end directly away from the boat. Once started, the deck was easily rolled up.

The technique of sealing the deck in place was as follows. The boat was at first held fairly firm between two pins on a wooden bar clamped to the table. The deck, already waxed on top around the edge, was laid in place, then a brass plate was clamped down upon it. This plate was narrower than the deck, but wider than the opening in the boat. It ensured two things, first, that any part of the deck, once waxed, would not be loosened by warmth due to the waxing of an adjacent portion, and, second, that the deck just around the hole in the boat would remain cool, preventing wax from flowing in under against the powder. The waxing was done with a small nail warmed over a Bunsen burner. The wax sometimes adhered to the brass plate and might be loosened when this was raised. The easiest way to deal with this difficulty was apparently to wrap aluminum foil (0.01 mm. thick, from chocolate packages) around the plate, which could then be lifted free after the waxing. The aluminum could next be peeled off without loosening the wax. Wax was run across under the deck near the bow, so that none was needed near the wire. Premature wiggling of the wire, unless excessive, would then not endanger the seal.

The best wax, mechanically, of those we tried was picein. Picein, however, like many waxes, shows below 30° a variation in apparent specific heat, due no doubt to incipient melting. This causes the practical heat capacity of the calorimeter to vary with temperature by an amount depending on how much wax was used. With picein, however, the variation from 22 to 30° is 0.1 cal. per gram[4] per degree. Not over 200 mg. was needed, so the variation was actually 0.02 cal. per degree or 25 parts per million of the total capacity of 800 cal. per degree. Several times as much as that would ordinarily be safely negligible.

Summary

A thermochemical calorimetric mixing device will liberate powders into a solution very rapidly after they have been immersed so as to reach the calorimeter temperature. The method of opening is particularly convenient. The tightness of each seal against any sort of leakage of acid can be thoroughly tested with ease. Made for use in hydrofluoric acid, the apparatus is made of Bakelite, nitrocellulose film, and the very adherent wax, picein.

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[4] The corresponding variation with some solid paraffins, due probably mostly to crystal inversions, is 7 times as great. Such waxes, in any quantity, would not be safe. More complete values on a number of waxes will be published later.

WASHINGTON, D. C. RECEIVED MAY 8, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Saturated Standard Cells with Small Temperature Coefficients. II

BY W. C. VOSBURGH, MARY GUAGENTY AND WILLIAM J. CLAYTON

It has been shown by Vosburgh[1] that adding sufficient lead or tin to the amalgam of a saturated Weston cell makes a cell that is as reproducible as the Weston cell, but has a smaller temperature coefficient. The electromotive force and temperature coefficient of the Weston cell can be altered by additions to the cadmium sulfate solution also, and it is the purpose of this paper to show the effect of adding sodium sulfate.

When another component is added to the electrolyte, another phase must be added also if a change in the variability of the system is to be prevented. Accordingly, the saturated cadmium sulfate solution of the Weston cell was replaced by a solution saturated with both cadmium sulfate, $3CdSO_4 \cdot 8H_2O$, and the double salt of sodium and cadmium sulfates, $CdSO_4 \cdot Na_2SO_4 \cdot 2H_2O$.[2] The result was a cell with an electromotive force of 1.01668 v. at 25° and a temperature coefficient about 10% higher than that of the Weston cell. By replacing the cadmium amalgam of this cell with a cadmium–bismuth amalgam[1] (p. 2537) a cell was obtained having an electromotive force of 1.0184 v. at 25° and a positive temperature coefficient between one-quarter and one-third of that of the saturated Weston cell.

Materials.[3]—Mercury was purified by distillation in a current of air. One preparation of mercurous sulfate was made by precipitation from mercurous nitrate and sulfuric

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[1] Vosburgh, THIS JOURNAL, 47, 2531 (1925).

[2] A solution saturated with sodium sulfate and the double salt might also be used, but this system has a transition point at 31° according to "International Critical Tables," Vol. IV, p. 340.

[3] For the preparation of some of the materials the authors are indebted to Mr. Gerald R. Cooper and Miss Barbara Pettengill.

acid and another was made electrolytically from mercury and sulfuric acid. Cadmium sulfate and sodium sulfate were recrystallized, and the double salt was prepared from the recrystallized component salts. Cadmium amalgam containing about 10% cadmium was prepared electrolytically. Two preparations of cadmium–bismuth amalgam were made, both of a composition of about 8.9% cadmium and 11.1% bismuth. This is equivalent to the addition of 12.5 g. of bismuth to 100 g. of 10% cadmium amalgam. An attempt was made to prepare one amalgam electrolytically, but by mistake too much cadmium was added and to correct the composition more mercury and some bismuth were added. The other amalgam was made by adding the calculated quantity of bismuth to some 10% cadmium amalgam and heating. The two gave the same results in cells.

