THERMODYNAMICS OF CONCENTRATION CELLS

By Henry S. Carhart

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INTRODUCTION

The most general expression of the laws of thermodynamics for an isothermal process, of which the well-known equation of Helmholtz for the electromotive force of voltaic cells is a particular example, may be written in the form

$$A = H + T\frac{dA}{dT}.$$

H denotes the change in the internal energy of the system and A the maximum work or the change of free energy for a reversible physical or chemical process conducted isothermally.

If A for 1 gram equivalent of an ion is expressed in terms of electrical work as nFE (n the valence of the cation, F the number of coulombs transported through an electrolyte by a gram equivalent, and E the emf), the equation becomes that of Helmholtz, namely,

$$nFE = H + TnF\frac{dE}{dT}, \text{ or } E = \frac{H}{nF} + T\frac{dE}{dT}.$$

A number of distinct cases occur in the application of the general equation.

First. $dA/dT = 0$ at all temperatures. This case is an expression of the so-called Thomson principle as applied to voltaic cells, which makes $dE/dT = 0$. In fact, the Daniell cell, set up with saturated copper sulphate and very dilute zinc sulphate (specific gravity 1.04)[1] as the electrolytes, and the Weston cell without cadmium sulphate crystals, have electromotive forces very nearly independent of temperature. They may therefore be classed under this head.

Another case in point is the purely physical transformation of the potential energy of gravity into the energy of electric transfer. The Des Coudres' cell,[2] consisting of two mercury columns of different height, joined by a solution of mercurous nitrate, the longer column being retained in position by a porous diaphragm, is another illustration of case one. The measurement of the emf in this arrangement is not very satisfactory, but the results are of the same order of magnitude as the calculated values. A single example will suffice.

The difference between the measured heights of the columns was 141.1 cm. Then, when 1 gram equivalent (200 g) of mercurous mercury is transferred electrolytically from the one elevation to the other, the decrease in potential energy is $141.1 \times 200 \times 980 =$ 27 655 600 ergs $= 2.76556$ joules. The corresponding emf is $\frac{2.76556}{96530} = 0.0000286$ volt; the measured value was 0.000030.

Second. H has a constant value. The general equation above gives $\frac{dA}{A-H} = \frac{dT}{T}$. By integration $\ln (A-H) = \ln T + \ln a = \ln aT$. Whence $A - H = aT$. Since a is the constant of integration, $A - H$ is proportional to the absolute temperature T and $dA/dT = a$. It appears, therefore, that when dA/dT or dE/dT is a constant, H is either zero or has a constant value. Illustrations will follow later.

[1] Helmholtz: Sitzungsber, Ber. Akad., pp. 22–39; 1882.

[2] Wied. Ann., **46**, p. 292; 1892.

Third. $A = 0$, and $H = -T\,dA/dT$. This condition can obtain only at some definite point of temperature where A passes through a zero value. Examples are several cases of transition, such as $ZnSO_4.7\,H_2O$ into $ZnSO_4.6\,H_2O$ at 39°, and white tin into gray tin at 20°. At the transition temperature the two phases are in equilibrium, like water and ice at 0°, and there is no free energy. But at the transition point dA/dT may be large, and $H = -T\,dA/dT$.

Fourth. As a fourth case we may include Nernst's recent modification of the general equation. Nernst [3] assumes the following empirical expressions for A and H in terms of the integral powers of the absolute temperature:

$$A = A_0 + a'T + b'T^2 + c'T^3 +$$
$$H = H_0 + aT + bT^2 + cT^3 +$$

From the general thermodynamic equation, when $T = 0$, $A_0 = H_0$; hence

$$\frac{A-H}{T} = \frac{dA}{dT} = (a'-a) + (b'-b)T + (c'-c)T^2 = a' + 2b'T + 3c'T^2.$$

Whence $a' = a' - a$, or $a = 0$; $2b' = b' - b$, or $b' = -b$; $3c' = c' - c$, or $c' = -\frac{1}{2}c$.

Finally, then,

$$A = A_0 + a'T - bT^2 - \tfrac{1}{2}cT^3 -$$
$$H = H_0 + bT^2 + cT^3 +$$

Since the same constants now appear in both equations, the a' may be replaced by a.

When the constants b and c are zero, the expression for A reduces to the simpler one containing only the first power of T, $A - H = aT$, and $dA/dT = a$, a constant as in case two, or the relation between A and T is a linear one.

Nernst assumes without sufficient justification that both $\frac{dA}{dT}$ and $\frac{dH}{dT}$ are zero when T is zero. The equations above show that $\frac{dA}{dT} = a$ when $T = 0$; hence the term aT in the expansion for A is not zero as Nernst has it. If it were zero, the expression for A would exclude the case of concentration cells, in which A

[3] Thermodynamics and Chemistry, Sitzungsber. Berl. Akad.; 1909.

is proportional to the absolute temperature (for very dilute solutions), or is equal to a constant H plus a term proportional to the first power of the absolute temperature.

