AN EUROPIUM-CHLORINE
-OXYGEN-HYDROGEN CYCLE FOR
THE PRODUCTION OF HYDROGEN
AND OXYGEN FROM WATER

Interim Progress Report
Budget Activity NT 04-02-02-01

D. S. Martin and J. R. Long

AMES LABORATORY, USERDA
IOWA STATE UNIVERSITY
AMES, IOWA

Date Transmitted: April, 1975

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT W-7405-eng-82

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

AN EUROPIUM-CHLORINE-OXYGEN-HYDROGEN
CYCLE FOR THE PRODUCTION OF HYDROGEN AND
OXYGEN FROM WATER

Interim Progress Report

Budget Activity NT 04-02-02-01

D. S. Martin and J. R. Long

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Ames Laboratory

Iowa State University

Ames, Iowa 50010

Date Transmitted: April, 1975

PREPARED FOR THE ENERGY RESEARCH AND DEVELOPMENT
ADMINISTRATION UNDER CONTRACT NO W-7402-ENG-82

MASTER

DISTRIBUTION OF THIS DOCUMENT UNLIMITED

—NOTICE—

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Available from: National Technical Information Service
U. S. Department of Commerce
P.O. Box 1553
Springfield, VA 22161

Price: Microfiche \$2.25

SPECIAL DISTRIBUTION

Energy Development and Research Agency, Washington

F. D. Stevenson (7)

J. O. Roberts

Atomic Energy Commission, Albuquerque Operations

R. S. George

Argonne National Laboratory

B. M. Abraham

Brookhaven National Laboratory

F. J. Salzano

Livermore Berkeley Laboratory

Leo Brewer

Lawrence Livermore Laboratory

O. H. Krikorian

Sandia Laboratories - Albuquerque

R. W. Lynch

J. E. Schirber

Sandia Laboratories - Livermore

J. W. Swisher

S. W. Zehr

Oak Ridge National Laboratory

W. R. Grimes

C. E. Bamberger

D. S. Martin and J. R. Long (80)

Chicago Operations Office

Patent Section (1)

Energy Research and Development Administration

Technical Information Center (27)

Ames Laboratory

Library (8)

ABSTRACT

A Eu-Cl-O-H cycle for the thermal decomposition of H_2O to H_2 and O_2 is considered with the five steps.

1. $\text{EuCl}_3(\text{s}) \rightarrow \text{EuCl}_2(\text{s}) + \text{Cl}_2(\text{g})$
2. $2\text{EuCl}_2(\text{s}) + 2\text{HCl}(\text{g}) + 12\text{H}_2\text{O}(\ell) \rightarrow 2\text{EuCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) + \text{H}_2(\text{g})$
3. $2\text{EuCl}_3 \cdot 6\text{H}_2\text{O}(\text{s}) \rightarrow 2\text{EuCl}_3(\text{s}) + 12\text{H}_2\text{O}(\text{g})$
4. $11\text{H}_2\text{O}(\text{g}) \rightarrow 11\text{H}_2\text{O}(\ell)$
5. $\text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$

The thermodynamics for the reactions in this cycle are summarized from a literature review. Exploratory laboratory studies of reactions 1 and 3 are described.

I. A Eu-Cl-O-H Cycle.

A. Introduction

The chemical behavior of europium chlorides indicated that they might be incorporated into a chemical cycle, operating under 1000°K for the decomposition of H_2O into H_2 and O_2 . For example, the Eu^{2+} ion has a capability of reducing H^+ to H_2 from aqueous solutions. In addition, at high temperatures, EuCl_3 is known to decompose with the evolution of chlorine. A study of various aspects of the following five-reaction cycle, based upon known compounds has been undertaken for feasibility considerations.

