from, the "law of mass action" is proposed. This theory is in accord with and affords an explanation of Reichinstein's "Constant Sum Hypothesis." An outline is given of the application of this theory to heterogeneous gas reactions and to enzyme action.

The second part of this paper will deal with the Structure of Liquids with particular reference to surface tension phenomena. It will be shown that the surface tension of organic liquids is a characteristic *chemical* phenomena. It depends particularly upon the *shapes* of the group molecules and upon the relative intensities of the chemical activity of *different portions* of the molecules. A method will be described (together with experimental data) by which the *cross sections*, *lengths* and other dimensions of group molecules of liquids may be determined.

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THE THERMODYNAMIC PROPERTIES OF SILVER AND LEAD IODIDES.

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Received July 10, 1916.

The thermodymanic properties of silver and lead iodides have been the subject of considerable recent experimental investigation. The object of the work has been to obtain accurate data on the free energies and heats of formation with a view to testing the newer thermodynamic conceptions relative to these two magnitudes.

The relation between free energy and heat of formation is representable, according to the two laws of thermodynamics, by the fundamental equation,

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

With the aid of this equation, given the maximum work or free energy, A, at any temperature, T, together with its temperature coefficient dA/dT, it is possible to evaluate the heat effect of the reaction U. The values obtained by such a procedure should show concordance with the direct calorimetric observations. Alternatively, if it be desired to proceed from the thermal data to an evaluation of the free energy, classical thermodynamics, without the aid of new assumptions, is inadequate. This will readily be grasped if the form of the above equation be somewhat modified. Since

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

it follows that

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

Dividing each side by T^2 there results,

$$\frac{\mathrm{A}\,d\mathrm{T} - \mathrm{T}\,d\mathrm{A}}{\mathrm{T}^2} = \frac{\mathrm{U}\,d\mathrm{T}}{\mathrm{T}^2},$$

whence

$$\mathrm{A} = -\mathrm{T}\int\frac{\mathrm{U}\,d\mathrm{T}}{\mathrm{T}^2} + \mathrm{IT}$$

where I is the constant of integration.

Obviously, in order to evaluate A from the thermal data it is necessary to know U as a temperature function and also the value of the integration constant I. As regards the variation of U with temperature it is well known that this magnitude varies with the specific heats of the reacting substances (Kirchhoff's Law) according to the equation

$$d\mathrm{U}/d\mathrm{T} = \Sigma n\mathrm{C}$$

the summation sign indicating an algebraic summation (reactants positive, resultants negative) of the molecular heats of the substances participating, multiplied by their respective molecular coefficients, *n*. The necessity of evaluating this equation has led to the determination of specific heats of many substances down to very low temperatures with a resultant considerable development in the theory of specific heats, some of the newer features of which will later be developed. Concerning the constant of integration, I, classical thermodynamics teaches nothing. New assumptions are necessary, the consequences of which must be submitted to experimental verification before they are finally accepted.

The fundamental assumption made by Nernst in the Nernst heat theorem is

$$\lim\,(d\mathrm{U}/d\mathrm{T}) = \lim\,(d\mathrm{A}/d\mathrm{T}) \text{ for } \mathrm{T} = 0$$

for all reactions which take place in condensed systems, *i. e.*, in systems which persist continuously, without change of state of aggregation, down to the absolute zero of temperature. Obviously, therefore, this assumption applies to reactions between pure solids and liquids which supercool but not to those between gases and solutions. The deductions which may be made from this assumption are independent of the manner in which A and U are expressed as functions of temperature provided the functions be continuous. Thus, the fundamental thermodynamic equation may be generalized to give

$$\varphi(\mathrm{T}) = f(\mathrm{T}) + \mathrm{T}\varphi'(\mathrm{T}),$$

in which $\mathrm{A} = \varphi(\mathrm{T})$, $\mathrm{U} = f(\mathrm{T})$, and $d\mathrm{A}/d\mathrm{T} = \varphi'(\mathrm{T})$.

This yields on differentiation,

$$\varphi'(\mathrm{T}) = f'(\mathrm{T}) + \mathrm{T}\varphi''(\mathrm{T}) + \varphi'(\mathrm{T})$$

whence

$$\varphi''(\mathrm{T}) = -1/\mathrm{T}\,.\,f'(\mathrm{T}).$$

If this equation be integrated, there follows

$$\varphi'(\mathrm{T}) = -\int 1/\mathrm{T}\,f'(\mathrm{T})d\mathrm{T} + \mathrm{I}.$$

