Ni present.	Ni found.	Co present.	Dimethylglyoxime added (1% solution). Cc.	Co found.
0.0468	0.04664	0.00862	30	0.00822
0.0468	0.04657	0.00862	30	0.00822
0.0468	0.04662	0.00431	30	0.00383

Solution and washings diluted to 100 cc.; comparisons made with cobalt solutions containing 0.00431 g. of Co and 5 cc. of dimethylglyoxime reagent in 100 cc.

Many other results on other concentrations of the salts gave data comparable with the above.

While the method gives very good results for small amounts of cobalt in the presence of much larger amounts of nickel some points should be kept in mind. The solution or filtrate should be allowed to cool slowly as the intensity of color seems to vary slightly with the rate of cooling and in the sodium acetate solution copper and iron must of course be absent.

Summary.

1. It has been found that dimethylglyoxime always gives a brown colored solution with cobalt which does not disappear upon the addition of mineral acids as does the color of other metal glyoximes and hence can be used as a sensitive qualitative test for cobalt, in the absence of such interfering substances as copper and iron.

2. In the absence of the elements which give colored solutions or precipitates with sodium acetate or dimethylglyoxime (with the exception of nickel) the brown color of cobalt dimethylglyoxime is proportional to the concentration and hence can be used as a colorimetric method for this element, when the solution is prepared by use of acetic acid and sodium acetate.

URBANA, ILLINOIS.

THE THERMOCHEMICAL DATA OF CADMIUM CHLORIDE AND IODIDE.

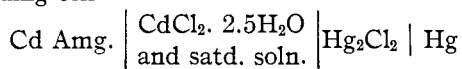By HUGH STOTT TAYLOR AND GEORGE ST. JOHN PERROTT.

In a communication[1] relative to the thermodynamic properties of silver and lead iodides, opportunity was taken to subject the Nernst heat theorem to a careful test employing data obtained from a study of the cell combination Ag | AgI | XN KI solution | PbI$_2$ | Pb. Since the cell operated in a homogeneous liquid medium the difficulties of correction for liquid potential and osmotic work factors were eliminated and the values obtained by direct measurement could be employed in the calculations involved. This represents a marked advantage over such cases in which this procedure is not possible. The combination, however, like

[1] Taylor, THIS JOURNAL, **38**, 2295 (1916).

many which preceded it, was open to criticism in that the potentials obtained were dependent to a certain degree upon the concentration of the potassium iodide solution employed; whereas in the calculations which followed it was tacitly assumed that the reaction proceeding when the cell operated did not at all involve the potassium iodide. Thus the heat of the reaction $Pb + 2AgI = PbI_2 + 2Ag$ as determined from the cell combination using $0.05\ N$ and $0.10\ N$ potassium iodide was 11500 and 11610 calories, respectively. The discrepancy between the 2 values was greater than the reproducibility of the cells would have warranted. Efforts were made to determine the magnitude of the quantity with the aid of cells weaker in potassium iodide and also in aqueous solutions, but the electromotive forces observed were unsatisfactory as regards constancy and reproducibility.

In the succeeding work (of which the present contribution is the first instalment) an effort has been made to study reactions by means of cell combinations in which the presence of substances foreign to the reaction was unnecessary, maintaining, however, as in the previous work, a homogeneous liquid medium. Certain such combinations have already been studied. Pollitzer's investigations of the Clark cell[1] and the recent studies by Seibert, Hulett, and Taylor[2] on the saturated Weston and cadmium chloride cells are cases in point. These systems, however, since mercury is one of the components, become condensed systems only below $234°$ K, the freezing point of mercury, so that the application of the Nernst heat theorem involves either a long and uncertain extrapolation to this low temperature or a complicated calculation with the aid of the Gibbs-Helmholz equation. In the first place, it was decided to investigate cell combinations containing a saturated solution of cadmium chloride as the liquid medium, employing a cadmium amalgam as one electrode, the other electrode being either lead or silver in contact with the corresponding halide.

