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THE REDUCTION OF CADMIUM BY MERCURY AND THE ELECTROMOTIVE FORCE OF CADMIUM AMALGAMS.

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The present work was undertaken in order to get some idea of the equilibrium conditions in the system, mercury, cadmium sulphate and water. From the behavior of standard cells it seemed probable that mercury reduced a cadmium sulphate solution and formed a very dilute amalgam with an equivalant amount of mercury passing into the solution. It is known that silver will not completely reduce a mercury nitrate solution while mercury will displace some silver from solution and it has been found that a definite equilibrium is established from whichever side approached.[1] The equilibrium conditions have been expressed by the following relation, due to Nernst: $\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$ where P_1 and P_2 represent the solution pressures of the metals, p_1 and p_2 their ionic osmotic pressures and n_1 and n_2 their respective valencies. Where P_1 and P_2 are widely separated in the electrochemical series and P_2 is less than P_1 then the concentration of P_1 in the metal phase and P_2 in the electrolyte will be exceedingly small. This is the case under consideration and since electromotive forces depend upon relative and not absolute concentrations the electromotive force of very dilute cadmium amalgams seemed most likely to disclose the equilibrium point in question, or at least to give some idea of the equilibrium concentrations involved.

A great deal of preliminary investigation was required to overcome the experimental difficulties encountered. The potentials of the dilute amalgams were found to steadily increase with time and thus indicated

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[1] Ogg, *Z. physik. Chem.*, **27**, 285. Reinders, *Ibid.*, **54**, 609.

a loss of cadmium to the solution. The ease with which metals, dissolved in mercury, oxidize has been encountered in all work with amalgams and this is responsible for our lack of information on the potentials of dilute amalgams. Even with more concentrated amalgams C. Meyer[1] found that the combination—cadmium amalgam 1 | solution | cadmium amalgam 2—showed a noticeably increasing e. m. f. which he attributed to oxidation, and found it necessary to take the very first readings. Richards and Lewis[2] minimized this difficulty by first treating the electrolyte with the amalgam in order to remove the active agent. In later work Richards and Forbes[3] took very elaborate precautions to exclude oxygen from their cells and to determine, analytically, the metal lost to the solution by oxidation. They found that the effect due to oxidation was most pronounced with the dilute amalgams. Our experience particularly confirmed this point and showed that all the precautions hitherto taken still left enough oxygen in the cell to materially alter the potential of an amalgam containing only 1 part of cadmium to 10000 parts of mercury.

In all previous work on the e. m. f. of concentration cells, the e. m. f. of two amalgams of different concentrations have been measured, and as the amalgams lost base metal by oxidation the e. m. f. has always been observed to increase. The potentials of amalgams decrease as they lose base metal, but the e. m. f., which is the algebraic sum of two potentials, depends only on the ratio of the concentrations and is proportional to the logarithm of this ratio; consequently if two amalgams lost metal in proportion to their concentrations there would be no change in the value of the ratio or the e. m. f. It appears therefore that the dilute amalgams lost base metal at a proportionally greater rate than the more concentrated ones and evidently the observed change or drift of the e. m. f. of concentration cells has not shown the real loss due to oxidation, so this difficulty is a more serious one than has been assumed. It became necessary therefore to have an unchanging, reproducible basis of reference for all potential measurements; such a basis we have obtained by employing a two-phase amalgam as a reference electrode. All cadmium amalgams between 6 and 13 per cent. of cadmium have the same potential against an electrolyte because at room temperature any amalgam in this range is made up of two phases and the composition of the liquid phase depends only on the temperature. When the temperature is fixed there results one of the most reproducible concentrations we have and it is immaterial whether such an electrode loses cadmium by oxidation or in other ways. This constant reproducible electrode has made it possible to detect at once the loss of cadmium from the amalgams and to determine the loss quantitatively by the logarithmic formula.

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[1] *Z. physik. Chem.*, 7, 482.

[2] *Ibid.*, 28, 7.

[3] *Ibid.*, 58, 693.

It has not been found possible to keep oxygen from entering the cells unless they were either glass sealed or had only ground glass joints which were sealed with marine glue, but with these precautions amalgams were preserved for over a year without indications of oxidation. In the preliminary work the oxygen was displaced by hydrogen and precautions were taken to make the exclusion of oxygen as effective as possible, but it was found that there was still enough oxygen left in the cells to change the potential of the dilute amalgams. For example a 1 to 10000 cadmium amalgam decreased a quarter of a millivolt in three weeks, indicating a loss of 3 per cent. of its cadmium.

The following method was finally employed in removing the residual oxygen before the dilute amalgams were introduced into the cells. In the space above the electrolyte a short spiral of 1/20 mm. platinum wire was fixed and the larger lead wires were fused into the sides of the cell. After the cell and contents had been saturated with hydrogen the platinum spiral was brought to a glow with an electric current and caused the hydrogen to combine with the residual oxygen. The gaseous mixture in the vicinity of the wire immediately came to equilibrium, diffused away and soon the whole mixture was at the equilibrium conditions corresponding to the temperature of the wire. That this actually takes place and very rapidly has been shown by Nernst and his fellow-workers.[1] They have also given us the necessary data for calculating the equilibrium constant for any temperature. Our wire was at about 700° or 1000° absolute and the equilibrium constant for $2H_2O \rightleftarrows 2H_2 + O_2$ at this temperature is 5.2×10^{-19}. Taking the hydrogen pressure as 740 mm. and the water vapor 20 mm. the calculated partial pressure of the oxygen is 4×10^{-16} mm. This is an extrapolated value but no doubt gives the order of magnitude and shows that as far as our requirements are concerned the oxygen was "out" of the gas phase. The electrolyte, saturated with hydrogen, was agitated in this atmosphere for several days and was also in contact with the two-phase amalgam all the time. When the residual oxygen had been removed by this treatment the cell was opened and the dilute amalgam was introduced against a rapid stream of hydrogen. These precautions made it possible to observe the potential of a dilute amalgam (1 part of cadmium to 10000 of mercury) for three weeks without a detectable decrease.

Density and Composition of Cadmium Amalgams.—A knowledge of the composition of the liquid phase of the constant electrode at the temperature of the experiments, 25°, was desirable and this has been determined. Measurements had already been made on the densities and composition of cadmium amalgams at 20° by Richards and Forbes[2]

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[1] *Thermodynamics and Chemistry*, Nernst. Langmuir, THIS JOURNAL, 28, 1357.

