of vaporization of bismuth, it was impossible to evaluate the term $[(\Delta U_1^0)^{1/2} - (\Delta U_2^0)^{1/2}]^2$. However, as a test for regular solution behavior, the quantity "b" was calculated from the experimental data and its approximate constancy with variation of composition demonstrated. The results of these calculations are given in Table XI and plotted in Fig. 7. Also, it may be shown that from the above $dE_1/dT = -R/nF \ln N_1$ for regular solutions; that is, the slope of the electromotive force–temperature curve should be a function of composition only. This is true for the lead–bismuth liquid alloys, as shown by the values in Table XII.

TABLE XI

N_2	N_2^2	a_1/N_1	$\log_{10} a_1/N_1$	"b"
0.152	0.023	0.989	−0.0048	− 666
.280	.079	.950	− .0223	− 911
.400	.160	.880	− .0555	−1112
.504	.254	.803	− .0953	−1202
.586	.343	.734	− .1345	−1255
.672	.452	.677	− .1694	−1202
.770	.594	.604	− .2190	−1182
.889	.792	.519	− .2848	−1153

TABLE XII

N_2	$\log_{10} N_1$	dE/dT, calcd. volts/°C. × 10^6	dE/dT, obsd. volts/°C. × 10^6
0.152	−0.0716	7.2	7.4
.280	− .1427	14.2	14.4
.400	− .2218	22.0	20.8
.504	− .3045	30.2	27.8
.586	− .3830	38.0	37.6
.672	− .4841	48.0	46.4
.770	− .6383	63.3	64.4
.889	− .9547	94.7	102.0

Summary

1. Methods of calculation have been presented whereby thermodynamic data can be used to establish accurately the conditions of phase equilibria in binary systems.

2. The activities and relative partial molal heat contents of lead and bismuth in their liquid alloys have been determined, and it is shown that the alloys may be classified as regular solutions.

3. The activities and relative partial molal heat contents of lead in solid solutions of lead and bismuth have been determined accurately up to 20% bismuth, and the approximate activities have been established from 22.5 to 33% bismuth.

4. The eutectic composition and temperature are fixed at 54.7 atomic per cent. bismuth and 125°. The compositions of the two solid phases comprising the eutectic solid have been found to be 36.5 atomic per cent. bismuth and practically pure bismuth.

5. The liquidus curve on the bismuth side of the eutectic and the solidus on the lead side up to 20% bismuth have been calculated.

6. The indicated existence of a peritectic at 184° on the lead side of the system has been verified by thermal analysis.

7. A revised phase diagram of the system is presented.

PITTSBURGH, PENNA. RECEIVED JUNE 22, 1936

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Zinc and Zinc Amalgam Electrodes

BY WILLIAM J. CLAYTON AND WARREN C. VOSBURGH

The difference of potential between zinc and saturated zinc amalgam electrodes in a solution containing zinc ion was considered by Cohen in 1900 to be practically zero.[1] This conclusion was based partly on the results of earlier workers and partly on some measurements of his own. The results of the latter measurements, given in a footnote in the same article[1] (pp. 618–619), are 0.570 mv. at 25° and 0.488 mv. at 0° for the cell

$$\text{Zn(s)/Zn}^{++}\text{/Zn (satd. amalgam)} \qquad (1)$$

On the basis of these results Scatchard and Tefft[2] and Shrawder, Cowperthwaite and La Mer[3] used the value 0.6 mv. at 25° in the calculation of the normal electrode potential of zinc. Puschin[4] found a value of about −2 mv. for cell 1. Garner, Green and Yost[5] have assumed that the electromotive force of cell 1 is zero.

In this investigation the electromotive force of cell 1 has been found to be zero. A similar cell in which a superficially amalgamated zinc electrode was substituted for the pure zinc electrode was found to have zero electromotive force also. The

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[1] Cohen, *Z. physik. Chem.*, **34**, 612 (1900).

