was found to be 1.630, and its mean compressibility between 6000 and 12,000 bars at about 22°, 4.8×10^{-6} per bar. A method for calculating the heat of fusion from solubility data gives a value which is in fair agreement with that determined from the initial slope of the melting curve, the average value being 32 cal. per g. of $NaCl\cdot 2H_2O$.

A secondary pressure increase, that is, a continued rise of pressure following a sudden increase, was observed at pressures near the maximum on the curve, and an explanation is given for this phenomenon.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE SEPARATION OF YTTERBIUM BY ELECTROLYTIC REDUCTION.

OBSERVATIONS ON THE RARE EARTHS. XXXVI

BY ROBERT W. BALL[1] WITH L. F. YNTEMA

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Recently it was found that europium can be separated from a mixture of samarium, europium and gadolinium chlorides by electrolytic reduction in acid solution in the presence of the sulfate ion.[2] Europous sulfate, $EuSO_4$, precipitated as a white, finely crystalline compound, stable when heated in air at 65° and insoluble in dilute acids. It was readily oxidized by dilute nitric acid.

In 1929 Klemm and Schüth[3] reported the preparation of ytterbous chloride, $YbCl_2$, similar to samarous chloride, $SmCl_2$,[4,5] and europous chloride, $EuCl_2$[6,7] by treatment of ytterbium oxide, Yb_2O_3, with a stream of Cl_2–S_2Cl_2 at 600–620°.

These facts suggested the possibility of separating ytterbium from the other rare earths of the yttrium group by electrolytic reduction in the presence of the sulfate ion.

Experimental

I. Electrolysis of Rare Earths with Low Ytterbium Content.—Ten grams of pink yttrium group oxides, containing yttrium and erbium with small percentages of thulium and ytterbium, were dissolved in hydrochloric

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[1] An extract from a thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Chemistry in the Graduate School of the University of Illinois.

[2] Yntema, THIS JOURNAL, **52**, 2782 (1930).

[3] Klemm and Schüth, *Z. anorg. allgem. Chem.*, **184**, 352 (1929).

[4] Matignon and Cazes, *Compt. rend.*, **142**, 83 (1906).

[5] Jantsch, Rüping and Kunze, *Z. anorg. allgem. Chem.*, **161**, 210 (1927).

[6] Urbain and Burion, *Compt. rend.*, **153**, 1155 (1911).

[7] Jantsch, Alber and Grubitsch, *Monatsh.*, **53**, **54**, 305 (1929).

acid. The excess acid was evaporated, the solution diluted to 400 cc. and 4 cc. of sulfuric acid (sp. gr. 1.84) was added.

This solution was put into the cathode compartment of an electrolytic cell with a mercury cathode.[2] The anode compartment was filled to the same level with approximately 0.05 *N* hydrochloric acid. A current of 0.1 ampere, corresponding to a current density at the cathode of 0.025 amp./sq. cm., was used. The voltage drop between electrodes was 110 volts.

The solution was electrolyzed almost continuously for one hundred and ten hours. The only interruptions were during the nights when enough of the hydrogen evolved would get into the salt bridge to shut it off. During the first hour of the electrolysis the solution became dark. This soon cleared up and after thirty-two hours the solution, which was originally pink, had become clear green in color. Visual examination of the solution with a hand spectroscope still showed the absorption spectrum of erbium while there was also general absorption in the red part of the spectrum. At the end of eighty hours a greenish-white crystalline precipitate started to form. At the end of one hundred and ten hours the precipitate was filtered off, washed with boiled distilled water and dissolved in nitric acid. It dissolved in concentrated nitric acid with the evolution of brown fumes, indicating that it was a reduced compound. Any heavy metals with which the precipitate might have become contaminated were removed with hydrogen sulfide. The rare earths were precipitated as oxalate and ignited to the oxide, which was white in color. A qualitative test showed that the anion of the precipitate was sulfate.

Photographs were made of the arc spectra on carbon electrodes of the original mixed oxides and of the oxide from the precipitate.

The more prominent lines on this photograph were examined. The results obtained are shown in Table I.