For the small temperature dT above the absolute zero, this equation yields

$$\varphi'(dT) = -f'(dT) + I,$$

which is only reconcilable with the assumption of Nernst, *i. e.*,

$$\lim f'(T) = \lim \varphi'(T) \text{ for } T = 0$$

if,

$$(a)\ \lim \varphi'(T) = \lim f'(T) = 0$$

and

$$(b)\ I = 0.$$

Accordingly, if the Nernst hypothesis be accepted, it follows that the integration constant is zero and the evaluation of free energy from thermal data becomes at once possible when U is known as a temperature function since the IT term of the original equation becomes zero and consequently,

$$A = -T\int\frac{U\,dT}{T^2}.$$

Nernst was led to his assumption reasoning from the approximate equality of A and U at moderate temperatures with reactions between solids and pure liquids in agreement with the Berthelot principle. Its final acceptance or rejection will depend however on experimental verification, to which end accurate determinations of heats of reaction, free energies and specific heats will all be requisite.

For such purposes of experimental measurement the halides of several of the metals have been eminently suitable owing to the relative simplicity of structure and of the reactions which result in their formation and interaction. Also, they have proved suitable for direct determination of the free energy magnitudes and of the calorimetric data. In the case of one of these salts, silver iodide, an examination of the literature reveals that the conclusions reached by different workers as a result of careful experimental investigation are not only not concordant but are actually diametrically opposed as to the value which must be assigned to the integration constant.

Ulrich Fischer in a research on the affinity between iodine and silver[1]—elsewhere characterized by Nernst as "der sehr eingehend und genau untersuchte Fall der Bildung des Jodsilbers"—determined electrometrically and with the aid of the fundamental thermodynamic equation by measurements of the electromotive force and temperature coefficient of cells of the type

$$Ag \mid AgI \mid N/x \text{ KI solution} \mid I_2$$

the heat of the reaction

$$Ag + I = AgI.$$

This was supplemented by a calorimetric determination of the same

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[1] *Z. anorg. Chem.*, 78, 41 (1912).

quantity. Concordant values by both methods yielded as a mean for T = 288° K. a value for U of 15,000 calories with a maximum deviation from the mean of 180 calories. Calculating from the electromotive forces of the cells with the aid of the Nernst heat theorem (assuming I = 0) a value of 15,079 calories was obtained, forming strong evidence in support of the truth of the theorem.

More recently, a publication by Jones and Hartman[1] described similar measurements with cells of the same type, though different in construction, for which a considerably higher degree of constancy and reproducibility is claimed than was obtained by Fischer. From measurements of the electromotive force at two temperatures with the aid of the most reliable specific heat data it was concluded that the integration constant was not zero but had a value equal to 2.33 calories per degree, so that in the free energy equation not only was IT not equal to zero but on the contrary at 273° K. possessed a value 273 × 2.33 = 636 calories, greater in magnitude than the sum of all the terms involving the specific heats of the substances concerned.

It is evident therefore that between these two investigations there exists a considerable discrepancy which is more manifest in view of the following considerations. Calculation with the aid of the Gibbs-Helmholz equation using the values for A and dA/dT obtained by Jones and Hartmann yields as a mean value for U the heat of reaction, 14,565 calories, a deviation from the mean obtained by Fischer of 435 calories. Independently, and apparently overlooked by Jones and Hartmann, the calorimetric determination of the heat of formation of silver iodide was carried out by Braune and Koref[2] and found to be 15,100 calories, somewhat higher than that determined by Fischer using the same method, and deviating still further from the value of Jones and Hartmann. With the aid of new determinations of the specific heat of silver iodide, Braune and Koref recalculated the value of U according to the Nernst heat theorem and obtained a value, 15,188 calories.

The divergencies between the three sets of data are readily grasped from the following table:

U from dA/dT and A.	U thermochemically.	U from Nernst heat theorem.	Author.
15169	14820	15079	Fischer
...	15100	15135	Braune & Koref
14565	...	14500	Jones & Hartmann

The values of Jones and Hartmann have been calculated by the author from their electromotive force data and according to the theorem from their value for U_0, since they did not attempt determination of U but

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[1] THIS JOURNAL, 37, 752 (1915).

[2] *Z. anorg. Chem.*, 87, 175 (1914).

concentrated attention on the method for determining I from measurements of the temperature coefficients of the cells.

It will be obvious that any experimental evidence which can help to a decision on the merits of the several sets of determinations will be of extreme importance, since the conclusions from these investigations involve important evidence on the general theorem that I = 0.