The same conclusion may be reached by a different demonstration, assuming only the one expansion,

$$H = H_0 + aT + bT^2 + cT^3 +$$

The general equation $A = H + T\frac{dA}{dT}$ gives $AdT - TdA = HdT$, or $\frac{TdA - AdT}{T^2} = -\frac{H}{T^2}dT$. Integrating,

$$\frac{A}{T} = \frac{H_0}{T} + a' - a\ln T - bT - \tfrac{1}{2}cT^2, \text{ or } A = H_0 + a'T - aT\ln T - bT^2 - \tfrac{1}{2}cT^3.$$

Then $$\frac{dA}{dT} = a' - a\ln T - a - 2bT - \frac{3}{2}cT^2.$$

If now this expression for A is generally true, it must be true when dA/dT is a constant. But in case two it was shown that dA/dT is a constant when dH/dT is zero for $T = 0$, as in the last solution. Hence a in the expressions above for both A and H is zero, and the two reduce as before to

$$A = A_0 + a'T - bT^2 - \tfrac{1}{2}cT^3 -$$
$$H = H_0 + bT^2 + cT^3 +$$

The reader will note that these demonstrations show only that while the coefficient of T in the expansion for H is always zero, it is not necessarily zero in the expansion for A.

THE EVIDENCE OF EXPERIMENT

It would appear antecedently probable that a concentration cell such as *Zn amal. conc.* | $ZnSO_4$ *solution* | *Zn amal. dil.* (where the dilute amalgam at least must be of a lower concentration than that corresponding to a saturated or two-phase condition) should have constant heat of dilution for the two amalgams; or, in other words, H should be constant. This proves to be true, for the emf as a function of the temperature is linear.

For two amalgams with a concentration ratio by weight equal to two, the per cent of zinc in the more concentrated amalgam being approximately 1.2, the equation representing the emf was found to be

$$E = -0.001455 + 0.00003084\ T.$$

For the centigrade scale this is equivalent to

$$E_t = 0.006964(1 + 0.00443\ t).$$

The constant 0.00443 is the temperature coefficient $\frac{1}{E_0}\frac{dE}{dT}$. It is much larger than the temperature coefficient of a perfect gas.

In the following table are the observed values of the emf compared with those computed by the first equation:

Temp.	Obs. emf	Comp. emf	Per cent difference
11°.1	0.007300	0.007307	+0.10
15°.4	7444	7439	− .07
19°.8	7574	7575	+ .01
24°.6	7720	7723	+ .04
29°.4	7870	7871	+ .01
32°.8	7983	7976	− .09
36°.6	8086	8094	+ .10
42°.0	8262	8259	− .04
47°.0	8417	8414	− .04

The greatest difference between the observed and the computed values is 0.008 millivolt. The experimental cell was placed in a large water bath with double walls, and a stirrer driven by an electric motor was used to insure equal temperatures of the two legs of the cell. The emf was measured by a Wolff's potentiometer and a Weston Normal cell.

The cell was then taken apart, the amalgams washed, and the cell was again assembled with a concentrated solution of $ZnCl_2$ as the electrolyte. The observations are best represented by the same linear equation as the one applying to the $ZnSO_4$. Both the heat of dilution of the amalgams and the temperature coefficient, therefore, remain unchanged when the anion Cl replaces

the anion SO_4. The observed and computed values are compared in the table.

Temp.	Obs. emf	Comp. emf	Per cent difference
10°.1	0.007275	0.007276	+0.01
14°.9	7424	7424	.00
19°.6	7567	7569	+ .03
25°.3	7733	7744	+ .14
32°.1	7943	7954	+ .14
37°.3	8106	8114	+ .10
41°.8	8256	8253	− .04
47°.9	8460	8441	− .22
49°.3	8486	8485	− .01

In the diagram Fig. 1 the circles denote the observations for $ZnSO_4$ and the crosses those for $ZnCl_2$.