[2] *Loc. cit.*

but their results extend only to 3 per cent. amalgams while the work of Kerp and Boettger[1] and Bijl[2] on the composition of the saturated amalgams did not aim at the accuracy required by the e. m. f. measurements. Richards and Forbes have found that the density is a linear function of the composition of cadmium amalgams from pure mercury to 3 per cent. of cadmium and we have found that this relation holds up to the saturated amalgam or 5.57 per cent. of cadmium. After this curve had been accurately located, it was only necessary to determine the density of the saturated amalgam in order to calculate its percentage composition.

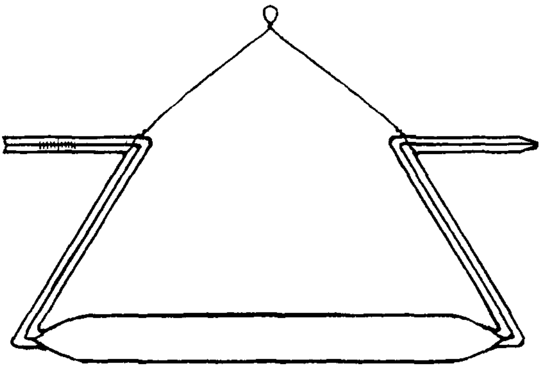

Fig. 1.

The pycnometer used is represented in Fig. 1. This form was much more effectively wiped and dried than the usual form, while it was convenient to handle in the bath and the long body rapidly took up the desired temperature. It could also be placed directly on the balance pan with the stem resting against the bows. This pycnometer was weighed several times during the period of six weeks and the weight was found to be 21.21702 g. On two occasions it was filled with mercury at 25° and the weights were 138.15175 and 138.15043, which gave as the masses of mercury in the pycnometer, 116.9277 and 116.9264, and from the density of mercury at 25°, 13.53396, the volume of the pycnometer was calculated to be 8.63950 ± 0.00005. With this instrument the densities of the saturated cadmium amalgam and also a 3 and a 5 per cent. amalgam were determined. The saturated amalgam was made by using an excess of cadmium with mercury at 25°, while the metals were directly weighed for the 3 and 5 per cent. amalgams, the weight of mercury was adjusted to the amount required by the pieces of cadmium which had been weighed out. All weights were made by substituting calibrated weights for the "tared" metal and the vacuum correction was applied to the

Weight of cadmium	3.89350	10.49564
Weight of mercury	125.89738	199.42941
Vacuum correction	−0.00755	−0.01196
Mass of mercury	125.88983	199.41745
Percentage of the amalgam	3.0000	4.9999

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[1] *Z. anorg. Chem.*, **25**, 1.

[2] *Z. physik. Chem.*, **41**, 641.

mercury weights but as cadmium has essentially the same density as the brass weights the correction for it was negligible.

There is no difficulty in measuring the amount of metals for an amalgam of definite percentage with a high degree of precision, but the subsequent loss by oxidation is a difficulty that has always been encountered in making amalgams of known composition. A scum forms as soon as the metals are brought together. Under certain solutions bright amalgams are obtained but the oxide is formed and dissolves in the solution, so unless the loss is determined the composition of the amalgam is in doubt. Richards and Forbes[1] analyzed the ammonia solution under which the amalgams were made but even then subsequent loss was to be guarded against. This uncertainty has been entirely avoided by the following simple device: The mercury was first placed in a dish under distilled water and made cathode by a 10-volt circuit, a little platinum spiral in the water serving as anode. When the cadmium was dropped through the water and on the mercury it dissolved without a coat appearing and the amalgam remained bright indefinitely unless the circuit was broken. The water was readily pipetted off and it left the amalgam surface clean, bright and dry and the amalgam was then drawn into the pycnometer.

In making the saturated amalgams two tubes were prepared, one containing a 6 per cent. and the other a 7.3 per cent. amalgam. The tubes were sealed and rotated in a bath at 25° ± 0.01° for several days. The solid phase is an isomorphous mixture of cadmium and mercury and is lighter than the saturated amalgam, consequently it was necessary to use a filter pipette (Fig. 2) to separate the two phases. The filter was a layer of asbestos between two layers of glass wool, the top layer of glass wool being used to prevent the asbestos from becoming packed into the small inside tube. This filter tube was brought to the temperature of the bath before the liquid amalgam was drawn into it and thus the two phases were effectively separated at the bath temperature. The liquid was at once placed under distilled water and preserved as just described.

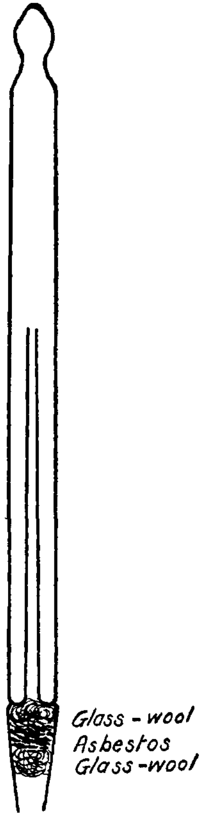

Fig. 2

The average value for the density of the saturated amalgam from the two tubes is 13.1967. On plotting the densities of pure mercury, 13.5340, and for the 3 and 5 per cent. amalgams they were found to lie very exactly

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[1] *Loc. cit.*

in a straight line and on extending this line to the value 13.1967, the density of the saturated amalgam, a percentage composition of 5.570 was indicated.

	5 per cent. amalgam.		3 per cent. amalgam.
Pycnometer + amalgam	135.52334	135.53441	136.59236
Pycnometer	21.21702	21.21702	21.21702
Weight of amalgam	114.30632	113.31739	115.37534
Vacuum correction	−0.00686	−0.00686	−0.00692
Mass of amalgam	114.29946	114.31053	115.36842
Density	13.22990	13.23090	13.35360

	From the 7.5 per cent. tube.		From the 6 per cent. tube.	
Pycnometer + amalgam	135.2202	135.2421	135.2520	135.2361
Pycnometer	21.2170	21.2170	21.2170	21.2170
Weight of mercury	114.0032	114.0251	114.0350	114.0191
Correction	−0.0068	−0.0068	−0.0068	−0.0068
Mass of amalgam	113.9964	114.0183	114.0282	114.0133
Density	13.1948	13.1973	13.1985	13.1967

As a check on this work the liquid amalgam from the rotated tubes was subjected to analysis. The amalgam was treated with concentrated hydrochloric acid and the cadmium dissolved with an energetic evolution of hydrogen, a method employed by Kerp and Boettger.[1] However, we found that a little mercury always dissolved with the cadmium and curiously enough more than would dissolve from pure mercury under the same conditions and in the same time. The trace of mercury that passed into the solution with the cadmium was determined colorimetrically. This was easily done, as it was found that hydrogen sulphide did not precipitate cadmium from the strong acid solution, while the black sulphide of mercury was precipitated and the color obtained in the diluted solution was compared to that formed by hydrogen sulphide in similar solutions which contained known amounts of mercury.

