^{+3} Molarity	Heat Evolved (cal)	$\Delta H_{293.2}$ Kcal/mole
HCl 1.0 N				
Sat. with O$_2$	439.3	2.61×10^{-4}	0.2395	-87.7 ± 0.8
"	414.2	2.46×10^{-4}	0.2311	-89.8 ± 0.7
"	359.5	2.13×10^{-4}	0.1957	-87.5 ± 0.7
"	305.0	1.82×10^{-4}	0.1636	-86.3 ± 0.6
			Average	-87.8 ± 0.7

HEATS OF FORMATION OF AQUEOUS
TRIPOSITIVE LANTHANIDE IONS