[2] Scatchard and Tefft, THIS JOURNAL, **52**, 2280 (1930).

[3] Shrawder, Cowperthwaite and La Mer, *ibid.*, **56**, 2348 (1934).

[4] Puschin, *Z. anorg. Chem.*, **63**, 230 (1903).

[5] Garner, Green and Yost, THIS JOURNAL, **57**, 2055 (1935).

latter would be expected because Clark cells made with superficially amalgamated zinc electrodes agree in electromotive force with those made with saturated amalgam electrodes, as pointed out by Cohen[1] (p. 613).

Materials and Apparatus.—Mercury was purified by washing with a solution of nitric acid and mercurous nitrate and distilling in a current of air. Zinc sulfate was recrystallized. The zinc chloride used was of the best commercial grade. Most of the zinc used was the best grade of commercial stick zinc, but a few measurements were made with some spectroscopically pure zinc which the Research Division of the New Jersey Zinc Company kindly furnished, and a few with strips of sheet zinc intended for standardizing. The treatment of the stick zinc in making the electrodes was found to be of considerable importance, and is described below. Zinc amalgam containing 5% of zinc was prepared electrolytically with stick zinc as the anode and zinc chloride as the electrolyte.

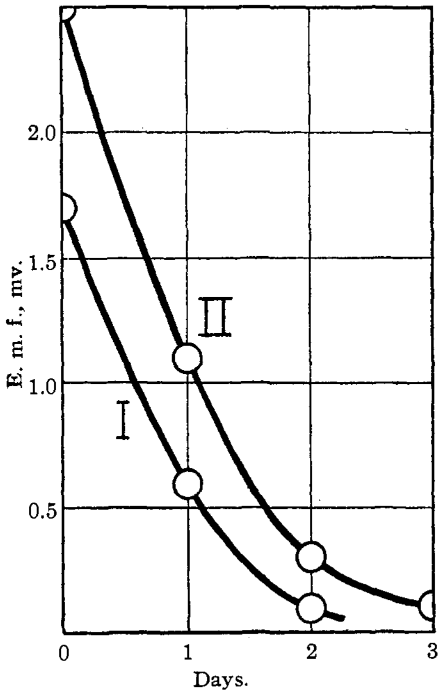

Fig. 1.—Electromotive force of the cell Zn(stick)/Zn^{++}/Zn (Hg) when the stick zinc electrode has been immersed in acidified zinc chloride solution from one to three days.

Zinc sulfate solution for use in the cells was made by dividing a solution containing 20 g. per liter of hydrated zinc sulfate in two equal parts, digesting one part with precipitated zinc hydroxide, filtering off the excess and reuniting the two parts. Zinc chloride solution for use in the cells was prepared by dissolving 20 g. of anhydrous zinc chloride per liter with the addition of enough hydrochloric acid to prevent precipitation of basic material and digesting with zinc oxide. Zinc acetate solution was prepared in the same manner as the zinc chloride solution, using 20 g. of hydrated zinc acetate per liter.

Nitrogen was prepared by passing air through four bottles of ammoniacal cuprous chloride solution.[6] The solution in the last bottle remained colorless.

Preparation of Zinc Stick Electrodes.—Most of the zinc sticks used as pure zinc electrodes were annealed, and all were treated as described below with an acidified solution of zinc chloride. Annealing was accomplished by sealing the zinc inside a glass tube and heating it in a muffle furnace to a temperature near or in some cases above the melting point, and cooling very slowly. The treatment with an acidified zinc chloride solution was best carried out in the following manner. The zinc sticks were immersed in a concentrated zinc chloride solution (200 g. of anhydrous zinc chloride to 100 ml. of water) and concentrated hydrochloric acid was added until hydrogen was generated uniformly over the surface of the zinc. Additional small portions of acid were added from time to time (about six or seven times a day) to keep the reaction going slowly.