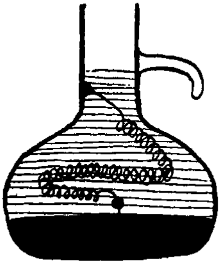

Fig. 3

The amalgam was prepared, separated from the solid amalgam and preserved as just described and then it was brought into a little flask represented by Fig. 3. The weights of the flask and the flask plus the amalgam were carefully determined and then the flask was nearly filled with concentrated hydrochloric acid. The platinum spiral, indicated in the cut, made contact with the mercury and presented a large surface of platinum to the acid and was very efficient in reducing the time needed to complete the reaction. It was found that the mercury would amalgamate and creep up the wire, thus decreasing its effectiveness, so a little glass bead was fused

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[1] *Z. anorg. Chem.*, 25, 1.

on the wire just above the point reached by the mercury surface. In a few hours most of the cadmium passed into solution and then the solution was replaced with fresh acid and left for a day or so; finally the acid was removed with a pipette, water was added and removed in the same way and this washing with distilled water was repeated until the acid and dissolved cadmium had been completely removed. The flask with mercury was then placed in a vacuum desiccator over calcium chloride where the residual wash water rapidly disappeared. The mercury that passed into solution was accurately determined colorimetrically and added to the weight of the mercury left in the flask, thus the loss in weight represented the cadmium. An analysis of the amalgams of known composition showed that the method was capable of giving very exact results.

	A.	23 hours.	50 hours.	B.	23 hours.	50 hours.
Flask +amalgam	93.42976	88.66348	88.66245	55.81394	53.05296	53.05206
Flask	7.96332			7.96332		
Weight of amalgam	85.46644			49.53308		
Mass of amalgam	85.46122			49.53010		
Dissolved by the acid		4.76628	4.76731		2.76098	2.76188
Mercury dissolved		0.00200	0.00287		0.00110	0.00186
Mass of cadmium		4.76428	4.76444		2.75989	2.76002
Per cent. of cadmium		5.5749			5.5735	

The average from these analyses gave 5.574 as the percentage composition of the liquid phase of cadmium amalgam saturated at 25°; and from the density-composition curve previously obtained, the density of a cadmium amalgam containing 5.574 per cent. of cadmium was 13.1962 while the direct determination of this density gave 13.1967. The results of the two independent methods agree to 1 part in 1500 on the composition, but the analysis should be given the greater weight, so if we take 5.573 as the percentage composition of our saturated amalgam the value is probably correct in the third decimal place and since the density of these amalgams is a linear function of the composition, the relation may be very accurately expressed. The density at 25° of any cadmium amalgam is $D = 13.5340 - 0.0666 \times p$ where p is the percentage composition. On plotting the results of Richards and Forbes on the density and composition of cadmium amalgams at 20° the most probable curve was found to diverge slightly from the one for our results at 25°, indicating that cadmium amalgams have a slightly greater temperature coefficient than pure mercury. The divergence of the two curves gave the change of the temperature coefficient with percentage composition. The decrease in the density of pure mercury at 25° is -0.0024 per degree and for the cadmium amalgams it was found to be $-(0.0024 + 0.0003\ p)$. These relations, $D_{25} = 13.5340 + 0.0606\ p$ with a temperature coefficient $-(0.0024 + 0.0003\ p)$ give the means of accurately calculating one magnitude from the other for any liquid cadmium amalgam at any ordinary temperature.

Purification of Materials.—All the mercury used in this work was purified chemically and then distilled under diminished pressure with some air passing over with the mercury vapor.[1] This method insures the removal of such metals as zinc and cadmium and leaves no question as to the purity of the mercury. Cadmium sulphate was the starting point for the other materials, and advantage was taken of the fact that the sulphide of cadmium is distinctly more soluble than the sulphides of the other heavy metals, except zinc. The cadmium sulphate solution was treated with hydrogen sulphide until cadmium sulphide was distinctly in evidence and the whole was digested for a day or two before filtering. The cadmium was now precipitated as the sulphide while, from the acid solution, only a trace of the zinc sulphide was carried down with the cadmium sulphide. This product was washed and changed to the sulphate with nitric and sulphuric acids, heated to remove the excess of acids and then recrystallized. Fortunately cadmium sulphate is not isomorphous with other sulphates and the clear crystals, which may be readily separated from the cloudy ones, are quite free from inclusions so it was possible to obtain this salt in an exceptional state of purity. The preparation of metallic cadmium in a satisfactory state required more attention; it was easy to obtain the metal electrolytically from the purified sulphate and in a very attractive looking condition but this crystalline, electrolytic cadmium was found to contain occluded mother liquor which we were not able to remove by washing or by vacuum drying; *indeed it was retained by the metal until it was melted.* In one experiment 125 g. of the electrolytic cadmium gave off hardly perceptible amounts of moisture until the melting point was reached and then there was a sudden evolution of water which was collected and found to be about 80 mg. or 0.06 per cent. The dross formed contained sulphate, sulphide and probably oxide as the molten metal seems to have reduced the sulphate and it was feared that both the oxide and sulphide had a certain solubility in the metal. With this in mind the metal was made the anode in a pure cadmium sulphate solution and the resulting electrolytic cadmium was washed, dried and mixed with ammonium chloride. This mixture was heated to the melting point of cadmium in an atmosphere of hydrogen, the ammonium chloride absorbed the occluded mother liquor, melted and was relied upon to effectively take care of the impurities. The button of metal obtained in this way was perfectly bright and when distilled in a vacuum did not leave a residue. It was distilled a second time in a vacuum and run into the drawn-out end of the combustion tube. The metal was silver white and was easily cut into convenient pieces with a clean piece of steel. When preserved in a dry atmosphere it did not tarnish and has been entirely satisfactory.

