chloric acid in water solution, both the water layer and the alcohol layer become pink. If, however, the concentration of the acid used be 0.125 *N*, the water layer will become pink but the alcohol layer will remain yellow. The mid-point between the pink and the yellow color in the alcohol layer is obtained when the acid used has a concentration of about 0.2 *N*. If nitric acid be used instead of hydrochloric, the mid-point is obtained with nearly the same concentration of acid as in the case of the hydrochloric. With sulfuric acid solutions, however, the yellow color persists in the alcohol layer until nearly normal acid is used.

BOULDER, COLORADO.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF PRINCETON UNIVERSITY.]

STANDARD CELLS AND THE NERNST HEAT THEOREM.

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A considerable amount of exact information has been accumulated as to the reactions, the electromotive forces and the temperature coefficients of the various combinations of standard cells. For the purposes of thermodynamic calculation over the ordinary range of temperature these data are sufficient. On the other hand, if it be desired to extend the calculations over a wide range of temperature it is necessary in addition to know the specific heats of the several reacting substances. With this information secured standard cells provide a most interesting means of testing the Nernst heat theorem.

The assumptions made by Nernst are applicable only to condensed systems, so that in case the system consists in part of a solution, calculations according to the theorem of Nernst can only be made below the cryohydrate temperature. At temperatures above this the Gibbs-Helmholz equation must be used. Consequently, with standard cells, it is necessary to carry out the thermodynamic calculations in two stages, below the cryohydrate temperature with the aid of the Nernst heat theorem, above this temperature with the fundamental equation.

The present work was undertaken in order to test the applicability of the Nernst heat theorem to the well-known Weston standard cell

$$\begin{array}{c|c|c} \text{Cd} & CdSO_4.8/3H_2O \quad Hg_2SO_4 & \text{Hg} \\ \text{amalgam} & & \end{array}$$

and to a standard cell lately studied in this laboratory,[1]

$$\begin{array}{c|c|c} \text{Cd} & CdCl_2.5/2H_2O \quad Hg_2Cl_2 & \text{Hg.} \\ \text{amalgam} & & \end{array}$$

The electromotive forces and the temperature coefficients of these cells

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[1] Lipscomb and Hulett, THIS JOURNAL, 38, 20 (1916).

have been most carefully determined. The specific heats of all the materials composing the cell, with the exception of the two cadmium salts, have been previously determined at various temperatures ranging from 273° K.[1] downwards. The data for the cadmium salts are supplied by the present investigation.

The investigations of Pollitzer[2] on the Clark standard cell form a typical example of this class of work. He obtained the necessary specific heat data as well as other essentials for calculations with regard to the combinations:

$$\begin{array}{llll} Zn & \mid ZnSO_4.7H_2O & Hg_2SO_4 & \mid Hg \\ Hg & \mid Hg_2Cl_2 & PbCl_2 & \mid Pb \\ Hg & \mid Hg_2Cl_2 & AgCl & \mid Ag \end{array}$$

The results obtained by the use of the Nernst heat theorem were compared with the electromotive forces of the combinations as actually measured.

For example, with the Clark cell in which the reaction is as follows:

$$Zn + Hg_2SO_4 + \underset{liquid}{7H_2O} = ZnSO_4.7H_2O + \underset{liquid}{2Hg},$$

it was shown that

$A_0 = U_0 = 67195$ cals. $A_{234° K} = 67227$ cals. $U_{234° K} = 66318$ cals.

By calculating these results to 266° K. the cryohydrate point of zinc sulfate, a value for the electromotive force by calculation, $E_{266° K} = 1.4610$ volts, was obtained whereas the observed value is 1.4556 volts.

Historical.

Specific heat investigations at temperatures below 273° K. were not made previous to 1849. Regnault used alcohol cooled by solid carbon dioxide and obtained temperatures down to 197° K. In his investigations he worked on boron, carbon, silicon, potassium, bromine, lead and mercury from 253° K. to 197° K. He used his results to test out the Dulong-Petit law but found it did not hold for boron, carbon and silicon. Weber pointed out later that the lower the temperature the more these substances deviated from the Dulong-Petit law.

Still lower temperatures were not obtainable until a decade later when the permanent gases were liquefied. In 1891 Zakrzewski constructed an apparatus for determining the specific heats of metals at the temperature of liquid ethylene, which is about 173° K. Considerable deviations of some substances from the Dulong-Petit law were noticed, amounting to 2.9% for silver and 30.8% for carbon.

Dewar devised an apparatus whereby he could obtain the specific heats of substances over various ranges at low temperatures by measuring

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[1] Degrees Kelvin or absolute temperatures.

