[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Antimony Electrode. I. Normal Electrode Potential. II. The Potential of the Antimony Electrode as a Function of Hydrogen Ion Concentration

BY FRANK HOVORKA AND GERALD H. CHAPMAN*

Many investigations have been carried out on electrodes of the metal–metal oxide type. The only one of these which has met with much success is the antimony–antimony oxide electrode. The use of this electrode for continuous *p*H determination of industrial solutions has been possible for a number of years. The results for this electrode have been summarized by Parks and Beard[1] and by Perley.[2]

The values reported in the literature for E_0 and for the slope of the curves vary widely. In this investigation an attempt has been made to determine more accurately the true E_0 and the slope of the *p*H curve of the antimony–antimony oxide electrode to see how closely this system approximates the Nernst equation.

The antimony electrodes were prepared by the method developed by Hovorka and Schoenfeld.[3]

Antimony was plated on platinum from a hydrofluoric acid solution of doubly distilled antimony trichloride. The antimony was removed from the platinum and cast into sticks 7 mm. in diameter in Corning no. 172 glass tubing under a vacuum. The sticks were polished to a higher luster using 1/0, 2/0, 3/0, and 4/0 polishing paper, respectively. A copper lead was attached to the electrode and the electrode was sealed in a glass tube with deKhotinsky cement. About 2 cm. of antimony extended from this tube for immersion in the solution under investigation. However, the electrode was never immersed more than 8 mm. Each time the electrode was placed in use in a new solution, it was electrolyzed in sodium carbonate solution and repolished.

The thermostat used maintained the temperature at 25 ± 0.01°.

The electrode vessels were constructed of three Pyrex test-tubes, 15 cm. long, connected by 6 mm. Pyrex tubing attached at the bottoms and to a 3-way mercury seal stopcock. The stopcock was T-bored and the arms to the test-tubes were 10 cm. long. By turning the stopcock, it was possible to connect any two of the electrode vessels or all three at one time. Two of the tubes were used for antimony electrodes while the third held the hydrogen electrode.

The electrode vessels and the wash bottles were mounted on a form that could be lifted from the thermostat or be submerged to any desired depth. This apparatus is similar to that described by Hovorka and Dearing.[4]

The hydrogen electrodes were constructed of B. and S. no. 18 platinum wire sealed in small glass tubing with 2 cm. of the wire extended for a working surface. The other ends were soldered to copper wire leads. Two such electrodes were fitted into a rubber stopper and used as a unit. This unit fitted into a larger tube that had a side arm for the introduction of hydrogen. The electrode wires extended to the end of this tube. Two holes for the escape of hydrogen were placed about 5 mm. from the bottom and on opposite sides of this jacket. This unit was fitted to the electrode vessel by means of a rubber stopper which contained a hole for the escape of hydrogen. The platinum wires were polished with fine scouring powder and a soft cloth before each run. They were then cleaned by electrolysis in 10% sulfuric acid solution at 4 volts, the potential being reversed from time to time. When the evolution of gas was even, the wires were rinsed in distilled water and platinized at 4 volts, reversing the potential from time to time, in 3% solution of H_2PtCl_6. The potential between these electrodes was easily maintained. to 0.00002 volt. If at any time a drift of potential was greater, they were removed and replatinized.

The hydrogen used, from a tank of electrolytic hydrogen, was washed in concentrated potassium hydroxide solution, and in water, then passed over platinum wire heated to 450° and finely bubbled through a wash bottle of the solution under investigation just before introduction to the electrode vessel.

The antimony electrodes were fitted in a two hole stopper. Two units were used, one in each of the remaining electrode vessels. The potential between these electrodes was held to 0.00002 volt. In case of greater deviation, they were removed and repolished.

All electrode connections were made by screw clamps. The switchboard connections were soldered, and the lead wires were made of B. and S. no. 16 rubber insulated copper wire. The switchboard was so constructed that the deviations within electrode units or the potentials between any combination of units could easily be read.

The potentials were measured by means of a Leeds and Northrup type K potentiometer and a type R galvanometer lamp and scale. The standard cell was of the unsaturated cadmium type, manufactured by the Eppley Laboratories and certified by the Bureau of Standards. This cell was checked frequently with another certified cell. The system was shielded and free from appreciable stray currents.

The chemicals and the different *p*H standard solutions used were prepared according to the directions given by Clark.[5]

The measurements were made with the hydrogen and antimony electrodes both immersed in the same *p*H solution. However, since the connecting glass tubing was long and the stopper holding the antimony electrodes fitted

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(1) Parks and Beard, THIS JOURNAL, **54**, 856 (1932).

(2) Perley, *Ind. Eng. Chem.*, *Anal. Ed.*, **11**, 316, 319 (1939).

(3) Schoenfeld, Thesis, Western Reserve University, 1937.

(4) Hovorka and Dearing, THIS JOURNAL, **57**, 446 (1935).

(5) W. M. Clark, "Determination of Hydrogen Ions," 3rd ed., Chap. IX, The Williams and Wilkins Co., Baltimore, Md., 1928.

tightly, there was very little mixing of the solution in the electrode vessels.

The e. m. f. observed was constant to 0.0001 volt or less in all of the *p*H standard solutions tested with the exception of *p*H 3. In this solution the hydrogen apparently reduced the potassium acid phthalate causing the *p*H of the solution to change so rapidly that readings in the millivolt range were not stable.

