obtained by Perley is a fairly good check with the value of 0.2552 obtained in this work.

Summary

Very satisfactory antimony electrodes were obtained by electrolysis of pure antimony from hydrofluoric acid solution. The antimony so obtained was cast into sticks under reduced pressure. The resulting castings, which were free from surface pits and had a high luster, were cleaned by electrolysis in a sodium carbonate solution and repolished before use.

The potential developed by the antimony electrode was found to be

$$E = 0.2552 - 0.5893\ p\text{H at } 25°$$

when referred to the normal hydrogen electrode.

A deviation of the potential at *p*H 8 reported by other investigators was confirmed.

It was found that between a *p*H of 2.2 and 8 the slope of the curve is a constant having a value of 0.05893. This value approaches that of the theoretical value of 0.05912 quite closely.

CLEVELAND, OHIO RECEIVED DECEMBER 23, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 84]

Reaction of Anhydrous Rare Earth Bromides with Ethyl Benzoate and the Separation of Neodymium from Lanthanum

BY RALPH C. YOUNG, ARNOLD ARCH AND WILLIAM V. SHYNE, JR.

The anhydrous bromides of lanthanum, neodymium, praseodymium, and samarium have been found to react with ethyl benzoate at a relatively low temperature in a manner analogous to the reaction of thorium bromide[1] and aluminum chloride[2] with this reagent.

$$LaBr_3 + 3C_6H_5COOC_2H_5 = La(C_6H_5COO)_3 + 3C_2H_5Br$$

The rates of this reaction for the different rare earth bromides vary. Those for lanthanum and neodymium have been studied at 154° by a measurement of the ethyl bromide evolved from 1 g. of the bromide and excess ethyl benzoate. A closed apparatus of about 1400-ml. capacity with calibrated mercury manometer was used for this study, Fig. 1. The percentage conversion to the benzoate and the time of heating are given in Table I.

TABLE I

PER CENT. CONVERSION OF RARE EARTH BROMIDES TO BENZOATES

Time in hours		5	10	15	20	25
Conversion to benzoate, %	Nd	26	54	70	78	84
	La	3	13	24	31	36

According to these data a favorable separation might be obtained if the reaction were carried to 30% of completion provided a large percentage of the substances formed were insoluble in water.

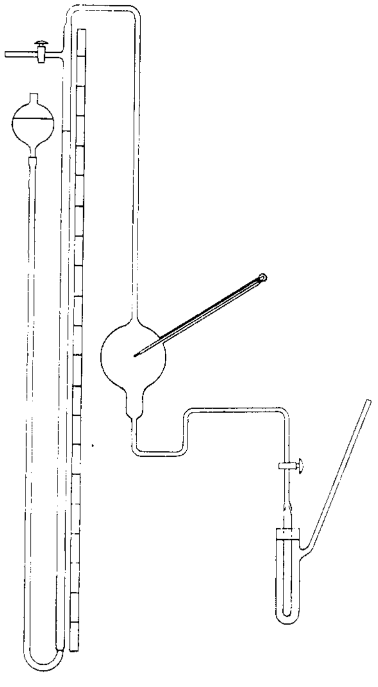

Fig. 1.—Apparatus for measurement of rate of reaction of rare earth bromides with ethyl benzoate.

Samples[3] of about 2 g. of a nearly equimolal mixture of the bromides of lanthanum and neodymium were heated with 5 ml. of ethyl benzoate in the apparatus mentioned for about five hours at 154° (bath of boiling bromoben-

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[1] Young, THIS JOURNAL, 56, 29 (1934).

[2] Norris and Klemka, *ibid.*, 62, 1432 (1940).

[3] Oxides of neodymium and lanthanum were separately weighed and then united and dissolved in hydrochloric acid. From the solution the mixed oxalates were precipitated, converted to the oxides, and from the latter the bromides were formed.

zene). The cooled reaction product was treated with petroleum ether to remove the excess ethyl benzoate, and extracted several times with 25 ml. of water to dissolve the soluble portion and finally allowed to stand in contact with water for twenty-four hours. The residue consisted of rare earth benzoates and contained no bromide. The insoluble and soluble portions were separately converted to the oxides.