[2] *Z. Elektrochem.*, 17, 5 (1911).

the gas liberated when the substance at a known temperature was dropped into a liquefied gas. The results, however, were not very concordant, but Barshall later improved this method and obtained fairly good results. The most recent and extensive specific heat determinations have been made by Nernst and his associates. Nernst,[1] Koref and Lindemann in their investigations developed a copper calorimeter. It consisted of a copper block in a vacuum vessel in a bath at a constant temperature. The substance, which was at a known temperature, was dropped into the copper block and the rise in temperature of the block measured by means of a thermocouple.

They were able to measure the mean specific heats of many substances over various temperature intervals. Since this method gave only mean specific heats, Nernst[2] and his associates devised another apparatus which enabled them to determine the mean specific heats of substances at various temperatures over small intervals, the interval generally being between two or three degrees. In its first form, the calorimeter was suspended in a glass tube and so arranged that a high vacuum could be maintained about the calorimeter. The heating was then done by means of a known electric current. The platinum wire used in the heating also served as a resistance thermometer to determine the temperatures and temperature changes. In a later form a heating coil was inserted inside the calorimeter and the platinum wire used for measuring the temperature was placed on the outside of the calorimeter.

Experimental Details.

The apparatus used in the present investigation was similar to that described by Nernst[3] and Schwers.

A copper cylinder (6 cm. long and 4 cm. wide) weighing approximately 35 g., served as the calorimeter shell. Closely fitting inside the calorimeter was a coil of constantan wire which had a resistance of about 100 ohms at 273° K. and served as the heating coil. The terminals of this coil were brought through the lower end of the copper cylinder, through small platinum tubes which were brazed to the copper. Small platinum wires were embedded in glass inside the platinum tubes so as to insulate them from the platinum and copper and at the same time make the apparatus gas-tight. On the inside the platinum wires were soldered to the constantan coil.

On the outside of the calorimeter was wound a coil of platinum wire (0.25 m. in diameter and having a resistance of 63.127 ohms at 273° K.), which served as the thermometer. In order to insulate it from the copper cylinder a very thin layer of mica was placed between the shell and the

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[1] *Sitz. Berlin Akad.*, **1**, 247 (1910); *Ann. Physik*, **36**, 395 (1911).

[2] Nernst, *Ann. Physik*, **36**, 395 (1911).

[3] *Sitzb. Preuss. Akad.*, Berlin, 355 (1914).

platinum coil. As an additional precaution against any electrical leakage the platinum wire was coated with an insulating enamel.[1]

In the top of the calorimeter was an opening of about 6 mm. through which the material under investigation was inserted. This opening was closed by means of a plug which was soldered into place so as to make the whole apparatus gas-tight. In all experiments the calorimeter was filled with hydrogen.

Following the experience in Nernst's laboratory the calorimeter was mounted inside another somewhat larger copper guard tube and insulated from it by small ivory plugs. In the top of this guard tube was fitted a heavy lead block with a central hole for the leads from the calorimeter. On the outside of this guard tube was wound a second platinum resistance thermometer which was employed as a check thermometer.

During the experiments the calorimeter was suspended in a large 60 mm. tube which was immersed in the bath liquid contained in a Dewar tube. This calorimeter tube was closed by a stopper of test-tube shape which extended well down into the calorimeter tube. The tubes were closed above by means of a well-ground joint.

The heating and thermometer lead wires, joined to platinum wires, were sealed through the bottom of this test-tube stopper, and also the calorimeter was suspended from the bottom of this tube. The main purpose of this stopper tube was to serve as a receptacle for some of the bath liquid, thus making it possible to surround the calorimeter not only on the sides and bottom but also on the top with the bath liquid. We employed this modification in order to lessen heat losses by conduction along the wires and by radiation from the calorimeter, which should be taken into consideration when working from 100° to 200° from room temperature.

The space in which the calorimeter was suspended was evacuated through a side tube connected to a Gaede mercury pump with its necessary auxiliary. A large tube containing cocoanut charcoal was connected to the apparatus and the pumps so that during an experiment, by immersion of the charcoal tube in liquid air, the vacuum obtained by the pump was considerably improved.

For the temperature measurements, by the potential drop method, we needed a small but very constant current. This we obtained from a special unsaturated Clark cell with a large (530 cm.) cathode area. The bottom of a desiccator was covered with a layer of mercury and a thin layer of mercurous sulfate, the nearly saturated zinc sulfate solution extended above the perforated porcelain plate of the desiccator. This porce-

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[1] We are indebted to John A. Roebling Sons & Co., of Trenton, N. J., for enameling our resistance wire.

lain plate was covered with a filter paper and supported several sticks of amalgamated zinc, which were connected with platinum wires and served as anode. The constancy of the current from this cell added much to the convenience and accuracy of the temperature measurements. A standard 100 ohm coil, a resistance box, the calorimeter thermometer and the guard thermometer were connected in series. A current of about 0.7 milliampere flowed through this circuit continuously.

