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APPLICATION OF GIBBS-HELMHOLTZ EQUATION TO CONCENTRATION CELLS.

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INTRODUCTION.

UP to the present time there is no theory that satisfactorily accounts for the E.M.F. of concentration cells. The Nernst equation, which is based upon the gas law, applies only to very dilute solutions — millinormal and under. For somewhat greater concentrations it has to be modified, and for strong solutions it no longer holds. It has been pointed out[1] that the Gibbs-Helmholtz equation applies when the heats of reaction and dilution are so small that they may be neglected. This also restricts the solutions to very dilute ones. The present research has for its object, in general, the application of the Gibbs-Helmholtz equation to concentration cells, and in particular, to cells in which the heat of dilution is not negligible, and to show how to take this factor into account. The class of cells to which application is made is that in which the two electrodes are composed of amalgams of the same metal immersed in a salt solution of the metal, the concentration of the amalgams being the same, but that of the solution being different at the two electrodes.

HISTORICAL.

Robert Mayer[2] was one of the first to point out that there existed a relation between the change in chemical energy and the electrical

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[1] Trans. Am. Electrochem. Soc., 1, 32, 1906.

[2] Mayer, Die Organische Bewegung in ihrem Zusammenhange mit dem Stoffwechsel.

energy of the current. Helmholtz[1] was of the opinion that all the chemical energy lost reappeared in the electrical form. This opinion was also held by Sir William Thomson,[2] J. Bosscha[3] and others. Later investigations by Raoult,[4] Thomsen[5] and Braun[6] showed experimentally that the electrical energy may be either greater or less than the heat of chemical reaction. Gibbs[7] and Helmholtz[8] theoretically came to the same conclusion. Helmholtz finally put this theory into the form in which it is usually found. He called that portion of the whole heat energy which can be transformed into electrical energy, "free energy," that portion which cannot be transformed, "bound energy" and the sum of these two "total energy." The theory stated in this form is known as the Gibbs-Helmholtz equation.

Numerous examples[9] of the Gibbs-Helmholtz equation have been worked out for voltaic cells, but no general application has been made to concentration cells. Richard and Lewis[10] applied the equation to concentration cells for determining the heats of amalgamation from the temperature coefficient when amalgam was used for one of the electrodes and pure metal for the other.

Carhart,[11] in his thermoelectric theory of concentration cells, maintains that concentration cells are devices for converting heat of their surroundings into electrical energy, and that whenever the heat of reaction and dilution is negligible, the last term only of the Gibbs-Helmholtz equation, $T \cdot dE/dT$, remains and represents the E.M.F.

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[1] Ostwald, Klassiker der exakten Wissenschaften, Nr. 1.

[2] Phil. Mag., 2, 429, 1851; 2, 551, 1851.

[3] Pog. Ann. Phys., 101-517, 1857; 103, 1858; 105, 396, 1858.

[4] Ann. de Chimie et de Phys., 4, 392, 1856.

[5] Wied. Ann. Phys., 11, 246, 1880.

[6] Wied. Ann. Phys., 5, 183, 1878; 16, 561, 1882; 17, 593, 1882.

[7] Trans. of Connecticut Acad., 3, 588, 1878.

[8] Berl. Sitsungs., 22, 1884.

[9] Czapski, Wied. Ann. Phys., 21, 209, 1884. Gockel, Wied. Ann. Phys., 24, 618, 1885. Jahn, Wied. Ann. Phys., 28, 21, 1886; 28, 491, 1886; 28, 498, 1886. Nernst & Bugarsky, Zeit. f. anorg. Chem., 14, 145, 1890. Poincaré, Ann. de Chimie et de Phys., 21, 344, 1890. Oswald & Miller, Zeit. Phys. Chem., 34, 62, 1900; 34, 612, 1900. Cohen, Zeit. Phys. Chem., 60, 707, 1901. Lorenz, Electrolysis of Fused Salts, Vol. 3. Lorenz, Zeit. Phys. Chem., 63, 121, 1908.

[10] Am. Acad. of Arts and Sciences, 34, 87, 1898.

[11] Trans. Am. Electrochem. Soc., 2, 123, 1902.

of the cell. Application[1] was made to two cells of the type, Ag — $AgNo_3$ conc. — $AgNo_3$ dil. — Ag, and Cd.Hg — *n*/10 $CdSO_4$ — *n*/100 $CdSO_4$ — Cd.Hg. The agreement between the calculated values and the observed values was very good but in both cases the calculated values were low because the heat of dilution was not taken into account.

In 1907 Richards and Forbes[2] reported work done on concentration cells in which the difference of concentration was in the amalgams comprising the electrodes. Heats of dilution of cadmium and zinc amalgams were measured with a specially devised calorimeter. The heat of dilution of a 3 per cent. cadmium amalgam was so small as to be negligible. In this case the last term of the Gibbs-Helmholtz equation was found to represent the E.M.F. of the cell. For the zinc amalgam, the heat of dilution is not negligible. No application of the Gibbs-Helmholtz equation was made to such cells.

For the last two decades numerous examples of concentration cells have been worked out for the purpose of verifying the equations of Nernst and Planck, but as far as is known to the writer the Gibbs-Helmholtz equation has not been applied to concentration cells of any type so as to take into account the heat of dilution.

THEORETICAL.

According to the Gibbs-Helmholtz equation wich is based upon fundamental principles of thermodynamics,

$$E = \frac{H}{nF} + T\frac{dE}{dT}, \tag{1}$$

in which E represents the E.M.F. of the cell; H the heat of reaction; n the valence of the ion; F the number of coulombs transported by a gram equivalent of the ion; T the absolute temperature.