To show the changes taking place during the treatment with acidified zinc chloride solution, the treatment of eight zinc sticks was interrupted at one-day intervals and the difference of potential between the sticks and zinc amalgam electrodes was determined by the procedure described below. The results are shown in Fig. 1. Curve I shows the change in the average electromotive force as the treatment progressed for four annealed electrodes and curve II for four unannealed electrodes. In two days for the annealed electrodes and three days for the unannealed the electromotive force had fallen to about 0.1 mv. Experience with other electrodes showed that a further slow decrease goes on for two to three weeks, after which no further change takes place, and the electrodes are in very good agreement with each other.

It is shown in Fig. 1 that for commercial stick zinc the annealing process is of less importance than the treatment with the acidified zinc chloride solution. Occasionally unannealed electrodes had to be rejected for disagreement with the others, but annealed electrodes could always be brought to excellent agreement. The annealing was essential for electrodes cast in the laboratory in Pyrex tubes.

Some of the spectroscopically pure zinc was treated with acidified zinc chloride solution, and some was not treated, but used for electrodes as received. No attempt was made to anneal it.

Superficially amalgamated zinc electrodes were prepared by immersing zinc sticks about 0.5 cm. in diameter to a depth of 4 cm. in 0.1 *M* hydrochloric acid solution at 40° and touching them to three or four small droplets of mercury about 1 mm. in diameter. By rubbing two sticks together the spreading of the mercury over the surface was hastened. No annealing or other treatment was necessary.

Preparation of the Cells.—Figure 2 is a diagram of the cell vessel used, with the electrodes in place. Stick electrodes, either of pure or superficially amalgamated zinc, were soldered to brass rods of small diameter which were passed through one-holed rubber stoppers. The strips of sheet zinc were treated similarly. A clean, dry cell vessel was connected by means of the tube projecting downward from the cross-arm to the three-way stopcock of the

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[6] Van Brunt, THIS JOURNAL, **36**, 1448 (1914).

apparatus shown in Fig. 3, using a rubber tube for a connector. The cell vessel was stoppered and evacuated and filled with nitrogen. Some amalgam was washed with dilute acid and water, then dried and heated to a temperature near its boiling point. It was then passed through a small hole in a filter paper into the two legs of the cell vessel, with a stream of nitrogen flowing to protect from oxidation. The stick electrodes which had been treated as described above were next washed with dilute hydrochloric acid, water and alcohol and then quickly placed in an empty cell vessel, the rubber stoppers fitting tightly in the tops of the vertical tubes. The vessel was immediately evacuated and the alcohol all evaporated. The electrodes were then transferred to the cell vessel containing the amalgam electrodes. The cell vessel was evacuated for at least forty-five minutes by means of an efficient vacuum pump:[7] Then some zinc sulfate solution was allowed to flow into the flask of the apparatus of Fig. 3. The low pressure caused it to boil, expelling dissolved gases. By allowing air to enter the flask, part of the solution was forced into the cell vessel. The vessel was filled to the lower part of the stick electrodes, then the three-way stopcock was turned to allow the entrance of nitrogen. Care was taken that no nitrogen bubbles stuck to the electrodes, as these seemed to cause disagreement. The cell was removed from the apparatus of Fig. 3 by closing the rubber tube connection by means of a screw clamp and disconnecting from tube A. Some of the cells were placed in a constant-temperature air-bath for measurement, and some were measured at room temperature.