$$\Delta H_{298}^{\circ} = 223.2 \text{ kJ}$$

$$\Delta S_{298}^{\circ} = 200.7 \text{ J/deg.}$$

$$\Delta G_{298}^{\circ} = 163.2 \text{ kJ.}$$

$$\Delta H_{298}^{\circ} = -309.4 \text{ kJ}$$

$$\Delta S_{298}^{\circ} = -570.3 \text{ J/deg.}$$

$$\Delta G_{298}^{\circ} = -139.5 \text{ kJ}$$

$$\Delta H_{298}^{\circ} = 796.4 \text{ kJ}$$

$$\Delta S_{298}^{\circ} = 1775.2 \text{ J/deg.}$$

$$\Delta G_{298}^{\circ} = 267.4 \text{ kJ}$$

$$\Delta H_{298}^{\circ} = -481.8 \text{ kJ}$$

$$\Delta S_{298}^{\circ} = -1306.8 \text{ J/deg.}$$

$$\Delta G_{298}^{\circ} = -92.4 \text{ kJ}$$

$$\Delta H_{298}^{\circ} = 57.2 \text{ kJ}$$

$$\Delta S_{298}^{\circ} = 64.3 \text{ J/deg.}$$

$$\Delta G_{298}^{\circ} = 38.0 \text{ kJ}$$

Overall Reaction

B. Literature Review

A literature review of the components in this cycle has been conducted. The thermodynamic parameters for the reactions in the cycle are based on recently published standard enthalpy and entropy data where it was available. Some estimates for the entropies of the anhydrous halides were required. The enthalpies and Gibbs free energies of formation together with the entropies upon which these thermodynamic parameters were based are included in Table 1. The reactivities of the europium halides have in the past and continue to introduce some ambiguities and uncertainties into the thermal data. However, it can guide preliminary feasibility considerations of a cycle, although it is anticipated that discrepancies in the data may well indicate need for some additional experimental investigations.

In reaction 3 the $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ is dehydrated by heating. The possible formation of EuOCl in this process was of some concern since thermogravimetric studies² had indicated that it was produced. However, when samples of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ were heated to 200°C in a dynamic

vacuum or in a stream of argon, the dehydration was accomplished cleanly to the EuCl_3 phase, which was identified by x-ray diffraction powder patterns. The dehydration therefore requires only the exclusion of oxygen. Reaction 3 absorbs the largest amount of heat of any of the five steps. A considerable portion of the heat is utilized to vaporize 12 mols of H_2O and the heat of condensation for 11 mols of H_2O are given up by the system in reaction 4. Thus if the efficiency of the cycle is approximated by the expression:

$$\text{Eff.} = \frac{-\Delta G_{f298}^{\circ} (\text{H}_2\text{O} - \ell)}{\sum \text{Positive } \Delta H_{298}^{\circ}},$$

the efficiency is only 22.0%. However the efficiency can be increased very substantially if heat of condensation of reaction 4 can be re-used to provide some of the heat needed for step 3. In the limit where all the heat of reaction 4 is recovered, the efficiency becomes 39.8%.

Reaction 5 is the reverse Deacon process. It would need to be operated at the maximum available temperature to obtain the minimum ΔG° . This step is included in many of the hydrogen cycles.

C. High Temperature Reaction 1

To determine the thermodynamic parameters for reaction 1 at high temperatures, heat capacities are needed. Since no experiment values were found in the literature, approximations were utilized. For EuCl_2^3

$$C_p = 69.4 + .0216T \text{ J/mol deg.}$$

The lattice heat capacity for EuCl_3 was estimated in a similar fashion from the heat capacities at room temperature of FeCl_3 and ZrCl_3 ⁴ and Kubaschewski's⁵ approximation that the melting point $C_p = 30.3 \text{ J/deg}_{\text{mol}}$ (no. of atoms/formula unit). For EuCl_3 C_p (Lattice) = $83.7 + .042T$ J/mol deg. To this was added the electronic contribution.⁶ From these computations

$T^\circ\text{K}$	$\Delta H^\circ (\text{kJ})$	$\Delta S^\circ (\text{J/deg})$	$\Delta G^\circ (\text{kJ})$
298	223.2	200.7	163.4
773	207.5	171.0	75.31
873	203.0	162.9	60.7

In case the two phases remain insoluble, the indicated pressure of Cl_2 at 500°C is 6×10^{-3} mmHg and at 600°C is 0.18 mmHg. Polyachenok and Novikov⁷ estimated from the chlorine pressure over melts that the vapor pressure of the solid near the mp. of EuCl_3 , 620°C , should be about 5 mm. Thus the pessimistically low calculated pressure may reflect some errors in the thermodynamic data.