Preparing and Handling the Amalgams.—In preparing an amalgam of

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[1] *Phys. Rev.*, **21**, 388.

definite composition a piece of cadmium was weighed on a balance sensitive to 0.01 mg. and the mass of the cadmium determined by the substitution of carefully calibrated weights. The weights corresponding to the desired air weight of mercury were placed in a little porcelain dish, the dish and weights were tared on a balance and then the weights were replaced by mercury. The addition of the last of the mercury was made with a fine capillary joined to a rubber tubing and it was found possible to make the final adjustment of mercury to within one or two-tenths of a milligram. This mercury was covered with distilled water and made the cathode on a ten-volt circuit, contact being made with the mercury by means of a very fine platinum wire and only the point of this wire extended through the little glass tube which protected it from the water. The anode was a small platinum spiral in the water and there was a slow generation of oxygen on this spiral but hydrogen was not noticed at the mercury cathode so it must have dissolved and diffused away as fast as formed. When cadmium is dropped on mercury it generally floats for some time without dissolving, but we found that the mercury cathode at once "wet" the cadmium and solution followed immediately. If the cadmium was bright it dissolved without forming a coat. Amalgams have been kept this way for months without a sign of oxidation unless the current was accidentally broken, but then the oxide appeared in a short time. It was found possible to completely remove the water with a pipette except for the small amount left in the capillary depression next to the dish, and then the amalgam was removed quite free from water. Little glass ladles were made from very thin glass and the amalgams dipped up by and weighed in these ladles. It was found that unless the glass was very smooth and clean, tiny drops of amalgam would cling to the ladle and readily escape detection, so the ladle was reweighed after the amalgam had been poured out and it was always cleaned with nitric acid and dried by warming before being used.

Having obtained the weight of an amalgam of known composition, it was necessary to calculate the amounts of cadmium and mercury present in order to determine the amount of mercury to be added for the next dilution. This amount of mercury was weighed out and made cathode under water and the amalgam poured in. Sometimes a slight coat would appear when the amalgam was poured into the mercury, for the merest trace of oxide is readily detected on a clean mercury surface, but even this oxide was very soon reduced by the current and so it was found possible to make these amalgams with almost mathematical accuracy and to any required dilution. Great care was needed in double checking all weighings and calculations, as an error effected all subsequent dilutions.

The form of cell used in the measurements of the electromotive forces is represented in Fig. 4. The body of the cell was 40 mm. in diameter and about 160 mm. long. There were four little partitions or dams straight across the bottom and about one centimeter high and the glass between these dams was slightly concave so that the globule of amalgam or mercury rested in the middle of the compartment when the tube was level and it was then in contact with the platinum wire. The glass tubes carrying these contact platinum wires made well-ground joints with the tubes *a*, *b*, *c*, *d* and *e*, so that a very little marine glue, when warmed, effectively and neatly closed these joints. The electrolyte filled the cell to a depth of 15 mm. and when the cell was tilted it flowed over the dams and was most thoroughly mixed while the amalgams remained in their compartments but were free to move about and, due to resting on a flat surface, made as little contact as possible with the glass. The cell was evacuated through the side tube *f* and then hydrogen gas was let in and this process repeated until the oxygen was effectively removed. When materials were introduced through one of the tubes, hydrogen was forced in at *f* and out through the tube in question so that the materials were thoroughly washed with hydrogen as they entered the compartment. A large supply of pure hydrogen was provided and so arranged that it passed a glowing platinum wire immediately before it was used and thus was assuredly oxygen free.

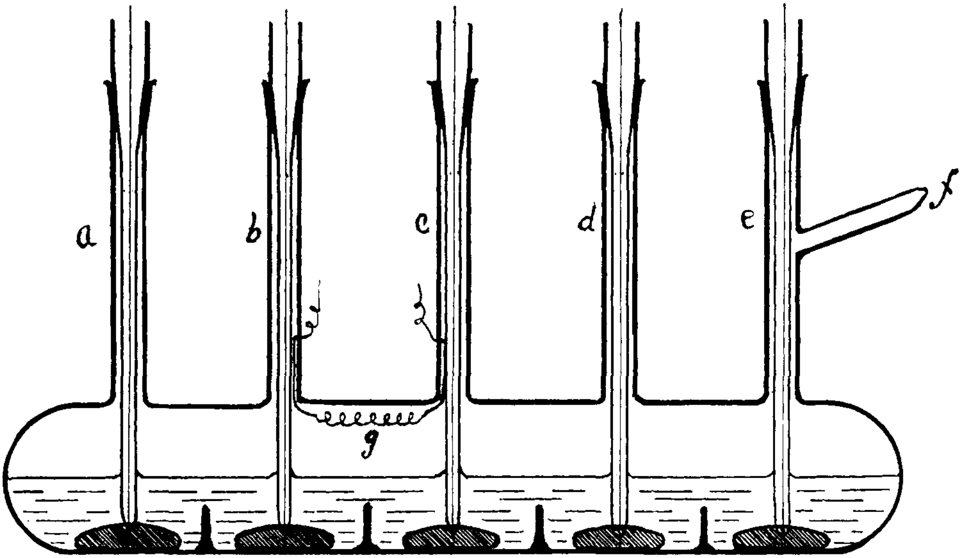

Fig. 4.

The electrolyte was made from equal weights of clear cadmium sulphate crystals and water and particular attention was given to removing the oxygen from this solution. A separatory funnel was partly filled with the solution and the glass stopper inserted. The stem of the separatory funnel was now joined to a vacuum pump and the air evacuated, the cock closed and the solution vigorously shaken in a vacuum. After this process had been effectively carried out, hydrogen was admitted and by shaking, the solution was rapidly saturated with this gas, but this gas was removed and the solution resaturated, repeating the operation several times in order to make the exclusion of oxygen as effective as possible. Shaking a liquid in a vacuum is undoubtedly the most effective way of releasing the persistent supersaturation of gases in liquids. A "T" tube with two stopcocks was joined to the stem of the separatory funnel, the vacuum pump and the hydrogen generator and then these operations were rapidly and easily carried out. The separatory funnel proved to be a convenient instrument for preserving or delivering desired amounts of the solution.

After the electrolyte and a two-phase amalgam had been put into the cell, an electric current was passed through the platinum spiral *g* until it was at about 700°. The glowing spiral soon established equilibrium in the gas phase and then it was made up of hydrogen at a pressure of 740 mm., water vapor 20 mm. and a calculated pressure of 4×10^{-16} mm. of oxygen. The platinum wire maintained these conditions while the solution was agitated. A mechanical device slowly lifted one end of the tube at regular intervals and caused the solution to flow back and forth over the dams and it was thus not only thoroughly mixed with the gas phase but was also brought into intimate and continuous contact with the two-phase amalgam. Several days of this treatment were judged to be sufficient to really remove the residual oxygen and the subsequent behavior of dilute amalgams in these solutions confirmed this supposition.

