The "fit" of this equation is indicated by the deviation in millivolts ($\Delta = E^0$ (obsd.) $- E^0$ (Eq. 2)) given in the last column.

Comparison with the corresponding values reported by Harned, Keston and Donelson[3] shows that our results are higher by two or three tenths of a millivolt, the agreement being best at the higher temperatures. In view of the indirect nature of our method and the combined uncertainties of the extrapolations for E^0_{HCl} and E^0_{HBr} involved in the comparison, it is probable that the agreement obtained is as good as could be expected. Nevertheless it should be remarked that Donelson's data for the 0.01 molal hydrobromic acid cell (fused silver bromide) are also two or three tenths of a millivolt higher than Keston's at the same concentration.[9]

Upon this basis we regard the reliability of electrode comparisons in borax buffers as established, and the accuracy of the method as limited only by the reproducibility of the measurements and the absolute accuracy of the electrode employed as standard.

Summary

1. The normal electrode potential of the silver–silver bromide (fused) electrode has been determined from 5 to 40° by comparison with the silver–silver chloride electrode in borax solutions without liquid junctions.

2. The reliability of the method is indicated by satisfactory agreement with results obtained with similar electrodes in hydrobromic acid solutions.[3]

3. By using materials from a variety of sources and subjected to different degrees of purification, it was shown that the silver–silver bromide (fused) electrode is highly reproducible.

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[9] In a private communication Mr. Donelson informs us that the extrapolation of his data on the cells $H_2 \mid HBr_{(0.01)}, LiBr_{(m)} \mid AgBr - Ag$ leads to values of E^0_{HBr} in excellent agreement with our own—maximum difference about 0.1 mv.

Contribution to the Chemistry of Europium

BY HERBERT N. MCCOY

Introduction.—The easy preparation of bivalent europium salts which, though powerful reducing agents, are sufficiently stable to be handled, invited further study of these unique rare earth compounds. This work has included determination of the velocity of oxidation by air of such europous compounds, the measurement of their reduction potential, the development of new methods of electrolytic reduction, the observation of the absorption spectrum of europous solutions, and the discovery that this spectrum is wholly different from that of trivalent europium solutions. As no method for the determination of europium in both of its stages of oxidation had been described, the first necessity for the work was the development of such a method.

Determination of Europium.—In a preliminary note[1] it was mentioned that europium may be determined iodometrically. The method may be illustrated by the following example.

A solution of europium chloride was made by dissolving 2.1619 g. of nearly pure europium oxide in 8.2 ml. of 6 *N* hydrochloric acid and diluting to 250 ml. Standard iodine and thiosulfate solutions, approximately 0.04 *N*, were prepared. The Jones reductor used[1] contained 150 g. of 20 to 30 mesh amalgamated zinc which gave a column 1.7 cm. in diameter and 21 cm. high. Immediately before each series of titrations 0.05 *N* hydrochloric acid was poured into the reductor tube and the zinc and acid were well shaken together. The reductor was then thoroughly flushed with more of the dilute acid, leaving sufficient barely to cover the top of the zinc column. The nozzle of the reductor dipped into a measured volume (usually 20 ml.) of standard iodine solution in a 400-ml. covered beaker into which a stream of carbon dioxide was passed to exclude air. For an analysis, 20 ml. of the europium chloride solution was run through the reductor, followed by a wash of 150 ml. of approximately 0.05 *N* hydrochloric acid. Reduction and washing required about twenty minutes.

The excess iodine was titrated with standard thiosulfate. The reactions are $2EuCl_3 + Zn \longrightarrow 2EuCl_2 + ZnCl_2$ and $Eu^{++} + I \longrightarrow Eu^{+++} + I^-$. In four determinations the net volumes of iodine solution required were 18.12, 18.05, 18.08 and 18.11 ml., mean 18.10 ml. indicating 0.1685 g. of europium oxide (Eu = 152.0) while the amount of oxide taken was 0.1730 g. The purity of the oxide was therefore 97.5%. In determinations, when no carbon dioxide was used, the results were 1 to 3% too low, due, doubtless, to partial oxidation of reduced europium by air.