In order to obtain the resistance of the calorimeter thermometer the potential drop was measured across the standard 100 ohm coil and then by means of a mercury switch, not shown in the diagram, the potential drop was measured across the thermometer. From these data the resistances of the thermometers were obtained. All the measurements in this work were carried out in this manner since the potential method was found to be more convenient for our purpose than the ordinary bridge method for measuring resistances. We used a White double combination potentiometer,[1] with which readings were easily obtained to 1 microvolt.

The Determination of Specific Heats.

The principle of the method is as follows: A known quantity of heat is generated in the calorimeter containing the given quantity of the substance. The rise of temperature is measured by a suitable method and from these data the heat capacity of the calorimeter plus the substance can be calculated. A similar determination with the empty calorimeter gives a correction which is to be applied to the original measurement in order to obtain the specific heat of the substance itself.

A complete diagram of all electrical circuits is shown in Fig 1. In the present work the apparatus was brought to the desired temperature by immersion in a suitable bath. The glass tube containing the calorimeter was exhausted. A known quantity of heat was then added to the calorimeter and the rise in temperature measured.

A large 100-volt storage battery furnished a satisfactory and constant current with which to supply heat to the system. In series with the heating current was a small silver coulometer which served to measure the number of coulombs of electricity. This procedure was adopted as a substitute for methods previously employed. Hitherto the energy has been determined by measuring the time of heating and the amperes. Considerable difficulty may frequently be experienced in maintaining a constant current. The use of the coulometer eliminates this difficulty as well as the necessity of measuring the time. The amount of heat liberated in the calorimeter was accurately known from the relation:

$$\text{calories} = E \times Q \times 0.2388,$$

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[1] This Journal, 36, 1856, 1868, 2011, 2292–2313 (1914).

where Q = the number of coulombs, E = potential drop over the calorimeter heater.

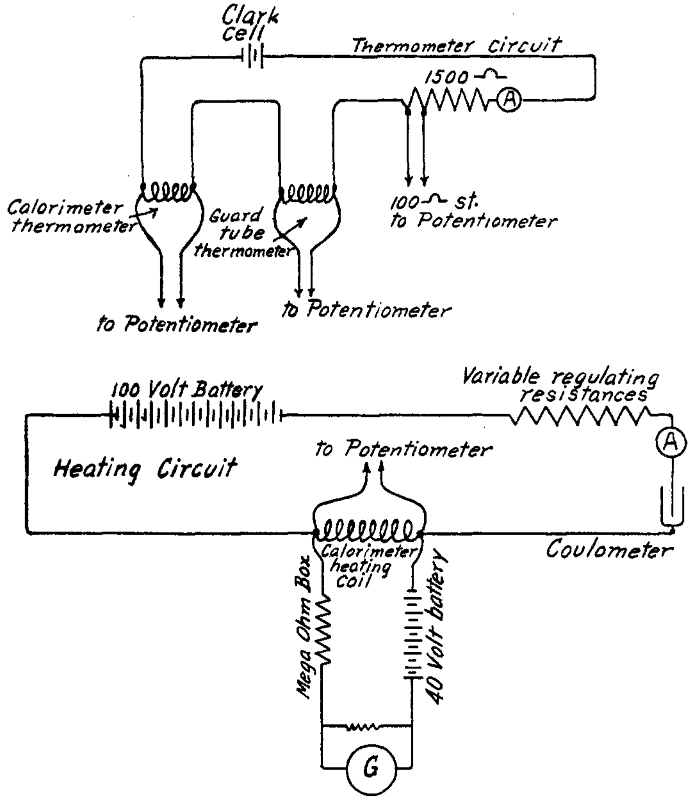

Fig. 1.

In order to secure a constant voltage drop over the heating circuit, a small so-called high tension battery was connected in series with an ordinary wall type of galvanometer and a megohm box. This circuit was attached to the end of the calorimeter heater. By adjusting the voltage from the high tension battery so that it was a few tenths of a volt in excess of the voltage from the battery which served for the heating, a deflection of the galvanometer was observed. Then, by means of the regulating resistances the galvanometer was maintained steady. At the same time the potential drop was measured across the terminals of the heater. From this voltage and the quantity of silver deposited in the coulometer the number of calories liberated was obtained.

Calibration of Thermometers.

Above 273° K. the resistance of a platinum thermometer can be represented with great accuracy by means of a quadratic equation, but below about 233° K. this loses its validity and no simple relation is known which will accurately express the resistance as a function of the temperature. Consequently, F. Henning[1] has established a series of results from which any platinum thermometer can be calibrated, providing it has a resistance ratio between certain limits which include nearly all samples of pure platinum. Henning's[2] tables include all temperatures between 80° K. and 273° K. By resistance ratio is meant

$$R_1 = R_t/R_o,$$

where R_t is the resistance at any temperature, t, and R_o is the resistance at the ice-water point.