From the researches of Jones and Hartmann it would seem that the integration constant is not equal to zero, while the work of Fischer and of Braune and Koref suggests the opposite conclusion. This latter verdict is supported by work of Braune and Koref on the corresponding reaction with lead and iodine. In a manner similar to that employed by Fischer they investigated calorimetrically the heat of formation of lead iodide and also the electrometric relationships of cells of the type

$$\mathrm{Pb} \mid \mathrm{PbI_2} \mid N/x \text{ KI Solution} \mid \mathrm{I_2},$$

using, to attain reproducible electrodes, 0.72 per cent. lead amalgam instead of lead. The results obtained were reduced to those of metallic lead electrodes by use of the accurate data of Brönsted[1] on the e. m. f. of lead—lead amalgam cells. Concordant results were obtained by the several methods and they agreed with the value calculated from the Nernst theorem as the following summary shows:

REACTION: $Pb + I_2 = PbI_2$ (T = 293° K.).

From $TdA/dT = A - U$	U = 41960 calories.
Thermochemically	U = 41850 calories.
According to the theorem	U = 42034 calories.

In the present research an attempt has been made to throw light on the point at issue by investigation of a cell which consists essentially of a combination of the two cells previously discussed. It was apparent that if such a cell could be constructed and yielded constant and reproducible results information would be obtained allowing of a test of the two earlier combinations.

It is evident that a cell of the type

$$\mathrm{Pb} \mid \mathrm{PbI_2} \mid N/x \text{ KI Solution} \mid \mathrm{AgI} \mid \mathrm{Ag}$$

possesses certain advantages over cells of the type

$$\mathrm{M} \mid \mathrm{MI}_x \mid \mathrm{I_2},$$

since by elimination of the iodine electrode there is eliminated from the system a liquid potential effect at the junction of the two halves of the cell and also an osmotic work effect caused by the different concentrations of iodide ions on the two sides. The corrections for these two effects are considerable and, at the same time, are uncertain as compared with the accuracy with which the cells may be reproduced. Thus, in the cell of Jones and Hartmann with 0.05 N KI at 25° C. the liquid poten-

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[1] *Z. physik. Chem.*, **56,** 668 (1906).

tial correction amounted to +0.0032 volt while the osmotic work correction amounted to —0.0177 volt, a considerable percentage of the total e. m. f. measured, *viz.*, 0.6992 volt. On the contrary, with insoluble salts like silver and lead iodides a homogeneous electrolyte was readily obtainable and the various corrections disappear.

From a determination of the electromotive force of the combination and its temperature coefficient, a value for the heat of the reaction

$$Pb + 2AgI = PbI_2 + 2Ag$$

may be deduced. The results obtained may then be compared with the electrometric and calorimetric data previously detailed and may also be employed in calculations according to the Nernst theorem. In the following the results of such an investigation are presented.

Experimental.

Preparation of the Silver-Silver Iodide Electrodes.—Constant and reproducible silver electrodes were readily obtained, after a little experience, by following closely the detailed directions supplied by Jones and Hartmann, so that the method of preparation does not call for further detailment here. The reproducibility obtained was excellent as the table below shows. The several electrodes (5–9) were separately and successively made from June 2nd to 4th. After preparation, they were kept in a solution of potassium iodide saturated with silver iodide and of the same normality as that in which it was designed to use them.

Electrode 5 against........	6	7	8	9
June 7th. Difference......	—0.00002	+0.00006	+0.00002	+0.00003 volt

The maximum difference of any pair is 0.00008 volt.

The average difference from the mean is 0.00002 volt.

The Lead Amalgam Electrodes.—Lead amalgam was prepared, of strength exactly 0.72% lead by weight, from three times distilled mercury and the very purest lead procurable. The lead employed was bright and lustrous, the coating of oxide being removed from the sample from which the lead employed was cut. The amalgam showed a marked tendency to oxidize. If made in contact with the air it was soon covered with oxidation products. Accordingly, the weighed quantity of mercury was covered with a solution of potassium iodide of the same strength as was later to be used with the amalgam in the cells. From this solution the oxygen was removed by bubbling through pure hydrogen, after which the lead was added in small pieces and in the calculated amount. Hydrogen was bubbled through until the amalgam was homogeneous. By this method of preparation clean bright amalgam was obtained. Its constancy and reproducibility is manifest from the constancy of the complete element described below.

The Cell.—Since the solution could be homogeneous and it was necessary only to limit the diffusion between the two electrodes, the H type of cell was chosen. Into one limb the amalgam was introduced, contact with the outside being established by means of a platinum wire sealed through the base of the limb. Over the amalgam was placed, about 1 cm. deep, a layer of a paste composed of lead iodide and the solution of potassium iodide of the normality chosen. Each limb was then filled to the cross-piece with a solution of potassium iodide saturated, the one with silver iodide, the other with lead iodide, the latter naturally over the lead amalgam. Contact between the two limbs was then made by filling the H-piece carefully with the pure potassium iodide solution. Into the limb containing the silver iodide in potassium iodide the silver-silver iodide electrode was introduced. The electrode was held in position by means of a cork which served also to close the limb. The other limb was closed by means of an ordinary cork stopper. After setting up, the cells were immediately placed in an oil-bath thermostat regulated carefully to 25° ± 0.01°.