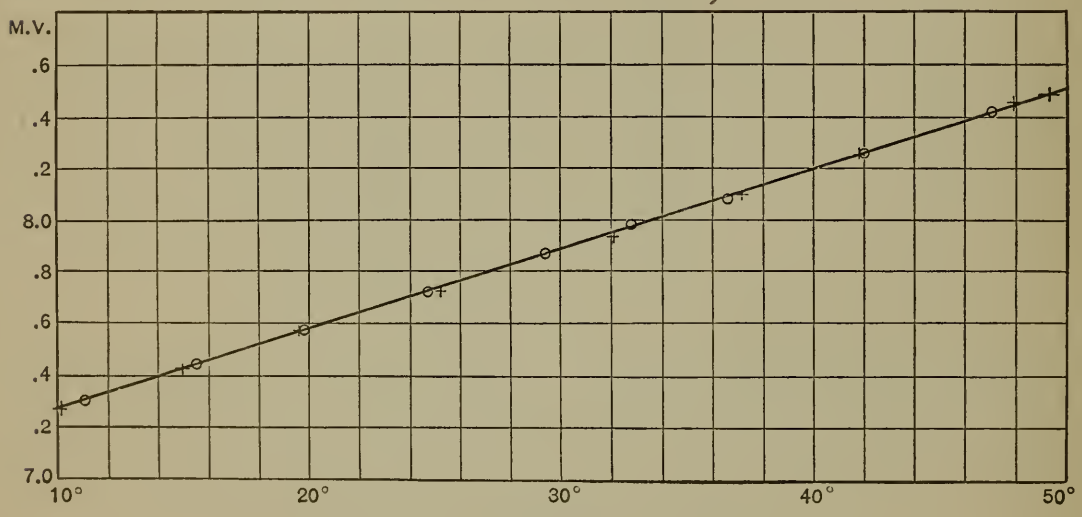

Fig. 1

Since the equation representing the emf is linear, it follows that dE/dT is a constant. The constancy of dE/dT may be shown in another manner. From the Helmholtz equation and the constant of the last equation, $\frac{dE}{dT} = \frac{E + 0.001455}{T}$.

Then for 11°.1, $\frac{dE}{dT}=\frac{0.007300+0.001455}{248.1}$		=0.00003082
15°.4		3085
19°.8		3083
24°.6		3083
29°.4		3083
32°.8		3086
36°.6		3082
42°.0		3085
47°.0		3085
	Mean	0.00003084

Cady[4] measured the emf of a sodium amalgam cell with the amalgams in a solution of *NaI* in pyridin. He assumed the correctness of the formula in the Nernst form for the emf of the cell as 0.0002 $T \log \frac{c_1}{c_2}$, in which the ratio of the concentrations replaces that of the osmotic pressures of the sodium in the amalgams. From his data the following values have been calculated:

For 4°, $\frac{dE}{dT}=\frac{0.0648-0.03}{277}$		=0.0001256
7°		1264
9°		1262
19°		1260
22°		1264
	Mean	0.0001261

The constant 0.03 was the difference between the observed electromotive forces and those calculated from the Nernst formula. This constant is evidently too large. Calculating it by the Helmholtz equation for 7°, for example, it is 0.0265. Then, substituting this in place of 0.03 in the equation for dE/dT, the resulting value is 0.0001384. Again correcting the heat of dilution by this new approximate value of dE/dT, the emf due to the heat of dilution comes out 0.02665. The substitution of this value in

[4] J. Phys. Chem., **2**; 1898.

place of 0.03 in the Helmholtz equation to determine dE/dT gives as the mean value 0.0001381. This is materially larger than Cady's value from the same data.

The equation for the emf is accordingly

$$E = 0.02665 + 0.0001381\ T.$$

The observed and computed values are the following:

Temp.	Obs. emf	Comp. emf	Per cent difference
4°	0.0648	0.06480	0.0
7°	654	6532	−.12
9°	656	6559	−.02
19°	668	6698	+.25
22°	673	6729	−.02

The heat of dilution of the sodium amalgam with mercury, computed from the equation for E, is 612.9 calories per gram molecule.

The following examples have been calculated from data given by Richards (Carnegie Institution of Washington, Publication No. 118):

Thallium, per cent of metal in the denser amalgam, 0.41.

$$\text{For } 0°, \frac{dE}{dT} = \frac{0.031543 - 0.001813}{273} = 0.0001089$$

$$15° \qquad \frac{0.033166 - 0.001813}{283} = 0.0001089$$

$$30° \qquad \frac{0.034810 - 0.001813}{303} = 0.0001089$$

Thallium, per cent of metal in denser amalgam, 0.111.

$$\text{For } 0°, \frac{dE}{dT} = \frac{0.016360 - 0.000436}{273} = 0.00005833$$

$$15° \qquad \frac{0.017238 - 0.000436}{288} = 0.00005833$$

$$30° \qquad \frac{0.018110 - 0.000436}{303} = 0.00005833$$

The linear equations for these two cases are:

$$E = 0.001813 + 0.0001089\ T.$$

$$E = 0.000436 + 0.00005833\ T.$$

The heat of dilution and the temperature coefficient are constant in both cases; both therefore negative the hypothesis of Nernst that the coefficient of T in the expression for A (or E) is zero. The relation between the emf and the temperature in all these amalgams is a purely linear one. The range of temperatures must be restricted to limits within which there is no change of phase in the materials composing the cell.

In addition to the cell with zinc amalgams the writer finds also that a concentration cell composed of cadmium amalgams and cadmium sulphate has an emf following the linear relation. The two amalgams had concentrations of approximately 2 per cent and 0.783 per cent. The following are the measured emf's compared with those computed by the equation

$$E = -0.000219 + 0.00003915\ T:$$

Temp.	Obs. emf	Comp. emf	Per cent difference
10°.05	0.010862	0.010862	0.0
15°.10	11063	11060	− .03
18°.42	11190	11190	.0
22°.10	11336	11334	− .02
26°.80	11517	11518	+ .01
33°.40	11773	11776	+ .03
38°.00	11942	11956	+ .12
43°.20	12160	12160	0.0

The heat of dilution comes out a small negative quantity of −10 calories per gram molecule of cadmium. The observations are plotted in Fig. 2, the straight line representing the equation for E.