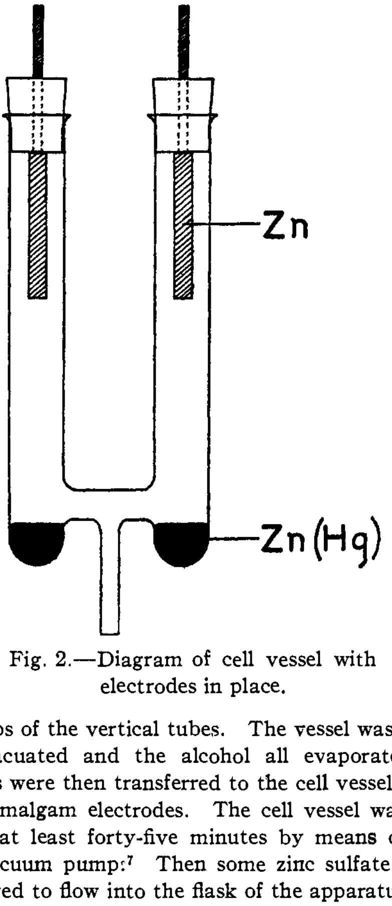

Fig. 2.—Diagram of cell vessel with electrodes in place.

The spectroscopically pure zinc was used in the form of irregular chunks as received. Chunks of the proper size were soldered to platinum wires which at the opposite ends were sealed into glass tubes. The level of the electrolyte was adjusted so that only part of the zinc electrode was immersed and the platinum wire did not touch the electrolyte.

Electromotive Force Measurements.—In the best cells, as soon as temperature equilibrium was attained, the electromotive force became constant at a value very near zero for all combinations of the electrodes and remained so indefinitely. As an example of the agreement obtainable between similar electrodes, the potential difference between pure zinc stick electrodes averaged 0.01 mv. for eight pairs, between amalgamated stick electrodes 0.006 mv. for five pairs, and between amalgam electrodes 0.006 mv. for eight pairs. Average potential differences between zinc and amalgam electrodes in cells in which the electrolyte was zinc sulfate are given in Table I. A positive value indicates that the zinc electrode was negative. In giving the number of cells, each cell as described above is counted as two, since it contained two of each kind of electrode. For cells with pure zinc electrodes the average deviation from the mean value in the table was 0.01 mv. and for the amalgamated stick electrodes the average deviation was 0.003 mv.

It was found that a zinc chloride solution or a zinc acetate solution if prepared as described above could be used in the cells in place of the zinc sulfate solution. The results so obtained were practically the same as those shown in Table I, and need not be given in detail.

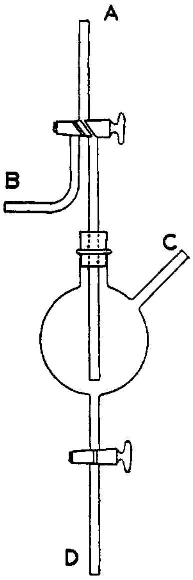

Fig. 3.—Apparatus used in evacuating the cell vessels and introducing the electrolyte without contact with air. The cell vessel was connected at A. Tube B was connected with a source of nitrogen, and tube C with either a vacuum pump or the atmosphere by means of a three-way stopcock. The electrolyte was introduced through D.

The strips of sheet zinc as purchased were covered with grease. Washing with alcohol (without further treatment) gave electrodes that were positive toward amalgam to the extent of 3.5 to 4.5 mv. Washing the same strips with ether left a surface that still seemed to be greasy but

TABLE I

ELECTROMOTIVE FORCE OF THE CELL Zn(s)/Zn^{++}/Zn (SATD. AMALGAM)

Zinc electrode	No. of cells	Average, e. m. f. 20°	25°	30°
Amalgamated stick	18	−0.002	0.002	0.001
Annealed stick	12	.000	.005	.002
Unannealed stick	4	.02	.01	.01
Spectroscopic (treated)	4	...	.005	.001
Spectroscopic (untreated)	4	...	− .002	− .005

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(7) The evacuation is an important part of the process. When properly carried out equilibrium was reached in the cells as soon as the temperature became uniform. When a water pump was used for the evacuation more time was required for equilibrium, but about 80% of the cells came to excellent agreement within three or four days.

lowered the potential difference to about 0.5 mv. Immersion of the ether-washed electrodes in very dilute hydrochloric acid solution resulted in potential differences within 0.1 mv. of zero against amalgam electrodes. On greasing these electrodes with petrolatum the performance could be repeated.

