

TABLE IV

-Phenoarsinic acid	M. p., °C.	Formula	Calcd.	Arsenic analyses, %	
				Calcd.	Found
$\gamma$ -Benzo	278-280	$C_{16}H_{11}O_2As$	22.98	23.04	23.00
8-Methyl- $\gamma$ -benzo	205-270 <sup>a</sup>	$C_{17}H_{13}O_2As$	22.04	22.04	22.08
10-Methyl- $\gamma$ -benzo	215-217	$C_{17}H_{13}O_2As$	22.04	22.04	22.06
8-Chloro- $\gamma$ -benzo	216-218	$C_{16}H_{10}O_2ClAs$	20.79	20.90	20.92
10-Chloro- $\gamma$ -benzo	214	$C_{16}H_{10}O_2ClAs$	20.79	20.78	20.76

<sup>a</sup> Substance partially melts at 205°, then solidifies and finally melts sharply at 270°.

fication was necessary if the corresponding phenoxynaphthaleneearsonic acids used were pure. All were insoluble in sodium carbonate and cold sodium hydroxide solutions, but were soluble in hot sodium hydroxide solutions.

### Summary

1. The isomeric 1,2- and 2,1-chloronaphthaleneearsonic acids have been prepared for the first time. The synthesis of the latter involved the developing of methods for the quantity production of the intermediates 2-chloro-1-nitronaphthalene and 2-chloro-1-aminonaphthalene and the necessary modifications of the Bart reaction.

2. Two new series of naphthyl phenyl ether derivatives have been prepared by the condensation of the parent compounds with phenol and substituted phenols. 1-Chloro-2-naphthalene-

earsonic acid has been condensed with phenol and *o*-cresol. 2-Chloro-1-naphthaleneearsonic acid has been condensed with phenol, *o*- and *p*-cresols, and *o*- and *p*-chlorophenols.

3. By the elimination of water, heterocyclic benzophenoarsinic acids have been prepared from all the above naphthyl phenyl ethers. No benzophenoarsinic acids have been reported previously.

4. No condensations were possible, under the conditions employed, with either aniline, the aliphatic amines or the aliphatic alcohols.

5. Chlorine in these naphthaleneearsonic acids was found less reactive than chlorine in a similar position in the benzene nucleus.

LINCOLN, NEBRASKA

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

## The Normal Potential of the Silver-Silver Bromide Electrode from 5 to 40<sup>o</sup>

BY BENTON BROOKS OWEN AND LOUISE FOERING

Experimental difficulties inherent in the direct comparison of certain electrodes with the hydrogen standard have led to the extensive use of secondary standards such as the familiar calomel half-cells. Because of the thermodynamic objections to the estimation of liquid junction potential involved in the ordinary use of such standards, it is important to be able to perform the comparison in cells without liquid junctions. It has recently been shown<sup>2</sup> that cells containing dilute borax buffers can be very conveniently employed in this connection. Although the method is general in principle, the use of borax solutions, under certain prescribed conditions, has the peculiar advantage of eliminating the need for an extrapolation to infinite dilution. This labor-

saving feature and the convenience of borax as a buffering agent make it desirable to test the accuracy and reliability of the method by investigating a system which can be readily checked by more orthodox procedures.

For this purpose we have measured the electromotive forces of cells of the type

$H_2 | HBO_2(m), Na_2BO_2(m), KX(m) | AgX - Ag$   
in which X represents either bromide or chloride, and  $m \approx 0.005$  molal. After a small correction<sup>2</sup> to the electromotive forces to make them correspond exactly to  $m = 0.005$ , the equation

$$E_{HBr}^0 = E_{HCl}^0 + E_{KBr}^{0.005} - E_{KCl}^{0.005} \quad (1)$$

permits the calculation of  $E_{HBr}^0$  in terms of known values of  $E_{HCl}^0$  taken as standard. Comparison can then be made with values of  $E_{HBr}^0$  obtained by direct extrapolation of measurements on cells containing dilute hydrobromic acid. We have employed electrodes containing fused silver bromide because the corresponding normal potentials have

(1) This communication embodies part of the experimental material to be presented by Louise Foering to the Graduate School of Yale University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Owen, THIS JOURNAL, 57, 1526 (1935). Full particulars regarding the calculations are given.

TABLE I  
OBSERVED VALUES OF  $E_{\text{KBr}}^{0.005}$  AND THE CORRESPONDING VALUES OF  $E_{\text{HBr}}^0 = -E_{\text{AgBr}}^0$

$t^\circ$	(1)	(2)	$E_{\text{KBr}}^{0.005}$ (3)	(4)	(5)	$E_{\text{HBr}}^0$ Average	$\Delta$
5	0.72777	0.72786	0.72775	0.72769	0.72777 <sup>b</sup>	0.07986	0
10	.73417	.73423	.73417	.73409	.73416 <sup>b</sup>	.07801	1
15	.74061	.74061	.74071	.74059	.74053 <sup>b</sup>	.07599	3
20	.74703	.74709	.74714	.74707	.74714	.07372	-2
25	.75362	.75366 <sup>a</sup>	.75365	.75356	.75377	.07128	-6
30	.76011	.76008 <sup>a</sup>	.76011	.76006	.76014	.06871	-5
35	.76668	.76661 <sup>a</sup>	.76661	.76656	.76663	.06600	0
40	.77300	.77300 <sup>a</sup>	.77300	.77312	.77312	.06307	1
$m \times 10^5$	4902	4939	4997	4840	5031		

<sup>a</sup>  $m \times 10^5 = 5061$ . <sup>b</sup>  $m \times 10^5 = 4719$ .

recently been reported<sup>3</sup> over a wide temperature range.