The constancy and reproducibility obtained by Lipscomb and Hulett[3] in the corresponding cell

$$\text{Cd Amg.} \left| \begin{array}{c} \text{CdCl}_2.\ 2.5\text{H}_2\text{O} \\ \text{and satd. soln.} \end{array} \right| \text{Hg}_2\text{Cl}_2\ |\ \text{Hg}$$

has again been obtained in the present instance and the cells studied have proved very suitable to the investigations planned. From the values obtained with the several cell combinations various other electromotive forces could be deduced and the experimental work checked against the results of previous investigations.

In the second place, the corresponding cells obtained by substituting

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

[2] Seibert, Hulett and Taylor, THIS JOURNAL, **39**, 38 (1916).

[3] Lipscomb and Hulett, *ibid.*, **38**, 20-7 (1916).

the iodide for the chloride have also been studied. Such cells possess the added advantage that they are systems in which the halide in equilibrium with the saturated solution contains no water of hydration, the system being therefore a true condensed system at all temperatures. Accordingly, the electromotive forces of the 2 cell combinations Cd Amg. | CdI$_2$ and saturated soln. | AgI | Ag and Cd Amg. | CdI$_2$ and saturated soln. | PbI$_2$ | Pb Amg. were measured, the experimental data thus obtained being further useful as by combination they yielded a check on the measurements of Taylor with the combination Ag | AgI | PbI$_2$ | Pb Amg. in solutions of potassium iodide and would tend to demonstrate the effect of the potassium iodide in such cell combinations.

Experimental.

The **Cadmium Chloride-Silver Chloride Cell.**—The silver-silver chloride electrodes, which were made up by a modification of the Jones and Hartmann[1] method for silver-silver iodide electrodes, consisted of platinum spirals electrolytically covered with silver and filled in with porous silver obtained by heating the spirals filled with oxide to 400–500°. The electrodes were then coated with silver chloride by making them anode in a solution of potassium chloride. They showed excellent reproducibility when mea·sured against each other in a solution of potassium chloride saturated with silver chloride. Electrode 1 against electrodes 2, 3, 4 and 5 showed a difference of 0.01, 0.02, 0.02 and 0.00 mv., respectively.

The cadmium amalgam employed was 9% cadmium by weight and was thus chosen in accordance with the investigations of Bijl[2] so that, at 0° C., there should still be present a quantity of the liquid amalgam phase. The cadmium chloride employed was a recrystallized sample of a good grade product. It consisted of large clear crystals of $CdCl_2.2H_2O$.

The cells were the simple test-tube variety, having the cadmium amalgam at the bottom covered by a layer of cadmium chloride crystals and a saturated solution of the salt into which the silver-silver chloride electrode was introduced. This latter was kept in position by means of a cork which served also to close the cell.

The **Cadmium Chloride-Lead Chloride Cell.**—The lead amalgam was prepared of strength exactly 0.72% by weight in the manner described by one of us in the earlier communication.[3] The electrode was covered with a paste of lead chloride and cadmium chloride crystals in a saturated solution of cadmium chloride. The lead salt was pre·pared from a high grade material by precipitation from the conc. hydrochloric acid solution of the salt, merely by dilution with water. The cadmium chloride electrode was again composed of 9% amalgam and was covered with a layer of cadmium chloride crystals. To minimize diffusion in this case owing to the greater solubility of lead chloride, the H-type cell was chosen.

The potentials yielded by the cells were measured at 25° and 0°, and the values given for 5 cells in each case show that desirable constancy and reproducibility were readily attained. Thus, for the cell Cd Amg.|CdCl$_2$.2.5H$_2$O and satd. solution|AgCl|Ag at 25°, the mean voltage was 0.62478, and the maximum deviation among 5 cells was 0.00006 volt; while at 0°, the mean voltage was 0.6249, and the maximum deviation was 0.0001.

[1] Jones and Hartmann, THIS JOURNAL, **37**, 752 (1915).
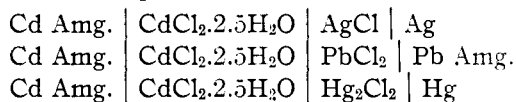
[2] Bijl, *Z. physik. Chem.*, **41**, 641 (1902).