The potentials of the cells immediately after setting up were low and varied among themselves, but rose steadily to constant and concordant values. The cells apparently maintain their constancy for a considerable period of time and with varying treatment. The tables communicated below show that after a series of constant measurements extending over several days had been obtained at 25° C. the cells gave concordant values for a further period of time at 0°, returning to their original values when replaced in the 25° thermostat.

Two strengths of potassium iodide solution were used, 0.1 and 0.05 *N*. As regards constancy, there is little to choose between the two dilutions. Tables I and II record typical measurements at 0° and 25° with the two sets of cells.

TABLE I.

0.05 *N* Potassium Iodide Solution.

Cell No.		1	2	3	4	5
Silver Electrode No.		5	6	7	8	9
Date of construction.	Temp.	June 7th.	June 7th.	June 7th.	June 7th.	June 7th.
June 8th, A.M.	25°	0.19860	0.19995	0.19915	0.19833	0.19817
8th, P.M.	25	0.20051	0.20050	0.20044	0.20031	0.20037
9th, A.M.	25	0.20067	0.20072	0.20056	0.20054	0.20050
9th, P.M.	25	0.20070	0.20072	0.20065	0.20057	0.20060
10th, P.M.	25	0.20076	0.20072	0.20056	0.20064	0.20065
11th, P.M.	25	0.20075	0.20075	0.20062	0.20065	0.20065
12th, A.M.	25	0.20065	0.20065	0.20056	0.20065	0.20055
13th, A.M.	25	0.20058	0.20058	0.20067	0.02071	0.20045
Placed in ice June 13th, A.M.						
June 13th, P.M.	0°	0.2093	0.2096	0.2094	0.2099	0.2096
14th, A.M.	0	0.20930	0.20964	0.20965	0.20993	0.20968
14th, P.M.	0	0.20926	0.20965	0.20980	0.20985	0.20977
15th, P.M.	0	0.20930	0.20982	0.20955	0.20985	0.20978
Replaced in bath at 25°.						
June 17th, P.M.		0.20046	0.20035	0.20049	0.20078	0.20066

TABLE II.

0.10 *N* Potassium Iodide Solution.

Cell No.		9	10	12	13	14
Silver Electrode No.		13	14	10	11	12
Date of construction.	Temp.	June 11th.	June 11th.	June 15th.	June 15th.	June 15th.
June 12th, A.M.	25°	0.19982	0.19980	...	...	...
13th, A.M.	25	0.19995	0.19973	...	...	...
14th, A.M.	25	0.20010	0.19950	...	...	...
15th, A.M.	25	0.20014	0.19950	...	...	...
16th, A.M.	25	0.20013	0.19920	0.19823	0.19865	0.19814
17th, A.M.	25	0.20006	0.19293	0.19944	0.19974	0.19964
18th, A.M.	25	0.20003	0.09520	0.19946	0.19975	0.19976
19th, A.M.	25	0.20008	0.11500	0.19959	0.19988	0.19978
20th, P.M.	25	0.20003	Discontinued.	0.19959	0.19988	0.19980
Placed in ice June 21st, A.M.						
June 21st, P.M.	0	0.20932	...	0.20906	0.20904	0.20890
22nd, A.M.	0	0.20925	...	0.20905	0.20894	0.20890
22nd, P.M.	0	0.20931	...	0.20908	0.20908	0.20903
23rd, A.M.	0	0.20922	...	0.20896	0.20904	0.20909
24th, A.M.	0	0.20909	...	0.20890	0.20900	0.20903
25th, P.M.	25	0.19998	...	0.19965	0.20003	0.19969

A certain percentage of the cells set up showed initially a normal potential, but, in the course of a few days fell away in electromotive force and gave irregular and fluctuating values. In several cases this was identified with the passage of suspended silver iodide through the H-piece and deposition on the lead iodide. Presumably when this penetrated thus far the irregularities observed were obtained. A typical example of this behavior is recorded in Table II, Cell 10.

The potential measurements were made with the aid of a Wolff direct-reading potentiometer and a Leeds and Northrup high sensitivity galvanometer. For the potentiometer settings, use was made of the exceptional facilities of this laboratory in the matter of standard cells, so that the electromotive forces determined could readily be checked to the hundredth of a millivolt.

In Table III are recorded the accepted means for the different cells at the two temperatures and the accepted means for the two combinations.

TABLE III.