Using this technique, the europium content of rare earth mixtures containing 1% or even less of this element may be determined if other reducible substances are

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[1] McCoy, THIS JOURNAL, 57, 1756 (1935).

absent. A chloride solution of the rare earths of monazite in nearly their natural proportions was freed from iron, phosphate and sulfate. This material had been precipitated previously as double sodium sulfate and in consequence was nearly free from ytterbium, which may react like europium. The solution had a density of 1.13 and contained 0.11 g. of oxides per ml. Fifty ml. of this solution was reduced and titrated. Its titer indicated a europium oxide content of 0.0033 g., assuming no other reducing substances present. To two further 50-ml. portions of this solution known amounts of europium were added. Analyses gave the following results.

	I	II
Eu_2O_3 in 50 ml. sol., g.	0.0033	0.0033
Eu_2O_3 added, g.	.0625	.0424
Total	0.0658	0.0457
Found	0.0659	0.0440

Oxidation of Europium by Air.—The observation of Urbain[2] that a dilute solution of europous chloride can be kept and that it is not oxidized by iodine or nitric acid even at 100° can only mean that complete oxidation by air had occurred before the small amount of material in hand was tested. A like explanation may be made regarding the statement of Jantsch, Alber and Grubitsch[3] who were unable to titrate with iodine a solution thought to contain europous chloride and concluded that a state of equilibrium was reached. Yntema[4] and also Selwood[5] found no difficulty in oxidizing solid europous sulfate with nitric acid.

On exposure to air a solution of europous chloride is oxidized more or less rapidly depending on conditions. A few ml. of a dilute solution in an open beaker may be oxidized completely in an hour or less, but 300 to 400 ml. of a 30% solution has often stood three or four days under similar conditions without being wholly oxidized. When thus oxidized, solutions with excess hydrochloric acid remain clear, europium trichloride being formed. If there is a deficiency of acid, white basic material precipitates.

A rough determination of the speed of oxidation of europous chloride by air was made. A 30 to 50-fold excess of air was blown through dilute solutions under such conditions that the concentrations of the dissolved oxygen remained nearly constant. The set-up used comprised a 70-ml. wide-mouthed jar with a rubber stopper carrying a small zinc reductor, the tip of a buret for standard iodine solution, a tube through which either carbon dioxide or air could be led to the bottom of the jar, and a narrow vent for the escape of gases. The solutions used were half molar europium chloride, normal and decinormal hydrochloric acid, and 0.04 N iodine and thiosulfate; only the last two were standardized. In making a run, 5 ml. of N acid was put in the jar, the stopper with attached tubes adjusted, and the air displaced by carbon dioxide. Two ml. (exactly) of the europium solution followed by 25 ml. of decinormal acid were run through the reductor in five or six minutes while a slow stream of carbon dioxide was passed into the jar.

This finished, the latter gas stream was replaced at zero time by 8 or 10 bubbles of air per second for an exactly measured interval. Next a measured excess of iodine solution was run in rapidly and, after waiting a few minutes for the completion of the ensuing reaction, the excess of iodine was titrated with thiosulfate. A fresh 2-ml. portion of europium solution was used for each oxidation run. The results lead to a fair constant for a first order reaction.

SPEED OF OXIDATION OF $EuCl_2$ SOLUTIONS BY AIR AT 23°

Interval, min.	Net ml. $N/25$ I	$K \times 10$
0	26.33	..
1	21.99	1.80
2	18.32	1.81
3	15.09	1.85
5	11.53	1.65
7	7.31	1.83
9	4.62	1.93
	Mean	1.81

It is thus seen that a 0.04 molar solution is half oxidized in about four minutes in a solution kept saturated with oxygen from air. The speed of oxidation by air of a concentrated solution standing in a beaker is very much slower for obvious reasons.