[3] Taylor, *Loc. cit.*

The cells at 0° possessed a high internal resistance owing to the separation of solid cadmium chloride hydrate from the solution and the sensitivity of the measurements was thereby considerably diminished. The recovery of the cells after reinsertion in the bath at 25° was also extremely slow so that considerable time elapsed before the original value was again reached.
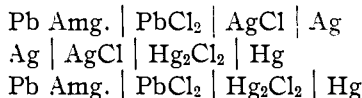
For the cell Cd Amg. | $CdCl_2. 2.5H_2O$ and satd. soln. | $PbCl_2$ | Pb Amg. at 25°, the mean voltage was 0.14840, and the maximum deviation among 5 cells was 0.00002 v.; while at 0° the mean voltage was 0.1484, and the maximum deviation was 0.0003.

In this combination also the internal resistance was so great at 0° that unsatisfactory results were obtained. The values obtained showed only a slight variation in the fourth decimal place from the value obtained at 25°. This rather unexpected result was confirmed by the process of calculation outlined in the following paragraph.

Comparison of Results.—An excellent check on the measurements given above was obtained by suitable combination of these results with themselves and with the standard cadmium chloride cell investigated by Lipscomb and Hulett,[1] and by comparison of the results obtained with direct measurements of the resulting cell combinations by other workers. Thus from the potentials of the cells

Cd Amg. | $CdCl_2.5H_2O$ | AgCl | Ag
Cd Amg. | $CdCl_2.5H_2O$ | $PbCl_2$ | Pb Amg.
Cd Amg. | $CdCl_2.5H_2O$ | Hg_2Cl_2 | Hg

the potentials of the following combinations could be derived:

Pb Amg. | $PbCl_2$ | AgCl | Ag
Ag | AgCl | Hg_2Cl_2 | Hg
Pb Amg. | $PbCl_2$ | Hg_2Cl_2 | Hg

All these have been carefully measured by Brönsted[2] and so a comparison of the direct and indirect values is possible. The results of such a comparison are given in Table I.

TABLE I.

	° C.	Brönsted—Direct.	Indirect (T. and P.).
Pb Amg.|$PbCl_2$|AgCl|Ag	25.......	0.4766	0.4763
	0.......	0.4864	0.4864
Hg|Hg_2Cl_2|AgCl|Ag	25.......	0.0456	0.0460
	0.......	0.0368	0.0369
Pb Amg.|$PbCl_2$|Hg_2Cl_2|Hg	25.......	0.5225	0.5224
	0.......	0.5233	0.5234

The e. m. f. at 0° of the cell Cd | $CdCl_2.5H_2O$ | Hg_2Cl_2 | Hg was calculated from the equation representing the experimental measurements of Lipscomb and Hulett. The values of the e. m. f.'s for lead amalgam cells were obtained with the aid of Brönsted's values at 0° and 25° for the cell Pb | $PbCl_2$ solution | Pb Amg. (0.72%), which are representable by the linear interpolation formula $E = 0.0051 + 0.000233\ t$.

[1] *Loc. cit.*
[2] Brönsted, *Z. physik. Chem.*, **56**, 668 (1906); *Z. Elektrochem.*, **19**, 754 (1913).

The Cadmium Iodide-Silver Iodide Cell.—Reproducible silver iodide electrodes were prepared after the method of Jones and Hartmann. 9% cadmium amalgam was used as in the previous work with the cadmium chloride cell. The cadmium iodide used was of a pure grade, samples from widely different sources showing no difference in electromotive force. The cells were of the simple test-tube variety, closed with a cork which also served to hold the silver electrode.

The Cadmium Iodide-Lead Iodide Cell.—Lead amalgam was prepared from lead of the highest purity of strength exactly 0.72% by weight as in the cadmium chloride cell. The electrode was covered with a paste of lead iodide and covered with crystals of cadmium iodide and saturated cadmium iodide solution. The cells used were of the H-type in order to minimize diffusion.