If the resistance ratio of any thermometer to be calibrated is R_2 and that of the Henning standard at the same temperature be R_1, the relationship between the two may be expressed by an equation of the form

$$R_2 = R_1 + A(R_1 - 1) + B(R_1 - 1)^2,$$

in which the two constants A and B can be determined from the values of R_1 and R_2 at two fixed temperatures. The boiling point of oxygen and the sublimation point of solid carbon dioxide were employed as the two fixed points. The experimental determination at these temperatures yielded for our calorimeter thermometer the following:

$$R_2 = R_1 - 0.0015932(R_1 - 1) + 0.003673(R_1 - 1)^2.$$

With this equation it was possible from any measurement of R_2 to determine the corresponding ratio R_1 and hence, from Henning's tables, the actual temperature.

Typical Example.—As an example of the method of obtaining data for an experiment, the determination of the specific heat of 50.12 g. of $CdSO_48/3H_2O$ at the temperature of a mixture of solid carbon dioxide and petroleum ether will be detailed.

After the calorimeter had taken up approximately the temperature of the bath the glass apparatus containing the calorimeter was evacuated by means of the Gaede mercury pump, while the charcoal was heated to dull redness for about 10 minutes, allowed to cool and then cooled with liquid air. A vacuum was thus established such that no discharge was observed in the Geissler tube when the auxiliary spark gap was reduced below 4 centimeters. A series of readings were then taken prior to heating.

Cal. thermo. potential drop.	Std. 100 ohm potential drop.	Time.
0.035507	0.081303	1 : 50 P.M.
0.035505	0.081303	1 : 55
0.035503	0.081302	2 : 02

From 2 : 04 : 30 to 2 : 07 : 00, a constant current was passed through the calorimeter heater at a potential drop of 9.472 volts. A series of readings after discontinuing the heating gave the following:

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[1] *Ann. Physik*, **40**, 465 (1913).

[2] *Ibid.*, **43**, 282 (1914).

Cal. thermo. volts.	Std. 100 ohm coil volts.	Time.	
		Min.	Sec.
0.035990	....	7	30
0.035986	....	8	..
0.035977	....	8	30
0.035970	....	9	..
0.035965	....	9	30
0.035961	0.081274	10	..
0.035955	....	11	..
0.035954	....	11	30
0.035952	....	12	..
0.035951	....	12	30
0.035949	....	13	..
0.035947	....	13	30
0.035947	....	14	..
0.035945	....	14	30
0.035944	0.081274	15	..
0.035943	....	15	30
0.035941	....	16	..
0.035940	....	..	30
0.035939	....	17	..
0.035937	....	18	..
0.035935	....	..	30
0.035934	....	19	..
0.035931	....	20	..
0.035929	0.081274	21	..
0.035926	....	22	..
0.035924	....	23	..
0.035921	0.081273	24	..
0.035919	....	25	..

These results were plotted and at the mid-point of the heating by extrapolation the reading of the calorimeter thermometer was found to be 0.035966. This gives as the resistance ratio:

$$\text{after heating } \frac{0.035966}{0.081274} \times \frac{1}{63.127} = 0.70101$$

$$\text{before heating } \frac{0.035501}{0.081302} \times \frac{1}{63.127} = 0.69171,$$

the value 63.127 being the resistance of the thermometer at 273° K. From Henning's tables the rise in temperature was calculated to be:

$$\frac{0.70101 - 0.69171}{408} = 2.279^\circ$$

The weight of silver deposited in the coulometer amounted to 15.71 milligrams.

The coulometer consisted of an ordinary 30 cc. platinum crucible as cathode in which we electrolyzed a *pure* 10% solution of silver nitrate. The silver anode was inclosed in a small "alundum" test-tube so that the anode and any anode slime could be easily removed after a run. The manipulation of washing, drying and recovering lost silver followed the standard coulometer practice. We seldom found loose silver with this form of coulometer and the current densities used, and it was possible to get results to 0.01 mg. with our constant temperature balance room and facilities for weighing.

Heat supplied in calories = 9.472 × 15.71/1.118 × 0.2388 = 31.78. Specific heat of the calorimeter plus $CdSO_4 8/3H_2O$ = 31.78/2.279 = 13.94. The water equivalent of the calorimeter and connections subtracted from this value gave 13.94 — 4.90 = 9.04 calories. Calculated for one mol of the salt this gives 9.04/0.1954 = 46.26. The resistance ratio, 0.69171, corresponds to a temperature of 196.2° K.

Experimental Results.

In the following table are given the results for the water equivalent of the calorimeter and connections at various temperatures.