The existence of solid solutions or the formation of intermediate compounds can serve to reduce the chlorine pressure. A phase diagram for the EuCl_2 - EuCl_3 system was included in a research report under an Air Force contract with little experimental detail. Four intermediate compounds are indicated. It indicated the melting point of EuCl_3 as 620°C . A compound $\text{EuCl}_{2.5}$ melted congruently at 600°C with a eutectic between EuCl_3 and $\text{EuCl}_{2.5}$ at 500°C . The compound $\text{EuCl}_{3.4}$ melted incongruently at 630°C , and $\text{EuCl}_{2.33}$ melted incongruently at 685° . A

compound $\text{EuCl}_{2.2}$ melted congruently at 755° whereas EuCl_2 melted at 750°C . The report indicated that $\text{EuCl}_{2.6}$ was blue. EuCl_2 is nearly white. EuCl_3 is yellow, and its color intensifies at higher temperatures.

D. Experimental Results

For the study of reaction 1, millimole samples of EuCl_3 , contained in boats of various materials, have been heated in a tube furnace to various temperatures. The boats with the EuCl_3 were heated in an enclosed system through which an inert gas was passed at a controlled rate or which could be evacuated by a mechanical pump. The flowing gas leaving the furnace was bubbled through KI solution. The evolution of chlorine could be monitored visually by the appearance of iodine color in the KI. The iodine produced was then measured quantitatively by titration or sometimes by colorimetric techniques. In an evacuated system the Cl_2 evolved was first condensed in a liquid nitrogen trap and subsequently passed into the KI solution by a flowing gas stream as the trap was warmed. The europium halides were handled by dry box techniques; the x-ray diffraction powder patterns and gravimetric analyses served to characterize the products.

Initial experiments proved that oxygen must be very vigorously excluded from the system. When cylinder argon was used as the sweeping gas, the product, when heating was continued to $650\text{-}700^{\circ}\text{C}$, invariably contained major quantities of EuOCl , formed by the reaction:

Since this reaction yields more Cl_2 per mole of EuCl_3 , the determination of Cl_2 must be supplemented in these studies by the identification of the product phases. With a tight vacuum system the formation of EuOCl was considerably reduced. Recently, when argon stream has been passed over hot zirconium-titanium turnings, the formation of EuOCl has been eliminated below 750°C .

The results have also indicated that there will be container problems in the system which need solutions. For example, the fused halides have badly etched vycor boats. Reaction with LECO and alundum boats has been observed. A glazed porcelain boat has been the most resistant ceramic material found to date. Also, platinum has not been attacked in a preliminary study.

The following pattern of decomposition of EuCl_3 has been established in a series of experiments. Chlorine evolution begins at about 500°C and continues for some time at that temperature. Since this is close to the first eutectic temperature, apparently melting does not occur. The evolution of chlorine continues as the temperature increases to 650°C . Heating to higher temperatures did not yield further chlorine. When the samples were cooled from 650°C to room temperature, the solid was bright blue and appeared to have not been melted. A weight loss of 13.7% was expected and the observed weight loss was 13.0%. Typical analyses of the product were: Eu 68.3% Calcd. 68.2%. Cl 30.8 Calcd. 31.7 Total 99.1%. The powder patterns of the product, however, were not consistently identical with the ASTM file pattern for EuCl_2 which is reported as a white

solid. In one case the quantity of chlorine transported by the flowing Ar stream at 500°C corresponded to a partial pressure of Cl_2 of the order of 1 mm Hg. In these experiments although a product close to the composition of EuCl_2 has been obtained, the recovery of chlorine has consistently not been higher than 55-65%. It has also been noted that a yellow-white film condensed on the cool surfaces of the furnace tube just outside the furnace, as though a volatile component in the hot zone had condensed. This film did not have the characteristics of europium chlorides in that it did not react with H_2O . This film is presently believed to originate by the high temperature reaction of chlorine with the vycor reaction tubes or ceramic materials in the boats. If such attack of ceramics occurs at 600-700°C, then difficulties will be encountered with many of the proposed hydrogen cycles which generate chlorine at these temperatures. The attack of SiO_2 by chlorine to form a volatile compound would probably release O_2 . Such a process seems likely since whenever the europium chloride samples were heated to high temperatures, above 750-800°C, in an evacuated system, some EuOCl was invariably formed.