Equation (1) when written

$$nFE = H + nFT\frac{dE}{dT} \tag{2}$$

gives the conditions under which the electrical energy nFE, is a

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[1] Trans. Am. Electrochem. Soc., 1, 32, 1906.

[2] Zeit. Phys. Chem., 58, 683, 1907.

measure of the heat of reaction of a cell. It is to be observed that $nFE = H$ whenever $dE/dT = 0$, or $T = 0$. In other words, the electrical energy of a cell is equal to the heat of reaction, (1) when the temperature coefficient is zero, (2) when the absolute temperature is zero. If $dE/dT > 0$, or the temperature coefficient is positive, the electrical energy is greater than the heat of reaction. If $dE/dT < 0$, or the temperature coefficient negative, the electrical energy is less that the heat of reaction. In the former case the cell absorbs heat from the surroundings; in the latter, it evolves heat. The total electrical energy of the cell may be calculated by determining the heat of reaction and the temperature coefficient.

If equation (2) is written

$$H = nF\left(E - T\frac{dE}{dT}\right) \tag{3}$$

an expression is obtained by means of which the heat of reaction may be calculated by merely measuring the E.M.F. at different temperatures. It is to be noted in this case that $H = 0$ whenever $E = T \cdot dE/dT$, or the heat of reaction is equal to zero whenever the E.M.F. of the cells equals $T \cdot dE/dT$ as is approximately the case for concentration cells with dilute solutions; $H > 0$ whenever $E > T \cdot dE/dT$, or the heat of reaction is positive whenever the E.M.F. of the cell is greater than $T \cdot dE/dT$; $H < 0$ whenever $E < T \cdot dE/dT$, or the heat of reaction is negative whenever the E.M.F. is less than $T \cdot dE/dT$.

These equations were applied to cells of the following general type: Amalgam — concentrated salt solution of metal in amalgam — dilute salt solution of metal in amalgam — amalgam. In all cases the amalgam used for the two electrodes was of the same kind and concentration; the solutions in the two legs of the cell were of the same salt but of different concentration. Only those solutions were used for which the heats of dilution were known.

For cells of the above type the heat of dilution becomes the heat of reaction. If we dilute from any initial concentration to the concentrations of the solutions in the two legs of the cell, the heats of dilution, in general, are different. This difference is available as energy to produce E.M.F. represented by the first term of the

Gibbs-Helmholtz equation. The electrode in the more dilute solution is the anode, that is, the electrode by which the current enters the cell. Whenever the heat of dilution is positive, that is, when dilution generates heat, then more heat is generated for the entrance of a gram-equivalent of the electrode at the anode than is absorbed by the removal of an equal amount at the cathode. If the heat of dilution is negative, that is, if dilution absorbs heat, then more heat is absorbed at the anode than is generated at the cathode. Let us suppose the quantities of the two solutions so great that the entrance of a gram-equivalent at the anode and the removal of an equal amount from the solution about the cathode do not change the concentration of the solutions. Now when the gram-equivalent of metal at the anode goes into solution it becomes a salt and is diluted down to the same concentration as that of the solution surrounding the anode; at the same time an equal amount of the metal is removed from the more concentrated solution surrounding the cathode. When the heat of dilution is positive, this latter operation absorbs less energy than is derived from the former; when negative the former absorbs more energy than is generated by the latter. This difference of energy is available to produce E.M.F. When it is positive the E.M.F. is directed within the cell from the more dilute to the concentrated solution; when negative, from the concentrated to the more dilute.

Description of Apparatus.

For the accurate determination of the E.M.F. of concentration cells in which the electrolytes on the two sides of the cell are of different concentration two things are especially desired in the construction of the apparatus. First, that the temperature of the two legs of the cell be kept the same and remain constant for any desired length of time; and second, that during this time there shall be no mixing of the electrolytes. To satisfy the first condition, three thermostats were employed, one for the warm bath, the second for the intermediate, and a third for the cold. The temperature in these could be maintained constant to within 0.02° C. by means of a toluene-mercury regulator. Beckmann thermometers were employed for reading the temperatures. The E.M.F. was measured by means of an Otto Wolff potentiometer which reads directly to 0.00001 volt. A Weston normal cell was used as a standard of comparison.

The concentration cell was set up as shown in Fig. 1. A_1 and A_2 represent the two legs of the cell, which are connected by means of a bent tube containing a filter paper plug *h* and provided with a glass stop-cock *S*; *a*, *a*, the two electrodes; *b*, *b*, the two electrolytes. The electrodes *a*, *a* are composed of glass cups *c*, *c* about 2 cm. in diameter, into which are fused glass tubes. Through the tubes near the bottom are sealed short platinum wires *d*, *d*, which make connection with the amalgams *e*, *e* in the cups and the mercury *f*, *f* inside the tubes. Copper wires *g*, *g* lead from the mercury in the tube direct to the potentiometer.

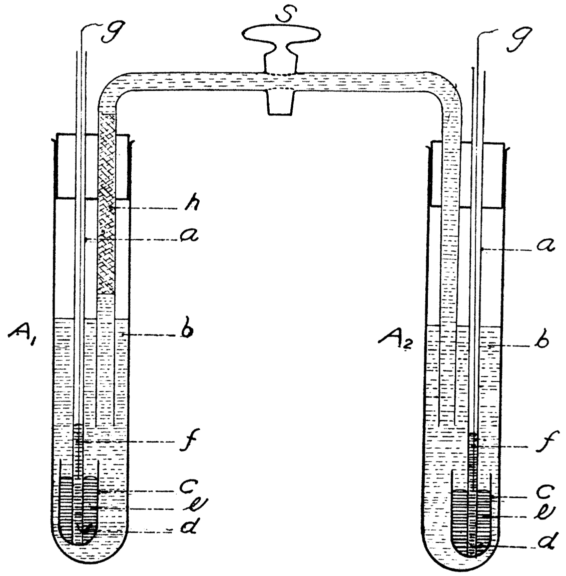

Fig. 1.