#### Materials and Technique

Since the concordance among some of the earlier estimations of  $E_{\text{HBr}}^0$  is not very satisfactory, we have paid particular attention to the purity of our materials upon the supposition that the uncertainty in the older measurements may have been due to impurities in the hydrobromic acid.

We employed two samples of potassium bromide. Sample A was prepared from carefully purified potassium oxalate and bromine, and recrystallized three times from conductivity water. The purification of the bromine was essentially the procedure used by Baxter and Grover.<sup>4</sup> Sample B consisted of Baker "analyzed" potassium bromide recrystallized six times from conductivity water. Both samples were dried over solid sodium hydroxide, and then heated in platinum to constant weight at 120°.

The borax was a re-fused Kahlbaum product previously described.<sup>5</sup>

All concentrations were calculated from the weights of the "dry" salts, and expressed as moles per kilogram of solvent weighed *in vacuo*. The effect of the presence of 0.1% of moisture in the borax would be unmeasurable under the conditions of our experiment, but would amount to 0.02 or 0.03 mv. if present in the potassium bromide.

The silver-silver bromide electrodes were prepared by heating a mixture of 90% silver oxide and 10% silver bromate for seven minutes at 650°.<sup>6</sup> Several different samples of silver bromate were employed. One was a recrystallized fresh preparation, and the other two were carried over from previous researches.<sup>6,7</sup> Fresh and old<sup>2</sup> silver oxides were also used. Six electrodes were prepared from a silver bromate-silver oxide mixture left in the laboratory by Dr. Keston. They were used in the measurement marked by the superscript *a* in Table I.

Intercomparison of electrodes prepared from various combinations of these silver compounds showed them to be indistinguishable. They were kept dry until used, and no effort was made to protect them from diffuse daylight.<sup>2</sup>

Special care was taken in washing the hydrogen electrodes free from chlorides of the platinizing bath, and in

the exclusion<sup>2,8</sup> of oxygen during the preparation and use of the cell solutions. Solutions were always used within one to four days after their preparation.

#### Discussion of the Results

The observed electromotive forces of the cells containing borax and potassium bromide were corrected to a partial pressure of hydrogen of one atmosphere, and to the round concentration  $m = 0.005$ . They are recorded as  $E_{\text{KBr}}^{0.005}$  in Table I.

The actual concentrations,  $m$ , of the solutions used in each series of cells is also included. Each value of  $E_{\text{KBr}}^{0.005}$  is the mean value of five or six independently filled cells agreeing within 0.1 mv. The same set of cells was never used over a temperature range greater than 20°.

Solutions (1) and (2) were prepared from sample B of potassium bromide. The others were made from the elaborately purified sample A. It can be seen that no *consistent* difference was observed in the electrochemical behavior of the two samples of potassium bromide. Since the source of the bromate and oxide used in the electrodes was also without noticeable effect upon the results, it is reasonable to conclude that the silver bromide electrode is not sensitive to such traces of impurities as may have remained in *any* of our chemicals.

In the calculation of  $E_{\text{HBr}}^0$  by equation (1), we employed the smoothed values of  $E_{\text{HCl}}^0$  given by equation (7) of Harned and Ehlers,<sup>8</sup> the mean values of  $E_{\text{KCl}}^{0.005}$  previously reported,<sup>2</sup> and the mean values of  $E_{\text{KBr}}^{0.005}$  derivable from the data given in Table I. The resulting values of  $E_{\text{HBr}}^0$  are recorded in the next to last column. Their temperature variation can be represented empirically by the quadratic equation

$$E_{\text{HBr}}^0 = 0.07134 - 498 \times 10^{-6} (t - 25) - 3.6 \times 10^{-6} (t - 25)^2 \quad (2)$$

(8) Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

(3) Harned, Keston and Donelson, *THIS JOURNAL*, **58**, 989 (1936).

(4) Baxter and Grover, *ibid.*, **37**, 1027 (1915).

(5) Owen, *ibid.*, **56**, 1695 (1934).

(6) Keston, *ibid.*, **57**, 1671 (1935).

(7) Owen, *ibid.*, **55**, 1922 (1933).

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<sup>3</sup> 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  $E_{\text{HCl}}^0$  and  $E_{\text{HBr}}^0$  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.<sup>9</sup>

Upon this basis we regard the reliability of

(9) In a private communication Mr. Donelson informs us that the extrapolation of his data on the cells  $\text{H}_2 | \text{HBr}(0.01), \text{LiBr}(m) | \text{AgBr} - \text{Ag}$  leads to values of  $E_{\text{HBr}}^0$  in excellent agreement with our own—maximum difference about 0.1 mv.

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.<sup>3</sup>

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.

NEW HAVEN, CONN.

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## 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<sup>1</sup> 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<sup>1</sup> 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  $2\text{EuCl}_3 + \text{Zn} \longrightarrow 2\text{EuCl}_2 + \text{ZnCl}_2$  and  $\text{Eu}^{++} + \text{I} \longrightarrow \text{Eu}^{+++} + \text{I}^-$ . 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 ( $\text{Eu} = 152.0$ ) 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

(1) McCoy, *THIS JOURNAL*, **57**, 1756 (1935).