Cell electrolytes were prepared by dissolving sodium and cadmium sulfates in the proportions to give a solution saturated with both cadmium sulfate and the double salt, using as the solvent either 0.015 molar sulfuric acid solution or 0.1 molar acetic acid solution.[4] Cell vessels of the usual H type were used for all of the cells.

Preparation of the Cells.—Four cells, Nos. 745–748, were made in which one electrode was a cadmium–bismuth amalgam and the other a plain cadmium amalgam. The electrolyte was a saturated cadmium sulfate solution with excess of the crystals present. These cells are designated below as amalgam cells.

Cells 740–744 were modified Weston cells made with plain cadmium amalgam and with electrolytes saturated with both cadmium sulfate and the double salt, with excess of both crystals present at both electrodes. The solution was about 0.01 molar with respect to sulfuric acid. The mercurous sulfate electrodes were prepared as in Weston cells. No protection from air was attempted in the preparation of these cells. The vessels were closed with rubber stoppers.

Cells 749–758 were made with cadmium–bismuth amalgam and with electrolytes saturated with both cadmium sulfate and the double salt. Air was excluded during the preparation of the cells by a current of nitrogen. In the preparation of the amalgam electrodes the amalgam was treated by the vacuum procedure used by Clayton and Vosburgh[5] for zinc amalgam electrodes. It is believed that this treatment was at least partly responsible for these cells assuming electromotive forces within 0.01 mv. of their final values as soon after preparation as temperature equilibrium was attained. Cells 749–753 were made with a solution containing sulfuric acid and Cells 754–758 with a solution containing acetic acid. All of these cells were sealed with a nitrogen atmosphere inside.

Electromotive Force Measurements.—The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer. The standard cell used was checked by the measurement of five non-portable saturated Weston cells that had recently been standardized by the National Bureau of Standards. The error of measurement was probably less than 0.01 mv. The temperatures of the cells were maintained by means of a constant-temperature oil-bath, and were within 0.05° of the values given.

The results for the amalgam cells at various temperatures are given in Table I. Some of the temperatures were approached from both above and below with good agreement. The cells were maintained at each temperature for not less than two days before final measurements were made. The four cells agreed within 0.01 mv. at all temperatures except at 10°. The electromotive forces at 25, 30 and 35° agree within 0.02 mv. with the results of Vosburgh[2] for similar cells.

TABLE I

THE CELL: Cd(Bi, Hg)/$3CdSO_4 \cdot 8H_2O$(satd.)/Cd(Hg)

t, °C.	9.85	14.7	19.85	25.05	29.9	34.85
E_t, 4 cells, mv.	0.91	1.12	1.37	1.71	2.06	2.48
E_t, ref. 2, mv.	..	...	...	1.71$_8$	2.07$_2$	2.49$_6$

The results for the cells with cadmium amalgams and with sodium sulfate in the electrolyte are given in Table II. These cells did not agree well when first prepared, but came to good agreement within two weeks. Within the subsequent seven months when no measurements were made the average electromotive force increased 0.02 mv. There is no reason to believe, however, that the presence of sodium sulfate has harmful effect on the cell. The five cells usually agreed within 0.01 mv. when fully aged. The measurements recorded in Table II were made when the cells were nine to ten months old.

TABLE II

THE CELL: Cd(Hg)/$3CdSO_4 \cdot 8H_2O$, $CdSO_4 \cdot Na_2SO_4 \cdot 2H_2O$, Hg_2SO_4/Hg; E_{25} = 1.01668 v.

t, °C.	9.85	14.7	19.85	29.9	34.85
$E_t - E_{25}$, 5 cells, mv.	0.62	0.46	0.25	−0.28	−0.63

The results for the cells made with the ternary amalgam and with solutions containing sodium sulfate are shown in Table III. The measurements recorded in Table III were made when the cells were between one and two months old. The electromotive force of these cells should be equal to the sum of the electromotive forces of

TABLE III

THE CELL: Cd(Bi, Hg)/$3CdSO_4 \cdot 8H_2O$, $CdSO_4 \cdot Na_2SO_4 \cdot 2H_2O$, Hg_2SO_4/Hg. FOR CELLS 749–753, E_{25} = 1.01841$_5$; FOR CELLS 753–758, E_{25} = 1.01839$_5$; CALCULATED, TABLES I AND II, E_{25} = 1.01839

t, °C.	9.85	14.7	19.85	29.9	34.85
$E_t - E_{25}$, Cells 749–753, mv.	−0.17$_5$	−0.13	−0.06$_5$	0.07	0.14
$E_t - E_{25}$, Cells 754–758, mv.	− .18	− .12	− .05	.07	.14$_5$
$E_t - E_{25}$, Tables I and II, mv.	− .17	− .13	− .09	.07	.14

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[4] See Cells 659–660 made by Priepke and Vosburgh, THIS JOURNAL, **55**, 1803 (1933). These cells are in use at present as reference standards, along with a number of cells made with sulfuric acid.

