

[CONTRIBUTION FROM THE WOLCOTT GIBBS MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

THE ELECTROCHEMICAL BEHAVIOR OF LIQUID SODIUM AMALGAMS

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The significance of the electrochemical behavior of amalgams in relation to the general behavior and nature of solutions as well as in relation to the laws of thermodynamics has already been often emphasized. The literature upon the subject is copious, and lack of space prevents a detailed review. Some of the more important papers are named in the accompanying list, in which the several Harvard investigations upon this subject during the last 23 years are placed at the conclusion.¹

Sodium amalgam presents points of especial interest not only because the substance is so much used as a reducing agent, but also because the great affinities involved might lead one to expect extreme deviation from the simple concentration laws. Moreover, conflicting data concerning it have been published, without as yet having been reconciled.²

Accordingly the careful investigation of sodium amalgam was undertaken some years ago. The electrochemical part was finished early in 1916; the thermochemical part, which will soon be published, was studied with the help of Mr. John Russell in 1921.

¹ Tammann, *Z. physik. Chem.*, **3**, 441 (1889). Ramsay, *J. Chem. Soc.*, **55**, 521 (1889). Von Türin, *Z. physik. Chem.*, **5**, 340 (1890). Meyer, *Wied. Ann.*, **40**, 244 (1890). Meyer, *Z. physik. Chem.*, **7**, 477 (1891). Kerp, *Z. anorg. Chem.*, **17**, 284 (1898); **25**, 1 (1900). Cady, *J. Phys. Chem.*, **2**, 551 (1898); **3**, 107 (1899) (corr.). Schoeller, *Z. Elektrochem.*, **5**, 259 (1898). Maey, *Z. physik. Chem.*, **29**, 119 (1899). Kurnakov, *Z. anorg. Chem.*, **23**, 439 (1900). Haber, *Z. physik. Chem.*, **41**, 399 (1902). Haber and Sack, *Z. Elektrochem.*, **8**, 245 (1902). Schüller, *Z. anorg. Chem.*, **40**, 385 (1904). G. McP. Smith, *Am. Chem. J.*, **36**, 124 (1906); **37**, 506 (1907); **38**, 671 (1907). Von Wogau, *Ann. Physik.*, **23**, 345 (1907). Smith, *Z. anorg. Chem.*, **58**, 394 (1908). G. A. Hulett and DeLury, *THIS JOURNAL*, **30**, 1805 (1908). Smith and Bennett, *THIS JOURNAL*, **32**, 622 (1910). K. Bornemann and others, *Metallurgie*, **7**, 396 (1910); **9**, 473 (1912); Lewis and Kraus, *THIS JOURNAL*, **32**, 1459 (1910). Vanstone, *Chem. News*, **103**, 181 (1911); *J. Chem. Soc.*, **105**, 2617 (1914). Hildebrand and Eastman, *THIS JOURNAL*, **36**, 2020 (1914); **37**, 2452 (1915). MacInnes and Parker, *ibid.*, **37**, 1451 (1915). Richards and Lewis, *Proc. Am. Acad.*, **34**, 87 (1898). Richards, Wilson and Garrod-Thomas, *Carnegie Inst. Pub.*, **118**, 1 to 72 (1909). Richards and Daniels, *Trans. Am. Electrochem. Soc.*, **22**, 343 (1912); *THIS JOURNAL*, **41**, 1732 (1919).

A fairly complete historical account of the earlier work is found in the paper by Richards and Forbes, *Carnegie Inst. Pub.*, **56**, 1 (1906). This has been brought up to 1918 in the thesis presented for the doctor's degree to the Faculty of Arts and Sciences of Harvard University by Farrington Daniels, June, 1918.

² Meyer, *Wied. Ann.*, **40**, 244 (1890). Cady, *J. Phys. Chem.*, **2**, 551 (1898); with correction, **3**, 107 (1899). Schoeller, *Z. Elektrochem.*, **5**, 259 (1898). Haber and Sack, *ibid.*, **8**, 245 (1902). Lewis and Kraus, *THIS JOURNAL*, **32**, 1459 (1910).