Analyses of both the original mixture and products were made for neodymium with an absorption spectrophotometer (Cenco Spectrophotelometer). Measurements on solutions of the chlorides were made on the absorption band of neodymium at a wave length of 521 mμ and calibration was accomplished by use of standard solutions of neodymium chloride of concentrations varying from 0.1 to 0.001 *m*. As a check on these results, analyses for lanthanum were made with a 35-foot Wadsworth mounted spectrograph. For the calibration data mixtures of neodymium and lanthanum oxides were used containing percentages of lanthanum which varied from 10% lanthanum to 0.01%. The results of typical runs are given in Table II. The accuracy is considered to be within a range of ±5%.

TABLE II

SEPARATION OF NEODYMIUM FROM MIXTURES OF NEODYMIUM AND LANTHANUM

Mixed bromides used, g.	$NdBr_3$ in mixture ± 5%, %	Recovery Water insol. portion, oxide, g.	Recovery % Nd ± 5%	Recovery Water sol. portion, oxide, g.	Recovery % Nd ± 5%
2.0	38.1	0.1034	99	0.6899	32
2.6	56	.1568	97	.6156	49
2.3	56	.0635	100	.7985	49
2.0	56	.4473	72	.3892	44

The rare earth bromides react with diethyl oxalate and form ethyl bromide and the oxalates of the rare earths. A study of the reaction between the rare earth chlorides and both esters is planned.

Summary

The anhydrous bromides of the rare earth elements react with ethyl benzoate at 154° and produce ethyl bromide and the rare earth benzoate. Since the rates differ for the different rare earths and the benzoates are insoluble in water, this reaction affords a means of separation. From nearly equimolal mixtures of neodymium and lanthanum bromides, 25% of the neodymium is obtained in a degree of purity of 95% in one operation since neodymium bromide reacts at a much faster rate than lanthanum bromide to produce the benzoate.

CAMBRIDGE, MASS. RECEIVED JANUARY 22, 1941

[CONTRIBUTION NO. 419 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Heats of Dilution, Relative Molal Heat Contents and Heat Capacities of Aqueous Sodium Sulfate Solutions[1]

BY W. E. WALLACE AND A. L. ROBINSON

In the past numerous investigations[2,3] of the thermal properties of very dilute solutions of electrolytes have been shown[4,5] to yield results which, for the low valence types (1–1, 1–2, 2–1), are in substantial agreement with theory.[6,7] Most of these studies involved measurements at a single temperature, 25°. For this reason reliable data for the temperature dependent properties of dilute solutions are available in comparatively few cases.[3,8] In this paper are presented measurements of the intermediate heats of dilution of aqueous sodium sulfate solutions from 0.4 to 0.0001 molal at 15 and 20° and from 0.4 to 0.1 molal at 25°. These results, when combined with the extremely precise data of Lange and Streeck[9] for the very low concentration range at 25°, permit the evaluation of the partial molal heat contents at the three temperatures and the (average) heat capacities (15 to 25°) from zero to approximately 0.4 molal.

Experimental.—The apparatus was essentially that used by Dunkelberger and Robinson[8] with a few minor changes.

The Julius suspension, previously used for the support of the galvanometer, was replaced by a supporting shelf similar to that used by Amdur and Pearlman.[10] The details of the construction are given elsewhere.[11] This type of support proved to be so satisfactory that the scale dis-

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(1) From a thesis submitted by Mr. W. E. Wallace in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Pittsburgh, 1940.

(2) E. Lange and A. L. Robinson, *Chem. Rev.*, **9**, 89 (1931).

(3) E. A. Gulbransen and A. L. Robinson, THIS JOURNAL, **56**, 2637 (1934).

(4) T. F. Young and W. L. Gronier, *ibid.*, **58**, 187 (1936).

(5) T. F. Young and P. Seligmann, *ibid.*, **60**, 2379 (1938).

(6) P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

(7) N. Bjerrum, *Z. physik. Chem.*, **119**, 145 (1926).

(8) T. H. Dunkelberger and A. L. Robinson, THIS JOURNAL, **60**, 1301 (1938).

(9) E. Lange and H. Streeck, *Z. physik. Chem.*, **157A**, 1 (1931).

(10) I. Amdur and H. Pearlman, *Rev. Sci. Instruments*, **9**, 194 (1938).

(11) W. E. Wallace, Thesis, University of Pittsburgh, 1940.