The zinc strip electrodes could not be treated successfully with an acidified zinc chloride solution because the dissolution of some of the zinc left the strip so fragile that it was difficult to avoid bending it in subsequent operations. Bending caused an electrode potential considerably more negative than that of the amalgam, as might be expected.

The Normal Electrode Potential of Zinc.—The electromotive force of cell 1 is shown to be zero within the rather narrow limits of experimental error. A correction of −0.6 mv. is therefore necessary to the values for the electrode potential of zinc given by Scatchard and Tefft and Shrawder, Cowperthwaite and La Mer. Application of this correction makes better agreement between these two values and the value of Getman[8] which was obtained from cells with pure zinc electrodes. The three values are as follows:

Scatchard and Tefft (corr.)	0.7610 v.
Getman	.7613
Shrawder, Cowperthwaite and La Mer (corr.)	.7614

Additional Observations.—Of the three kinds of zinc electrode, namely, pure zinc, amalgamated zinc stick and zinc amalgam, the first is the most troublesome to prepare in a highly reproducible condition. The amalgamated stick electrode is easy to prepare and handle, and gives the same potential difference against a zinc salt solution as a pure zinc electrode when measured as described above. For some purposes this electrode might be preferable to amalgam electrodes. Amalgamated electrodes rubbed with filter paper for the purpose of spreading the mercury over the zinc surface were found to be about 0.2 more negative than zinc amalgam when first put in contact with an electrolyte in the presence of air. This value persisted for some time when the electrolyte contained a small amount of free acid, but when the electrolyte had been treated with zinc oxide or hydroxide the electromotive force soon dropped to zero.

Sticks of pure zinc prepared as described above when partially immersed in a 60% slightly acidified zinc chloride solution in contact with air agreed within 0.02 mv. However, when such a solution was used as a cell electrolyte, with exclusion of oxygen, the agreement of the zinc electrodes was poor.

Zinc salt solutions containing added acid, or even the quantity of acid resulting from hydrolysis, gave erratic results in the cells. The treatment of the solutions with zinc oxide as described above was necessary for the best results. The disturbing effect of acid was less in the presence of air than in its absence.

Twelve cells with amalgamated stick electrodes prepared with slightly acid electrolytes and with fairly good protection from air differed rather widely for some time, but after four months the electromotive forces were between −0.01 and +0.05 mv.

The introduction of hydrogen into a cell in place of nitrogen caused the pure zinc electrodes to be more positive than the amalgams by 0.2 to 0.3 mv. When bubbles stuck to the electrode the values were a little higher. Air when introduced caused a large temporary effect and a more or less permanent effect of the same order of magnitude as that of hydrogen. A few cells were allowed to come to thermal equilibrium and measured before the introduction of the nitrogen. These gave the same values as after the introduction of nitrogen, showing that nitrogen has no effect on the electrodes. This seems to disagree somewhat with Getman's[9] conclusion on the effect of nitrogen.

Finely divided zinc samples prepared both by electrolysis and by reduction by magnesium and also zinc deposited by electrolysis on platinum wires were tried. A few samples of the finely divided zinc came to good agreement with the stick electrodes. Most of the difficulty was probably in washing this zinc properly. The zinc deposited on platinum wires was always positive with relation to the other electrodes.

Summary

The electromotive force of the cell Zn(s)/Zn^{++}/Zn (satd. amalgam) is zero. The symbol Zn(s) may be understood to stand for either a pure zinc electrode or a superficially amalgamated zinc electrode, these two having the same electrode potential.

DURHAM, N. C. RECEIVED AUGUST 3, 1936

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[8] Getman, *J. Phys. Chem.*, **35**, 2755 (1931).

[9] Getman, *ibid.*, **36**, 2662 (1932).