[5] Clayton and Vosburgh, *ibid.*, **58**, 2093 (1936).

the cells of Tables I and II. Addition of these two series of electromotive forces gives the values in the last line of Table III.

The relation between electromotive force and temperature can be expressed within 0.02 mv. by the equation $E_t = E_{25} + 0.000013(t - 25)$. However, the relation is not exactly linear and an additional term would improve the equation. The temperature coefficient, 0.000013, is less than one-third of the average temperature coefficient of the Weston cell between 20 and 30°.

The lag in adjustment to equilibrium after a decrease in temperature was about the same as has been observed in regular Weston cells. An exact comparison cannot be made, because no Weston cells were made of the same materials.

There is no apparent reason why the cell of Table III should be less constant or less reproducible than the saturated Weston cell. If experience shows this to be the case, the new cell should be superior to the unsaturated Weston cell as a practical standard for use at room temperature. Its temperature coefficient is small enough so that a change in temperature of 8° is required for 0.01% change in electromotive force,[6] and a temperature correction may be applied, if desired. Its electromotive force is within the customary range for unsaturated cells. It is planned to continue the study of this cell and also to construct some similar cells with other added salts in the hope of finding a cell still better adapted for use as a practical standard at room temperature.

Summary

Substitution of cadmium–bismuth amalgam for the cadmium amalgam of the Weston cell and saturation of the electrolyte with the double salt of sodium and cadmium sulfates as well as with cadmium sulfate gives a cell with an electromotive force of 1.0184 v. at 25° and a temperature coefficient of 0.000013 v. per degree.

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(6) An unsaturated cell may be expected to decrease 0.01% in electromotive force in the course of one to three years: (a) Vosburgh, *J. Optical Soc. Am.*, **11**, 59 (1925); (b) Smith, *Rev. Sci. Instruments*, **5**, 425 (1934).

DURHAM, N. C. RECEIVED MAY 5, 1937

[CONTRIBUTION FROM THE NEW YORK STATE AGRICULTURAL EXPERIMENT STATION]

Further Phase Rule Studies of the Calcium Arsenates[1]

BY G. W. PEARCE AND A. W. AVENS

In a previous paper[2] the equilibrium conditions in the system $CaO–As_2O_5–H_2O$ at 90° are described. Since the calcium arsenates exhibit a negative coefficient of solubility and most of them are hydrolyzed readily, it was believed that the system would be quite different at other temperatures. Accordingly the present paper deals with the equilibrium conditions in the system $CaO–As_2O_5–H_2O$ at 35°. The study has been confined to the more basic part of the system in which Smith[3] and others[4] apparently were unable to reach equilibrium.

Experimental

The methods of analysis and their limitations as well as the apparatus and reagents are the same as described in the report on the system at 90°.[2] In that study a technique was developed for rapid attainment of equilibrium. The same technique has been applied to the system at 35°.

Using the data obtained at 90°[2] as a basis for calculating the approximate concentrations required, preliminary experiments at 35° were carried out. Samples were prepared in one-liter, wide-mouthed, Pyrex Erlenmeyer flasks by adding a saturated solution of lime to a solution of arsenic acid partially saturated with lime and cooled to about 10°, until the first perceptible precipitation occurred. The samples were brought to a volume of about 600 cc., placed in a constant temperature bath maintained at 35 ± 0.1°, and connected to the multiple stirring device previously described.[2] After remaining in the bath with intermittent stirring for periods of five to ten days, the samples were removed and examined according to the procedure used for the study at 90°.[2]

The results of the preliminary runs were used in calculations for confirmatory experiments. In the latter instance the proportions of lime, arsenic acid and water were calculated so that known amounts of solids would precipitate at 35°. The samples were made up at room temperature because as a rule no precipitation occurred until they were brought to 35°. In the few cases where partial precipitation occurred before placing in the bath, the results indicated that no error was introduced, probably because there is no great difference in the system at room temperature

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(1) Approved by the Director of the New York State Agricultural Experiment Station for publication as Journal Paper No. 200, April 15, 1937.

(2) Pearce and Norton, THIS JOURNAL, **58**, 1104 (1936).

(3) Smith, *ibid.*, **42**, 259 (1920).

(4) Clifford and Cameron, *Ind. Eng. Chem.*, **21**, 69 (1929).