It was now necessary to give particular attention to the operation of introducing the dilute amalgams into the cells without allowing oxygen to enter at the same time. A glass bulb with a capillary stem and a little funnel was made, Fig. 5. Hydrogen was forced in through the tube *h* until the air was completely removed (this was done immediately after the instrument was blown, as the glass is then free from the surface air film). When hydrogen was issuing freely from the funnel and the stem *i*, this stem was introduced into a tube leading to a compartment of the cell and then amalgam was poured into the funnel. The amalgam in passing from the funnel into the bulb fell through an at-

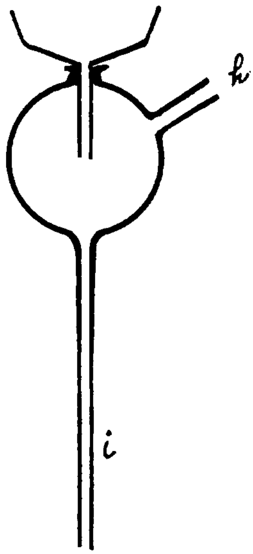

Fig. 5.

mosphere of hydrogen and then a second time as it entered the compartment it was washed with hydrogen. During all this time the platinum spiral was heated to glowing and hydrogen passed in through the tube *j*.

Measurement of Electromotive Forces. The basis of the e. m. f. measurements was Clark cells which had been made at intervals since 1903 and which were all in good agreement. These cells were made with chemically pure materials while particular attention had been given to the depolarizer; precautions were taken to avoid the formation of the basic salt in the preparation of the mercurous sulphate and to avoid hydrolysis in making the paste. With these precautions the Clark cell is reproducible to better than 1 part in 50000 and does not change with time. The absolute value of these cells at 25° is 1.42040 as determined by K. E. Guthe.[1] This is also about the average value of all previous absolute determinations on the Clark cell. For this work a large 100-liter oil-bath was used. It was electrically heated and controlled and did not vary over 0.01° at any time from 25°. The thermometer used in locating this temperature was checked at the transition point of sodium sulphate, 32.383° (Richards and Wells).

All e. m. f. measurements were made by the "null" method; the instruments used were a high resistance potentiometer made by Otto Wolff, Berlin, a Broca galvanometer with 1000 ohm coils, Nernst glower lamp and scale, regulating resistance and two standard batteries[2] which gave an exceedingly steady and constant current. The corrections for the resistances of the potentiometer coils were almost negligible but the instrument was carefully calibrated and the whole system was thoroughly insulated. For accurate measurements this was quite essential and especially was it found that dust or moisture on the hard rubber base of the potentiometer introduced very measurable disturbances, so the instrument was kept scrupulously clean and dry. It was found possible to test this point by short-circuiting the lead wires, placing the switches at zero reading and closing the galvanometer circuit. There was no deflection of the galvanometer if all was in order; otherwise cleaning between the coil plugs of the potentiometer generally corrected the fault, but in damp weather even this would not do and then no measurements were attempted.

The cells used for the amalgams had from 3 to 5 compartments and each amalgam was measured with the constant electrode. The total e. m. f. is made up of the potential of the constant electrode minus the potential of the amalgam under consideration, since the two are opposed, and while we cannot measure a single potential we have here elected to measure each one with the constant electrode and by taking any two

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[1] *Bull. Bureau of Standards*, **2**, 3.

[2] *Phys. Rev.*, **27**, 33.

of these values we get the e. m. f. between the two dilute amalgams under consideration and with an accuracy that depends only on the accuracy of the measurements. Since it was possible to directly compare any two amalgams in a cell there was a check on the accuracy of the measurements. For example one cell contained the amalgams lettered *a*, *b*, *c*, *d* and *e*, where *a* was the constant electrode. The following observations are taken at random from a series of measurements: *a–b* 0.023382, *a–c* 0.052942, *a–d* 0.082603, *a–e* 0.112005. From these values the differences *b–c*, *c–d*, and *d–e* were obtained and they were also directly measured.

	Observed.	By difference.
b–c..............	0.029560	0.029560
c–d..............	0.029660	0.029661
d–e..............	0.029401	0.029402

Many checks of this kind were made and in general it was found unnecessary to do more than compare each amalgam with the constant electrode. With the direct reading potentiometer there was little chance of errors in reading; the galvanometer gave 10 full millimeters deviation for 0.00001 volt. The possibility that the measuring current might change the concentrations of the amalgams was considered. Until the balance was nearly obtained at least 100000 ohms was in the cell circuit and with the high resistance galvanometer the momentary infinitesimal current used was entirely to be disregarded. In making the final balance, the small current necessary was generally reversed to about the same amount and a measurable effect on the concentration of the amalgams was not observed, even in the case of the dilute amalgams.

Some evidence was obtained on the reproducibility of the constant electrode by placing a 10 and 7 per cent. amalgam in the same cell; as both of these amalgams form two-phase electrodes at 25° there should be no e. m. f. between them;

June 21.............	*a–b*	+0.0000012 V.
" 22.............	"	+0.0000012 "
" 27.............	"	.... "
July 5.............	"	+0.0000007 "
Dec. 1.............	"	.... "
" 20.............	"	—0.0000005 "

The cell stood in the laboratory, subjected to changing temperature, during the summer and fall. It was evident that the constant electrode was really independent of the total amount of cadmium present and it is probably one of the most reproducible concentrations we have. One of the many advantages gained by measuring all potentials with this constant electrode is that the results for any two cells are directly comparable, since the e. m. f. of an amalgam concentration cell is quite independent of the kind or concentration of the electrolyte. Two amalgams in different cells each compared to the constant electrode, when the cells are at the same temperature, give values which show the e. m. f. between these two amalgams as accurately as if they had been directly compared in the same cell.

The composition of the liquid phase of the constant electrode at 25° we have found to be 5.573 per cent. of cadmium which is 5.902 grams of cadmium to 100 grams of mercury and for our purpose it has been found most convenient to express concentrations as fractions, the numerator giving grams of cadmium and the denominator grams of mercury. The saturated amalgam is then 5.902/100 and an amalgam containing one gram of cadmium to 10000 grams of mercury is represented as $1/10^4$, etc. Since it was possible to make the amalgams of a definite composition and to entirely avoid loss by oxidation it is unnecessary to give the details of weighings as the amalgams were generally made on the decimal scale starting with a 1/100 amalgam.