The *p*H 3 reading was finally obtained by placing the hydrogen electrode in a 0.05 *N* potassium acid phthalate half cell and the antimony electrode in the *p*H 3 solution. With this arrangement, the potential was constant to 0.0001 volt. To convert this reading to the same basis of the other *p*H values, it was necessary to know the potential of the half cell. This potential was obtained by measuring it against a hydrogen electrode in normal hydrochloric acid. An e. m. f. of 0.23529 v. equivalent to a *p*H of 3.979 was obtained. This was in close agreement with the value 3.980 reported by Hovorka and Schoenfeld.[3] Neither of these values agreed with that reported by MacInnes,[6] who states that the *p*H was 4.00 at 12° and at 25°, and 4.015 at 38°. Grant[7] stated on page 22 of his book that the *p*H is "3.92 at 18–30°, which rose only to 3.94 at 50–60°." He indicated the *p*H changed with temperature, although his *p*H values are apparently in error. However, on page 67 of the same text he reported a *p*H of 3.97 for this half cell—a value that confirms that found in this investigation.

TABLE I

ANTIMONY ELECTRODE AS A FUNCTION OF HYDROGEN ION CONCENTRATION

*p*H		*E* (obsd.)	*E* (cor.)	*E* av.
2.20	(*a*)	0.25476 ± 0.044	0.25538	0.25536
	(*b*)	.25474 ± .043	.25534	
3.00	(*a*)	.31250 ± .041	.25512	.25512
	(*b*)	.31235 ± .043	.25512	
4.20	(*a*)	.25437 ± .042	.25509	.25510
	(*b*)	.25444 ± .042	.25510	
5.00	(*a*)	.25439 ± .041	.25501	.25501
	(*b*)	.25450 ± .041	.25500	
6.00	(*a*)	.25493 ± .043	.25561	.25551
	(*b*)	.25484 ± .042	.25541	
6.80	(*a*)	.25541 ± .041	.25591	.25583
	(*b*)	.25526 ± .043	.25574	
8.00	(*a*)	.25601 ± .041	.25671	.25672
	(*b*)	.25601 ± .041	.25672	

Table I contains the results of this investigation. In each case *a* and *b* represent different sets of three to six readings made over intervals of sixty to one hundred and fifty minutes in new solutions. All readings have been corrected to reduce the hydrogen pressure to 760 mm. at 0°. The correction also involved a consideration of the vapor pressure of the solution and the hydrostatic pressure caused by the immersion of the hydrogen electrode.

The curve obtained by plotting the potentials of the antimony electrode against various *p*H values intercepts the abscissa at 0.2552. The slope of the line is 0.05893. Therefore, the equation for the antimony electrode is

$$E = 0.2552 - 0.05893\ p\text{H at } 25°$$

when referred to the hydrogen electrode. According to the Nernst equation the value should be $E = E_0 - 0.05912\ p\text{H}$ at 25°. The value for the slope found in this investigation approaches the theoretical value quite closely.

Parks and Beard[1] found that the *p*H curve was not a straight line function above a *p*H of 7. This phenomenon has also been noticed by Hovorka and Schoenfeld, and King.[8] This finding was confirmed by this investigation as at *p*H 8 there was a definite increase in the e. m. f. value.

King suggests that this increase is due to the salt error of the potassium chloride used in the buffer solution. He quotes a private communication with R. J. Brest in which the salt error of 0.4 of a *p*H due to 1 *N* potassium chloride is recorded. King investigated the salt error over a wide range of *p*H. He reports that the error is 0.4 of a *p*H but adds that a deviation of only 2 millivolts occurs. This deviation is 0.033 of a *p*H.

Parks and Beard[1] have reported a value of $E = 0.2528 - 0.05915\ p\text{H}$ for the antimony stick electrode in an unstirred solution in contact with air at equilibrium with both antimony and antimony trioxide. However, the slope of the curve calculated from their data does not seem to be 0.05915 as reported. An examination of their results reveals that the nearest approach to this value is 0.05928 for the slope between a *p*H of 3.32 and 7.67.

Perley[2] reports for the antimony/saturated calomel electrode system at 25° the value $E_{\text{Sb}} = -0.008 + 0.059\ p\text{H}$. When the equation is referred to the hydrogen electrode at 25° it becomes: $E_{\text{Sb}} = 0.2538 + 0.059\ p\text{H}$.

It is interesting to note the E_0 value of 0.2538

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(6) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Co., New York, N. Y., 1939, p. 278.

(7) J. Grant, "The Measurement of Hydrogen Ion Concentration," Longmans, Green and Co., New York, N. Y., 1930.

(8) King, *Ind. Eng. Chem., Anal. Ed.*, **5**, 323 (1933).

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.

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

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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.

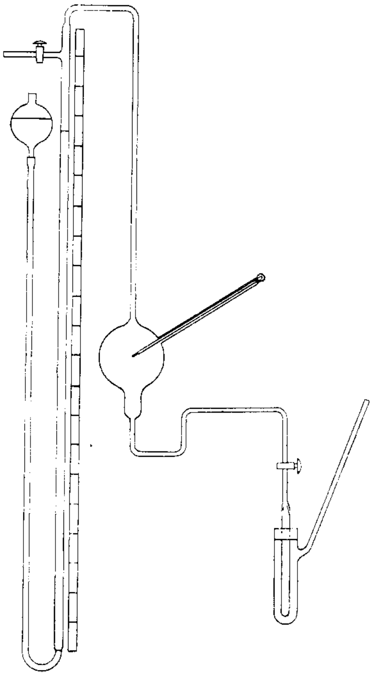

Fig. 1.—Apparatus for measurement of rate of reaction of rare earth bromides with ethyl benzoate.

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.