The Preparation of Substances

After several rather unsuccessful attempts, the method of preparing the sodium amalgams from mercury and the solid metal used by Lewis and his collaborators³ and MacInnes and Parker⁴ was rejected as inconvenient and the amalgam was prepared by electrolysis.⁵ A saturated solution of pure sodium carbonate (four times recrystallized and centrifuged) was electrolyzed in a cell consisting of an ample mercury cathode and an anode of platinum foil; a wide-mouthed half-liter bottle served as the container. After passing a current of 4 amperes for a few hours, the amalgam became pasty and the process was stopped. The electrolyte was poured off as completely as possible and the amalgam was thoroughly agitated with 4 or 5 fresh portions of distilled water and subsequently with 2 portions of alcohol. It was transferred to a small flask which was evacuated and heated for some minutes. Having been thus dried, it was placed while still hot in a desiccator where it remained until it was diluted, filtered through a capillary tube (which eliminated the film of hydroxide) and transferred directly to the electrodes, as described below.

The sodium hydroxide solution used as electrolyte in the measuring cells was prepared from pure sodium amalgam and water, the action being hastened by making the amalgam the anode in a suitable cell. This solution was approximately 0.5 N.

Mercury was purified by repeatedly dropping it in a fine stream through a solution of mercurous nitrate and nitric acid. It was subsequently distilled in a current of air and then in a current of pure hydrogen.

Hydrogen was prepared by the electrolysis of dil. sodium hydroxide solution, and was passed through a tower of glass beads covered with sodium hydroxide solution, through a hot tube containing platinized asbestos, over solid potassium hydroxide and finally over phosphorus pentoxide.

The Cell and Its Manipulation

The cell previously used by one⁶ of us could not be used in this research because of the rapid action between sodium amalgam and aqueous solutions. There were two alternatives,—either to work in an anhydrous medium or to use an aqueous electrolyte and circumvent the action of the amalgam on the water by the use of a special form of electrode. The first alternative had been chosen by Cady and Haber, the second by Meyer, Schoeller, and MacInnes and Parker, while Lewis used both methods.⁷ To us the second alternative seemed to be the most convenient. Lewis's

³ G. N. Lewis and Kraus, Ref. 1.

⁴ MacInnes and Parker, *THIS JOURNAL*, **37**, 1451 (1915). They prepared potassium not sodium amalgam.

⁵ After this method had been elaborated, Lewis, Adams and Lanman published a somewhat similar method, having abandoned the earlier process. *THIS JOURNAL*, **37**, 2656 (1915).

⁶ Richards and Forbes, *Carnegie Inst. Pub.*, **56** (1906).

⁷ Lewis and Kraus, Ref. 1.

electrode was consequently taken as a model; numerous modifications of it were tried before a satisfactory apparatus was obtained.

We found that the cell must meet the following requirements: (1) each amalgam should be measurable against several other amalgams; (2) each amalgam should be held in a protecting container, which should always deliver an amalgam of the same composition for potential measurements and for analysis; (3) the two amalgam surfaces between which the potential is being measured should be constantly changing, and the movements of the two surfaces should be as nearly as possible synchronous.

These specifications were fulfilled by a cell composed of two electrodes constructed as shown in the accompanying illustration.

Each electrode (Fig. 1) had its own reservoir of amalgam and was provided with a side-tube B and a leveling bulb A containing mercury which ensured sufficient pressure to cause the amalgam to flow out when desired. The capillary tube D was likewise filled with the amalgam, electrical contact being made by means of a sealed-in platinum wire and a side-tube E containing mercury. The shape of the orifice is of great importance, since with an ordinary opening there is a tendency for the amalgam to recede after each drop has been ejected, thereby drawing in small amounts of the electrolyte and also greatly changing the resistance of the cell. An excellent aperture (see Fig. 2) was obtained by allowing the end of the capillary tube to fall together in a flame and subsequently grinding away the glass until the top of the arch-shaped cavity was reached. A file-scratch was cut in each stopcock in the usual way, thus allowing the rate of egress of the amalgam to be easily and accurately adjusted. The stopcock was not greased in the middle, in order to avoid contaminating the amalgams.