Electrolytic Reduction of Europium.—In the electrolytic reduction of a europium chloride solution Yntema[4] used a two-compartment cell which required 65 volts to give a current of 0.18 amp. Its high resistance was due to the great separation of the electrodes. A one compartment cell having electrodes close together fails to give much reduction because of the reverse change at the anode.

The electrolysis of europium formate (made from the oxide and acid) overcomes these difficulties. The cathode is mercury, the anode a short stout platinum wire. At the anode carbon dioxide and hydrogen from the formate ion come off steadily. In a one-compartment cell with 50 ml. of 0.1 molar formate 6 volts (4 no. 6 dry cells) give an almost steady current of 0.08 amp. Practically no hydrogen is liberated at the cathode, which remains bright and mirror-like until the larger part of the europium is reduced. Finally when 75 or 80% has been reduced hydrogen begins to be liberated at the cathode and the current efficiency falls off. Europous formate so made shows the typical reactions of europous solutions, including the immediate formation of the insoluble sulfate when treated with a solution of sulfuric acid or a sulfate. Europium may be separated from other rare earths by the electrolysis of formate solutions containing some sulfate.

The electrolysis of the acetate works well. It is also possible to reduce a chloride solution in a one-compartment cell, using a silver anode.

The Reduction Potential of the Eu^{++}/Eu^{+++} Electrode.—The many indications that a solution of Eu^{++} has a high reducing potential were confirmed by direct measurement which led to a value of E_0 of about 0.43 volt. The arrangement of the cell was as follows: Pt/$Eu(COOH)_3$ + $Eu(COOH)_2$ + HCOOH + N KCl/ + N KCl/N KCl + Hg_2Cl_2/Hg. For the potential measure-

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(2) Urbain, *Compt. rend.*, **153**, 1155 (1911).

(3) Jantsch, Alber and Grubitsch, *Monatsh.*, **53–54**, 305 (1929).

(4) Yntema, THIS JOURNAL, **52**, 2782 (1930).

(5) Selwood, *ibid.*, **57**, 1145 (1935).

ments the following Leeds and Northrup instruments[6] were used: potentiometer, galvanometer, double throw switch, Eppley standard cell and Hildebrand (normal) calomel electrode. The total concentration of the europium was approximately 0.1 molar, the concentration of the free formic acid was small and variable, being sufficient only to prevent precipitation of the base by reason of oxidation by air during the measurements. A 150-ml. tall form beaker (without lip) with a fiber board cover and rubber band seal served both for the partial electrolytic reduction of the europium formate solution and later for the measurement of the electrode potential. In the beaker were placed 20 ml. of pure mercury and 50 ml. of approximately 0.1 molar europium formate containing a small excess of formic acid. The cover had seven holes, one central, the others peripheral. The central hole carried the glass insulated anode for the electrolysis, 1.5 cm. of stout platinum wire. Three glass-insulated platinum wires passed through other holes—one led to the mercury, the others, 3 mm. exposed lengths of small wires, served as alternate electrodes for the potential measurements. These electrodes were made of new wire carefully cleaned and kept in acidified europous chloride solution for twenty-four hours before being used. They quickly came to definite potentials during measurements. A salt bridge with normal potassium chloride connecting with a normal calomel electrode and a glass mechanically operated reciprocating stirrer passed through two holes while the seventh hole, closed by a plug, permitted the introduction of a 5-ml. pipet. The electrolysis was carried out as already described with four dry cells. The current of 0.07 to 0.08 amp. ran for two to two and one-half hours and reduced half or more of the europium to the bivalent state. The electrolyzing circuit was now disconnected and sufficient solid potassium chloride was dissolved in the reduced solution to make the concentration of this salt exactly one molar. If this addition is made prior to the electrolysis several difficulties arise.