(a) Water equivalent of the calorimeter.	Mean temperature K°.	(a) Water equivalent of the calorimeter.	Mean temperature K°.	(a) Water equivalent of the calorimeter.	Mean temperature K°.
5.78	274.3	4.91	197.0	2.73	86.8
5.73	274.3	4.89	197.2	2.68	86.8
5.67	274.3	4.89	197.2	2.71	87.8
5.75	274.3				
Mean = 5.73		Mean = 4.90		Mean = 2.71	

The two salts were prepared from high grade samples by several recrystallizations. Only the very clear crystals were chosen for an experiment. Both materials were analyzed for their water content and corresponded to the formulas employed. The following tables give a résumé of the results:

(1) $CdCl_2.2^1/_2H_2O$.

Mean temp. K°.	Heat capacity of material + calorimeter.	Heat capacity of material.	Molecular heat.
274.4	16.23	10.50	56.47
274.4	16.16	10.43	56.10
198.2	12.72	7.82	42.06
198.5	12.58	7.68	41.30
87.2	6.56	3.85	20.71
89.2	6.62	3.89	20.92

(2) $CdSO_4.8/3H_2O$.

Mean temp. K°.	Heat capacity of material + calorimeter.	Heat capacity of material.	Molecular heat.
274.3	18.88	13.15	67.30
274.3	18.69	12.96	66.33
197.6	14.15	9.25	47.34
197.3	13.94	9.04	46.26
198.6	13.92	9.02	46.16
198.6	14.21	9.31	47.64
87.3	7.01	4.30	22.01
89.3	7.21	4.48	22.82

Theory of Specific Heats.

On the basis of the quantum theory[1] Einstein developed an equation for the specific heats of solids and supercooled liquids. In its original form the expression for the heat energy was

$$W = {}^3/_2 R\left(\frac{\beta\nu}{e^{\beta\nu/T} - 1}\right),$$

which, on differentiation, gives

$$C_v = \frac{dW}{dT} = 3R\left[\frac{(\beta\nu/T)^2\, e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2}\right].$$

Einstein assumed only one oscillating frequency of the atom. Extended observations on specific heats at very low temperatures showed that the Einstein equation was inadequate for the reproduction of the experimentally determined values at the temperature of liquid hydrogen.[2] Nernst and Lindemann therefore modified the original Einstein equation by add-

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[1] *Ann. Physik,* [4] **22,** 184, 800 (1907).

[2] *Z. Elektrochem.,* 17, 817 (1911).

ing another term which served as a correction factor. It differs from the original equation in that the second term contains a $^1/_2\beta\nu/\mathrm{T}$ function:

$$\mathrm{C}_v = {}^3/_2\,\mathrm{R}\left[\frac{(\beta\nu/\mathrm{T})^2\,e^{\beta\nu/\mathrm{T}}}{(e^{\beta\nu/\mathrm{T}}-1)^2}+\frac{(\beta\nu/2\mathrm{T})^2\,e^{\beta\nu/2\mathrm{T}}}{(e^{\beta\nu/2\mathrm{T}}-1)^2}\right]$$

Now, under ordinary experimental conditions, specific heat determinations are carried out at constant pressure, while the latter expression refers to specific heats at constant volume. It is therefore necessary to have a relationship connecting these two magnitudes. Nernst and Lindemann, from certain considerations and with the aid of thermodynamics, obtained such a relation. If a denotes the coefficient of linear expansion, v the molecular volume, and K the compressibility, then

$$\mathrm{C}_p = \mathrm{C}_v\left(1+\frac{9a^2v\mathrm{T}}{\mathrm{KC}_v}\right).$$

Since knowledge with regard to K is meagre, it is necessary to substitute for the last term in the expression an empirically determined quantity, $k\mathrm{T}^{3/2}$, where k is a constant characteristic for a given substance. The expression then becomes

$$\mathrm{C}_p = \mathrm{C}_v + k\mathrm{T}^{3/2}.$$

This has proved to be an adequate correction term in the interpretation of the experimental run of the curves.

The original Einstein equation becomes therefore

$$\mathrm{C}_p = 3\mathrm{R}\Sigma n\,\frac{(\beta\nu/\mathrm{T})^2\,e^{\beta\nu/\mathrm{T}}}{(e^{\beta\nu/\mathrm{T}}-1)^2}+k\mathrm{T}^{3/2},$$

while that of Nernst and Lindemann becomes

$$\mathrm{C}_p = \frac{3\mathrm{R}}{2}\,\Sigma n\left[\frac{(\beta\nu/\mathrm{T})^2\,e^{\beta\nu/\mathrm{T}}}{(e^{\beta\nu/\mathrm{T}}-1)^2}+\frac{(\beta\nu/2\mathrm{T})^2\,e^{\beta\nu/\mathrm{T}}}{(e^{\beta\nu/2\mathrm{T}}-1)^2}\right]+k\mathrm{T}^{3/2}.$$

In the present work the results have been interpreted with the aid of the latter equation.

For calculating the molecular heats of the two salts the following data were employed. They represent empirically determined magnitudes which fit closely the experimental measurements.