	0.05 *N* KI solution.			0.10 *N* KI solution.	
Cell No.	Accepted value, 0°.	Accepted value, 25°.	Cell No.	Accepted value, 0°.	Accepted value, 25°.
1	0.20930	0.20069	9	0.20920	0.20006
2	0.20965	0.20069	12	0.20900	0.19950
3	0.20965	0.20060	13	0.20900	0.19979
4	0.20990	0.20060	14	0.20905	0.19972
5	0.20971	0.20057	....	...	...
Mean value..	0.20965	0.20065	....	0.20905	0.19977

Cells were set up in which water was used as the liquid medium but neither constancy nor reproducibility was attainable. This is doubtless due to secondary reactions—probably at the amalgam electrode—as it was found that in preparing the amalgam in the manner previously described, if distilled water were used as the protecting liquid, lead hydroxide readily formed and was noted by the resulting cloudiness of the aqueous layer. The small solubility of the two iodides may also have contributed to the observed irregularities.

Evaluation of the Results.

To convert the values obtained with the amalgam cells to those obtaining in the case of metallic lead as electrode, use was made of the formula of Brönsted for lead—lead amalgam cells. Brönsted showed that such cells gave constant and reproducible values over a wide temperature range, representable by a linear interpolation formula

$$E = 0.0051 + 0.000233t,$$

where t is the temperature in degrees centigrade. Hence it follows, that to the observed means in the present series must be added (*a*) at 0° 0.0051 volt, and (*b*) at 25° 0.01092 volt. This yields for the electromotive forces of the combinations $Pb \mid PbI_2 \mid N/x\ KI \mid AgI \mid Ag$.

(*a*) $x = 0.05$. At 25° 0.21157 volt.
At 0° 0.21475 volt.
(*b*) $x = 0.10$. At 25° 0.21069 volt.
At 0° 0.21415 volt.

The temperature coefficients of the two combinations are, respectively,

$$(a) \quad \frac{0.21157 - 0.21475}{25} = -0.000127 \text{ volt per degree.}$$

$$(b) \quad \frac{0.21069 - 0.21415}{25} = -0.000138 \text{ volt per degree.}$$

These two sets of data, when employed in the Gibbs–Helmholz equation, give values for U

(*a*) 11500 calories. (*b*) 11610 calories.

The mean value for U from the two sets of determinations is, therefore,

$$U = 11550 \pm 50 \text{ calories,}$$

which represents the heat of the reaction

$$Pb + 2AgI = PbI_2 + 2Ag$$

as determined by means of the cell combination employed.

A comparison of this value with the data obtained from the previously tabulated results of Fischer, Braune and Koref, and Jones and Hartmann is most interesting.

Calorimetrically, from the data of Braune and Koref one obtains

$$U = 41850 - 2(15100) = 11650 \text{ calories}$$

in good agreement with the value found above.

Combining the electrometric data of Fischer and Braune and Koref, there results

$$U = 41960 - 2(15170) = 11620 \text{ calories,}$$

also in good agreement with the observed value.

Combining the electrometric data of Braune and Koref with those of Jones and Hartmann for silver iodide there results

$$U = 41960 - 2(14565) = 12830 \text{ calories,}$$

or a discrepancy of more than 1000 calories.

This conclusion is somewhat anomalous, judged from the standpoint of the experimental work, since the determinations of Jones and Hartmann are, apparently, considerably more concordant and reproducible than are those of Fischer, while those of the present work are comparable in every way with those of Jones and Hartmann in this regard.

It should be observed that both Fischer, and Braune and Koref omitted to allow for the liquid potential effect and that therefore their results are in error to the extent of about 3 millivolts or about 0.4 % in the case of the silver cell and 0.3% in the case of the lead cell. Further, according to Jones and Hartmann, the correction employed by the earlier workers for the osmotic work due to the presence of triiodide causes an error in the value for the electromotive force of the cell and also in the value for the temperature coefficient. These facts vitiate any combination of the measurements of Jones and Hartmann with those of Braune and Koref.

Recalculating the results of Fischer in accordance with the method of Jones, it can readily be shown that U in the Gibbs-Helmholz equation would be 15010 calories or 200 calories less than the value deduced by Fischer. Since Braune and Koref adopted the same procedure as Fischer with regard to the two effects it is evident that the error thus caused in their value for U will be of the same magnitude. This brings down the discrepancy between the experimental values obtained in the present work and those derived from the values of Jones and Hartmann and of Braune and Koref to somewhat more than 600 calories, a still quite definite discrepancy.

An error of this number of calories in the electrometric determination of U for lead iodide by Braune and Koref would bring agreement between the present work and that of Jones and Hartmann. It would then be necessary to locate the divergencies between the calorimetric data and the electrometric data in the cases of the two iodine cells. The presence of polyiodides in the iodine cells and their absence in the calorimetric method (since the values were obtained from the heats of solution of iodine plus silver and of silver iodide in a solution of potassium cyanide) might contribute to such a discrepancy. Also, the possibility of the calorimetric data being affected by side reactions between iodine and potassium cyanide is not wholly excluded.