The potentials of the cells were measured at 0°, 25°, and 40°. With the silver iodide cell much trouble was at first experienced in obtaining reproducible results, the cells holding good values for several days and then beginning to fluctuate and sometimes differing from each other by a millivolt. This was evidently due to the formation of some cadmium-silver complex. A brown deposit formed over the cadmium electrode after a week. It was therefore found necessary to take frequent measurements of the cell for the period of a day at each temperature. Thus, for a series of measurements at 0°, 25°, and 40° lasting 3 days, the cells would agree among themselves and assume their original value when put into the bath at 25°. If kept for several days at 25° before beginning measurements at the different temperatures, reproducible results could not be obtained and the cells would not assume their original value when replaced in the bath at 25°.

The lead iodide cells were much more reproducible and could be kept for several weeks without showing signs of deterioration.

The results given are from a representative series from a large number of cells. Over 25 of each kind were set up at different times. The values finally used in calculations were chosen as being the most representative means.

For the cell Cd Amg.|CdI$_2$|CdI$_2$ sat. soln.|AgI|Ag at 0°, 25° and 40°, the mean voltages were 0.3006, 0.3035 and 0.3050, and the maximum deviations among 5 cells were 0.0010, 0.0003 and 0.0004, respectively.

For the cell Cd Amg.|CdI$_2$|CdI$_2$ satd. soln.|PbI$_2$|Pb, at the temperatures 0°, 25° and 40°, the mean voltages were 0.09655, 0.10725 and 0.11350, and the maximum deviations among 5 cells were 0.0003, 0.00013 and 0.0002, respectively.

Discussion.—The accepted means of the 2 cells at the different temperatures have been collected in Table II.

TABLE II.

	0°.	25°.	40°.
Cd Amg.|CdI$_2$ and satd. soln.|AgI|Ag	0.3006	0.3035	0.3050
Cd. Amg.|CdI$_2$ and satd. soln.|PbI$_2$|Pb Amg	0.09655	0.10725	0.11350

It is obvious that the algebraic sum of these 2 combinations should give the cell Ag | AgI | PbI$_2$ | Pb Amg. already investigated. Carrying out this addition gives results between 4 and 5 millivolts higher than those found by Taylor. It will be observed that the discrepancy is in the same direction as would be anticipated from results with cell combinations with potassium iodide containing concentrations of iodide ion similar to those obtaining in the present case. It emphasizes the observation made earlier as to the general unsatisfactoriness of cell combinations containing substances foreign to the reaction under observation.

TABLE III.

The Cell Ag | AgI | PbI₂ | Pb Amg.

KI N.	Taylor (obs.).		Calc. (T. and P.).	
	0°.	25°.	0°.	25°.
0.05	0.20965	0.20065	0.20405	0.19625
0.10	0.20905	0.19977		

Determination and Computation of Thermochemical Data.

The data obtained with the several cells may now be employed to determine the heats of the reactions occurring in the cells. For this purpose the electromotive force data were first corrected to the simple element electrodes in place of the amalgam electrodes actually employed. This was done with the aid of the data of Hulett[1] for cadmium amalgam and the data of Brönsted already cited, for the 0.72% lead amalgam. Hence, there follows for the combination Cd | CdCl₂.2.5H₂O | AgCl Ag, at 25° 0.62478 + 0.05053 = 0.67531 volt;[2] and at 0° 0.63490 + 0.05663 = 0.69153 volt. The temperature coefficient of the cell is therefore equal to —0.00065 volt per degree.

These data when employed in the Gibbs·Helmholz equation, $U = A - T(dA/dT)$, give a value for $U = 40030$ calories.

In a similar manner for the combination Cd | CdCl₂.2.5H₂O | PbCl₂ | Pb, at 25° 0.1484 + 0.05053 — 0.01092 = 0.18801 volt; and at 0° 0.1484 + 0.05663 — 0.0051 = 0.19993 volt. Whence $dE/dT = -0.00048$ volt per degree; and the heat of reaction is in like manner $U = 15250$ calories.