Each electrode was filled in the following manner. Clamped horizontally and sealed to a larger glass vessel [(A) Fig. 3] by means of a 0.2 mm. capillary tube (C), it was dried when warm by a current of very dry air drawn through the apparatus for 20 minutes. The desired amalgam was next introduced through B into the large reservoir (A). This amalgam had been prepared by suitably diluting with pure mercury some of the semi-solid electrolytic amalgam, rough analyses having determined approximately the desired concentration. After the introduction of the amalgam through B into A, the whole system was attached to a pump at B and alternately evacuated and filled with pure hydrogen and finally partially evacuated. The electrode system was now turned through 180° around a lengthwise horizontal axis and slightly inclined, the amalgam thus collecting in one end of A. By allowing hydrogen to enter at B, the amalgam was forced through the capillary tube C into the reservoir of the electrode, thus being filtered from its film of hydroxide. When the electrode

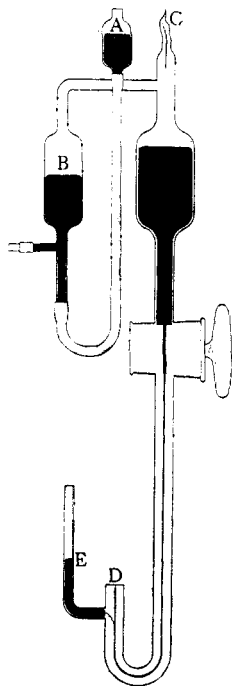


Fig. 1.—A single electrode, the amalgam being placed in C.

reservoir was full, the capillary tube was sealed off, the electrode returned to its normal vertical position, the apparatus filled with hydrogen through the projecting side-tube and mercury run into the leveling bulb. The capillary tube was next exhausted, dried, and completely filled with amalgam.

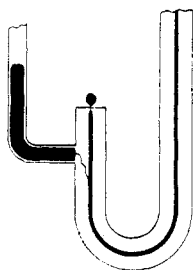


Fig. 2.—Detail of single electrode tip.

For the determination of the difference between their electromotive effects, two such electrodes were supported side by side in such a manner that the apertures at the ends of the capillary tubes were as close together as possible and about a centimeter below the surface of the electrolyte of pure sodium hydroxide solution which was contained in a half-liter beaker. Hydrogen was bubbled through the electrolyte, thus keeping it stirred and free from dissolved air. The temperature of the thermostat employed was held constant within 0.005° .

Lewis and Jackson,⁸ Walker,⁹ Baker¹⁰ and others have shown the great influence of traces of impurities upon the speed of reaction between water and sodium amalgam. By preparing pure sodium amalgam and pure sodium hydroxide it was hoped that this action might be made as slow as possible.

Preliminary measurements showed that when fresh globules of amalgam were allowed to form at each electrode and the surfaces then kept stationary, the potential between them was not constant for any length of time, but steadily increased. With amalgams containing more than 0.1% of sodium this increase was not more than 0.1 mv. in 5 or 10 minutes; but for more dilute amalgams the increase was so rapid that reproducible results with stationary electrodes could not be obtained. This

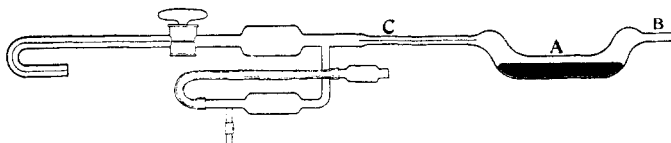


Fig. 3.—Method of filling electrode.

must be due to a greater *percentage* loss of sodium on the surface of dilute than on the surface of concentrated amalgams. In other words, the losses in sodium were more nearly identical in each case than were the original concentrations. Since the potential of the cell is a function of the *ratio* of the two concentrations, subtracting a nearly equal amount from both concentrations will increase the value of the ratio and consequently the observed electromotive force.

To obviate this change in potential and to enable the method to be used with amalgams of all concentrations, a device shown in Fig. 4 was

⁸ Lewis and Jackson, *Proc. Am. Acad.*, **41**, 403 (1906).

⁹ J. W. Walker and Paterson, *Trans. Am. Electrochem. Soc.*, **3**, 185 (1903).

