THE THERMOELECTRIC BEHAVIOR OF METALS IN
SOLUTIONS OF THEIR OWN SALTS.

II. CADMIUM AMALGAM IN A SOLUTION OF CADMIUM SULPHATE.

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INTRODUCTION.

THE present paper is the second in a series on the thermoelectric behavior of metals in solutions of their own salts. Paper I.¹ deals with the thermoelectric behavior of silver. The work herein recorded has to do with the thermoelectric behavior of cadmium amalgam in a solution of cadmium sulphate.

The object of this work is in general, an investigation of the relation of heat to electromotive force. The solution of this problem demands the specific investigation of the thermoelectric behavior of a large number of metals, with respect to the direction and magnitude of the thermoelectromotive force under given conditions, and to the relation of this electromotive force to the concentration of the electrolyte. The problem also involves a study of the subjects of osmotic pressure and solution pressure and allied topics, in so far as these forces play any rôle in the production of an electromotive force.

In pursuing the present investigation three specific objects have been kept in view, as follows: First, to determine the direction of the thermoelectromotive force of cadmium amalgam in a solution of cadmium sulphate; second, to determine the relation between the thermoelectromotive force and the concentration of the electrolyte; and third, to compare the thermoelectromotive force due to a given difference of temperature, with the electromotive force due to a corresponding difference of concentration.

When two electrodes of a given metal are immersed in a neutral solution of a salt of this metal, two causes may operate to produce

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an electromotive force. A difference of temperature at the electrodes will produce an E.M.F., commonly spoken of as a thermo-electromotive force. Also, a difference of concentration of the electrolyte will produce an E.M.F., which for the sake of convenience and clearness is sometimes referred to as a concentration-electromotive force. Whether these two electromotive forces are due to one and the same cause remains to be seen.

The apparatus used was very similar to that employed in the investigation on silver (Paper I.), and is shown in outline in Fig. 1. The letters A_1 and A_2 , as used in the figure, are employed to designate (*a*) the two legs of the cell, (*b*) the electrodes, or (*c*) the electrolyte contained therein.

Fig. 1.

Fig. 2.

The electrodes were prepared as shown in Fig. 2. A glass tube (*a*) was sealed into the bottom of a small glass cup (*b*), about 2 cm. in diameter, and 2.5 cm. in depth. Into the tube (*a*), near the bottom, was sealed a short piece of platinum wire (*c*). Tube (*a*) was then filled with cadmium amalgam. Finally, cup (*b*) after being thoroughly cleaned and dried, was filled with the amalgam under test, after which the entire cell was set up as shown in Fig. 1. The siphon which connects the two legs of the cell was provided with a stopcock (*s*).

Temperatures ranging from 0° to 30° centigrade were employed. The lower temperatures, those near 0°, were obtained by means of crushed ice placed in a large Dewar flask. Those of 25° and 30°

were obtained by means of a thermostat which held constant to within a few hundredths of a degree for days. Beckmann thermometers were used, for the most part.

E.M.F. readings were made by means of an Otto Wolff potentiometer, reading directly to 0.00001 volt.

The electrolyte was prepared by dissolving cadmium sulphate, recrystallized from Kahlbaum's C.P. salt, in water redistilled for conductivity purposes.

The cadmium amalgam was of twelve and one half per cent. strength, prepared by dissolving pure cadmium in redistilled mercury, in the ratio of one part by weight of cadmium to seven parts by weight of mercury.

The method of conducting a test was as follows: A solution of CdSO_4 , or a series of solutions as required, of the desired concentration was prepared as described. Enough amalgam was prepared so that for each test a fresh portion of the amalgam might be used. The electrode cups were cleaned in nitric acid, then washed with distilled water and dried. The amalgam was heated over a water bath until it came to a fluid state, after which the desired amount was transferred to the electrode cups by means of a pipette. The electrodes were then placed in the legs of the cell, and the electrolyte added. The siphon (*s*) was filled, and finally the entire cell adjusted as shown in Fig. 1. At the close of the test the cell was dismantled, and the entire operation then repeated for a new test, as just described.

DIRECTION OF THE THERMOELECTROMOTIVE FORCE.

The object here was to determine the direction of the thermoelectromotive force of a cell of the type, $\text{Cd Am.} - \text{CdSO}_4 - \text{Cd Am.}$, the temperature of electrode A_1 being kept at 0° , and that of A_2 , at 30° . The electrolyte was of the same concentration at both electrodes.

It was observed that cadmium amalgam when placed in a dilute solution of CdSO_4 loses, after a time, its bright metallic appearance, the surface becoming covered with a grayish colored film. It therefore seemed desirable to make a "time test" of a $\text{Cd Am.} - \text{CdSO}_4$ thermoelement, to determine how far this film affects the E.M.F.