The data which have been obtained have also been utilized in an effort to determine the magnitude of the integration constant of the thermodynamic equation. The calculation has been carried out by each of two methods, that employed by Nernst and that of Jones and Hartmann. The results are not without interest.

In the first place, the data compiled by Braune and Koref have been combined and applied to the present reaction. Thus, for the reaction

$$Pb + I_2 = PbI_2$$

it was shown that the following relations hold, assuming $I = 0$:

(1) $A_0 = A_{293} + 654$ calories.
(2) $U_{293} = U_0 + 160$ calories.

Correspondingly for the formation of silver iodide it was calculated

(1) $A_0 = A_{293} - 487$ calories.
(2) $U_{293} = U_0 - 40$ calories.

Combining these two sets of data it is apparent that for the new reaction

(1) $A_0 = A_{293} + 654 - 2(-487)$ calories
$A_{293} + 1628$ calories.

and

(2) $U_{293} = U_0 + 160 - 2(-40)$
$U_0 + 240$ calories.

By interpolation from the experimental results it is found that

(*a*) For 0.05 *N* KI $A_{293} = 9870$ calories.
(*b*) For 0.10 *N* KI $A_{293} = 9840$ calories.
Or, in the mean $A_{293} = 9855$ calories.
Hence, $A_0 = 9855 + 1628 = 11483$ calories.
and therefore $U_{293} = 11483 + 240 = 11723$ calories.

This value differs from the experimentally determined value by 173 calories, 1.5% of the total value, and from the calorimetrically determined value by 73 calories (0.6%), which must be considered in view of the uncertainty of specific heat data a satisfactory agreement.

In the second place use has been made of the procedure adopted by Jones and Hartmann for evaluation of I from measurements of the electromotive force at two temperatures, and insertion of the experimentally determined values in the corresponding equations for A. In this manner two equations are obtained of the form

$$A = U_0 + IT + \text{Terms involving the specific heats,}$$

from which U_0 may be eliminated and the equations solved for I. The procedure is in reality the accurate determination of dA/dT, the equation for which does not involve any term containing U_0, to which, it is claimed, an error of many hundred calories may be attached.

For the evaluation of the terms in the equation relative to the heat capacities of the reacting substances the formula of Debye for specific heats was used, since as was shown by Nernst and Lindemann[1] this formula gives the best representation of the experimental values at extremely low temperatures. The mode of employment of the Debye equation has been demonstrated by Nernst.[2] The formula for the specific heat as used by him is as follows:

$$C_v = 3R\left(\frac{4\pi^4}{5}\left(\frac{T}{\beta\nu}\right)^3 - \frac{3\,\beta\nu/T}{e^{\beta\nu/T}-1} - 12\,\frac{\beta\nu}{T}\sum_{n=1}^{n=\infty} e^{-n\,\beta\nu/T}\left(\frac{1}{n\,\beta\nu/T} + \frac{3}{n^2\,(\beta\nu/T)^2} + \frac{6}{n^3\,(\beta\nu/T)^3} + \ldots\right)\right)$$

which is derived from the Debye equation for U

$$U = \frac{9}{12}R\left(\frac{C_v}{C_\infty} + \frac{3x}{e^x - 1}\right)T$$

where $x = \beta\nu/T$ and $C_\infty = 3R$.

Developed as a series, this gives

$$U = 0.75\,\beta\nu\,R\left(\frac{77.94}{x^4} - 12\sum_{n=1}^{n=\infty} e^{-nx}\left(\frac{1}{nx} + \frac{3}{n^2x^2} + \frac{6}{n^3x^3} + \frac{6}{n^4x^4}\right)\right).$$

The integration of this formula according to the thermodynamic equation for A, *viz.*,

$$A = -T\int\frac{U\,dT}{T^2} + IT$$

gives the following expression for A:

$$A = U_0 + IT - 9R\left(\frac{2.1646}{x^3} - \Sigma\,e^{-nx}\left(\frac{1}{n^2x} + \frac{2}{n^3x^2} + \frac{2}{n^4x^3}\right)\right)T$$

In the development, use is made of the relationship

$$\int_x^\infty \frac{e^{-x}}{x^{n+1}}\,dx = \frac{1}{n}\,\frac{e^{-x}}{x^n} - \frac{1}{n}\int_x^\infty \frac{e^{-x}}{x^n}\,dx.$$

By combination of this formula for A with that for the specific heat, an equation is obtained of the form

$$A = U_0 + IT - 9R\left(\frac{C_v}{36\,C_\infty} + \frac{x}{12(e^x - 1)} + \Sigma\,\frac{e^{-nx}}{3n}\right)T,$$

which formula is more suitable for calculations. The equation may also be given the compact form

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[1] *Sitz. Preuss. Akad., Berlin,* 1160 (1912).