¹⁰ Baker and Parker, *J. Chem. Soc.*, **103**, 2060 (1913).

employed. A glass rod was bent and supported in such a way that it could be moved across the tops of the capillary tubes simultaneously, brushing off the two globules of amalgam. In determining the electromotive force of the cell the stopcocks were turned so that the amalgams slowly issued at about the same rate from their respective openings. After the glass arm had moved across, brushing a way the drops which were forming, the subsequent drops on each electrode started at the same moment and formed at approximately the same rate. If the potential was measured during this time, a definite, constant electromotive force of the cell could be determined. Only by the use of this method could consistent and reproducible results be obtained with the very dilute amalgams. When the amalgams were allowed to drop slowly from the electrode and the potential was determined without the aid of the arm, the results varied appreciably. This was probably due to the fact that unless the drops on each electrode started at the same moment, a comparatively large old surface might be measured against a small new one. That the results obtained by this method are much better than results from standing or irregular drops is clear. Whether with the most dilute amalgams the results were wholly free from error due to solution of sodium is uncertain. In the case of the most concentrated, more safely measured, amalgams the values obtained were identical with potentials measured with a stationary surface, and are probably to be depended on within 0.05 mv. Moreover, it will be shown later that the results were thermodynamically consistent.

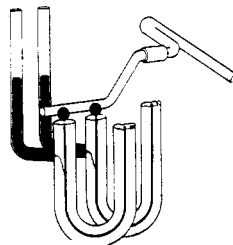


Fig. 4.—The details of two electrodes with arrangement for the removal of exuding drops synchronously.

The Analysis of the Amalgams

The method of analysis employed was in principle that employed in 1913 by one of us in collaboration with F. Daniels in the case of thallium,¹¹ and independently recommended by Lewis¹² in his recent paper on "The Electrical Transference in Amalgams."

After the rejection of the first 10 or 12 drops of amalgam (for obvious reasons, if the apparatus had been quiet for any considerable time) about 10 g. was run from the electrode into a previously weighed Erlenmeyer flask, which was then reweighed. A little more than the needed approximately known quantity of standardized 0.01667 *N* hydrochloric acid was run into the flask, which was again weighed, and the flask was stoppered and thoroughly shaken. Shaking was stopped as soon as the mercury broke up into minute permanent globules, showing complete extraction of the sodium.¹¹

¹¹ Richards and Daniels, *THIS JOURNAL*, 41, 1736 (1919). The publication was delayed by the war.

¹² Lewis, *ibid.*, 37, 2656 (1915).

The contents of the flask were now titrated with 0.0025 *N* barium hydroxide solution, the solution being stirred with a current of air free from carbon dioxide. Rosolic acid, used as the indicator gave an end-point within 0.1 cc. of hydroxide (or 0.00005 g. of sodium). Thus by using a 10 g. sample, an amalgam containing only 0.01% of sodium could be analyzed with an accuracy of about 0.5%. The barium hydroxide was standardized against carefully prepared 0.01 *N* oxalic acid. Duplicate analyses of amalgams (never more different than 0.5% and usually within 0.1%) were always made.

The Measurement of Electromotive Force

The potentiometer was a recent model Wolff instrument of the best quality. Actuated by two large dilute cadmium cells (according to Hulett), it was standardized by a number of other carefully prepared Weston cells (taken as 1.0184 volt -0.00004 ($t - 20^\circ$) volt) and used with a sensitive Leeds and Northrup d'Arsonval galvanometer. Incidentally, the potentiometer was compared with that used in the earlier work on thallium amalgams, and the two were found to give identical values (within a reasonable very small limit of error) for several zinc amalgam cells. Thus the two instruments mutually confirmed one another.

The potential of each sodium amalgam cell was determined by a series of approximations. The potentiometer having been set at nearly the potential to be measured, the amalgams were allowed to flow, and immediately after the electrode surfaces had been brushed with the arm, the galvanometer circuit was closed and the deflection noted. This procedure was repeated until two settings of the potentiometer were found that caused equal but opposite deflections of the galvanometer; the true electromotive force was taken as the mean of these two readings, which were usually about 0.00005 volt apart. To secure exact results the galvanometer circuit must be closed at the moment when fresh globules simultaneously start to form on both electrodes.

Summary of Results

The potentials of all the cells which were measured satisfactorily at 25° according to the procedure as described above are given in Table I. Three preliminary electrodes (6, 8, 12) containing very dilute amalgam, and measured before the technique for dilute amalgams had been mas-

TABLE I
MEASUREMENTS OF E.M.F. AT 25.00°

For the concentrations of the various amalgams see Table III

Cell composed of electrodes Nos.	E.m.f. at 25.0° Mv.	Cell composed of electrodes Nos.	E.m.f. at 25.0° Mv.
4-5	52.58	16-17	4.99
7-5	36.10	15-17	14.73
9-10	56.45	18-19	57.14
13-11	33.80	19-16A	46.36
13-14	42.18	18-16A	103.50
14-15	12.82	18-20	35.77
13-15	54.93	20-21	53.12
15-16	9.74	21-22	19.43

tered, were rejected. They gave values 1.5 mv. greater than Nos. 17 and 22.