Substance.	n_1.	$\beta\nu_1$.	n_2.	$\beta\nu_2$.	n_3.	$\beta\nu_3$.	Correction term.
$CdCl_2.5/2H_2O$	3	140	1	600	8	930	$e^{(\mathrm{T}-250)/15}$
$CdSO_4.8/3H_2O$	3	150	3	600	8	1000	$e^{(\mathrm{T}-240)/17}$

The correction term in the last column was employed since the results could not be satisfactorily interpreted with $\beta\nu$ values alone. It will be seen that these terms only become significant at temperatures above 240 or 250° K.

Below are given the calculated and observed molecular heats of the two substances at various temperatures:

$CdCl_2.5/2H_2O$.

Temp ° K.	Mol. heat observed.	Mol. heat calculated.
274.4	56.47	56.19
274.4	56.10	56.19
198.2	42.06	41.63
198.5	41.31	41.00
87.2	20.71	20.41
89.2	20.92	20.92

$CdSO_4.8/3H_2O$.

Temp. ° K.	Mol. heat observed.	Mol. heat calculated.
274.3	67.30	66.89
274.3	66.33	66.89
197.6	47.34	47.43
197.3	46.26	47.4
198.6	46.16	47.60
198.6	47.64	47.60
87.3	22.01	22.07
89.3	22.83	22.60

Calculation of the Results.

The cell

$$\mathrm{Cd} \mid \mathrm{CdCl_2.2^1/_2H_2O} \quad \mathrm{Hg_2Cl_2} \mid \mathrm{Hg}.$$

The heat of the reaction

$$\mathrm{Cd} + 2\mathrm{HgCl} + \underset{liquid}{5/2\,\mathrm{H_2O}} = \mathrm{CdCl_2.5/2\,H_2O} + \underset{liquid}{2\mathrm{Hg}}$$

amounts, as was shown by Lipscomb and Hulett,[1] to 35760 calories at 290° K.

Below the temperature of 262° K., the cryohydrate point of cadmium chloride,[2] the system is a true condensed system and may be treated as such in the theoretical investigations. At 234° K., however, the mercury changes from a liquid to the solid form, which must be taken into account in the calculations. These latter can be performed with solid mercury from 0° K. up to the melting point and then, since the maximum work A is the same for both crystal and melt, all the necessary data to carry A into the region of liquid mercury are available. Likewise, at 262° K. the same holds true with respect to the conversion of solid ice to liquid water. The following table gives the data employed in the calculations:

Substance.	n_1.	$\beta\nu_1$.	n_2.	$\beta\nu_2$.	n_3.	$\beta\nu_3$.	$k \times 10^5$.	Correction term.
Cd	1	146	..	...	..	....	3.3	....
$CdCl_2.5/2H_2O$	3	140	1	600	8	930	....	$e^{(T-250)/15}$
Ice	$^1/_2$	166	1	725	2	2500	....	$0.045\, e^{(T-220)/13}$
Hg_2Cl_2	1	80	1	236	..	....	12.0	....
Hg	1	97	..	...	..	....	21.0	....

The values of all substances except those of cadmium and cadmium chloride have been taken from the article of Pollitzer.[1] Those for cadmium were calculated from the formula of Lindemann.

For the calculations of the heat of reaction and of maximum work, the formula of Nernst and Lindemann gives the following equations:

$$\Sigma n C_p = \frac{dU}{dT} = \frac{3}{2} R \Sigma n \left[\frac{(\beta\nu/T)^2 e^{\beta\nu/T}}{(e^{\beta\nu/T} - 1)^2} + \frac{(\beta\nu/2T)^2 e^{\beta\nu/2T}}{(e^{\beta\nu/2T} - 1)^2} \right] + \Sigma n k T^{3/2} \quad (1)$$

which, on integration, gives:

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[1] *Loc. cit.*

[2] This temperature was easily determined by the cooling curve method and was quite sharp.

$$U = U_0 + {}^3/_2 R\Sigma n\left[\frac{\beta\nu}{(e^{\beta\nu/T} - 1)} + {}^1/_2\,\frac{\beta\nu}{(e^{\beta\nu/2T} - 1)}\right] + {}^2/_5\Sigma nkT^{5/2} \quad (2)$$

whence,

$$A = U_0 + {}^3/_2 R\Sigma n[\ln(e^{\beta\nu/T} - 1) - \ln(e^{\beta\nu/2T} - 1)] - {}^9/_4 R\Sigma n - {}^4/_{15}\Sigma nkT^{5/2}. \quad (3)$$