The filter paper plug *h* in the arm of the tube making connection with the two solutions deserves special attention, as it is this that prevents the mixing of the electrolytes, and thus meets the requirements of the second condition. The solutions in the two legs of the cell were maintained at the same level and the stop-cock kept open only while readings were being taken. The cell was suitably supported in the thermostat so that the temperature remained the same for both legs. The filter paper plug was near the end of the tube so that the junction of the liquids might be maintained at the same temperature as the electrodes.

PREPARATION OF MATERIALS.

Solutions.

Zinc and cadmium sulphates were prepared in practically the same manner. The chemically pure salt was dissolved in twice distilled water to form a saturated solution, which was allowed to evaporate until about three fourths of the salt had crystallized out. The crystals were washed several times with distilled water and then, before drying, transferred to a closed vessel where they were kept until ready for use. It is essential that the salt be dry but at the same time lose none of its water of crystallization; so a portion was carefully dried each time just before making up the solutions. The solutions were prepared as follows: $ZnSO_4 \cdot 50H_2O$, means that for every gram-molecule of anhydrous salt 50 gram-molecules of water, or 900.76 grams of water are required. One gram-molecule of $ZnSO_4 \cdot 7H_2O$ weighs 287.67 grams; of this 161.46 grams are anhydrous salt, and 126.11 grams water of crystallization. If hydrated salt be used, then 126.11 grams must be subtracted from 900.76 grams, thus leaving 774.65 grams of water to be added to the gram-molecule of the hydrated salt.

The lead nitrate was recrystallized from the pure salt, dried on a watch glass and kept in a desiccator until ready for use. The solutions were prepared by weight similar to the sulphate.

The preparation of the zinc chloride solutions will be described in connection with the zinc chloride cell.

Amalgams.

The mercury used for the amalgams was prepared by double distillation. For most of the work the amalgams were prepared, electrolytically from an acid solution of the purified salts; however, the observations showed no difference between these and others prepared by the fusion of the metal and mercury. Since the exact concentration of the amalgams is not essential, they were kept under an acid solution until ready for use, and then, just before using, thoroughly washed with distilled water.

EXPERIMENTS AND RESULTS.

Zinc Sulphate Cells.

Amalgam electrodes are best adapted for work on electrode potential. Since with pure metals it is very difficult to prevent oxidation or exclude occluded gases, variable and unsatisfactory results must necessarily follow. To obtain consistent results the electrodes must remain reasonably constant for days. Amalgams best fulfill these conditions. Preliminary tests were made to see what amalgams were best adapted for zinc sulphate cells. A series of amalgams ranging from .1 to 15 per cent. were used for this purpose. The amalgams must not change phase in the temperature interval employed, that is, they must remain either solid or liquid throughout the test. Change of phase causes a break in the temperature coefficient. Amalgams below one per cent. and above 10 per cent. fulfill these conditions, the former remaining liquid throughout; the latter, solid. Amalgams of a little less than one per cent. were finally chosen as best adapted to the following work because an amalgam which is much more dilute oxidizes readily, and the solid is less convenient to handle. The solutions used were prepared from the freshly dried $ZnSO_4 \cdot 7H_2O$ as described. High temperature could not be employed because zinc sulphate at 39° changes from the heptahydrate to the hexahydrate salt, and irregularities in readings occurred when this temperature was approached. These irregularities were probably due to the surface condition of the amalgam changing with the least possible current.

The cell was set up in the following manner: All parts were washed with nitric acid, then treated with cleansing solution, after which they were thoroughly rinsed with distilled water and carefully dried. The two legs of the cells were filled about two thirds full with their respective electrolytes. Into one end of the connecting tube was packed chemically pure filter paper, as shown in Fig. 1. The tube was then filled with the two electrolytes, the denser solution in the shorter arm and the more dilute in the longer arm, the two meeting at about the middle of the filter paper plug.

The amalgam, which had previously been prepared and kept under a dilute solution of sulphuric acid, was washed with distilled water and then transferred to the small cups by means of a clean pipette. The electrodes were at once put into the solutions of the two legs, leaving them exposed to the air but a few seconds; the connecting tube was put in place and the legs of the cell closed with rubber stoppers, which had been soaked in distilled water for several days. When all had been adjusted as shown in Fig. 1, the stoppers were covered with paraffin.

The following combination was first used:

$$Zn \cdot Hg - ZnSO_4 \cdot 50H_2O - ZnSO_4 \cdot 400H_2O - Zn \cdot Hg.$$

Before recording observations, the cell was allowed to stand a few hours, until equilibrium had been reached. In general it took a few hours before the readings of the cells became constant. There was no regularity in the shifting of the preliminary readings; some cells assumed a high initial value and gradually fell to constancy, others started with a low initial value and rose, while still others remained constant from the very first.

TABLE I.