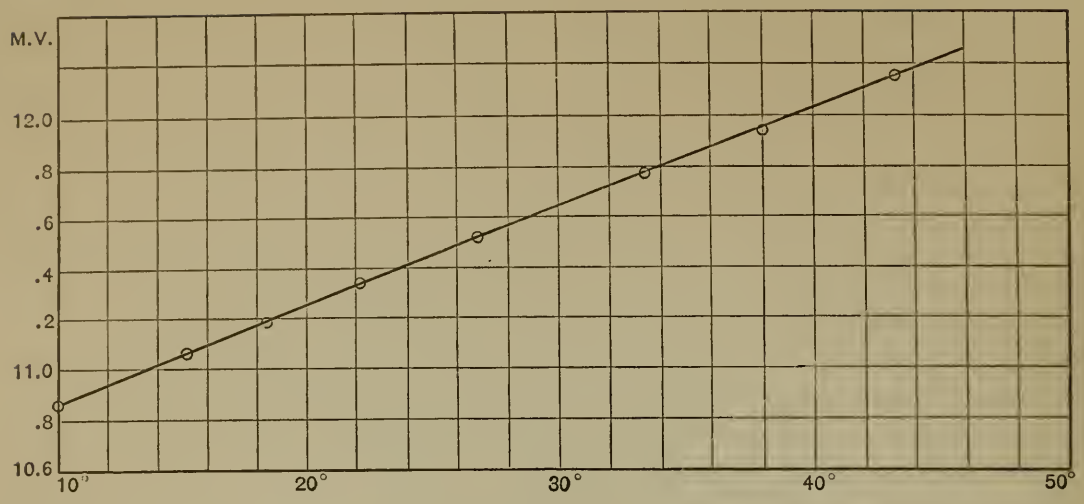

Fig. 2

THE SECOND TERM OF THE HELMHOLTZ EQUATION

The term $T\,dE/dT$, in cases where there is no change of phase in the materials, is a purely electrolytic thermoelectromotive force, which is very approximately linear. To illustrate this feature as applied to concentration cells, two amalgams were made by weighing out masses of mercury as one to two and depositing in them electrically the same quantity of zinc. The weight of zinc deposited was 0.6 and 1.2 per cent, respectively, of the weight of mercury. The concentration cell set up with these amalgams and a dense solution of zinc sulphate gave the following electromotive forces at the temperatures indicated:

Temp.	Obs. emf	Comp. emf
10°.70	0.007320	0.007319
14°.13	7420	7420
19°.62	7572	7581
24°.20	7713	7716
26°.25	7785	7776
31°.60	7940	7933
36°.80	8086	8086
39°.00	8146	8151

Equation: $E = -0.001022 + 0.0000294\ T.$

The corresponding heat of dilution of the two amalgams is -47 calories per gram molecule.

To measure the electrolytic thermoelectromotive force of the two amalgams, the two legs of the H-form of cell, identical in every respect as far as possible, were immersed in baths, one containing mixed ice and water, and the other water, the temperature of which was varied. The entire cell, except the short portion connecting the side tubes, was immersed. The results are the following:

Thermoelectromotive Force for the More Dilute Amalgam

Temp.	Obs. emf	Comp. emf
10°.30	0.01077	0.01077
15°.40	1611	1611
20°.47	2140	2141
25°.60	2676	2678
31°.10	3251	3253
36°.80	3852	3849
40°.20	4214	4205

Equation: $E_1 = 0.001046\ t.$

Thermoelectromotive Force for the More Concentrated Amalgam

Temp.	Obs. emf	Comp. emf
9°.41	0.00956	0.00957
14°.75	1496	1500
19°.65	1996	1998
25°.05	2542	2547
30°.60	3110	3112
35°.20	3582	3580
39°.30	4000	3993

Equation: $E_2 = 0.001017\ t.$

Then $\frac{dE}{dT} = \frac{E_1 - E_2}{t} = 0.001046 - 0.001017 = 0.0000290.$

Compare this with the value measured directly, namely, 0.0000294. The three tables are plotted in Fig. 3, with the scale for E on the left, and that for E_1 and E_2 on the right.