Consequently, from the heat of reaction, $U_{291^\circ} = 35760$ calories, it follows that:

$$U_{291^\circ} = U_0 + {}^3/_2 R\Sigma n\left[\frac{\beta\nu}{(e^{\beta\nu/T} - 1)} + {}^1/_2\,\frac{\beta\nu}{(e^{\beta\nu/2T} - 1)}\right] + 2/5\Sigma nkT^{5/2} +$$
$$5/2\,\sigma_{H_2O} - 2\,\sigma_{Hg} + 5/2\,\bar{c}_{H_2O}(T - 273) - 2\,\bar{c}_{Hg}(T - 234)$$

in which the heats of fusion of mercury and ice are denoted by the symbol σ; c denotes the mean specific heats of the liquids over the intervals of temperature designated. For these magnitudes the following figures have been used:

$\sigma_{H_2O} = 1436$ (Roth) $\quad \bar{c}_{H_2O}$ between $T = 273^\circ$ and $291^\circ = 18.06$

$\sigma_{Hg} = 555$ (Pollitzer) $\quad \bar{c}_{Hg}$ between $T = 234^\circ$ and $291^\circ = 6.68$

By inserting the $\beta\nu$ values given in the preceding table in this equation for U there was obtained:

$$35760 = U_0 + F\left(\frac{146}{T}\right) + 2F\left(\frac{80}{T}\right) + F\left(\frac{236}{T}\right) + 5/4F\left(\frac{166}{T}\right) + 5/2F\left(\frac{725}{T}\right)$$
$$+ 5F\left(\frac{2500}{T}\right) - 3F\left(\frac{140}{T}\right) - F\left(\frac{600}{T}\right) - 8F\left(\frac{930}{T}\right) - 2F\left(\frac{97}{T}\right)$$
$$+ 2/5(3.3 + 24.0) \times 10^{-5} \times 291^{5/2} - 42 \times 10^{-5} \times 234^{5/2}$$
$$+ 5/2(1436) - 2(555) + 5/2(18.06) \times 18 - 2 \times 6.68 \times 57$$

In this equation the function sign

$$F\left(\frac{\beta\nu}{T}\right) = \frac{5.955}{2}\left[\frac{\beta\nu/T}{(e^{\beta\nu/T} - 1)} + \frac{\beta\nu/2T}{(e^{\beta\nu/2T} - 1)}\right]$$

The evaluation of this function was obtained from tables supplied by Pollitzer.[1]

Simplification of this equation gave:

$$35760 = U_0 - 1210 + 17 + 3590 - 1110 + 812.5 - 761.5,$$

from which

$$U_0 = 34422 \text{ calories.}$$

It was now necessary to find the maximum work of the reaction at 234° K. By employing the value found for U_0 and with the aid of Pollitzer's tables for the $\beta\nu$ functions in Equation (3), there results:

$$A_{234^\circ} = 34422 + [- 6.204 - 2(9.201) - 2(4.103) - {}^5/_4(5.618)$$
$$- {}^5/_2(0.84) - 5(0.014) + 3(6.405) + 8(0.494) + 1.202$$
$$+ 2(8.200)]234 - {}^4/_{15}(3.3 + 24.0 - 42.0) \times 10^{-5} \times 234^{5/2}$$

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[1] *Sammlung chemischer Vorträge*, 17, 498 (1912).

whence

$$A_{234°} = 34422 - 293.6 + 33.$$
$$= 34160 \text{ calories.}$$

It is now necessary to obtain the heat of reaction for liquid mercury at 234° K. This is done in a manner similar to that just performed for U_0. There is thus obtained,

$$\underset{liquid}{U_{234°}} = 34422 - 561 - 49 - 1110 = 32702 \text{ calories.}$$

The terms for the heat of fusion of ice and for the average specific heats of liquid mercury and of water obviously do not come into calculations at this temperature.

Similarly at 262° K., the cryohydrate temperature, the heat of reaction may be calculated with the same formula but with an added term for the mean specific heat of liquid mercury from 234° to 262° K. Hence,

$$U_{262°} = 34422 - 871 - 20 - 1110 - 381 = 32040.$$

Now from Kirchhoff's law,

$$U = U_1 + \Sigma n\bar{c}\,(T - T_1),$$

where $\bar{c}$ is the mean specific heat over the given range of temperature.

Hence,

$$U_{262} = U_{234} + \Sigma n\bar{c}\,(262 - 234)$$

or

$$\Sigma n\bar{c} = -\frac{32702 - 32040}{28} = -23.6.$$

From a previous calculation we have $A_{234°} = 34160$. This value may now be used with the data for $U_{234°}$ and $\Sigma n\bar{c}$ for a determination of the value of A at the cryohydrate point. To accomplish this the thermodynamic equation in its integrated form is used.