These results obtained from the electrometric data can be compared with the available calorimetric data. For cadmium chloride the value 93.240 cals. from Thomsen was used. For the total heat change accompanying the formation of the hydrate in the saturated aqueous solution the recent determination of Cohen and Bruins[3], namely, 7710 cals., was employed. For mercurous, silver and lead chlorides the data of Braune and Koref,[4] 63584, 30410 and 85700 cals., respectively, were available. The comparisons obtained are presented in Table IV, in which also has been inserted a recalculation of the Lipscomb-Hulett cadmium chloride-calomel cell and a comparison with the calorimetric data from the same sources.

TABLE IV.

Reaction.	U electro-chemically.	U thermo-chemically.	Differ-ence.
Cd + 2AgCl + 2.5 H₂O = CdCl₂.2.5H₂O + 2Ag........	40030	39530	500
Cd + PbCl₂ + 2.5H₂O = CdCl₂.2.5H₂O + Pb..........	15250	14650	600
Cd + Hg₂Cl + 2.5H₂O = CdCl₂.2.5H₂O + 2Hg.........	37510	36765	745

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

[2] This value checks very well with that obtained by Horsch, THIS JOURNAL, **41**, 1794 (1919), for the e. m. f. of the cell Cd|CdCl₂ (6.6 mols per 1000 g. H₂O|AgCl|Ag, *viz.*, 0.67540 volt.

[3] Cohen and Bruins, *Verslag. Akad. Wetenschappen Amsterdam*, **26**, 587 (1917).

[4] Braune and Koref, *Z. anorg. Chem.*, **87**, 175 (1914).

The last column indicates the discrepancy between the 2 sets of data, of which the 2 former may be regarded as the more trustworthy since the thermochemical values for silver and lead chlorides were directly measured, that for mercurous chloride deduced from several indirect methods of calculation and for which an accuracy of not more than a few hundred calories is claimed. It is evident that an alteration of 550 calories in the value for cadmium chloride cited above would bring the thermochemical and electrochemical data for the 3 cells into excellent agreement, the value for the heat of formation of cadmium chloride deduced electrometrically becoming therefore 93,800 cals. Such a change gives a value for the heat change in the cell Cd Amg. | $CdCl_2.2.5H_2O$ | Hg_2Cl_2 | Hg practically identical with that reached by Cohen and Bruins in the paper above cited.

The e. m. f. of the cell Cd | CdI_2 and satd. soln. | AgI | Ag can be ex‑ pressed by the equation $E = 0.3572 — 0.0001205t — 0.0000003t^2$; whence $E_{20} = 0.3457$. The heat of reaction at 20° will therefore be, from the Gibbs-Helmholz equation, $U_{20} = 18300$ calories. Taking the value of Braune and Koref for the heat of formation of AgI there results for the heat of formation of cadmium iodide $2(15,100) + 18,300 = 48,500$ calories.

The e. m. f. of the cell Cd | CdI_2 and satd. soln. | PbI_2 | Pb can be represented by the equation $E = 0.14808 — 0.0000414 — 0.000000296t^2$; whence $E_{20} = 0.14713$ volt and $U_{20} = 7497$ calories.

Using the value of Braune and Koref for the heat of formation of lead iodide (41,850 calories) we obtain for the heat of formation of cadmium iodide

$$41,850 + 7497 = 49,350.$$

The same discrepancy between this value and that of the silver iodide cell is noted here as was previously discussed in connection with the com‑ parison of the algebraic sum of the voltages of our cells and the e. m. f. of the cell of Taylor. For U the difference is magnified by the fact that the temperature coefficients obtained by Taylor and in our cells were slightly different. In the Gibbs-Helmholz equation this is multiplied by the absolute temperature and so makes a much larger difference in U than in A.