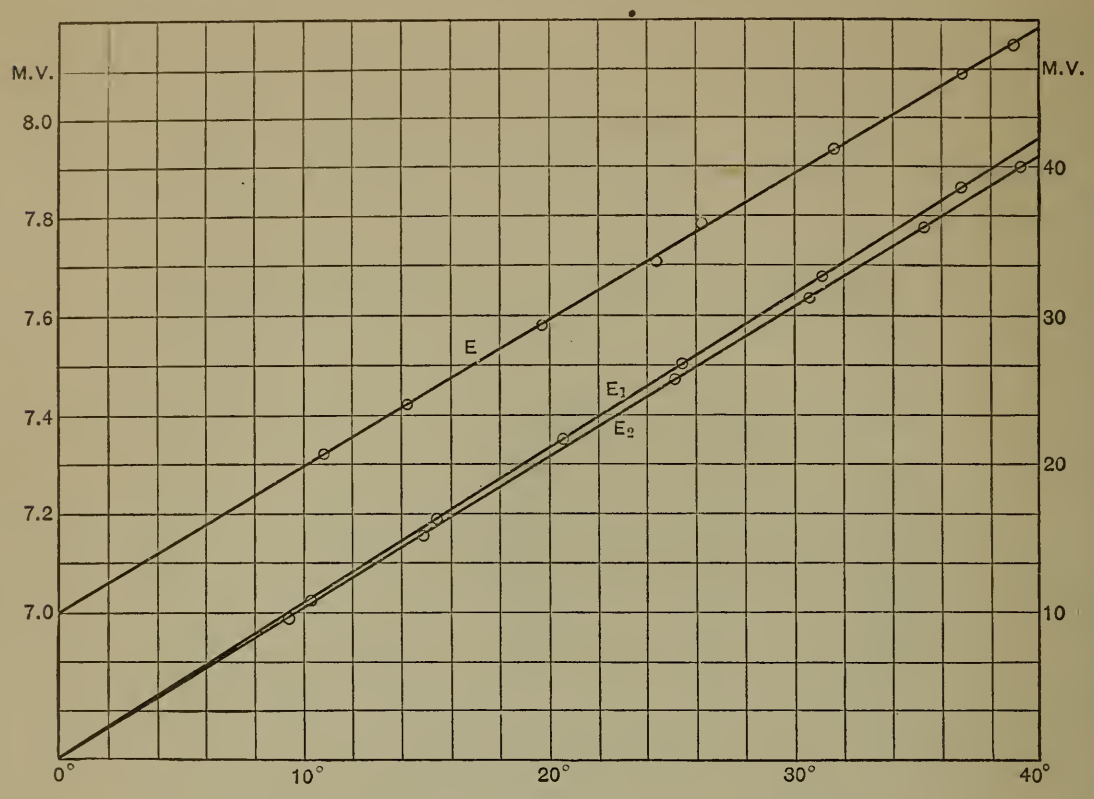

Fig. 3

The thermoelectromotive force is directed from the solution to the amalgam, and it increases as the *dilution* of the amalgam increases. In other words, the electrolytic thermoelectromotive force is a function of the concentration as well as of the temperature. Hence, the resulting emf of the cell is in favor of the dilute amalgam, which is thus the cathode of the cell. If the heat of dilution is positive, the emf derived from it is in the same direction as the emf resulting from the two thermoelectromotive forces; if the heat of dilution is negative, the corresponding emf is opposed.

The passage of a current through a concentration cell not only reduces the difference in concentration of the amalgam electrodes, but it tends to produce a temperature difference between them. At the anode the current encounters a back emf and heat is gen-

erated; at the cathode the thermoelectromotive force has the same direction as the current, and heat is absorbed. When the difference in concentration is entirely in the amalgam electrodes, the heat absorbed is greater than the heat generated, and such a cell converts its own heat and that of the surroundings into the energy of the electric current. It can not do so continuously, because its current reduces the difference of concentration on which the emf depends.

When the difference in concentration is in the electrolyte surrounding the electrodes, cases occur of positive heat of dilution and a negative temperature coefficient. An example is the following:

$$Zn \mid ZnCl_2.18.8\ H_2O \mid ZnCl_2.180\ H_2O \mid Zn$$

The quantity dE/dT for this cell[5] is -0.0000973; the heat of dilution is 4530 calories per gram molecule (Thomsen). The computed emf would be—

$$\text{emf due to heat of dilution,} \quad \frac{4530}{2 \times 23040} = 0.09831$$

$$\text{emf at } 25° \text{ equal to } T\frac{dE}{dT} = -298 \times 0.0000973 = -0.02900$$

$$E = 0.06931$$

The mean observed emf at 25° was 0.06719 volt.

This concentration cell is precisely like a voltaic cell with a negative temperature coefficient. Its energy is derived from the heat of dilution, and it is difficult to see how the Nernst formula for the emf of a concentration cell can have any application whatever to it.

Since the relation between the thermoelectromotive forces of the above amalgams and the temperature is a linear one, the potential difference at the liquid-amalgam junctions may be computed from the expression TdE/dT. Thus, the potential difference between the zinc sulphate solution and the dilute amalgam (0.6 per cent) at 27° is

$$0.001046 \times 300 = 0.3138 \text{ volt.}$$

For the concentrated amalgam (1.2 per cent) it is

$$0.001017 \times 300 = 0.3051 \text{ volt.}$$

[5] Phys. Rev., **29**, p. 329; 1909.