[2] *Ibid.,* 1172 (1912)

$$A = U_o + IT - 9R\left(\frac{C_v}{36\,C_\infty} + \frac{x}{12(e^x - 1)} - \frac{1}{3}\,C_v\,(1 - e^{-x})\right)T,$$

which is identical with the previous one when it is remembered that

$$-\ln(1 - y) = y + \frac{y^2}{2} + \frac{y^3}{3}$$

and

$$y = e^{-x}.$$

The formulas employed to represent the specific heats of the several substances are represented in the following table:

Substance.	C_v.
Pb	$F(93) + 7.8 \times 10^{-5}\,T^{3/2}$
Ag	$F(216) + 4.8 \times 10^{-5}\,T^{3/2}$
AgI	$F(68.4) + F(215) + 20 \times 10^{-5}\,T^{3/2}$
PbI_2	$2F(85) + F_1(129) + 31 \times 10^{-5}\,T^{3/2}$

F denotes the Debye function, F_1 the older Einstein function, which gives the better run of the curves at the higher temperatures. With the exception of silver iodide the same values were employed by Braune and Koref and interpret fairly accurately the experimental measurement. Their formula for silver iodide was not used since it was found that by its use the experimental data could not be reproduced.[1] The value chosen for silver iodide was that employed by Nernst in his recalculations of Fischer's work.

With these data and with the aid of tables compiled by Nernst and by Pollitzer, the following results were obtained:

$$A_{299} = A_o + IT_1 - 1789 \text{ calories}$$
$$A_{273} = A_o + IT_2 - 1624 \text{ calories}$$

The discrepancy between this calculation and that obtained by combining Braune and Koref's values has been traced to the silver iodide values, the values of the latter workers leading to a smaller negative value in calories in the A and U curves for the silver iodide-silver-iodine reaction.

Now the difference in magnitude of A_{298} and A_{273} can be obtained from the experimental determinations by multiplying the respective temperature coefficients of the two cells by the temperature difference of 25°. Converting to calories this gives in the two cases

(*a*) $0.05\,N$: $25(-0.000127)\,.\,96500\,.\,2\,.\,0.2388 = -146$ cals.
(*b*) $0.10\,N$: $25(-0.000138)\,.\,96500\,.\,2\,.\,0.2388 = -159$ cals.

Consequently the following two relations hold:

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[1] It is suggested that the cause of this is probably a typographical error in the $\beta\nu$ values in the original paper. The author has failed to reproduce both specific heat data and the A and U calculations of B. and K. with silver iodide although this was readily done in the other case. All the available evidence seems to indicate a typographical error as the cause.

(*a*) $-146 = I(298 - 273) - 165$

(*b*) $-159 = I(298 - 273) - 165$

It is apparent that the two strengths of solution do not give identical figures. To take the mean value is not justifiable until it is shown that there is not a progressive variation in the experimental value with increasing dilution of the solution of potassium iodide. As has been previously stated, reproducible values could not be obtained with an aqueous solution of the two iodides. Even with a 0.02 N solution of potassium iodide it has not yet been found possible to obtain results reproducible to less than 5 millivolts, so that for the present the above values must be considered alone. If it were permissible to take the mean, the following equation would be obtained:

$$-153 = I(298 - 273) - 165,$$

so that

$$25\ I = 12 \text{ cals.},$$

assuming that the experimental values for the electromotive forces and for the specific heats could be relied upon to one or two calories. On the other hand, if there is a possibility of error in the several determinations amounting to 10 or 20 calories it is obvious that the equation derived above might readily be in agreement with the hypothesis of Nernst and its deduction that $I = 0$, the difference being due to experimental error.

Some idea of the experimental error of the specific heat determinations can be obtained. Firstly, as was previously pointed out, there is a divergency between the present calculations and those of Braune and Koref, and this is due to the use by Braune and Koref of a new set of determinations of the specific heats of silver iodide. Their calculations lead to an expression for A at a temperature of 20° C.

$$A_{293} = A_o + IT - 1628 \text{ cals.}$$

With the values employed in the present calculations the corresponding equation is

$$A_{293} = A_o + IT - 1756 \text{ cals.}$$

It is obvious, therefore, that if one had used the same data as Braune and Koref the difference between the two specific heat terms would have been reduced by nearly 10% or to about 152 calories and that this would have yielded a value intermediate to those obtained experimentally with the two sets of cells for the difference between A_{298} and A_{273}.

Secondly, in the present calculations the value of $\beta\nu$ assumed for lead was 93. The more recent data of Eucken and Schwers[1] at low temperatures point to the value $\beta\nu = 88$ as more accurate and this is confirmed by the measurements of Kammerlingh Onnes and Keesom[2] at extremely

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[1] Eucken and Schwers, *Ber. Akad. Sitzb.*, p. 369 (1914).