A great many measurements were made on cells, containing amalgams of medium concentration, before the various details of the methods finally employed were worked out and only a few of these observations are of importance. A cell was charged in January, 1907, with a two-phase amalgam and with some mercury in a second compartment. After the amalgam had used up the residual oxygen cadmium was deposited electrolytically in the mercury forming a $265/10^4$ amalgam and the following observations were obtained:

Mar. 13, 1907	0.040378
Mar. 14, 1907	0.040382
Mar. 10, 1908	0.040379

The electrolyte was an acid solution of cadmium sulphate and it was evident that moderately dilute amalgams remained constant, even in an acid solution after the oxygen was removed and the cell was glass-sealed as in this case. A cell was charged with the following amalgams:

a.	*b.*	*c.*	*d.*	*e.*
5.902/100	4/100	2/100	1/100	1/1000

Days.	*a-b.*	*a-c.*	*a-d.*	*a-e.*
	0.0053663	0.014447	0.0123370	0.052936
1	64	51	76	55
3	15	46	68	37
6	66	44	72	44
24	70	52	80	24
38	60	40	75	40
70	60	45	80	45
	0.0053660	0.014444	0.0233740	0.052941

A cell charged with the following amalgams gave:

a. 5.902/100 Days.	*b.* 1/100 *a-b.*	*c.* $1/10^3$ *a-c.*	*d.* $1/10^4$ *a-d.*	*e.* $1/10^5$ *a-e.*
	0.023381	0.052936	0.082586	0.111893
1	82	42	603	2005
2	80	40	603	2088
6	80	40	622	2305
16	67	41	705	3050
24	71	46	852	4606
	0.023377	0.052941		

Here it will be seen that amalgam $1/10^4$ showed a distinct loss with time and in the case of the $1/10^5$ amalgam, the change was very marked indeed. About the same amount of amalgam was used in each case and a calculation showed that $1/10^4$ amalgam lost 3.1 per cent. of its cadmium while the $1/10^5$ amalgam had lost about 19 per cent. of its cadmium, so the dilute amalgam lost proportionally very much more than the more concentrated amalgam. The loss of cadmium is evidently not a reaction that depends alone upon the concentration of the cadmium in the amalgam. It would seem that the loss of cadmium was a secondary reaction, possibly the oxygen attacks the mercury largely and the product formed reacts with the dissolved cadmium.

The results just given are not the most constant that have been obtained with dilute amalgams but in the most favorable cases a $1/10^5$ amalgam showed some change in a month, and since all the evidence pointed to oxygen as the cause, further consideration was given to this point. The method of introducing the dilute amalgams seemed satisfactory but it was about the only chance oxygen had to enter the cell. The falling mercury must have carried a film of air, if oxygen did enter with it, in spite of the fact that it dropped through an atmosphere of hydrogen two distinct times. To get some evidence on this point the following experiment was performed, a cell was charged with the constant electrode, electrolyte and mercury in two compartments and then the residual oxygen was removed as described. A piece of cadmium was now lowered into the tube leading to one of the mercury compartments and held in the stream of hydrogen until the surface film was removed and it was then dropped on the mercury and the cell closed.

In compartment *b* was placed 46.481 g. of mercury, and 0.04648 g. of cadmium was dropped in, while the piece of cadmium dropped in compartment *c* weighed 0.00950 g., where 95. g. of mercury had previously been placed; the concentrations were therefore

a. 5.902/100 Days.	*b.* $1/10^3$ *a-b.*	*c.* $1/10^4$ *a-c.*
	0.052945	0.082545
1	46	54
2	43	50

Days.	*a-b.*	*a-c.*
3	36	41
5	41	41
8	35	45
15	30	45
	0.052940	0.082545

Here the results with a $1/10^4$ amalgam were more constant than in the previous experiment. In fact there was no evidence of a drift during the two weeks the cell was observed but the method offered little chance of working with very dilute solutions as the difficulty of weighing a small piece of cadmium with the required accuracy would soon be encountered. The idea at once presented itself of depositing the cadmium electrolytically in the mercury after the residual oxygen had been removed and thus making it unnecessary to open the cell at all. The cadmium was taken from the two-phase electrode without altering its potential value.

A cell was charged with a constant electrode, electrolyte and 35 g. of mercury in *b* and 70 g. in *c*. Agitation with the two-phase amalgam and exposure to the infinitesimal partial oxygen pressure, due to the glowing wire, was continued for several days. It was only necessary to close the amalgams *a–b* over a resistance in order to deposit cadmium in *b* but the e. m. f. changed very rapidly, especially at first, and did not permit a sufficiently accurate measurement of the quantity of electricity passed. A large storage battery of 200 volts was closed over large resistances and the cell was put in series with this circuit. The resistances included an accurately calibrated set and the fall of potential over a known resistance was followed with the potentiometer while the time was taken with a stop watch. For example it was desired to deposit 0.0003500 g. of cadmium in the 35 g. of mercury in order to make a $1/10^5$ amalgam. The circuit was closed, the current measured and the approximate time needed was calculated before the cell was switched into the circuit at

3:03	the potential over 1000 ohms was	0.23333 V.
:04		33
:08		34
:17		37
:18		38
:20		39
:21		41
:22		42
:24		41
:26		36
:28		32
:30		32
:32		31
:34		30

3:40		30
:42		29
:45: 52	broke the circuit	28
		0.23334

From these observations the average fall of potential over 1000 ohms was very accurately obtained. The current was 0.00023334 amp. for 42 minutes and 52 seconds or 2572 seconds which gave 0.60016 coulomb and as a coulomb deposits 0.0005825 gram of cadmium there were 0.00034960 gram of cadmium deposited in the 35 grams of mercury in *b* of the cell. Immediately after the circuit was broken the cell was rocked about 30 seconds and the measurements of this amalgam against the constant electrode were made with the following results:

1 minute	0.11210 V.
6 minutes	16 "
18 "	20 "
47 "	25 "
80 "	30 "
2 hours	35 "
4 "	37 "
6 "	42 "
18 "	43 "
66 "	45 "

There is some evidence of change here but the first reading taken is regarded as near the correct value for a $1/10^5$ amalgam, some previous results with dilute amalgams which had been introduced into the cell as previously described, gave values that indicated 0.112 volt.

Cadmium was now deposited in the 70 grams of mercury in compartment *c*. The current was 0.0001645 amp., and there was practically no variation for the 12 minutes and 10 seconds it was depositing cadmium, so this current for 730 seconds gave 0.1201 coulomb which deposited 0.00006995 gram of cadmium in the 70 grams of mercury making a $1/10^6$ amalgam. The cell was rocked ½ minute and then gave:

1 minute	0.14201 V.
2 minutes	0.14240 "
3 "	0.14125 "
12 "	0.14132 "
15 "	0.14161 "
75 "	0.14168 "
14 hours	0.14193 "
90 "	0.14246 "

Here with one part of cadmium in a million of mercury the cell was quite constant for a considerable time and we may take 0.1416 as the value of this amalgam.