Then the emf of the concentration cell composed of the two amalgams and the zinc sulphate as electrolyte, owing to the thermoelectromotive forces at 27°, is

$$0.3138 - 0.3051 = 0.0087 \text{ volt.}$$

But there is a loss on account of the negative heat of dilution equal to about 0.001 volt. Hence

$$E = 0.0087 - 0.0010 = 0.0077 \text{ volt.}$$

The measured value was 0.0078 volt.

A COMPOSITE CONCENTRATION CELL

A concentration cell, in which the difference in concentration is entirely in the two electrolytes bathing the electrodes, may be combined with one in which the concentration difference is in the amalgam electrodes in such a manner that the complete cell may have zero temperature coefficient, and thus come under case one of the general equation.

For example, the cell

$$Zn\ amal.\ |\ ZnSO_4.50\ H_2O\ |\ ZnSO_4.190\ H_2O\ |\ Zn\ amal.$$

has an emf represented approximately by the equation

$$E_2 = 0.001527 + 0.00003084\ T.$$

The positive is the electrode in the more concentrated solution. If this cell be combined with the one whose equation was found to be

$$E_1 = -0.001455 + 0.00003084\ T$$

with the dilute solution in contact with the dilute zinc amalgam, the resulting emf of the combination will be the difference between the two equations representing the two components of the composite cell. Then

$$\begin{aligned} E_2 &= +0.001527 + 0.00003084\ T \\ E_1 &= -0.001455 + 0.00003084\ T \\ \hline E &= \quad 0.002982 + 0.0 \end{aligned}$$

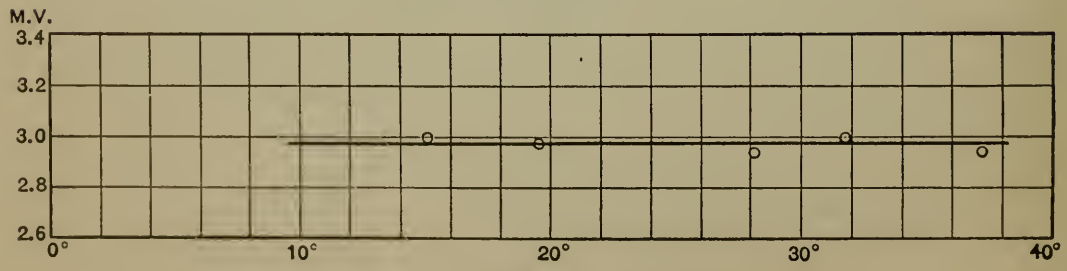

Fig. 4

The results of a single trial of such a cell are shown in Fig. 4. The amalgams were the same as those used in getting the data for Fig. 1. The equilibrium of the cell was rather uncertain and was easily disturbed by a jar.

$\frac{dE}{dT}$ FOR THE CALOMEL CELL

The analysis of the temperature coefficient already applied to the amalgams of a concentration cell (Fig. 3) is equally successful when applied to the calomel cell. The following measurements of electrolytic thermoelectromotive forces were made by the writer many years ago by means of an extemporized potentiometer, which permitted direct measurements to one ten-thousandth volt only. The density of the zinc chloride solution was 1.395 g per cm^3 at 15°, and metallic zinc wire was used as the zinc electrode. One electrode was kept in an ice bath while the temperature of the other was raised by short steps.

A. $Zn \mid ZnCl_2 \mid Zn$

Temp.	Obs. emf	Comp. emf	Difference
8°.1	0.00490	0.00478	−12
10°.5	612	608	− 4
12°.3	750	726	−24
17°.7	1040	1044	+ 4
22°.2	1301	1310	+ 9
25°.8	1499	1522	+23
28°.6	1668	1687	+19
32°.1	1913	1894	−19
34°.5	2050	2036	−14
39°.1	2295	2307	+12

The mercury electrode was then subjected to the same treatment with the following results:

B. $Hg \mid HgCl \mid ZnCl_2 \mid HgCl \mid Hg$

Temp.	Obs. emf	Comp. emf	Difference
7°.1	0.00517	0.00486	−31
10°.6	730	726	− 4
12°.9	882	884	+ 2
16°.5	1125	1130	+ 5
19°.8	1358	1356	− 2
22°.8	1561	1562	+ 1
25°.3	1729	1733	+ 4
27°.9	1928	1911	−17
31°.8	2170	2178	+ 8
34°.1	2340	2336	− 4
36°.8	2554	2521	−33

For A, $E_1 = 0.000590\ t$; for B, $E_2 = 0.000685\ t$. Whence for this calomel cell

$$\frac{dE}{dT} = \frac{E_2 - E_1}{t} = 0.000095.$$

The table following shows the observed emf's compared with those computed from the equation

$$E = 1.0005 + 0.000095\ (t - 15°)$$

up to about 35°; for higher temperatures the observed values exceed the computed ones, perhaps because of the increased solubility of the calomel at those temperatures.