Date.	Temp.	E.M.F.
August 30, 8:00 P. M.	0	0.01581
" " 8:30 "	0	0.01580
" " 8:40 "	0	0.01580
" 31, 9:00 A. M.	25	0.01708
" " 9:15 "	25	0.01708
" " 10:00 "	0	0.01578
" " 10:30 "	0	0.01578
" " 11:00 "	25	0.01711
" " 1:45 "	25	0.01712
" " 3:30 "	25	0.01713
" " 3:55 "	0	0.01580
" " 4:05 "	0	0.01577
" " 4:30 "	0	0.01578
" " 7:00 "	0	0.01579
" " 7:30 "	25	0.01708
" " 8:00 "	25	0.01710

Table I. gives the readings of cell 1*b* for a period of twenty-four hours after beginning to record observations. This is a fair sample of the constancy of the cells used. The readings show that the changes due to oxidation or other causes are so small as not to materially affect the results. The readings also show that the cell practically assumes the same value when brought back to the same temperature, otherwise it was discarded as in all subsequent work. Irregularities in nearly all cases were traced to some defect in the construction of the cells, such as a crack in the glass where the platinum was sealed through, or to change of phase for some of the materials. In fact, it seems that irregularities due to change of phase became evident several degrees before the temperature was reached at which this change nominally takes place. In most cases the temperature coefficient used was the mean of three different sets of readings as shown in Table I.

Table II. gives the results of the investigation of zinc sulphate cells. E_h is the E.M.F. due to the heat of dilution and $T \cdot dE/dT$ is the E.M.F. derived from the heat of the surroundings. All cells were set up and manipulated in the general manner just described. The solutions used were those for which the heats of dilution had been determined by Thomsen.[1] The most concentrated solution used was that of $ZnSO_4 \cdot 50H_2O$. $ZnSO_4 20H_2O$ was tried in the preliminary work, but the salt began to crystallize out before the lower temperature was reached, thus restricting the range for determining the temperature coefficient to higher readings. This fact made it undesirable as an electrolyte; consequently this solution was rejected. For the remaining solutions all possible combinations were made.

Two sets of comparisons are given in the table — one consisting of two columns of E.M.F.'s and the other consisting of two columns of heats of dilution. The computed E.M.F. for the first set is obtained in the following manner. According to Thomsen, for one gram-molecule of $ZnSO_4 \cdot 20H_2O$ diluted to $ZnSO_4 \cdot 50H_2O$, 318 calories of heat are generated. Also, $ZnSO_4 \cdot 20H_2O$ diluted to $ZnSO_4 \cdot 400H_2O$ generates 400 calories. Hence one gram-molecule of $ZnSO_4 \cdot 50H_2O$ diluted to $ZnSO_4 \cdot 400H_2O$ generates 82 calories. Since this heat of dilution is positive, it is free energy and gives rise to

$$\frac{82 \times 4.189}{2 \times 96,500} = 0.00178 \text{ volt E.M.F.}$$

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[1] Thermochem. Untersuchungen, J. Thomsen (see Table X.).

TABLE II.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25°.	E_h	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil. in Cal.	Obs. Heat of Dil. in Cal.
$ZnSO_4 \cdot 50H_2O$	1*a*	0.0000528	0.01573	0.00178	0.01751	0.01713	65	82
	1*b*	0.0000524	0.01561	"	0.01739	0.01710	69	"
$ZnSO_4 \cdot 400H_2O$	1*c*	0.0000510	0.01520	"	0.01698	0.01701	83	"
	1*d*	0.0000510	0.01520	"	0.01698	0.01711	88	"
	1	0.0000518	0.01544	0.00178	0.01722	0.01709	76	82
$ZnSO_4 \cdot 50H_2O$	2*a*	0.0000352	0.01029	0.00125	0.01193	0.01162	53	67
$ZnSO_4 \cdot 200H_2O$	2*b*	0.0000344	0.01045	"	0.01170	0.01159	62	"
	2*c*	0.0000340	0.01013	"	0.01158	0.01139	58	"
	2	0.0000345	0.01029	0.00125	0.01174	0.01153	57	67
$ZnSO_4 \cdot 100H_2O$	3*a*	0.0000340	0.01013	0.00072	0.01085	0.01090	35	33
	3*b*	0.0000344	0.01025	"	0.01097	0.01090	30	"
$ZnSO_4 \cdot 400H_2O$	3*c*	0.0000344	0.01025	"	0.01097	0.01081	26	"
	3	0.0000343	0.01021	0.00072	0.01093	0.01087	30	33
$ZnSO_4 \cdot 50H_2O$	4*a*	0.0000174	0.00518	0.00106	0.00624	0.00628	51	49
$ZnSO_4 \cdot 100H_2O$	4*b*	0.0000160	0.00477	"	0.00583	0.00607	60	"
	4	0.0000167	0.00498	0.00106	0.00604	0.00618	56	49
$ZnSO_4 \cdot 100H_2O$	5*a*	0.0000172	0.00512	0.00039	0.00551	0.00541	13	18
$ZnSO_4 \cdot 200H_2O$	5*b*	0.0000180	0.00536	"	0.00575	0.00552	7	"
	5	0.0000176	0.00524	0.00039	0.00563	0.00547	10	18
$ZnSO_4 \cdot 200H_2O$	6*a*	0.0000164	0.00489	0.00033	0.00522	0.00543	25	15
$ZnSO_4 \cdot 400H_2O$	6*b*	0.0000180	0.00536	"	0.00569	0.00556	9	"
	6	0.0000172	0.00513	0.00033	0.00546	0.00550	17	15
2+6	7	0.0000519	0.01542	0.00178	0.01720	0.01703	74	82
4+3	8	0.0000510	0.01519	0.00178	0.01697	0.01708	86	82
4+5+6	9	0.0000515	0.01535	0.00178	0.01713	0.01715	83	82
Mean of 1, 7, 8, 9	10	0.0000515	0.01535	0.00178	0.01713	0.01709	80	82

The temperature coefficient of (10) is 0.0000515, as a mean of the four independent determinations. Hence $T \cdot dE/dT$ at 25° is 298×0.0000515 equal to 0.01535. Then E computed equals $0.00178 + 0.01535 = 0.01713$ volt, as compared with 0.01709 volt, the observed value at 25°.