The consistency of the results was confirmed in the usual way by comparing the values of three electrodes measured in pairs. Typical results are given below. In no case was the difference between the sum of A-B and B-C, and the observed value of A-C greater than 0.08 mv., and it was usually less than 0.05.

TABLE II
COMPARISON OF VALUES
E.m.f. in millivolts

Electrode Nos.	E.m.f. in millivolts			IV Sum I + II	Difference III-IV
	I A → B	II B → C	III A → C		
15, 14, 13	12.82	42.18	54.93	55.00	-0.07
17, 16, 15	4.99	9.74	14.73	14.73	-0.00

From the values in Table I a consistent table of all the electromotive forces may obviously be built up in the usual way, basing all upon the most concentrated amalgam.¹³ These values (π_2) are given in the fifth column of Table III, the concentrations of each amalgam being recorded in the second column of this table. The fourth column gives the potentials which would have been observed if the simple thermodynamic concentration-equation

$$\pi_1 = \frac{RT}{F} \ln \frac{V_2}{V_1}$$

were fulfilled.

TABLE III
ELECTROMOTIVE FORCES
 V_2/V_1 , or
dilution in
terms of No. 9
Potential if No. 9=0
Calc.
 π_1
Obs.
 π_2
 $\Delta\pi$
Difference

Electrode No.	Na in amalgam %	V_2/V_1 , or dilution in terms of No. 9	Potential if No. 9=0 Calc. π_1	Obs. π_2	$\Delta\pi$ Difference
9	0.551
18	0.416	1.323	7.18	17.15	9.97
4	0.393	1.403	8.68	20.63	11.95
7	0.2895	1.903	16.51	37.11	20.60
20 ^a	0.1978	2.790	26.32	[52.92] ^a	[26.60] ^a
13 ^a	0.1862	2.960	27.83	[55.54] ^a	[27.70] ^a
10	0.1815	3.035	28.47	56.45	27.98
5	0.1174	4.69	39.65	73.21	33.56
19	0.1102	5.00	41.30	74.29	32.99
11	0.0707	7.795	52.69	89.34	36.65
14	0.0533	10.33	59.89	97.65	37.76
21	0.0396	13.90	67.51	106.04	38.53
15	0.0344	16.00	71.12	110.47	39.35
16	0.0240	22.98	80.41	120.20	39.79
16A	0.0236	23.35	80.83	120.65	39.82
17	0.0200	27.55	85.07	125.20	40.13
22	0.0197	27.95	85.45	125.47	40.02

^a The values for $\Delta\pi$ for electrodes Nos. 13 and 20 were found by interpolation from the other results; π_2 was then found by adding $\Delta\pi$ and π_1 .

¹³ See Ref. 6, pp. 35, 43.

The figures in the last column of the foregoing table, which give the differences ($\Delta\pi$) between the observed potentials (π_2) and the theoretical but obviously inadequate concentration effects (π_1) are at first more than half the observed value, the deficiency of the theoretical e.m.f. being almost exactly half the observed value between concentrations 0.55 and 0.19% by weight (or 4.7 and 1.65 atom-per cent.) This deficiency is considerably larger even than in the case of thallium,¹⁴ where the deficiency of the theoretical e.m.f. for a similar atom-per cent. relation was only about one-quarter instead of only half of the observed value. Evidently where great affinities are involved, as in the case of sodium and mercury, the concentration law is a very poor guide to potential. This matter will be considered in detail later.