TABLE I

SPECTRUM LINES

Wave lengths in I. A.	Element	Intensity of line in original	Intensity of line in precipitate	Wave lengths in I. A.	Element	Intensity of line in original	Intensity of line in precipitate
4935.51	Yb	0	7	4422.60	Y	10	1
4900.11	Y	7	1	4398.03	Y	8	2
4883.69	Y	7	1	4374.95	Y or Er	10	5
4854.88	Y	7	1	4358.72	Y	6	1
4823.31	Y	2	0	4309.62	Y	10	4
4786.60	Yb	0	7	4305.97	Yb	0	5
4781.90	Yb	0	7	3933.67	Ca	4	7
4564.00	Yb	0	3	3906.34	Er	4	1
4552.12	Er	3	3	3900.83	Yb	0	5
4527.80	Y	3	1	3472.5	Lu or Yb	4	4
4515.15	Yb	0	4	3467.88	Y	3	1
4439.22	Yb	0	8				

From this examination it was concluded that, while the original material contained only 1 or 2% of ytterbium, the precipitate consisted of ytterbium with very little of the other rare earths (estimated at 1 or 2%).

The authors wish to express their appreciation to Mr. P. W. Selwood for his assistance in the examination of the arc spectra of the original and precipitated oxides.

II. Electrolysis of Rare Earths with High Ytterbium Content and Analysis of the Precipitate.—Samples of ytterbium-rich oxide which were white in color and, when dissolved in hydrochloric acid, showed no absorption in the visible region of the spectrum, were also electrolyzed. The same color changes and precipitate formation as noted above took place although much more rapidly than in the solutions containing less ytterbium. When one or one and a half grams of precipitate had formed, the solution was decanted and the precipitate collected on a sintered glass crucible. It was found that the precipitate dissolved slowly if left in contact with the solution with constant evolution of gas. The decanted solution was clear green and bubbles of gas formed through its entire volume. At the end of about fifteen minutes it became colorless and no more gas was evolved.

The precipitate was washed successively with freshly boiled distilled water, alcohol and ether, and heated to constant weight at 72°. It was found that the precipitate gained weight when exposed to air at room temperatures; the crucible was therefore transferred to a glass-stoppered

TABLE II

RESULTS OF ANALYSES OF PRECIPITATES OBTAINED BY ELECTROLYSIS WITH MERCURY CATHODE OF RARE EARTHS WITH HIGH YTTERBIUM CONTENT

		IA	IB	II	IIIB	IIIC
1	Concn. of soln.	5 g. oxide in 200 cc.		10 g. oxide in 100 cc.	(Filtrate from Run III) 10 g. oxide in 100 cc.	Filtrate from Run IIIB
2	Hours. soln. elec.	37		6.5	3.0	5.5
3	Cur. dens., amps./sq. cm.	0.025	0.025	0.165	0.165	0.165
4	Wt. of precipitate, g.	.6585	.4736	.5879	.4595	.3727
5	Weight of Yb_2O_3, g.	.4549	.3215	.4023	.3113	.2388
6	Weight of $BaSO_4$, g.	.5200	.3481	.2969	.3044	.2533
7	Wt. of Yb (calcd. from No. 5), g.	.3996	.2825	.3534	.2735	.2098
8	Wt. of SO_4 (calcd. from No. 6), g.	.2140	.1433	.1222	.1253	.1043
9	Wt. of $YbSO_4$ (7 plus 8), g.	.6136	.4258	.4756	.3988	.3141
10	Weight of H_2O (?) and O_2 (?) (4 minus 9), g.	.0449	.0478	.1123	.0607	.0586
11	Mol. ratio SO_4:Yb	.968	.917	.625	.828	.898

weighing bottle before cooling. The analysis was carried out as described in a previous publication.[2] The results are given in Table II.

The ratio of sulfate to ytterbium was always less than unity. It was found that the material which approximated closest to a 1:1 ratio for ytterbium and sulfate was precipitated when the current density was low, the solution was dilute and the hydrogen-ion concentration fairly high. In this investigation no attempt was made to determine the optimum hydrogen-ion concentration for precipitation. The acid concentration in the cathode compartment of the cell at the start of a run was 0.37 *N* and this was decreased by the electrolysis. Care must be exercised, however, to prevent hydroxide formation through too low acidity. It is supposed that ytterbium is precipitated as $YbSO_4{\cdot}xH_2O$, in which the water content is unknown. The fact that the sulfate content is lower than is theoretically correct may be explained by assuming that there is hydrolysis after the precipitation has taken place. It should be pointed out that the completeness of separation is not affected by any change taking place in the precipitate after it has once formed.