Temp.	Obs. emf	Comp. emf
10°.0	1.0001	1.00003
15°.0	1.0005	1.00050
17°.2	1.0007	1.00071
20°.4	1.0010	1.00101
23°.7	1.0013	1.00133
26°.7	1.0016	1.00161
30°.2	1.0020	1.00194
36°.4	1.0025	1.00253

The results are plotted in Fig. 5. The inclined line at the bottom marked E is drawn from the above equation and passes through 9°.75, where the emf of the cell is 1 volt. The observed emf's are plotted along this line.

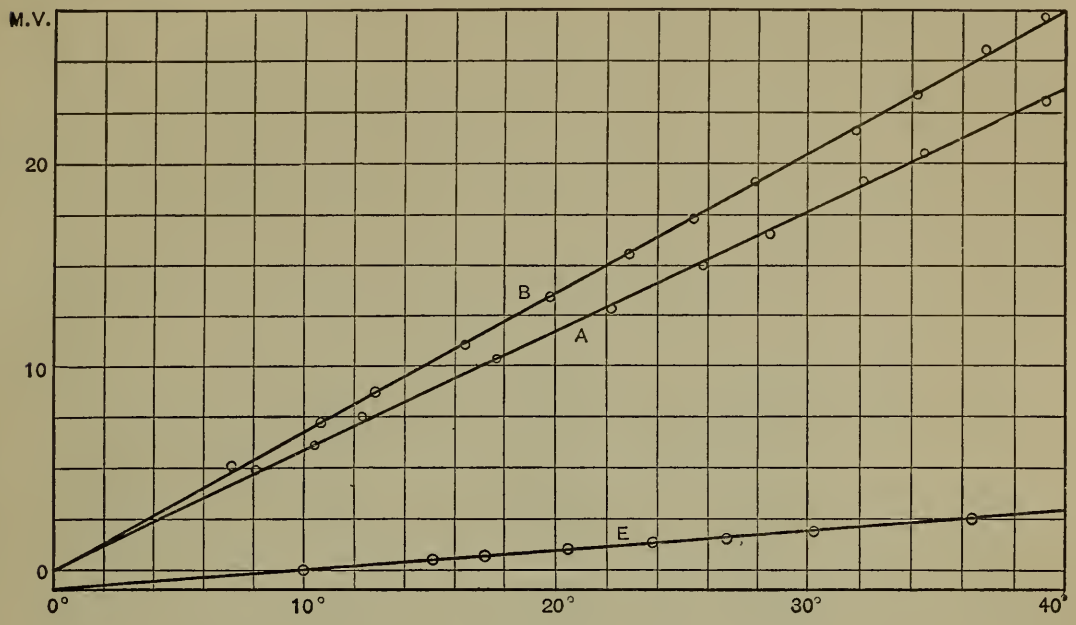

Fig. 5

A PAIR OF CALOMEL CELLS WITH CONSTANT EMF

The change of emf of the calomel cell with temperature is about 0.1 millivolt per degree and positive. The thermoelectromotive force at the mercury-mercurous chloride surface is thus higher than at the surface of the zinc.

Since the thermoelectromotive force between zinc sulphate and zinc amalgam increases as the concentration of the amalgam decreases, it is apparent that a calomel cell with a negative temperature coefficient is possible. Moreover, if the dilution of the amalgam produces a sufficient range in the thermoelectromotive force at its surface, it should be possible to make a calomel cell with a negative change of emf equal to 0.1 millivolt per degree. Such a cell in series with one set up with 10 per cent zinc amalgam would give a combined emf independent of temperature, at least over a range of 25 or 30 degrees.

A trial was made with a three-legged cell. One outer leg contained a 10 per cent zinc amalgam, the other an amalgam with about 0.8 per cent zinc; in the middle leg was placed mercury covered with mercurous chloride. The electrolyte was a solution of $ZnCl_2$, specific gravity 1.4. The cell was placed in a water bath and the potential difference between the two amalgams and the mercury as the positive electrode was measured at several temperatures. Let E_1 denote the emf of the cell with the 10 per cent amalgam and E_2 the other. A series of measurements is given in the following table:

Temp.	E_1	E_2	E_1+E_2	E_1-E_2
33°.3	0.99693	0.98456	1.98149	0.01237
30°.0	.99665	.98497	1.98162	.01168
26°.3	.99622	.98528	1.98150	.01094
22°.3	.99579	.98571	1.98150	.01008
18°.9	.99545	.98604	1.98149	.00941
14°.2	.99497	.98655	1.98152	.00842
9°.4	.99449	.98709	1.98158	.00740

These measurements were made within a period of two hours and the values correspond, therefore, to somewhat rapid changes of temperature. Nevertheless, E_1+E_2 remains nearly constant. The value of dE_1/dt is fairly represented by 0.000103 and dE_2/dt by -0.000103. If E_1-E_2 be denoted by E, then $dE/dt=0.000206$. The relation of these ratios to one another and to E_1+E_2 is shown graphically in Fig. 6.