To obtain the computed heat of dilution of the second set of comparisons, the process is reversed. The observed E.M.F. at 25°

equals 0.01709 volt, and $T \cdot dE/dT$ equals 0.01535 volt as before. Then 0.01709 — 0.01535 equals 0.00174 volt as the difference of the observed E.M.F. and that due to the heat from the surroundings. This surplus energy arises from the heat of dilution and is equivalent to 80 calories, as compared with 82 calories, observed by Thomsen.

By applying the principle of a cyclic system we obtain three checks on cell 1; the sum of 2 and 6 should equal 1; 3 and 4, equal 1; 4, 5 and 6, equal 1. Thus we obtain independently, four values for the combination $Zn \cdot Hg - ZnSO_4 \cdot 50H_2O - ZnSO_4 \cdot 400H_2O - Zn\ Hg$; (10) gives the mean of these four. From a comparison of these four it will be seen that the agreement is very satisfactory. If we compare the computed and observed E.M.F.'s the maximum difference is about one per cent., while for the mean it is less than one fourth of one per cent. Since the heats of dilution account for only about ten per cent. of the total E.M.F., the second set of comparisons is not so favorable from a percentage basis. Comparison of results on a percentage basis does not signify much unless we take into account all the factors which enter the quantities compared. To illustrate: one per cent. difference, between the computed and observed E.M.F. in cell 1, is equivalent to ten per cent. difference between the computed and observed heats of dilution; in cell 6 one per cent. difference in E.M.F. is equivalent to seventeen per cent. difference in heats of dilution.

For ten of the sixteen cells recorded in Table II. the calculated E.M.F. exceeds the observed; the mean difference, as shown above, is less than one fourth of one per cent. With the exception of *2c*, *4a* and *4b* the observed E.M.F. differs from the mean value by less than one per cent. The difference between the observed E.M.F. and that due to $T \cdot dE/dT$ is from five to eighteen per cent. of the whole E.M.F. of the cell and bears no direct relation to either, but is proportional to the heat of dilution as observed calorimetrically. The Gibbs-Helmholtz equation applies rigorously in this case, the deviation being less than the probable experimental error.

Cadmium Sulphate Cells.

For zinc sulphate cells the heat of dilution is relatively small, accounting for only a small portion of the total E.M.F. of the cell, the remainder being due to $T \cdot dE/dT$, the heat absorbed from the surroundings. Extending the investigation to solutions of cadmium sulphate we obtain a cell in which the heat of dilution is relatively large. The study of this cell was taken up in the general manner just described. The amalgam, however, proved more troublesome. With dilute amalgams, the E.M.F. did not consistently return to the same value when brought back to the same temperature. Evidently some change had taken place either in the amalgam or the electrolyte. Since there is no transition point in cadmium sulphate below 74° these irregularities cannot be ascribed to the salt. They might be due to oxidation, as the electrode in the more dilute solution gradually lost its brilliancy and became covered with a thin film. A "time test" made for a period of eighteen days, as given in Table III., shows that the cell remained remarkably constant. After reaching equilibrium, the maximum change in E.M.F. was only 0.00003 volt. Next, cells were set up from which the air had been thoroughly removed, and then saturated with hydrogen. These remained constant at 25° as before, but showed the same irregularities with change of temperature. Thus it seemed altogether unlikely that oxidation was the disturbing factor. Richards and Forbes[1] found that oxidation became evident only with very dilute amalgams.

The potential difference between cadmium amalgam and cad-

Table III.

Cell set up November 30, 1908.	25°	0.00532
December 1, 10:00 A. M.	"	0.00520
" 2, 9:00 "	"	0.00526
" 2, 1:20 P. M.	"	0.00525
" 3, 2:00 "	"	0.00527
" 5, 9:00 A. M.	"	0.00524
" 5, 4:00 P. M.	"	0.00526
" 6, 2:00 "	"	0.00527
" 9, 9:00 A. M.	"	0.00527
" 10,	"	0.00526
" 17,	"	0.00525

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[1] Zeit. Phys. Chem., 58, 683, 1907.

mium sulphate does not change for amalgams between five and fifteen per cent. Amalgams lying within this interval would therefore seem most favorable; hence six per cent. amalgam was chosen. This amalgam has the further advantage of being a liquid at ordinary temperature. Cells set up with it gave readings which were more constant, consequently more trustworthy. The temperature interval for determining the temperature coefficient was taken from 25° to 40°; at lower temperatures the solid phase appears.

Table IV.