During the series of potential measurements requiring about one hour, a little oxidation of the bivalent europium by air took place. For this reason potentiometric readings for each of the alternate platinum electrodes in the reduced solution were made immediately before and after removal of a 5-ml. sample for titration. This sample was run into a small (measured) excess of 0.04 N iodine. The excess was titrated with thiosulfate a few minutes later. Following the second pair of potential readings 5 ml. of a solution of europium trichloride and potassium chloride was run into the reduced solution. The former solution had exactly the same composition as the latter excepting that the europium of the solution added was entirely in the trivalent form. The ratio of Eu^{+++} to Eu^{++} of the solution in the cell was thus increased by stages. Following this addition, the titration of the excess iodine was made.

The solution in the cell was now stirred well for a few minutes and another series of potential measurements and another analysis were made, etc.

The two consecutive readings for the alternate electrodes usually agreed within 0.1 millivolt while the pair made before drawing the sample differed from those afterward by about one millivolt. The mean of the four readings of a set and the time of drawing the sample are given in the following table.

After the measurements were completed the total europium concentration was found by reduction of four 5-ml. portions in the zinc reductor and titration with standard iodine. The potential of a platinum electrode in the Eu^{+++} and Eu^{++} solution with normal potassium chloride was calculated by the equation

$$E_0 = (V - 0.2805) + 0.05915\ (\log_{10} Eu^{+++}/Eu^{++})$$

V being the observed e. m. f. including the normal calomel electrode. The reaction is $Eu^{++} = Eu^{+++} + e$. The platinum electrode in the europium solution is charged negatively.

POTENTIAL OF THE Eu^{+++}, Eu^{++} ELECTRODE

Temp. 25°. Total Eu concn. 0.0900 Molar

Time, min.	E. m. f., v.	Molar concn. Eu^{++}	Molar concn. Eu^{+++}	E_0, v.
0	0.7100	0.0437	0.0463	0.4310
19	.7007	.0358	.0542	.4309
30	.6933	.0289	.0611	.4321
40	.6864	.0239	.0661	.4321
50	.6797	.0201	.0699	.4312
65	.6720	.0162	.0738	.4304
			Mean	.4313

Another set of similar measurements gave $E_0 = 0.4283$ volt.

In these experiments liquid potentials have not been entirely eliminated, but it is thought that they have been made quite small by reason of the preponderating concentration of potassium chloride in all solutions. The value found for E_0, about 0.43 volt, is one of the highest reducing potentials so far observed.[7] It is in good accord with the powerful reducing properties of europous solutions.

Europous Sulfate.—Progress in the work of isolation of europium by the europous sulfate method[1,4,5] is easily followed by titration of this salt with standard permanganate. In a typical case the sulfate was made from a chloride solution which showed but faintly the strongest absorption bands of neodymium in addition to those of europium. After being well washed on the filter with dilute hydrochloric acid and methyl alcohol and dried at 75°, portions of about 0.1 g. were covered with 30 ml. of 3 N sulfuric acid and titrated with 0.04 N permanganate, 0.6 to 0.8 ml. excess being added and the excess titrated with standard ferrous solution after the difficultly soluble europous sulfate had completely dissolved.

	I	II
$EuSO_4$ taken, g.	0.1113	0.1119
0.04 N $KMnO_4$, ml.	10.83	10.86
Purity of $EuSO_4$, %	96.6	96.3

It is possible to titrate the sulfate with iodine but the solid dissolves so slowly that the method is tedious.

Europous sulfate exists in two forms: (α) tufts of minute needles which are feathery and bulky; and (β) still smaller crystals, appearing nearly globular when highly magnified, of high density and settling to a very

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(6) All kindly loaned by Professor L. D. Roberts, Univ. of Southern California.

(7) "Int Crit. Tables," Vol. VI, p. 332.

compact mass. The α-form is frequently obtained when a solution of europous chloride from a zinc reductor is run into a solution of magnesium sulfate or dilute sulfuric acid. It soon passes into the stable β-form. The latter is but slightly soluble in 3 *N* sulfuric acid, while the former is dissolved by acid of this concentration. The analyses quoted were of the β-form.