E. Future Plans

Larger quantities of the blue product will be prepared for further characterization and for use in testing the necessary conditions to generate hydrogen under reaction 2. The composition and characterization of the film condensing outside the furnace tube will be sought. In addition, various high temperature container materials will be tested for the high temperature reaction.

Table 1.
THERMODYNAMIC PARAMETERS
Eu-Cl-H-O System

298.1°K

Substance	ΔH_f° kJ	S° J/deg K	ΔG_f° kJ
Eu(s)	0	77.82 ^a	0
EuCl ₃ (s)	-936.0 ^a	155.0 ^c	-859.4
Eu ³⁺ (aq)	-604.8 ^a	-220.5 ^a	-515.9
EuCl ₃ (aq)	-1106.2 ^a	-54.9 ^a	-967.0
EuCl ₃ ·6H ₂ O(s)	-2785. ^a	+399.6 ^d	-2402.1
EuCl ₂ (s)	-824.4 ^a	143.9 ^c	-777.7
Eu ²⁺ (aq)	-527.8 ^a	-10 ^a	-501.6
EuCl ₂ (aq)	-862.1 ^e	-120.4 ^a	-802.4
EuOCl(s)	-910.4 ^e	110.3 ^e	-856.3
H ₂ O(l)	-285.6 ^b	+69.9 ^b	-237.1
H ₂ O(g)	-241.8 ^b	188.7 ^b	-228.6
HCl(g)	-92.3 ^b	186.7 ^b	-95.3
Cl ⁻ HCl (aq)	-167.4 ^b	55.2 ^b	-131.2
H ₂ (g)	0	130.5 ^b	0
O ₂ (g)	0	205.0 ^b	0
Cl ₂ (g)	0	222.9 ^b	0

^aM. H. Morss and H. O. Haug, J. Chem. Thermodynamics, 5, 513 (1973).

^bW. M. Latimer, "Oxidation Potentials", 2nd Edition, Prentice Hall, NY (1953).

^cRef. b Appednix III. Electronic contributions have been included

For Eu²⁺ $S^\circ(\text{el.}) = 17.2 \text{ J/}^\circ$

For Eu³⁺ $S^\circ(\text{el.}) = 9.41 \text{ J/}^\circ$

^dJ. Hinchey and J. W. Cobble, Inorg. Chem., 9, 917 (1970).

^eCalcd. from Expts for Sm and Gd by C. W. Kock and B. B. Cunningham, J. Am. Chem. Soc., 75, 796 (1953).

REFERENCES

1. D. J. Meier and C. S. Garner, J. Phys. Chem., 56, 853 (1952).
2. W. W. Wendlandt, J. Inorg. Nucl. Chem., 9, 136 (1959).
3. A. V. Hariharan and H. A. Eick, High Temp. Sci., 4, 91 (1974).
4. "JANAF Thermochemical Tables", 2nd Edition, D. R. Stull and H. Prophet, Project Directors, NSRDA-NBS37. U. S. National Bureau of Standards, Washington (1971).
5. O. Kubashewski and E. LL. Evans, "Metallurgical Thermochemistry", Pergamon Press, New York (1958).
6. David H. Dennison and Karl A. Gschneidner, USAEC Report, IS-1156 (1965).
7. O. G. Polyachenok and G. I. Novikov. Zhur. Neorg. Khim., 9, 773 (1964).
8. "Properties of Rare Earth and Transition Group Ions". Final Report U. S. Air Force Contract, AF 61(052)-677. B. Bleaney, Director, p. 16 (1965).