2. A design of apparatus is given.
3. Some of the properties of pure barium and strontium are enumerated.

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

BARIUM AND STRONTIUM AMALGAM ELECTRODES

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In a determination of the electrode potentials of barium and strontium by a method analogous to that employed by Lewis and his coworkers[2] in their determinations of the potentials of the alkali metals, it is necessary to know the potential of some amalgam of the metal against a standard electrode in an aqueous solution of the appropriate salt. The desirability of employing an amalgam of definite, constant and easily reproducible composition whenever measurements involving an amalgam electrode are made is entirely obvious. It has been pointed out[3] that these requirements are satisfied when a two-phase amalgam is used. A 0.1 M solution of a chloride with the standard calomel electrode is quite satisfactory for use with such an amalgam. Accordingly, measurements of the electromotive force of the following two cells have been made,

$$\text{Ba (2-phase amalgam), BaCl}_2(0.1\ M)\text{, HgCl, Hg} \qquad (1)$$

$$\text{Sr (2-phase amalgam), SrCl}_2(0.1\ M)\text{, HgCl, Hg} \qquad (2)$$

Design of Electrode Vessels.—Since no entirely satisfactory vessel has been described for use with amalgams which are as concentrated and consequently as reactive as are the two-phase amalgams, an extended investigation of this subject has been made.

The simple type of "dropping electrode" originally devised by Lewis and Kraus[2a] and since employed with various modifications by several other investigators is suited for use only where a continuous stream of dilute amalgam containing no solid phase may be kept running throughout a determination. When it becomes desirable to continue measurements with the same electrode for many hours either the quantity of amalgam which is necessary becomes very large and the apparatus unwieldy, or the flow of amalgam must be made intermittent. In the latter case the difficulty of preventing the solution from creeping in between the amalgam and the glass wall of the dropper tip increases rapidly with the concentration of the amalgam and with the time between renewals of the amalgam surface. When solution becomes trapped in this way between the amalgam and the vessel, reaction occurs which not only gives rise to fluctuating and erroneous

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[2] (a) Lewis and Kraus, THIS JOURNAL, **32,** 1459 (1910). (b) Lewis and Keyes, *ibid.*, **34,** 119 (1912); (c) **35,** 340 (1913). (d) Lewis and Argo, *ibid.*, **37,** 1983 (1915).

[3] (a) Gerke, THIS JOURNAL, **44,** 1686 (1922). (b) Danner, *ibid.*, **44,** 2837 (1922).

values of the electromotive force but also produces small bubbles of hydrogen which sooner or later break the electrical circuit and thus render the electrode inoperative. Still further requirements which are imposed upon the electrode vessel by the use of a two-phase amalgam are that no long capillary tubes which are liable to become clogged by particles of the solid amalgam shall be included and that the amalgam reservoir shall permit the exact temperature control necessary to insure equilibrium between the solid and liquid.

The electrode vessels which have been investigated have varied in character from one employing a very small, rapidly renewable surface of amalgam in contact with the same solution for a very short time, to the extreme opposite of a very large, constant surface of amalgam in contact with a renewable body of solution. The extreme types and one intermediate will be discussed.

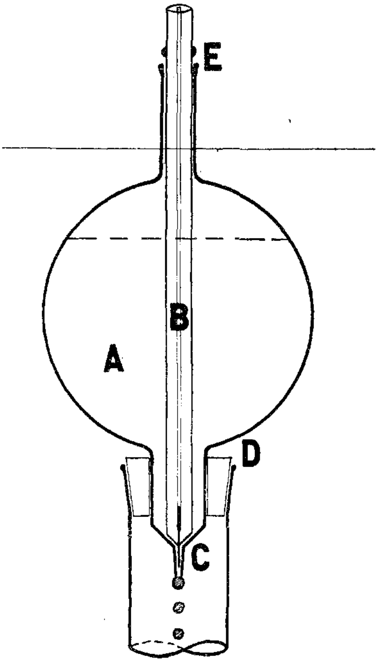

Fig. 1.

The first type is represented in Fig. 1.

The amalgam reservoir at A is made from a 150cc. round-bottom flask. The plunger at B is made from heavy-walled capillary tubing, is ground to a tight seat at C and has a platinum wire sealed through the tip which serves to make contact with the stream of amalgam issuing from the capillary which is drawn below C. This wire also serves to dislodge any particle of solid which may become fast in the capillary, though it is not often needed for this purpose as the solid is less dense than the liquid and stays well toward the surface. The bore of the capillary dropping tip is made just large enough to allow the desired rate of flow of amalgam and is different for each metal, as the viscosity of the various amalgams is quite different. The plunger may be firmly seated by a rubber connection at E. An appropriate cemented joint is made at D, depending upon the thermostat liquid. The amalgam must be introduced into the reservoir at a temperature somewhat above that of the thermostat and the whole apparatus quickly assembled and placed in the bath so that when the amalgam cools, its composition will be uniform throughout and it will be saturated at the temperature of the bath. The spent amalgam is removed by a device similar to that employed in a previous amalgam cell.[4]

This electrode may be operated intermittently over as long a period as desired since any bubble of gas formed by reacting liquid in the capillary will escape upward through the amalgam when the plunger is unseated while any solution in the capillary is forced downward by the rapid flow of amalgam.