Calculation from the results of Jones and Hartmann with the cell Ag | AgI | I_2 gives for the heat of formation of silver iodide 14,565 calories. Substituting this value we should get for the heat of formation of cadmium iodide $2(14,565) + 18,300 = 47,430$, a result differing by 1070 calories from the electrometrically determining value in the silver iodide cell, and by no less than 1920 calories from the value determined by the lead iodide cell. Accordingly it was decided to make a direct calorimetric determination of the heat of formation of cadmium iodide.

When iodine is dropped into a potassium iodide solution containing lead, silver, cadmium, zinc, etc., in a finely divided state, the solution is

rapidly decolorized with the formation of the iodides of the metals. This gives a simple method of determining the heat of combination directly. Braune and Koref have used this method for determining the heat of formation of silver and lead iodides. At first sight it might seem as if the state of combination of iodine in solution in potassium iodide would affect the result. But a consideration of Hess's law will show that the heat given up or absorbed during the formation of an iodine-potassium iodide complex will be exactly counterbalanced by that produced when the complex is decomposed by the formation of cadmium iodide.

$$KI + I_2 = KI_3 \pm q$$
$$KI_3 + Cd = CdI_2 + KI \pm q + Q$$
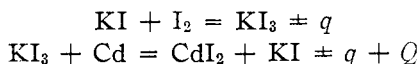
where q is the heat of formation of the complex and Q that of cadmium iodide plus its heat of solution. The possibility of side reactions may also be eliminated by varying the strength of the potassium iodide solution.

Apparatus.—The apparatus used was a duplicate of that used so successfully by Fischer and by Braune and Koref. The calorimeter vessel was a 90 mm. Dewar flask. It was provided with a felt-lined wooden cover containing holes for the admission of thermometer, stirrer, iodine container and electric heater. The stirrer was a pear-shaped glass bulb with 4 holes at the widest part of its circumference and one hole at the bottom. This served in a very efficient manner to draw the cadmium powder from the bottom and keep it distributed throughout the liquid. For a heater, a piece of 4 mm. glass tubing was bent in a circle at right angles to the tube and on this was wound a length of constantan wire having a resistance of 10.00 ohms. The leads of copper wire were put through holes at the bottom of the tube and came up inside the tube. The resistance of the heater plus the leads was 10.044 ohms. The drop of potential over the heater was measured by a Weston laboratory standard voltmeter which had been calibrated in November, 1916, immediately prior to its use. The resistance of the voltmeter was 2048.3 ohms. Correction was made for the current used by the volt-meter and for the resistance of the leads. The current was measured with a silver coulometer. This eliminated the necessity of measuring the time. The iodine was held in a stoppered tube. By raising the stopper, the iodine was dropped into the calorimeter. The tube was weighed before and after the experiment and afforded a simple and accurate means of getting a definite amount of iodine into the reaction mix-ture. This device also had the advantage that the iodine was at the same temperature as the calorimeter liquid. The temperature was measured with a Beckmann ther-mometer which had been calibrated at the Physikalische Technische Reichsanstalt.

Materials.—Finely divided cadmium was prepared from metal of the highest purity by filing and collecting the dust. This was dragged with a magnet and when tested for iron showed only the minutest trace.

Resublimed iodine of high grade was used after being powdered in a mortar.

Procedure.—In the calorimeter was placed 800 cc. of potassium iodide solution of the normality used and 30 g. of cadmium powder. Sufficient iodine to give a temperature rise of about 1° (3 g.) was weighed into the container. This was put in place in the cover and the latter with its stirrer and heater and thermometer were placed in position in the calorimeter. The stirrer was rotated by an electric motor at about 200 r. p. m. It caused a rise of temperature of about 0.001° per minute. Temperature

readings were taken at intervals of 1 minute for 15 minutes. Then the iodine was dropped in and readings taken until the temperature was again changing regularly and for 15 minutes thereafter. A known quantity of electricity was sent through the heater until a rise of temperature about equal to that caused by the addition of iodine had been attained and temperature readings were again taken until there was a constant change of temperature. From these data the heat of formation of cadmium iodide plus its heat of solution could be calculated.