Solutions.	Cells.	dE/dT	$T\cdot dE/dT$ at 25°.	E_h	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil. in Cal.	Obs. Heat of Dil. in Cal.
$CdSO_4 \cdot 3O \cdot 6H_2O$	1*a*	0.0000235	0.00700	0.01565	0.02265	0.02205	694	722
$CdSO_4 \cdot 400H_2O$	1*b*	0.0000244	0.00727	"	0.02292	0.02213	685	"
	1*c*	0.0000210	0.00626	"	0.02191	0.02213	732	"
	1	0.0000230	0.00684	0.01565	0.02249	0.02210	704	722
$CdSO_4 \cdot 3O \cdot 6H_2O$	2*a*	0.0000080	0.00238	0.00960	0.01199	0.01176	432	443
$CdSO_4 \cdot 100H_2O$	2*b*	0.0000078	0.00231	"	0.01191	0.01170	434	"
	2	0.0000079	0.00235	0.00960	0.01195	0.01173	433	443
$CdSO_4 \cdot 100H_2O$	3*a*	0.0000155	0.00462	0.00604	0.01066	0.01025	260	279
$CdSO_4 \cdot 400H_2O$	3*b*	0.0000156	0.00465	"	0.01069	0.01038	265	"
	3*c*	0.0000160	0.00477	"	0.01081	0.01052	266	"
	3	0.0000157	0.00468	0.00604	0.01072	0.01038	264	279
$CdSO_4 \cdot 50H_2O$	4*a*	0.0000192	0.00572	0.01082	0.01654	0.01638	492	499
$CdSO_4 \cdot 400H_2O$	4*b*	0.0000200	0.00596	"	0.01678	0.01637	481	"
	4*c*	0.0000185	0.00551	"	0.01633	0.01615	491	"
	4	0.0000192	0.00573	0.01082	0.01655	0.01629	488	499
$CdSO_4 \cdot 50H_2O$ $CdSO_4 \cdot 200H_2O$	5	0.0000090	0.00268	0.00747	0.01115	0.01107	387	391
$CdSO_4 \cdot 200H_2O$ $CdSO_4 \cdot 400H_2O$	6	0.0000095	0.00283	0.00234	0.00517	0.00496	98	108
2 3	7	0.0000236	0.00703	0.01565	0.00268	0.02211	697	722
5 6	8	0.0000185	0.00551	0.01082	0.01633	0.01603	485	499

Table IV. gives the results of thirteen different cells. As before 2 and 3 should equal 1, and 5 and 6 should equal 4. While the agreement is quite satisfactory, it is not so good as for the zinc sulphate. It will be seen that for all but one, 1*c*, of the thirteen cells, the computed E.M.F. exceeds the observed value; the difference between the two being about 2 per cent. It is further to be noted that this difference is comparatively constant, indicating an experimental error, rather than some defect in the principles involved.

The heat of dilution accounts for from fifty to eighty per cent. of the total E.M.F. of the cell.

Zinc Chloride Cells.

In the preceding experiments the cells have a positive heat of dilution and a positive temperature coefficient. Three other variations may arise, namely, (1) a positive heat of dilution with a negative temperature coefficient; (2) a negative heat of dilution with a positive temperature coefficient; (3) a negative heat of dilution with a negative temperature coefficient. In the third case the E.M.F. would be reversed, that is, the electrode in more dilute solution would become the cathode. In the other two cases the direction of the E.M.F. depends upon the relative magnitude of the quantities. For the solutions used the zinc chloride cell satisfies case (1) — a positive heat of dilution with a negative temperature coefficient — and will be next studied.

Upon diluting zinc chloride solutions hydrolysis takes place causing a change in concentration. The addition of the amalgam electrode sometimes brings about this change; even a change in temperature may produce it. Taking these things into account, it is difficult to prepare a solution of known concentration and to maintain it throughout the test.

The amalgam for this cell was a portion of that originally prepared for the zinc sulphate cells, and diluted to about one per cent. Solutions of approximately $ZnCl_2 \cdot 20H_2O$ and $ZnCl_2 \cdot 400H_2O$ were used for the preliminary tests. These were carefully filtered, then subjected to temperature changes and refiltered. Cells from these solutions remained reasonably constant but were not entirely free from hydrolysis (especially the more dilute solution) when subjected to temperature changes. The observed E.M.F. was higher than the computed value; this was probably due to the fact that the dilute solution hydrolyzed, thereby decreasing its concentration.

After trying solutions of different concentration under various conditions it was found that hydrolysis could be avoided by allowing the solutions to stand for some time; accordingly the two solutions from which the final determinations were made, $ZnCl_2 \cdot 18.84H_2O$ and $ZnCl_2 \cdot 180H_2O$, were allowed to stand for about six weeks. These solutions were carefully filtered before using. Great care was taken that all parts of the cell were perfectly dry and the solutions made contact in the middle of the filter paper plug in the connecting tube. Table V. gives the readings of the cell with these two solutions.

TABLE V.

Date.	Cell Set Up.	Temp.	E.M.F.
August 3,	5:00 P. M.	25	0.06737
" 4,	8:00 A. M.	25	0.06722
" 4,	8:45 "	25	0.06722
" 5,	9:00 "	25	0.06722
" 5,	3:00 P. M.	25	0.06720
" 6,	8:30 A. M.	25	0.06718
" 6,	11:30 "	25	0.06717

The total change, after equilibrium had been reached, was only 0.00005 volt. During this time, the temperature was lowered to 0° twice , and raised to 40° three times. The concentration of the solution was determined by titration against $AgNO_3$ using potassium chromate as an indicator. Heats of dilution were obtained by interpolation by means of a curve plotted from Thomsen's values. The curve as shown in Fig. 2 appears perfectly smooth, and when plotted on a large scale gives values which can be but little in error. To insure greater accuracy the solutions chosen were approximately those for which the heats of dilution had been determined.

Table VI. gives the results of three different cells from these solutions.

TABLE VI.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25°.	E_h'	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil. Cal.	Obs.[1] Heat of Dil. Cal.
$ZnCl_2 \cdot 18.8H_2O$	*a*	−0.000097	−0.02891	0.09832	0.06941	0.06722	4429	4530
$ZnCl_2 \cdot 180H_2O$	*b*	−0.000098	−0.02920	0.09832	0.06912	0.06723	4443	4530
	c	−0.000097	−0.02891	0.09832	0.06941	0.06712	4435	4530

[1] Thomsen (see Table IX.).

The agreement is very satisfactory, and as in the case of the cadmium sulphate cells, the computed E.M.F. is greater than the observed value.