Two such time tests were made. In the first, a cell of the form shown in Fig. 1 was used. The time was relatively short, readings being taken every ten minutes for an hour and a half. The electrodes A_1 and A_2 were maintained at a difference of temperature ($T_1 - T_2$) of 29.95° . In half an hour the thermoelectromotive force rose to 0.01175 volt, and this value remained unchanged for the following hour, during which readings were taken. Three hours later the cell showed an increase of only 0.00004 volt.

For the second time test a cell similar to that described in detail in Paper I. was set up. A glass tube, about 5 cm. in diameter and 70 cm. in length, sealed off at one end, was filled with a tenth molecular solution of CdSO_4 , and was set up vertically in such a manner that the lower half of the tube was contained in an ice bath, and the upper half in a water bath at 30° . One electrode was placed at the bottom of the cell, the other at the top. The difference of temperature of the electrodes was, therefore, equal to the difference of temperature between the ice bath and the water bath.

This test extended over a period of ten days. The results, as tabulated in Table I., show (a) that the E.M.F. is directed, in the external circuit, from the warm electrode to the cold—that is, the warm electrode is the cathode; and (b) the E.M.F. increases slightly with the time, due probably to the film mentioned. It must be noted, however, that this increase, over a period of ten days, was only 0.00033 volt.

TABLE I.

Time in Hours.	$T_1 - T_2$.	E.M.F. in Volts.	Time in Hours.	$T_1 - T_2$.	E.M.F. in Volts.
0	30.00°	0.00006	106	29.96°	1173
27	30.00	0.01162	118	29.99	1174
32	30.00	1163	123	30.02	1175
37	30.00	1162	142	29.98	1173
47	30.00	1163	154	29.96	1175
58	30.00	1164	174	30.00	1179
75	30.00	1172	192	29.95	1183
80	29.97	1173	214	29.95	1182
94	29.96	1172	220	29.96	1194
99	30.01	1176	244	29.96	1195

RELATION OF THE THERMOELECTROMOTIVE FORCE TO THE CONCENTRATION OF THE ELECTROLYTE.

For this test a series of solutions was prepared having the following concentrations: $n/80$, $n/40$, $n/20$, $n/10$, $n/5$. A normal solution as here used, means a gram molecule of the salt dissolved in one liter of water. The method pursued was as follows: The electrode cups (*b*, Fig. 2) were filled with cadmium amalgam, and then adjusted in the cell, as previously described. The eightieth normal solution ($n/80$) was used first. Electrode A_1 was placed in the ice bath; and A_2 in the 30° bath. The E.M.F. rapidly rose to a constant value, which was recorded.

The electrolyte was now removed and the cell washed and dried. The amalgam was also removed from the electrode cups, which were cleaned and dried, after which a fresh portion of the amalgam was added. A solution of the next higher concentration was then tested.

TABLE II.

Con.	$n/80$	$n/40$	$n/20$	$n/10$	$n/5$
T. E. M. F.	0.01024	0.01070	0.01107	0.01142	0.01172
"	1040	1081	1116	1148	1176
"	1029	1080	1111	1148	1175
"	1028	1083	1111	—	1173

Fig. 3.

Four series of readings were made, a record of which is given in Table II., and the corresponding curve in Fig. 3. Table II., which

shows an excellent agreement between the E.M.F. readings, indicates, together with the curve of Fig. 3, that the thermoelectromotive force *increases* with the concentration of the electrolyte.

COMPARISON OF THE E.M.F. DUE TO A GIVEN DIFFERENCE OF
ABSOLUTE TEMPERATURE, WITH THE E.M.F. DUE TO A
CORRESPONDING DIFFERENCE OF CONCENTRATION.

The object and conditions of the experiment were as follows: The entire cell was filled with a given solution, $n/10$ say, and the electrodes subjected to a difference of temperature of 30° , which produced a given E.M.F. The ratio of T_2/T_1 , measured on the absolute scale, was therefore, in this case equal to $303/273 = 1.11$.

Now it was desired to find what E.M.F., would be produced by a corresponding concentration ratio—that is $C_2/C_1 = 1.11$, the temperature of both electrodes being the same. To obtain the electromotive force due to this concentration ratio it was determined to plot two E.M.F. curves, obtained by different methods, such that one would serve as a check on the other. The two methods of procedure and the results are given in the following paragraph.

First Method.—A series of solutions of CdSO_4 was prepared, having the following concentrations: $5n/100$, $8n/100$, $10n/100$, $12n/100$, $15n/100$, $20n/100$. These particular concentrations were chosen, (*a*) because they gave a range which included the tenth molecular solution selected as a standard, and (*b*) because accurately calibrated pipettes capable of producing this series, were available.