SUMMARY

1. The general thermodynamic equation shows that when H is either zero or a constant, dA/dT is constant and $A=H+aT$.

2. A discussion of the expressions for A and H proposed by Nernst demonstrates that the term depending on the first power of T is not necessarily zero for A, as Nernst assumes it to be.

3. Concentration cells composed of zinc amalgams and either zinc sulphate or zinc chloride solutions, and cadmium amalgams

and cadmium sulphate solution, show a linear relation between their emf and temperature. This fact is contrary to Nernst's hypothesis.

4. dE/dT for these cells, and for others investigated by Richards, is a constant for each combination. H also is therefore constant and may be readily calculated from the Helmholtz equation for E.

5. The electrolytic thermoelectromotive force for zinc amalgams in contact with a solution of a salt of zinc is proportional to the

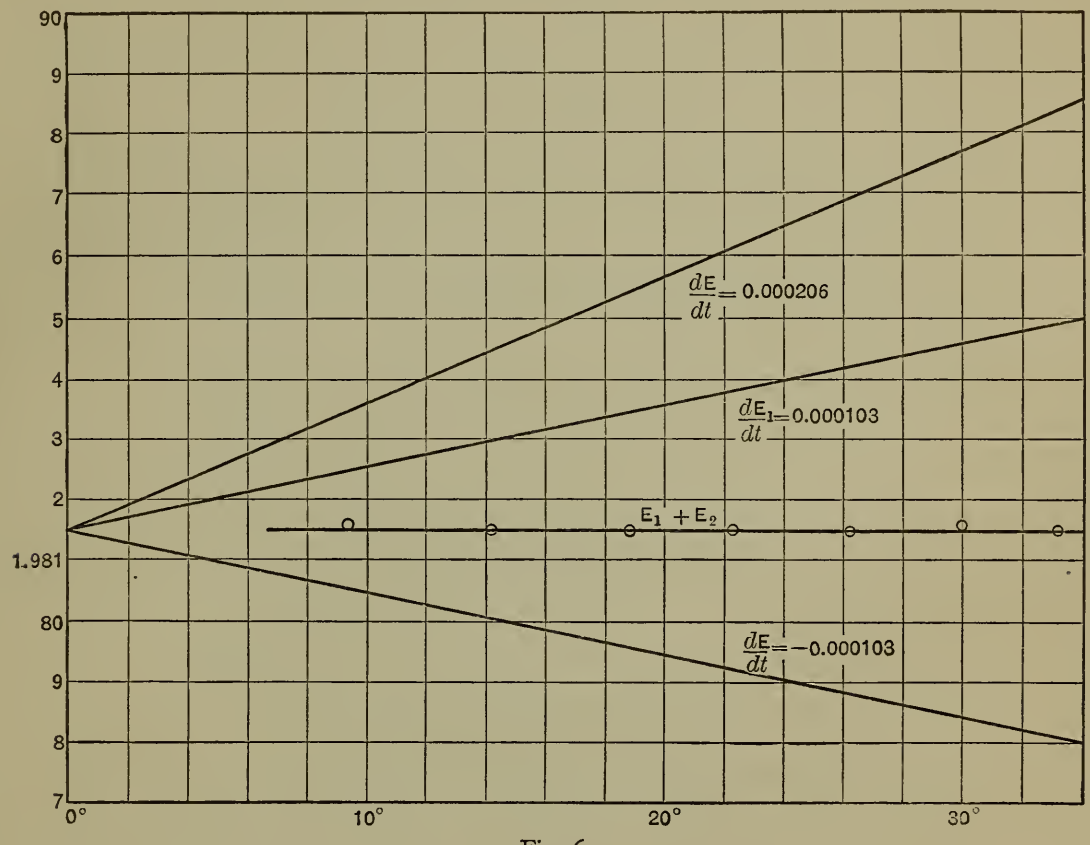

Fig. 6

temperature. In this instance, so long as there is no change of phase, H is zero and $E = aT$. When H is known for any two amalgams, the emf of the corresponding concentration cell may be calculated from H and the two thermoelectromotive forces.

6. By opposing the value of dE/dT for the amalgams by an equal and opposite value of dE/dT arising from a difference in the concentration of the electrolyte at the two electrodes, it is possible to

make a concentration cell independent of temperature. Its emf is derived entirely from the heat of dilution of the amalgams and of the electrolytes.

7. dE/dT for the calomel cell is positive, and is shown to be dependent on the difference between the thermoelectromotive forces at the two electrodes. By taking advantage of the fact that electrolytic thermoelectromotive forces vary with the concentration of amalgams, it is found possible to make a calomel cell with a negative temperature coefficient, numerically equal to that of the normal calomel cell, so that when the two are connected in series their combined emf is practically constant and independent of temperature over a range of 25 or 30 degrees.

The writer takes this opportunity to express to the Director of the Bureau of Standards his appreciation of the courtesies extended during the past few months, and his thanks for the privilege of carrying out the investigation described in this paper.

WASHINGTON, May 7, 1911.