$$A - U = T\,dA/dT$$

On integration, this becomes

$$\frac{A_2}{T_2} - \frac{A_1}{T_1} = -\int_{T_1}^{T_2} \frac{U dT}{T^2}.$$

For small temperature intervals in which U can be regarded as constant this gives

$$A_2 = A_1 \frac{T_2}{T_1} - U\,\frac{T_2 - T_1}{T_1}$$

or in case

$$U = U_1 + \Sigma n\bar{c}\,(T_2 - T_1)$$

the equation becomes:

$$A_2 = A_1 \frac{T_2}{T_1} - U_1 \frac{T_2 - T_1}{T_1} - \Sigma n\bar{c} \left[T_2 \ln \frac{T_2}{T_1} - (T_2 - T_1) \right]$$

On substitution in this equation there results

$$\begin{aligned} A_{262^\circ} &= 38287 - 3913 + 37 \\ &= 34374 \text{ calories.} \end{aligned}$$

Now, as before, one can proceed with the thermodynamic equation from 262° to 291° K. Over this range the mean specific heat calculates to

$$\Sigma nc_1 = 4.5,$$

and consequently,

$$\begin{aligned} A_{291} &= 38180 - 3944 - 9 \\ &= 34227 \text{ calories.} \end{aligned}$$

The electromotive force corresponding to this value for A is

$$E = \frac{34227}{46092} = 0.7426 \text{ volts. (Calc.)}$$

The experimentally determined value for the combination

$$Cd \mid CdCl_2.2^1/_2H_2O \quad Hg_2Cl_2 \mid Hg$$

may be obtained by a combination of the value for the standard cell with that determined by Hulett[1] for the combination

$$\begin{array}{c|c|c} \text{Cd} & \text{CdSO}_4 & \text{Cd} \\ \text{amalgam} & \text{solution} & \text{metal} \end{array}.$$

Such a combination yields for the experimentally determined value at 291° K. the value

$$0.6714 + 0.0522 = 0.7236 \text{ volts. (Found.)}$$

(2) The cell

$$Cd \mid CdSO_4.^8/_3H_2O, \quad Hg_2SO_4 \mid Hg.$$

Proceeding in a similar manner to (1) and employing the following data: For the heat of reaction at 291° K., the value deduced by Cohen[2] is:

$$U_{291^\circ} = 52972 \text{ calories.}$$

For the $\beta\nu$ values to represent the specific heats the following table embodies the values determined for cadmium sulfate and those of Pollitzer for the remaining substances.

Substance.	n_1.	$\beta\nu_1$.	n_2.	$\beta\nu_2$.	n_3.	$\beta\nu_3$.	$k \times 10^5$.	Correction term.
Cd	1	146	..	...	..	....	3.3	....
$CdSO.8/3H_2O$	3	150	3	600	8	1000	....	$e^{(T-240)/17}$
Ice	$^1/_2$	166	1	725	2	2500	....	$0.045\, e^{(T-220)/13}$
Hg_2SO_4	2	100	1	200	4	1050	....	....
Hg	1	97	..	...	..	....	21.0	....

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[1] *Trans. Am. Electrochem. Soc.*, 7, 333 (1905).

[2] *Z. physik. Chem.*, **89**, 287 (1915).

The calculations, carried through, as in the previous case, give:

$$52792 = U_0 - 1786 - 122 + 3829 - 1110 + 867 - 762,$$

whence

$$U_0 = 52056.$$

Similarly,

$$A_{234} = 52056 - 2355 + 86$$
$$= 49787$$
$$U_{234} \text{ (Hg liquid)} = 52056 - 1152 - 129 - 1110$$
$$= 49665.$$

The cryohydrate temperature was found to be 256° K. and so

$$U_{256} = 52056 - 1390 - 126 - 1110 - 299$$
$$= 49130.$$

From these values $\Sigma n\bar{c}$ is calculated to be —24.3.

Hence,

$$A_{256} = 54480 - 4670 + 24$$
$$= 49834.$$

Similarly,

$$\Sigma n\bar{c}_1 \text{ between } 256° \text{ and } 291° \text{ K.} = 0.33,$$

and therefore

$$A_{291} = 56650 - 7244 - 1$$
$$= 49405 \text{ calories.}$$

This corresponds to an electromotive force of 1.072 volts. (Calc.)

The experimentally determined value is obtained as before by combination of the Weston element with the Hulett[1] element, and gives:

$$1.01834 + 0.05223 = 1.071 \text{ volts. (Observed.)}$$

Summary.

Experiments have been described whereby the specific heats of cadmium chloride and cadmium sulfate have been determined between the limits of temperature 87° K. and 274° K.

The experimentally determined values have been expressed as functions of temperature with the aid of the Nernst-Lindemann specific heat equation.

The values so obtained have been utilized along with others available from the literature to investigate the thermodynamic relationships of the cadmium sulfate standard cell and the cadmium chloride standard cell. Satisfactory agreement has been obtained between the calculated and observed values with the assumption of Nernst for condensed systems and the consequent deduction that the integration constant in the thermodynamic equation is equal to zero.

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[1] *Trans. Am. Electrochem. Soc.*, 7, 333 (1905).