The dry β-form keeps surprisingly well. In one case a sample, kept in a corked vial, showed the same permanganate titer after two, sixteen and fifty-five days and but 2.8% less after one hundred and forty-three days. Another sample, known to contain some rare-earth contamination, showed a purity of 94.7% after sixty-four days. The resistance of europous sulfate to oxidation by air is doubtless in large measure due to its marked insolubility.

Europous sulfate can be oxidized by and dissolved in nitric acid.[4,5] It can also be oxidized by chlorine, bromine, bromic acid and other active oxidizing agents. When europous sulfate is boiled for a few minutes with a solution of one equivalent of sodium carbonate and 0.4 equivalent of sodium hydroxide it forms a yellow, compact, easily filtered carbonate (probably $EuCO_3$). The carbonate dissolves readily in most acids.

The Absorption Spectrum of Europous Chloride.—The chloride ($EuCl_2$) solution of 20 to 30% concentration has a greenish yellow color like that of a concentrated solution of chlorine. The absorption spectrum of this solution, in the visible range, differs in a remarkable way from one of the trichloride. It does not show any of the several bands of the latter.[8] Instead, below approximately 4480 Å. all visible light is absorbed. The exact maximum wave length at which complete absorption begins depends upon the concentration of the solution and the thickness of the layer. Characteristic results are obtained when 30 ml. of a 1.2 molar solution of europium trichloride is run through a zinc reductor and viewed in a 20-cm. tube. The spectrometer used was a Bausch and Lomb instrument Cat. no. 2700. The light was that of a 75-watt Mazda bulb. It thus appears that the shift of the valence electron in the change $Eu^{+++} \rightleftharpoons Eu^{++}$ is responsible for a profound change in the absorption spectrum.

Summary

1. New methods permit the electrolytic reduction of trivalent europium to bivalent in simple cells at 6 volts or less.
2. Solutions of bivalent europium do not show any of the bands of the absorption spectrum of the trivalent salts; instead, complete absorption of visible light occurs below 4480 Å.
3. The reduction potential E_0 of Eu^{++}, Eu^{+++} solutions is approximately 0.43 volt.
4. Dilute europous solutions are half oxidized by a rapid stream of air bubbles in about four minutes. Crystalline europous sulfate, $EuSO_4$, is quite stable in air.
5. Iodometric methods for the determination of europium are described.

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[8] If incompletely reduced the two strongest bands of Eu^{+++} may show faintly.

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The Vibrational Levels of Cyclopropane

BY GILBERT W. KING,[1] ROBERT T. ARMSTRONG AND LOUIS HARRIS

Cyclopropane has considerable interest stereochemically and from the point of view of the mechanics of vibration of polyatomic molecules. A unique assignment of frequencies to its normal vibrations is not possible from its Raman spectrum[2] alone; infra-red data, even of a semi-quantitative nature, would aid in such an assignment. Together, the two spectra permit an analysis of the fundamental modes of vibration of cyclopropane.

Infra-red Absorption.—The preparation and purification of the cyclopropane has been described in a previous paper.[3] The infra-red spectrum has been mapped in the following manner.

Region	Method of measurement	State of cyclopropane
I. 0.8 μ to 2.8 μ	Quartz monochromator. 1000 watt projection lamp. 15 mm. length quartz cell.	Liquid at −78°. Gas at 25° and 1 atm. pressure.
II. 0.8 μ to 1.1 μ	Hilger E1 spectrograph (Glass optics); also 21 ft. grating. 1000 watt projection lamp. 1 meter length cell, quartz windows.	Gas at 25° and 1 atm. pressure.

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[2] L. Harris, A. A. Ashdown and R. T. Armstrong, THIS JOURNAL, **58**, 852 (1936).

[3] A. A. Ashdown, L. Harris and R. T. Armstrong, *ibid.*, **58**, 850 (1936).