The zinc chloride cell furnishes a specially instructive illustration of the correctness of the principle involved, because the temperature coefficient is negative, as in most voltaic cells. The E.M.F. is accordingly less than the value derived from the heat of dilution.

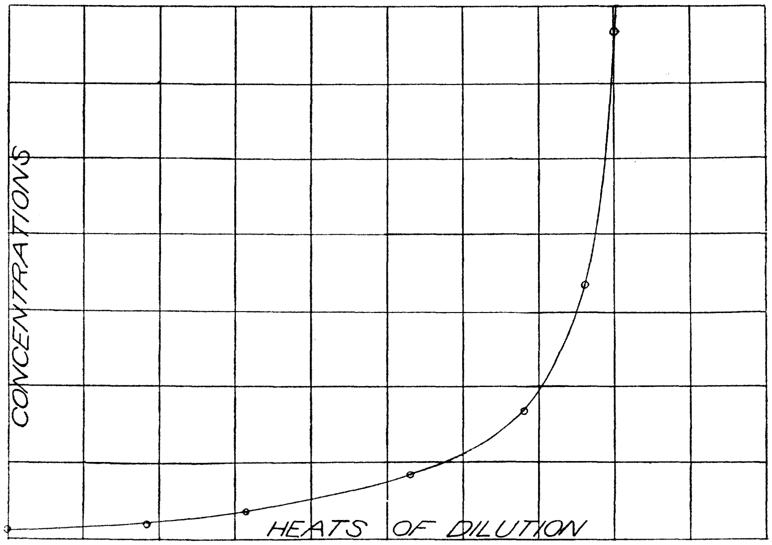

Fig. 2.

Lead Nitrate Cells.

Two more possible variations remain — a negative heat of dilution with either a positive or negative temperature coefficient. It becomes therefore a matter of great interest to know if the Gibbs-Helmholtz principle will apply to these. The lead nitrate cell fulfills one of these conditions, a negative heat of dilution with a positive temperature coefficient.

The solutions for this cell were prepared by weight from the recrystallized salt, similar to the sulphate; the amalgams, electrolytically, from an acid solution of the purified salt, and they were kept under an acid solution. Lead amalgams when left exposed to the air or in contact with aqueous solutions oxidize readily.

As a preliminary step, tests were made with reference to the constancy of the electrodes. With dilute amalgam and concentrated solutions the cell remained fairly constant, but when dilute solutions were used the readings were more variable. The electrodes in the dilute solutions became covered with a grayish film probably due to oxidation. Tests were made with $Pb(NO_3)_2 \cdot 400H_2O$, the most dilute solution used, to determine under what conditions oxidation might be prevented. It was found that by slightly acidulating the solution with nitric acid the film did not form and the readings became reasonably constant. Next, this test was extended to see what effect the acid had upon the initial readings of the cell. Equal portions of the two solutions from which the cell was set up were treated with the same quantity of nitric acid. The amount used was just enough to prevent the film from forming, and was determined beforehand. To make certain that both solutions were treated with the same amount, the conductivity water from which the solutions were made was acidulated before preparing the solutions. Such cells gave concordant values with change of temperature and remained reasonably constant. Furthermore, the readings were almost identical with the initial readings when no acid was used. For example, a cell without acid started with 0.01616 volt and reached apparent equilibrium at 0.01630 volt in about two hours, after which it slowly dropped in value. Table VII., which embodies the result of the final test, shows that this is in exact agreement with the mean of the three cells examined. Thus it is fair to suppose that the addition of the nitric acid did not affect the initial readings. It might be noted in this connection that all cells without the acid attained about the same initial readings at apparent equilibrium, and then slowly dropped in value. Constant agitation seemed to lessen this change, but did not completely eliminate it.

TABLE VII.

Solutions.	Cells.	dE/dT	$T \cdot dE/dT$ at 25° C.	E_h	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dil.	Obs.[1] Heat of Dil.
$Pb(NO_3)_2 \cdot 100H_2O$	*a*	0.000146	0.04351	−0.02756	0.01595	0.01620	−1659	−1270
$Pb(NO_3)_2 \cdot 400H_2O$	*b*	0.000145	0.04321	−0.02756	0.01565	0.01632	−1240	−1270
	c	0.000141	0.04202	−0.02756	0.01446	0.01636	−1183	−1270

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[1] Thomsen (see Table IX.).

Referring to Table VII., it will be noted that the computed E.M.F. is now less that the observed value. This was found to be true for all the preliminary determinations. The difference between the computed and observed values in cells *a* and *b* is well within the limits of experimental error. No reason can be assigned for the greater variation in cell *c* as it gave a good initial reading and remained fully as constant as the others.

Referring again to comparisons by percentage difference, it might be pointed out that if $T \cdot dE/dT$ observed be compared with $T \cdot dE/dT$ computed the percentage difference is only about one third of what it is for the E.M.F.'s and less than two thirds of what it is for the heats of dilution. For example, take cell *a*, $T \cdot dE/dT = 0.0435$ volt; $T \cdot dE/dT$ computed $= 0.04373$ volt; percentage difference is 0.5. The percentage difference between the observed and computed E.M.F. is about 1.4; between observed and computed heats of dilution, 0.8. The observed and computed E.M.F.'s do not give a fair comparison of the quantities involved unless the temperature coefficient and heat of dilution are both of the same sign.

This last case is particularly interesting since the chemical process is endothermic and the cell when in operation uses only a portion of the heat absorbed from the surroundings to be converted into electrical energy. It furnishes a striking proof of the incorrectness of the assumption that the heat of reaction is a measure of the electrical energy of a cell.

Discussion of Results.