[2] *Proc. Amsterdam Acad.*, p. 894 (1914).

low temperatures. If, now, this alteration be made in the calculations as carried out in the present communication, the following equations are obtained:

$$A_{298} = A_o + IT_1 - 1882$$
$$A_{273} = A_o + IT_2 - 1701,$$

or a difference in the two specific heats terms of 181 cals., nearly 30 calories greater than the experimental difference between A_{298} and A_{273}.

Consequently, for three successive changes in the values for one or other of the specific heat terms the value of I as calculated by this method has changed successively from 0.5 to 0.0 and then to 1.2. This indicates, with a considerable degree of reliability, the limitations of this particular method of calculating the integration constant. In case the experimental errors of the specific heats are small or in case the cell combination studied possesses a considerable temperature coefficient, the method may be utilized with a fair degree of certainty. When these conditions are not fulfilled great care must be exercised in drawing conclusions from the experimental facts; otherwise, grotesque results may be the outcome. It is evident that, in the present cell combination, even if the integration constant is not equal to zero, its value is considerably smaller than that to which the researches of Jones and Hartmann led in the case of silver iodide alone. This would involve as a consequence that the lead-lead iodide-iodine combination must have a value for the integration constant less than that of the present cell, and, therefore, very probably, a negative value, provided the value for the silver cell be correct.

It is obvious that a considerable increase of experimental evidence relative to the Nernst theorem is eminently desirable. The present investigations have indicated a promising new field of experimental possibilities to which attention is being devoted by the author and for which accurate electrometric and calorimetric determinations as well as the requisite specific heat data are being accumulated.

Summary.

By an investigation of the cell $Pb \mid PbI_2 \mid N/x\ KI \mid AgI \mid Ag$ the thermodynamic relationships of the iodides of silver and lead have been restudied.

It has been shown that the value for the heat of the reaction

$$Pb + 2AgI = PbI_2 + 2Ag,$$

as determined by means of the above cell combination agrees satisfactorily with the best calorimetric data for the substances taking part.

The data have been used in an investigation of the assumptions of the Nernst Heat Theorem and of the methods of testing the same. So far as the present experimental evidence relative to specific heats may be employed results favorable to the theorem have been obtained.

In conclusion, I wish to express my indebtedness to Mr. Earle A. Harding for his kind assistance in the preliminary work in connection with this investigation.

PRINCETON, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY.]

A STUDY OF THE TENTH-NORMAL HYDROCHLORIC ACID CALOMEL ELECTRODE.[1]

BY N. EDWARD LOOMIS AND MERLE R. MEACHAM.

Received August 8, 1916.

I. Purpose of the Investigation.

The purpose of this investigation was to carefully measure the electromotive force of the system

$$H_2\text{–}Pt\text{–}0.1\ N\ HCl\text{–}Hg_2Cl_2\text{–}Hg$$

at 25° with the view of comparing the value so obtained with that of the cell

$$H_2\text{–}Pt\text{–}0.1\ N\ HCl\ ||\ 0.1\ N\ KCl\text{–}Hg_2Cl_2\text{–}Hg,$$

from which the contact potential has been eliminated. From this comparison the relative potentials of the 0.1 N hydrochloric acid and the 0.1 N potassium chloride calomel electrodes can be determined and thereby the relative degrees of dissociation of the two electrolytes measured.

The degree of dissociation of an electrolyte, as commonly calculated from conductivity data, depends upon the assumption that the mobilities of the ions are independent of the concentration. This assumption was first questioned by Jahn[2] and considerable evidence against it has since been accumulated. The mobility of the hydrogen ion appears to increase with increasing concentration, and consequently the degrees of dissociation of the more concentrated solutions of hydrochloric acid, as determined by conductivity data, are probably too high.

In 1909 Lewis and Sargent[3] assumed that hydrochloric acid and potassium chloride are equally dissociated at equivalent concentrations, even though the apparent dissociation, as indicated by conductivity measurements, is considerably higher for the acid. If the two electrolytes are equally dissociated then the 0.1 N HCl calomel electrode should have the same potential as the 0.1 N KCl calomel electrode. This was assumed to be the case by Lewis and Sargent and their assumption has been adopted by several subsequent workers.

In 1912, however, Lewis[4] showed that the degree of dissociation of 0.1 N

[1] An abstract of this paper was presented at the Urbana meeting of the American Chemical Society.

[2] *Z. physik. Chem.*, 33, 545 (1900); 35, 1 (1900).

[3] THIS JOURNAL, 31, 363 (1909).

[4] *Idem.*, 34, 1631 (1912).