A cell was prepared with 35 and 70 grams of mercury and was used for observing the e. m. f. of 1/10⁷ and 1/10⁸ amalgams. First cadmium was deposited in the 35 grams of mercury by a current of 0.0000101515 amp. for 9 minutes and 33 seconds or 573 seconds giving 0.06025 coulomb or 0.000003508 gram of cadmium and the cell was rocked ½ minute and then measured:

1 minute	0.17320 V.
3 minutes	0.17325 "
5 "	0.17315 "
10 "	0.17309 "
50 "	0.17316 "
2 hours	0.17347 "
4 "	0.17402 "
6 "	0.17450 "
10 "	0.17503 "
30 "	0.17730 "

We may take the value of this amalgam which contained one part of cadmium in ten million parts of mercury to be 0.1732. It was sufficiently constant for the first hour.

Cadmium was now deposited in the 70 grams of mercury with a current of 0.00001051 amp. for 114 seconds or 0.001296 coulomb which represented 0.0000006986 gram of cadmium. The deposition required less than two minutes and after rocking the cell a few seconds the readings were taken:

1 minute	0.2215 V.
2 minutes	0.2280 "
3 "	0.2323 "
4 "	0.2351 "
5 "	0.2375 "
6 "	0.2396 "
7 "	0.2416 "
8 "	0.2485 "
11 "	0.2561 "
16 "	0.2736 "
45 "	0.3820 "
90 "	0.4910 "

The behavior of this amalgam, with only one part of cadmium in one hundred million parts of mercury, was noticeably different from the proceeding amalgams and the value can only be roughly estimated as something like 0.22 volt. Some experiments were made with these dilute amalgams in which the time required to deposit the cadmium was ten times greater than in the preceding, but the resulting e. m. f. was only about 3 per cent. greater, so only in the last experiment was the loss of cadmium to the solution, during the time of deposition, measurable.

The results may now be tabulated. The value of each amalgam measured against the constant electrode at 25° is given in the column marked "Observed." The "calculated" results will be explained immediately.

Amalgam.	Observed.	Differences.	Calculated.
5.902/100	0.000000 V	....	....
		0.005366	
4/100	0.005366	....	0.005580
		0.009079	
2/100	0.014445	....	0.014480
	....	0.008930	....
1/100	0.023375	....	0.023380
	....	0.0295685	....
1/1000	0.052940	....	0.052940
	....	0.029600	....
$1/10^4$	0.082540	....	0.082500
	....	0.029560	....
$1/10^5$	0.112100	....	0.112060
	....	0.029500	....
$1/10^6$	0.141600	....	0.141620
	....	0.031600	....
$1/10^7$	0.173200	....	0.171180
	....	0.046800	....
$1/10^8$	0.22	....	0.200740

An inspection of the observed values showed a uniform increase between the amalgams 1/100 and $1/10^6$ so it was evident that the logarithmic relation held for this very considerable range of concentrations and it seemed best to take some value in this range as the starting point of the calculated values. The most reliable value for this range seemed to be 0.052940 for the 1/1000 amalgam.

The Nernst relation for concentration cells is $E = RT \ln C_1/C_2$ where C_1 and C_2 in our case are the concentrations of the cadmium in the amalgams. R or p_0v_0/T we will take from $\frac{76 \times 13.596 \times 980.6}{273.1} = 0.83135$. E, the electrical energy, is equal to the product of the e. m. f., a "faraday," and the valence of the metal cadmium or $V. \times 2 \times 96540$. Collecting and changing to the Briggs logarithms we get $V. = 0.00009915\ T \lg C_1/C_2$ or for 25° $V. = 0.029560 \lg C_1/C_2$. In the above results where C_1/C_2 differ by 10, the logarithm of which is 1, the voltage should differ by 0.029560 to comply with the theory. Where $C_1/C_2 = 2$, the voltage differences should be 0.008900 and 0.004964 for $C_1/C_2 = 5.902/4$.

There is a noticeable difference between the observed and calculated values for the concentrated amalgams. Any two amalgams in the range from 1/100 to 6/100 give an e. m. f. distinctly greater then the theory requires and this agrees with the observations of Richards and Forbes.[1] A special consideration of these concentrated amalgams will be undertaken when some further experiments have been completed. We may now consider the very great range which follows this where the logarithmic relation is in excellent agreement with the observed values. Any

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[1] *Z. physik. Chem.*, **58**, 683.

two amalgams in this region from 1/100 to 1/10^6 show an e. m. f. which is in agreement with the requirements of the gas laws. If the cadmium dissolved in any two of these amalgams behaved as a perfect gas and exerted an osmotic pressure which lowered the vapor pressure proportionally to the concentration of the cadmium then these amalgams used as electrodes in an electrolyte of uniform concentration should give the electromotive forces actually observed. The great extent of the range, a variation of the cadmium concentration by 100000-fold, makes it probable that no factors have been overlooked and that the several assumptions made are correct.

Beyond 1/10^6 amalgams the logarithmic relation no longer holds and such a deviation was anticipated. Between the 1/10^6 and the 1/10^7 amalgams the observed e. m. f. is distinctly greater than the calculated and, since the potentials of these amalgams were opposed, the larger potential of 1/10^6 was too great or the smaller potential of the 1/10^7 amalgam was smaller than theory demanded. Now there was good reason to think that the potential of the 1/10^6 amalgam was normal so the 1/10^7 was to be regarded as too small, that is, there was really less cadmium present than had been assumed, or, if present, it did not for some reason exert its proper potential. The fact that this potential decreased with time showed that the amalgam was slowly losing cadmium (the constant electrode used as a basis leaves no doubt about the decrease or the exact amount of it). We must consider then the manner in which this amalgam, containing only one part of cadmium in ten million of mercury, could lose part of this cadmium. Oxygen dissolved in the solution about a cadmium amalgam does remove cadmium from that amalgam, just how is not known, but in the present case the method employed effectively disposed of the oxygen in the vapor phase while the solution was agitated for days with the constant electrode which was a cadmium amalgam some 60 million times more concentrated than the 1/10^7 amalgam under consideration, and it would seem that the two-phase amalgam must have removed the oxygen so completely that it could not have affected such a dilute amalgam. The solution was in contact with mercury before the oxygen was so completely removed and must have gained mercury decidedly beyond the amount that would be in equilibrium with the saturated amalgam, but whether this two-phase amalgam removed the mercury so completely from the solution that it could not reduce the dilute amalgam, may be questioned. In considering such extremely dilute solutions the rate of approaching the equilibrium point must be necessarily slow and it can hardly be assumed that the solution as a whole was at any time actually in equilibrium with the two-phase amalgam. The mercury in the other compartments would keep it far above this equilibrium point. However, they were all effective in removing the oxygen, so the loss of cadmium by these very dilute amalgams can hardly be attributed to oxygen.