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[4] Ref. 3 b, p. 2838, Fig. 4.

Upon varying the rate of flow of amalgam from 500 drops to 50 drops per minute the electromotive force of such an electrode, employing an alkali or alkaline earth amalgam, was invariably found to rise several tenths of a millivolt. This fact led to the modification shown in Fig. 2, which permits considerably larger globules of amalgam to be employed and held as long as desired before a new surface is formed. The difference, however, between a rate of flow of 50 drops per minute and one drop in two or three minutes was never more than 0.2 mv., and when the rate of flow became still less, the electromotive force began to show a rise and fall with each new drop due to aging of its surface. In this dropper more chance is offered for solution to creep in between the amalgam and the glass while the amalgam is not running so that, without modification, it was found to be less suitable for intermittent determinations than the former vessel. This defect was completely eliminated by coating that part of the surface of the dropper vessel which comes in contact with the solution with a thin layer of paraffin. The creeping of solution was so completely stopped by this procedure that an electrode could be continued in use for a time dependent only upon the size of the amalgam reservoir.

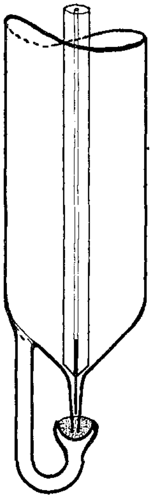

Fig. 2.

The results already enumerated show that the surface of an amalgam which has been separated from its solid phase is sufficiently depleted by reaction in one or two minutes to cause its electromotive force to begin to fall. However, the fact that the solid phase when present rises to the surface seemed to suggest that an electrode using a constant, rather large surface of amalgam containing considerable solid phase over which fresh liquid could be circulated from time to time might be worth trying. The vessel shown in Fig. 3 was accordingly designed.

A reservoir of solution of any desired size is shown at A, a body of amalgam at B, while tubes C and D connect with a standard electrode and a receiving reservoir, respectively.

When the plunger type of stopcock at E is unseated and a small air pressure is applied at F, solution is forced from the reservoir over the surface of the amalgam and out into a reservoir at D. The plunger at G serves to prevent stirring of the electrolyte in the standard electrode vessel while the solution is being circulated through the remainder of the vessel. Except with the most dilute solutions, sufficient conductivity is afforded even with this plunger tightly closed. The volume of amalgam is from 2 to 3 cc. and the volume of solution above it as small as possible, so that the reservoirs need not be extremely large to permit a large number of renewals of the contact surface between solution and amalgam. The inner surface of the amalgam chamber was coated with a layer of paraffin to prevent creeping of the solution.

When first prepared, electrodes of this type gave values of electromotive force which were entirely reproducible with renewal of the solution and which agreed entirely with the values obtained with the two previously described types of electrode. However, after the slow reaction which is inevitable had proceeded for half an hour the number of centers of reaction had so increased that the solid phase could not replace the metal as fast as it was used up and the value of the electromotive force read immediately after renewal of the solution was found to be considerably less than at first. It had previously been found that an amalgam surface which had been covered with a heavy paraffin oil[5] retained enough of that oil upon exposure to water so that the usual reaction was almost entirely eliminated.

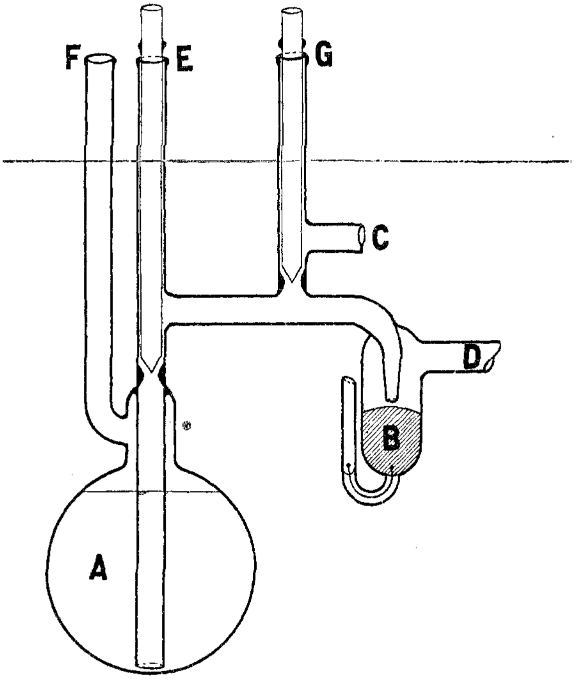

Fig. 3.

When this condition existed in a cell of this type it was found that the film of oil protected the amalgam surface so completely that even when the solution was not renewed the electromotive force would have fallen by only a few millivolts in several hours, and when the solution in contact with the amalgam was renewed the value of the electromotive force was reproducible to a couple of tenths of a millivolt over a period of several days. The magnitude of this electromotive force agreed with that obtained with the dropping electrode of Fig. 2, well within the limits of reproducibility.