One leg of the cell was filled with $10n/100$ solution and placed in the 30° bath. The concentration of this solution was unchanged throughout the experiment. The other leg of the cell was placed in the ice bath. The concentration of the electrolyte in this (the cold) portion of the cell was varied from $5n/100$ to $20n/100$.

To begin with, the E.M.F. of the cell was directed, in the external circuit, from the warm electrode to the cold electrode. It is evident therefore that the effect of increasing the concentration at the cold electrode would be to produce a counter E.M.F., which at a certain point would just balance the thermoelectromotive force. It is evident, also that the cell was operated both as a thermoelement and a concentration element at the same time, except at the

point at which the concentration at both electrodes became the same ($n/10$), at which instant the cell was functioning as a thermoelement only.

A record of the experiment is contained in Table III.

TABLE III.

$T_1 - T_2$	C. of Warm El.	C. of Cold El.	E.M.F.
30.02	10 <i>n</i> /100	5 <i>n</i> /100	0.01690
30.01	"	8/100	1352
30.02	"	10/100	1187
29.98	"	12/100	1072
30.00	"	15/100	905
30.00	"	20/100	738

Second Method.— The experiment was now repeated, though in a somewhat modified form, in order to obtain a second E.M.F. curve to serve as a check on the first.

The entire cell was placed in the 30° bath, both electrodes being therefore at the same temperature. The concentration of the electrolyte A_1 was held at 10*n*/100 throughout the experiment. The concentration of A_2 was varied from 5*n*/100 to 20*n*/100 as before. In this case the element was operated purely as a concentration cell.

The results of this series of tests are given in Table IV.

TABLE IV.

$T_1 - T_2$	C. of A_1 .	C. of A_2 .	E.M.F.
0.0	10 <i>n</i> /100	5 <i>n</i> /100	+0.00540
0.0	"	8/100	246
0.0	"	10/100	4
0.0	"	12/100	—0.00104
0.0	"	15/100	291
0.0	"	20/100	460

If now the concentrations be plotted as abscissas and the E.M.F. readings as ordinates, Tables III. and IV. give a pair of E.M.F. curves which theoretically should coincide when drawn with reference to x -axes 1,187 units apart.

Fig. 4 shows such a combination of E.M.F. curves. The continuous line represents E.M.F. readings due to both a difference of

temperature and concentration, as given in Table III. The curve represented by the broken line is taken from the data given in Table

Fig. 4.

IV., and is drawn with reference to the x -axis indicated by the horizontal dotted line.

The point (x) on curve I is the point at which the concentration ratio $C_2/C_1 = 1.11$ might be expected to produce an E.M.F. equal to that resulting from the absolute temperature ratio, $T_2/T_1 = 1.11$.

It will be noted, however, that there is at this point on the curve an outstanding E.M.F. of over 0.01100 volt. That is to say, a difference of concentration represented by the ratio $C_2/C_1 = 1.11$ will produce an E.M.F. equal to 0.00128 volt; while, on the other hand, corresponding difference of absolute temperature ($T_2/T_1 = 1.11$) will produce an E.M.F. equal to 0.01187 volt, a value nearly ten times as great.

SUMMARY.

1. Cadmium amalgam in a solution of cadmium sulphate gives between 0° and 30° , a thermoelectromotive force directed, in the

external circuit, from the warm electrode to the cold — that is, the warm electrode in the cathode. It was shown in Paper I. that in the case of silver the conditions are just the opposite, the *cold* electrode being the cathode. Further, with cadmium amalgam, the thermoelectromotive force is relatively constant, and for given concentrations is reproducible.

2. The thermoelectromotive force is a function not only of the temperature but also of the concentration of the electrolyte, an increase in concentration producing an increase of E.M.F. In the case of silver, the conditions are again reversed, an increase in concentration of the electrolyte producing a decrease of E.M.F.

3. Within a range of temperature from 0° to 30° , the thermoelectromotive force due to a given difference of absolute temperature is nearly ten times as great as the E.M.F. due to a corresponding difference of concentration. It therefore follows that the thermoelectromotive force observed cannot be accounted for on the assumption of an increase of osmotic pressure, since according to the theory a given increase of osmotic pressure due to a given difference of absolute temperature should be equal to that due to a corresponding difference of concentration. Nor can we well assign the large outstanding E.M.F., shown in Fig. 4, to a change of solution tension in the cadmium amalgam, unless we are willing to assume, since the warm electrode is the cathode, that the solution pressure of the metal *decreases* with an *increase of temperature*.

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