The heat of solution was determined in a like manner. 800 cc. of potassium iodide was put in the calorimeter and an amount of cadmium iodide about equal to that formed in each determination of the previous experiment was used. The difference between these 2 results gave the heat of reaction.

Two strengths of potassium iodide, N and $0.5\ N$, were used in order to make sure that this substance had no effect on the heat evolved. A typical experimental result is shown in Table V.

TABLE V.

Expt.	Rise in temp. °C.	Substance added. G.	Rise due to heating. °C.	Ag deposited. G.	Volts.	Heat of reaction.
5	0.850	3.521 g. I_2	0.832	0.3358	10.00	52350
8	0.082	6.6232 g. CdI_2	0.814	0.3305	10.00	3969

The mean results obtained with the two different concentrations of potassium iodide solution are collected in Table VI.

TABLE VI.

Concentration of N KI.	Heat of reaction of I_2 and Cd in solution. Calc.	Heat of solution of CdI_2. Calc.	Heat of formation of CdI_2. Calc.
1.0	52,380	3990	48390
0.5	52,360	3880	48480

Mean of both sets of determination, 48440

Within the limit of experimental error there is no difference between the heat of formation in N and in $0.5\ N$ potassium iodide solution. This means that the true heat of the reaction $Cd + I_2$ (solid) $= CdI_2 + Q$ is given by the heat evolved when the reaction takes place in such solutions. For, if there were any difference between the heat of reaction thus measured and the true heat of reaction, we should expect differences depending on the strength of the potassium iodide employed.

It is interesting to compare the thermochemical value with those obtained by means of the electrochemical data.
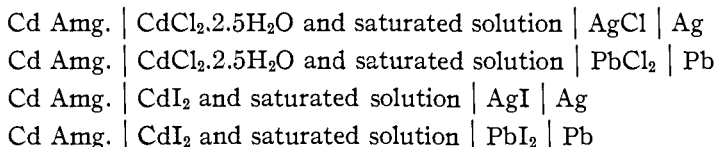
TABLE VII.

	U.
From the cell Cd$\|$CdI$_2\|$AgI$\|$Ag (Braune and Koref)................	48,500
(Jones and Hartmann).....................................	47,430
From the cell Cd$\|$CdI$_2\|$PbI$_2\|$Pb (Braune and Koref)..............	49,350
Thermochemically...	48,440

The application of these data to the thermodynamic relations of the several reactions concerned is in progress. To that end, further specific heat data at low temperatures are required. It is hoped to present the results of such investigations in a later communication. The experimental material thus far obtained tends to show that the earlier measurements of Seibert, Hulett and Taylor[1] contain a constant experimental error the cause of which has not yet been determined, but which tends to yield divergencies between the experimentally determined values for the e. m. f. of the several cells here studied and those calculable by use of the Nernst heat theorem. A brief communication relative to this matter is in course of preparation. Succeeding experimental work will, it is anticipated, reveal the causes of the discrepancy and establish agreement between the values found by experiment an d by application of the theorem of Nernst.

Summary.

A study has been made of the electromotive forces of the following cell combinations and of their temperature coefficients.

Cd Amg. | CdCl$_2$.2.5H$_2$O and saturated solution | AgCl | Ag

Cd Amg. | CdCl$_2$.2.5H$_2$O and saturated solution | PbCl$_2$ | Pb

Cd Amg. | CdI$_2$ and saturated solution | AgI | Ag

Cd Amg. | CdI$_2$ and saturated solution | PbI$_2$ | Pb

Values for the heats of formation of cadmium chloride and of cadmium iodide from their elementary constituents have been calculated from these electrical measurements. In the case of cadmium chloride it is deduced that a value of 93,800 calories, obtained from the electrometric measurements, is more trustworthy than the hitherto accepted value of Thomsen from thermochemical measurements. From the electrometric measurements involving cadmium iodide and from auxiliary thermochemical measurements it is concluded that the heat of formation of cadmium iodide is 48,500 calories.

PRINCETON, N. J.

[1] Seibert, Hulett and Taylor, THIS JOURNAL, **39**, 38 (1917).