If there is an equilibrium between the mercury and cadmium in the amalgam and in the solution it undoubtedly follows the relation proposed by Nernst,[1] $\sqrt[n_1]{\frac{P_1}{p_1}} = \sqrt[n_2]{\frac{P_2}{p_2}}$ where P_1 and P_2 represent the concentrations of cadmium and mercury in the amalgam and p_1, p_2 their respective concentrations in the solution. In our case the concentration (P_2) of mercury in the amalgam is constant as is the concentration (p_1) of cadmium in the solution, and as the mercury in solution is mercurous mercury $n_2 = 1$ and for cadmium $n_1 = 2$, so the relation reduces to $P_1 \times p_2^2 = K$, and evidently K is a very small number. If mercury is brought into a cadmium sulphate solution, as in our case, mercury should go into solution and reduce cadmium until the equilibrium constant is satisfied. In other words, our pure mercury must have gained cadmium in the cell and its potential must have increased, or against the constant electrode the e. m. f. must have decreased and this has been amply verified by observations on the cells before cadmium was deposited in the mercury. The e. m. f. measurements on pure mercury against the constant electrode showed values ranging from 0.60 to 0.70 volt with the average about 0.63 volt but they were always decreasing values and in time settled down to 0.50 volt. The value 0.508 was most frequently observed and it did not go below this value even with continued agitation, and agitation very much shortened the time required to change from 0.63 to 0.50 volt. This behavior is entirely in accord with the idea that mercury receives cadmium from solution and since the reaction is electrolytic a gram atom of cadmium entering the mercury would mean that two gram atoms of mercurous mercury had passed into the solution and it will at once be seen that the actual concentration of cadmium in the mercury will depend on the relative volumes of mercury and solution while the reaction proceeds until $P_1 \times p_2^2 = K$. In the case of the two-phase amalgam the concentration of P_1 is fixed and so the concentration of the mercury in the solution is fixed for a given temperature. In our cells the mercury in the electrolyte tends towards this concentration but with such exceedingly small mercury concentrations to work through the material actually transferred is correspondingly small and equilibrium conditions in the electrolyte are to be regarded as attained only at the surface of the amalgams while the system as a whole is not in equilibrium. When cadmium was deposited in this mercury electrolytically both cadmium and mercury were deposited in proportion to their concentrations, but in view of the small mercury concentration it is to be concluded that the cadmium deposited, even in the case of the most dilute amalgams,

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[1] *Z. physik. Chem.*, **22**, 539.

corresponded to the current passed, at least far beyond the accuracy of measurement of the coulombs. The deposition of cadmium disturbed equilibrium conditions and the cadmium at once began to leave the amalgam and reduce the mercury, or at least as soon as the cell was agitated and the "average" concentration of mercury in the electrolyte was brought into contact with the amalgam. Agitation would very decidedly hasten the interchange, as diffusion is very slow in the rather viscous cadmium sulphate solution; this conclusion was frequently verified as shaking rapidly increased the e. m. f.

The experimental results are all in accord with the idea that the reduction of mercury by cadmium is a reversible reaction which does not go to completion. Whenever a cadmium amalgam is put into a cadmium sulphate solution, it loses mercury and gains cadmium provided mercury was not originally in the solution. Pure mercury would always gain cadmium and go into solution even if there was mercury in the cadmium sulphate solution. In our cells the solution generally contained a greater concentration of mercury than corresponded to the equilibrium conditions for any amalgam used, so all the amalgams lost cadmium. The percentage loss of cadmium by any amalgam depended on the total amount of cadmium present in the amalgam and only when it was of the order of magnitude of the mercury concentration in the electrolyte did the loss of cadmium become sensible. It is to be concluded, therefore, that our amalgams of dilutions $1/10^7$ and $1/10^8$ were approaching the concentration of mercury in the electrolytes and this offers an explanation of the deviation of these amalgams from the logarithmic relation. In the case of zinc amalgams it is expected that this deviation from the logarithmic relation will not be encountered until much greater dilutions are reached since zinc is much more electropositive than cadmium and the equilibrium constant should be much smaller.

Summary.

The chief results of this investigation are:

A method of effectively preventing oxidation during the making or dilution of amalgams and methods of handling such amalgams.

The use of a two-phase amalgam as a constant reproducible electrode and as a basis for all measurements on the electromotive force of amalgams.

A determination of the composition and density of the liquid phase of a cadmium amalgam saturated at 25° which gave an exact relation between the density and composition of all cadmium amalgams at any ordinary temperature, $D = 13.5340 - 0.0606 \times p$ with a temperature coefficient of $-(0.0024 + 0.0003\ p)$ where p is the percentage of cadmium in the amalgam.

A method of removing oxygen from a solution and saturating it with hydrogen and of effectively removing the residual oxygen from a cell and its contents.

Measurements on the electromotive force of cadmium amalgams at 25°, extending from the saturated amalgam to a dilution of one part of cadmium in one hundred million of mercury. These observations were all based on a constant reproducible electrode and the values for amalgams in different cells are therefore directly comparable.

The discovery of a region between one gram of cadmium to 100 of mercury, and one gram of cadmium to one million of mercury, where the potential of any two amalgams corresponded to the requirements of the gas laws. A deviation from these requirements was found for amalgams containing less than one gram of cadmium to one million of mercury. This deviation was anticipated and is interpreted as evidence in favor of the reversibility of the reduction of mercury by cadmium, indicating that this reaction does not go to completion but that a definite equilibrium is established.

PRINCETON UNIVERSITY,
September, 1908.

THE MIXED BARIUM-STRONTIUM CHROMATE PRECIPITATE.

BY L. H. DUSCHAK.

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I. Introduction.

A study of the so-called occlusion of barium chloride by precipitated barium sulphate, carried out by G. A. Hulett and the author,[1] served as the starting point for the work now under consideration. In the first paper it was suggested that the presence of barium chloride as well as hydrochloric acid and water in the barium sulphate could most easily be explained by regarding the precipitate as an isomorphous mixture of barium sulphate with one or more complex salts of barium. It was stated further[1] (p. 217) that cases of isomorphism in which one component, owing to its ready solubility, was present in only a minute quantity were probably more common than one might at first suppose; and that many irregularities encountered in analysis might find their explanation in this circumstance.

The mixed barium sulphate precipitate which we studied belongs to one of the two general classes of simple isomorphous mixtures, namely, that mixture which contains several salts of the same metal. To the other class belong those mixtures containing two or more metals combined with the same acid radicle.

The mixed precipitate of barium and strontium chromates which is formed as an intermediate product in the separation of barium and stron-

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[1] *Z. anorg. Chem.*, **40**, 196 (1904).