All three types of electrode vessel have been employed using various

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[5] The heavy grade of "Nujol" was found very satisfactory.

alkali and alkaline earth amalgams; a set of values for two cells of each type is given in Table I which shows the average reproducibility and constancy of these electrodes.

TABLE I

THE BARIUM AMALGAM-CALOMEL CELL EMPLOYING DIFFERENT AMALGAM ELECTRODE VESSELS

	Type I		II		III	
	Amalgam running					
	Drops/min. 250–500	Drops/min. 30–50	Age of cell Hours	E.m.f. on renewing amalgam	Age of cell Hours	E.m.f. on renewing solution
Cell No. 1	2.0226	2.0236	1	2.0235	2	2.0240
	2.0229	2.0234	12	2.0238	7	2.0238
	2.0222	2.0234	36	2.0235	9	2.0240
	....	....	60	2.0236	24	2.0235
	....	....	..	....	45	2.0236
	....	....	..	....	53	2.0231
Cell No. 2	2.0230	2.0235	2	2.0236	2	2.0243
	2.0229	2.0236	4	2.0240	6	2.0240
	....	....	7	2.0240	10	2.0241
	....	....	15	2.0239	24	2.0238
	....	....	..	....	48	2.0239

There seems to be no reason to doubt that these electrode vessels would be equally applicable with the two-phase amalgams of the other alkali metals and it is possible that a modification of the first type might be used with the extremely reactive amalgams of calcium and magnesium.

The third type of electrode vessel is of especial interest because of its suggestiveness in the direction of electrometric analysis for the ions of the alkali and the alkaline earth metals.

Apparatus.—The potentiometer, thermostat and standard cells were the same as those used in an earlier investigation.[3b] The thermostat was constant to ±0.05°.

Materials.—The metal amalgams were prepared by the electrolysis of a saturated solution of the metal chloride onto a mercury cathode using a platinum anode. The salt had been twice recrystallized and the mercury distilled. The electrolysis was continued until a considerable quantity of the solid phase[6] was produced. The mixture of liquid and crystals was then completely dried and preserved under dry toluene.

The solutions used in constructing the cells were made from three or more times recrystallized salt and conductivity water, the salt having been dehydrated and heated to constant weight in platinum apparatus. Hydrolysis during this procedure is not detectable in the case of barium chloride and even with strontium chloride it is so small as to be entirely negligible.

Calomel was prepared by precipitation in aqueous solution and observation of the usual precautions.

Results.—In the case of barium a very large number of separate measurements are available since barium amalgam was largely used in the investigation of the various types of electrode vessel. The values chosen for several cells based, in each case, on a large number of renewals of the

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[6] Smith and Bennett, THIS JOURNAL, **32**, 622 (1910).

surface of contact between the amalgam and the solution, are recorded in Table II. All measurements were made at 25°.

Table II

Electromotive Force of Two-Phase Amalgam against Calomel in 0.1 M Chloride

Cell	1	2	3	4	5	6	7	Av.
Barium	2.0240	2.0241	2.0236	2.0240	2.0240	2.0241	2.0238	2.0240
Strontium	2.2474	2.2471	2.2472	....	....	....	....	2.2472

Taking the average values from Table II we may write,

Ba (2-phase amalgam), $BaCl_2$ (0.1 M), HgCl, Hg; $E = 2.0240$ (1)

and Sr (2-phase amalgam), $SrCl_2$ (0.1 M), HgCl, Hg; $E = 2.2472$ (2)

It is of interest to note that the magnitude of these electromotive forces with respect to each other is in agreement with the idea that the bond between the very electropositive barium and the mercury in their compound is a much firmer one than that between the less electropositive strontium and mercury and is thus further evidence of the salt-like character of the mercurides.

Summary

Design of an electrode vessel for use with two-phase alkali and alkaline earth amalgams is discussed.

Details of construction and operation of three such vessels are given.

Measurements of the potential of the two-phase barium and strontium amalgams against calomel are recorded.

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[Contribution from the Cobb Chemical Laboratory of the University of Virginia]

THE ADSORPTION OF ARSENIOUS ACID BY HYDROUS ALUMINUM OXIDE

By John H. Yoe

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Introduction

According to Lockemann and Paucke[1] arsenic, in the form of arsenite or arsenate, is completely removed from a dilute solution by aluminum hydroxide at the temperature of the water-bath (80–90°), but not at room temperature. The reverse, however, was found to be true in the case of ferric hydroxide. The authors explain this difference in adsorption as being due to the alumina precipitating incompletely in the cold but completely and in a flocculent condition from a hot solution, and hence offering a larger surface. The ferric hydroxide precipitates even from an ice-cold solution in a flocculent condition, and hence offers the combined ad-

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[1] Lockemann and Paucke, *Z. Kolloidchem.*, **8**, 273 (1911).