It was noticed that ytterbous sulfate was only stable in the acid solution when current was flowing and the cathode was one with a high overvoltage. When the current was shut off, the precipitate slowly dissolved with the evolution of hydrogen. The reaction is probably

$$2YbSO_4 + 2H^+ \longrightarrow 2Yb^{+++} + 2SO_4^{--} + H_2$$

Of particular interest is the green coloration which always appeared when ytterbium salts were reduced. Examination with a hand spectroscope showed no absorption bands, but general absorption in the red. When europium salts were reduced there was no change in color. When ytterbium was present, even if only in small amounts, the green coloration always appeared. It appeared before any precipitate formed and remained as long as the electrolysis was continued. On shutting off the current, or decanting the solution into a beaker, bubbles of hydrogen formed throughout the clear green acidic solution and within fifteen minutes the solution had become colorless. The reaction is probably

$$2Yb^{++} + 2H^+ \longrightarrow 2Yb^{+++} + H_2$$

The ytterbic ion, Yb^{+++}, is colorless, but the ytterbous ion, Yb^{++}, appears to be green.

Attempts to reduce ytterbium, using cadmium or platinum cathodes, were not very successful.

Summary

1. Bivalent ytterbium sulfate may be precipitated from an acid solution by electrolytic reduction in the presence of the sulfate ion.
2. Arc spectrum analysis indicates that ytterbium of 98% purity may

be separated in one operation from mixed yttrium group material containing 2% ytterbium.

3. Analysis of the precipitate showed it to be of variable composition approaching the formula $YbSO_4 \cdot xH_2O$. It is a very light green crystalline compound. It is soluble in dilute acids with the evolution of hydrogen and in nitric acid with evolution of oxides of nitrogen.

4. The ytterbous ion, Yb^{++}, is green.

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[CONTRIBUTION FROM FERTILIZER AND FIXED NITROGEN INVESTIGATIONS, BUREAU OF CHEMISTRY AND SOILS]

EQUILIBRIA IN THE Fe-H-O SYSTEM. INDIRECT CALCULATION OF THE WATER GAS EQUILIBRIUM CONSTANT

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In a previous paper[1] we have calculated the value of the equilibrium constant for the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad K_1 = (P_{CO})(P_{H_2O})/(P_{CO_2})(P_{H_2}) \qquad (1)$$

by combining the equilibrium constants obtained in our experiments[2] on the two reactions

$$Co + H_2O = CoO + H_2 \qquad K_2 = P_{H_2}/P_{H_2O} \qquad (2)$$

$$Co + CO_2 = CoO + CO \qquad K_3 = P_{CO}/P_{CO_2} \qquad (3)$$

The values so calculated were found to be in good agreement with those measured directly by Neumann and Köhler.[3] Such previous calculations made by Eastman and Evans,[4] Eastman[5] and Eastman and Robinson,[6] respectively, had, however, given values about 40% higher than the directly measured equilibrium constants. The first two of these calculations were based on the reactions

$$FeO + H_2 = Fe + H_2O \qquad K_4 = P_{H_2O}/P_{H_2} \qquad (4)$$

$$FeO + CO = Fe + CO_2 \qquad K_5 = P_{CO_2}/P_{CO} \qquad (5)$$

$$Fe_3O_4 + H_2 = H_2O + 3FeO \qquad K_6 = P_{H_2O}/P_{H_2} \qquad (6)$$

$$Fe_3O_4 + CO = 3FeO + CO_2 \qquad K_7 = P_{CO_2}/P_{CO} \qquad (7)$$

The calculations by Eastman and Robinson were made with the help of their own equilibrium data on the reactions

$$SnO_2 + 2H_2 = 2H_2O + Sn \qquad K_8 = P_{H_2O}/P_{H_2} \qquad (8)$$

$$SnO_2 + 2CO = Sn + 2CO_2 \qquad K_9 = P_{CO_2}/P_{CO} \qquad (9)$$

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[1] Emmett and Shultz, THIS JOURNAL, **52**, 1782–1793 (1930).

[2] Emmett and Shultz, *ibid.*, **51**, 3249–3262 (1929).

[3] Neumann and Köhler, *Z. Elektrochem.*, **34**, 218 (1928).

[4] Eastman and Evans, THIS JOURNAL, **46**, 888 (1924).

[5] Eastman, Bureau of Mines Information Circular 6125 (1929).

[6] Eastman and Robinson, THIS JOURNAL, **50**, 1106 (1928).