The observed values were plotted in the accompanying diagram, (Fig. 5), by first laying down 9, and 10, then 4 to 12, and finally placing 13 on the curve of the first series in a locus determined by its concentration. This is the graphic equivalent of the method used in constructing Table III. Evidently the results are very consistent: The points form a smooth and

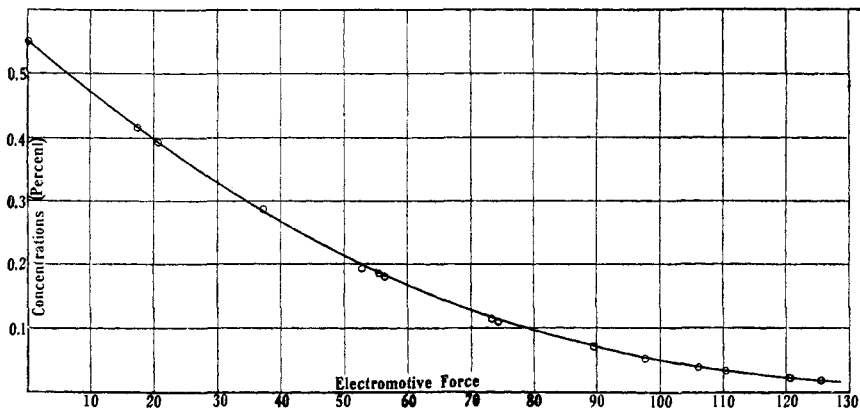


Fig. 5.—Graph of electromotive force between amalgams.

continuous curve. On the whole they seem to be quite as good as could be expected in an aqueous electrolyte with so reactive a substance as sodium amalgam.

On comparing these results with the few earlier values obtained by Meyer² and by Cady,² a fair degree of agreement between them all is found, although at the time the early values appeared to be mutually inconsistent. Cady's two cells gave potentials of 91 and 95 millivolts, respectively, whereas our corresponding values (found from the curve) are 93.5 and 99.8 respectively. Meyer's single crude measurement gave 12 instead of our estimate 17.4.

¹⁴ Richards and Daniels, Ref. 11, p. 1740. Amalgams B and D.

The Temperature Coefficients

The temperature coefficients of 4 cells were determined by measuring their electromotive forces at 15°, 25°, and 35°. By making all the measurements on each cell within a few hours, possible errors due to changes

TABLE IV
EFFECT OF TEMPERATURE ON E.M.F.

Electrodes Nos.	Electromotive force of the cell in millivolts			$\Delta\pi/\Delta T$		Average
	15°	25°	35°	15-25°	25-35°	
	18-20	34.84	35.77	36.67	0.156	
18-19	55.82	57.38 ^a	58.92	0.093	0.090	0.0915
20-21	51.48	53.12	54.73	0.164	0.161	0.1625
21-22	18.84	19.43	20.05	0.059	0.063	0.061

^a A different value from that given in Table I. The measurements above were made some days later, Amalgam 19 having slightly changed in concentration.

in concentration of the amalgams were avoided. The agreement between the value of the temperature coefficient as calculated from 15° to 25° and from 25° to 35° was satisfactory, and affords further evidence of the accuracy of all the results. Table IV records the measurements.

That these values of $\Delta\pi/\Delta T$ are much smaller than those demanded by the perfect gas law is shown by the following table, which gives $\frac{\Delta\pi}{\pi_{25^\circ}\Delta T}$, a quantity which should equal 0.003355 if the perfect gas law held in the mercurial solution.

TABLE V
RATIO OF TEMPERATURE COEFFICIENTS TO POTENTIAL

Sodium in first amalgam C ₁ %	Sodium in second amalgam C ₂ %	Av. Value of $\Delta\pi/\Delta T$	$\frac{\Delta\pi}{\pi_{25^\circ}\Delta T}$
0.416	0.1978	0.0915	0.00260
0.416	0.1102	0.155	0.00264
0.1978	0.0396	0.1625	0.00306
0.0396	0.01972	0.061	0.00314

Evidently the temperature coefficient approaches perfect regularity as dilution increases; at the point where the potential itself corresponds to the concentration law, the temperature coefficient would doubtless equal that required by the law of Charles.

The Helmholtz Equation and the Heat of Transfer of Sodium

Aside from a few rough experiments of Berthelot¹⁵ and a few more of Cady² on heats of dilution, there has been no thermochemical study of sodium amalgams. It has been shown that these data are not directly applicable to the thermodynamic consideration of the electrochemical results, because the latter involve not dilution, but rather transfer of

¹⁵ Berthelot, *Ann. chim. phys.*, [5] 18, 442 (1879).