One more variation remains — a negative heat of dilution with a negative temperature coefficient. As previously stated such a cell must have its E.M.F. reversed. This combination does not seem probable, for taking a current from such a cell would increase the difference in concentration of the solutions, thereby causing its E.M.F. to rise.

However, as it is, the results obtained are a very satisfactory confirmation of the principle involved. The deviation from the computed value in each case is comparatively constant indicating experimental errors. It now becomes a matter of interest to attempt an explanation of the probable cause of these small discrepancies.

The last term of the equation $T \cdot dE/dT$, is proportional to the absolute temperature, and therefore purely thermo-electric. According to Carhart's thermo-electric theory, the coefficient dE/dT is the algebraic sum of all the thermo-electric forces per degree arising at the several junctions. The temperature between the junction of the two liquids was considered the same as that at the electrodes. This perhaps is not strictly true because there would be more or less diffusion between the two solutions and the construction did not admit of immersing the whole cell. The thermo-electromotive force at the junction is accordingly less than the value which would be obtained with the junction at the same temperature as the electrodes. This assumption that the temperature of the junction is not always the same as that of the electrodes, and furthermore that it is variable, is borne out by the fact that the cells always remained the most constant at 25° or about room temperature. Results based on this assumption would indicate that for the zinc sulphate cell the thermo-electromotive force at the junction was practically negligible; for the cadmium and zinc chloride cells, it was directed from the concentrated to the more dilute solution; and in the lead nitrate cell, from the dilute to the more concentrated solution.

Secondly, the small difference may be explained on the assumption that the electrode in the more dilute solution oxidized to a greater extent than the other, thus establishing a counter E.M.F. In the case of the lead nitrate the observed E.M.F. is higher than the calculated value, which would indicate the reverse had taken place. This may be caused, however, by the addition of the nitric acid affecting the surface condition of the electrodes.

Thirdly, this difference between the observed and computed values may be due to the calorimetric determination of the heats of dilution. The heats of dilution as given may be inaccurate and are in need of revision because of modern facilities and a better knowledge of absolute units. Assuming the Gibbs-Helmholtz equation to apply rigorously in all cases, the results would indicate that the heats of dilution for the zinc sulphate solutions are correct as determined, that the heats of dilution for the cadmium sulphate and zinc chloride solutions are too large, and that the heats of dilution for the lead nitrate solutions are too small.

SUMMARY.

1. Simple concentration cells, made up of various solutions for which the heats of dilution have been determined, were investigated with reference to the application of the Gibbs-Helmholtz equation. The total heat of reaction becomes the heat of dilution and answers for the first term of the equation.

2. The four following cells were investigated: (1) Cadmium amalgam electrodes with cadmium sulphate of different concentration as electrolytes; (2) zinc amalgam electrodes with zinc sulphate of different concentration as electrolytes; (3) zinc amalgam electrodes with zinc chloride of different concentration as electrodes; (4) lead amalgam electrodes with lead nitrate of different concentration as electrolytes.

TABLE VIII.

Solutions.	E_h	$T \cdot dE/dT$	Comp. E.M.F.	Obs. E.M.F.	Comp. Heat of Dilution.	Obs. Heat of Dilution.
$ZnSO_4 \cdot 50H_2O$– $ZnSO_4 \cdot 400H_2O$	0.00178	0.01535	0.01713	0.01709	80 Cal.	82 Cal.
$CdSO_4 \cdot 30.6H_2O$– $CdSO_4 \cdot 400H_2O$	0.01565	0.00693	0.02258	0.02211	701 "	722 "
$ZnCl_2 \cdot 18.8H_2O$– $ZnCl_2 \cdot 180H_2O$	0.09832	–0.02901	0.06931	0.06719	4435 "	4530 "
$Pb(NO_3)_2 \cdot 100H_2O$ $Pb(NO_3)_2 \cdot 400H_2O$–	0.02756	0.04336	0.01580	0.01626	–1250 "	–1270 "

3. A filter paper plug in the connecting tube was used to prevent the mixing of the two solutions and to reduce diffusion to a minimum.

4. A method was found for successfully preventing oxidation of the lead amalgams under lead nitrate solution without vitiating the values of the readings of the cell. Zinc chloride solutions were also used without hydrolysis.

5. Table IX. gives a brief summary of the four cells investigated. For the lead nitrate cell the mean of cells *a* and *b* only are used.

The first cell has a large positive temperature coefficient with a relatively small heat of dilution; the second, a small temperature coefficient with a relatively large heat of dilution; the third, a negative temperature coefficient with a large positive heat of dilution; the fourth, a positive temperature coefficient with a relatively large negative heat of dilution. Of the two variables E_h and $T \cdot dE/dT$ which go to make up the E.M.F. of the cell, three of the four possible variations worked out.

6. The Gibbs-Helmholtz equation applies rigorously in all cases, the difference being less than the probable experimental error.

Table IX.

mn	$ZnSO_4$ *n* 20	$CdSO_4$ *n* 30.6	$ZnCl_2$ *n* 5	$Pb(NO_3)_2$ *n* 40
10			1850	
20			3150	
50	318	223	5320	
100	367	443	6810	−1230
200	385	614	7630	−1980
400	400	722	8020	−2500

In conclusion the writer wishes to express his thanks to Professor Carhart under whose direction this investigation was conducted for his interest and helpful suggestions.

For convenience of reference a table of the heats of dilution for the solutions used is appended. The heats of dilution are given in gram calories. *m* is the number of gram-molecules of water added to the solution when it already contains *n* gram-molecules of water to one gram-molecule of the anhydrous salt.

University of Michigan,
Ann Arbor, Mich.,
May, 1909.