sodium from a more concentrated to a more dilute amalgam.¹⁶ The total energy change involved in this latter process may, of course, be calculated from the Helmholtz equation using the results tabulated above; in this case it is practically equal to the change in heat content. The following table records the values of

$$U = n\pi F - nFT \frac{\Delta\pi}{\Delta T}$$

TABLE VI
TOTAL ENERGY CHANGE

Sodium		π_{25}°	$\Delta\pi/\Delta T$	π/F	$FT \frac{\Delta\pi}{\Delta T}$	U in joules
C_1 %	C_2 %					
0.416	0.1978	0.03577	0.0000915	3451	2632	819
0.416	0.1102	0.05738	0.000155	5540	4459	1081
0.1978	0.0396	0.05312	0.0001625	5129	4674	455
0.0396	0.01972	0.01943	0.000061	1875	1755	120

These values have been confirmed by actual measurements of the heat of dilution of amalgams, which will be recounted in a later paper.

As would be expected the heat of transfer (U) decreases rapidly with increasing dilution. With concentrated solutions the amount of heat evolved is greater than for equivalent proportions (on the gram atom basis) of the other amalgams investigated in this laboratory. The amount of heat evolved in the transfer of a gram atom of thallium¹⁷ over the range corresponding to the first of the above cells is not over 650 joules instead of 819.

In 1898 Cady² proposed the following equation,

$$\pi = \frac{RT}{nF} \ln \frac{C_1}{C_2} + \frac{U}{nF}$$

This can be true only when the simple concentration law holds for the osmotic part of the effect, and when no change of heat capacity occurs.¹⁸ When combined with the Helmholtz equation, it gives the following relationship,

$$\frac{R}{nF} \ln \frac{C_1}{C_2} = \frac{\Delta\pi}{\Delta T}$$

an expression which gives a method of testing the Cady equation without determining U .¹⁹ A comparison of the two members of the above equation taken from the foregoing data is given in Table VI. Obviously in all cases except the most dilute solution the two members show considerable lack of equality. This is probably due chiefly to failure of the concentration law, but perhaps partly to the effect of changing heat capacity.

¹⁶ Ref. 11, p. 1761.

¹⁷ Ref. 11, p. 1760. The value is taken from the curve.

¹⁸ Richards, *Z. physik. Chem.*, **42**, 145 (1902); *Proc. Am. Acad.*, **38**, 308 (1902).

¹⁹ Richards, Wilson and Garrod-Thomas, Ref. 1, p. 59.

Here again the concentration law gives too small quantities. We are inclined to accept the often suggested explanation of hydrargyration of the dissolved sodium.

TABLE VII
CONCENTRATION EFFECT AND TEMPERATURE COEFFICIENTS

C_1	C_2	C_1/C_2	$\frac{R \ln C_1/C_2}{F}$	$\frac{\Delta \pi}{\Delta T}$
0.416	0.1978	2.109	0.0642	0.0915
0.416	0.1102	3.780	0.1145	0.1550
0.1978	0.0396	4.990	0.1380	0.1625
0.0396	0.01972	2.010	0.0600	0.0610

Further theoretical considerations are postponed until the thermochemical data are ready for publication.

We are greatly indebted to the Carnegie Institution of Washington for much of our apparatus.

Summary

1. Improvements have been effected in the electrolytic preparation and the subsequent manipulation of pure liquid sodium amalgam, as well as in the apparatus for the measurement of the electromotive force of sodium amalgam concentration cells with aqueous electrolyte.

2. The electromotive forces of many concentration cells of liquid sodium amalgam have been measured at 25° and a few cells also at 15° and 35°.

3. The deviations of these potentials from the simple concentration-law were found to be greater in sodium amalgam than with any other mercurial solution hitherto studied in detail.

4. The heats of transfer of sodium from one amalgam to another calculated by the Helmholtz equation, are found to be unusually large.

CAMBRIDGE 38, MASSACHUSETTS

NOTES

The Rapid Analysis of Potassium Perchlorate.—In reviewing the various methods proposed for the analysis of potassium perchlorate, it is noted that the only principle that has been successfully applied is that of heating the perchlorate, either alone or mixed with some other substance. In the practical application of the principle the loss by volatilization of the resulting potassium chloride is the greatest source of error.

The method of heating the perchlorate with manganese dioxide has given such satisfactory results that it has been thought worth while to record the procedure.

A 0.5g. sample of potassium perchlorate is intimately mixed in an agate mortar with 1.0 g. of manganese dioxide. The charge is transferred to a porcelain crucible and heated for 15 minutes at a temperature of 600–