on the activity coefficients of the ions, so that interionic association is always considerable; (2) large differences in the extent of solvation of the various ionic and molecular species present in the solutions. Thus it seems probable that association with the solvent is very complete in the case of the stronger bases but very incomplete in the pure solutions of the weaker bases.

In the absence of independent information concerning the colligative properties of such solutions as we have studied, it seems undesirable at present to elaborate further mechanical hypotheses to account for their observed peculiarities.

Summary

Diagrams and tables are given which show the effect of the following influences on the shape of the titration curves of bases dissolved in acetic acid: the nature of the titrating acid, the concentration and the strength of the base. It is shown that the weaker bases give anomalous titration curves while the curves of bases which act like strong bases in water conform to the theory of such titrations. The effect of dilution on the hydrogen-ion activity of solutions of bases is studied by the electromotive force method, and it is shown that even the "strongest" bases are truly weak electrolytes in this solvent. It is shown that these results practically demonstrate the effective constancy of the liquid junction potential between saturated aqueous potassium chloride and the various acetic acid solutions used. The value of the electromotive force method in studying the effect of dilution on dissociation is emphasized in the discussion.

CAMBRIDGE, MASSACHUSETTS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE STATE UNIVERSITY OF IOWA AND THE EPPLEY LABORATORY]

A LEAD-MERCUROUS IODIDE VOLTAIC CELL

BY WARREN C. VOSBURGH

RECEIVED JUNE 4, 1928 PUBLISHED SEPTEMBER 5, 1928

The results of measurements of voltaic cells with mercurous iodide electrodes are not very concordant. Gerke[1] has calculated the electromotive force of the cell

$$\mathrm{Hg} \mid \mathrm{Hg_2I_2} + \mathrm{HI}\ (a = 1) \mid \mathrm{HI}\ (a = 1) \mid \mathrm{H_2(Pt)} \qquad (1)$$

from the results of Bugarsky[2] and from the results of Oeholm,[3] obtaining the values 0.0432 v. and 0.0414 v. at 25°, respectively. Cohen and Bruins[4]

---

[1] Gerke, *Chem. Reviews*, **1**, 385 (1925).

[2] Bugarsky, *Z. anorg. Chem.*, **14**, 145 (1897).

[3] Oeholm, *Acta Soc. Scientarum Fennicae*, **41**, 1 (1913); *C. A.*, **7**, 2718 (1913).

[4] (a) Cohen and Bruins, *Z. physik. Chem.*, **93**, 53 (1918); (b) see also, Yoshida, *J. Chem. Soc. Japan*, **48**, 435 (1927).

found for the cell

$$\text{Cd(Hg)} \mid \text{CdI}_2\text{, sat.} \mid \text{CdI}_2\text{, sat.} + \text{Hg}_2\text{I}_2 \mid \text{Hg} \qquad (2)$$

the value $E_{25} = 0.41712$ v.[5]

From this and the value calculated by Gerke[1] for the cell

$$\text{Cd(Hg)} \mid \text{CdI}_2 \text{ sat.} + \text{HI } (a = 1) \mid \text{H}_2 \text{ (Pt)} \qquad (3)$$

the value $E_{25} = 0.0403$ v. can be calculated for Cell 1. The electromotive force of Cell 3 was calculated from some results of Obata[6] with which some later results of the author[7] were in good agreement. A third value for Cell 1 given by Gerke, namely, $E_{25} = 0.0404$ v., was calculated from some results obtained in this investigation. It is in good agreement with the value calculated from the results of Cohen and Bruins. Ishikawa and Shibata[8] have determined the electromotive force of the cell

$$\text{Zn(Hg)} \mid \text{ZnI}_2 \mid \text{ZnI}_2 + \text{Hg}_2\text{I}_2 \mid \text{Hg};\ E_{25} = 0.5243 \text{ v.} \qquad (4)$$

By combining their value with values for the cells

$$\text{Ag} \mid \text{AgI} + \text{HI } (a = 1) \mid \text{HI } (a = 1) \mid \text{H}_2 \text{ (Pt)};\ E_{25} = 0.1501 \text{ v.}^1 \qquad (5)$$

$$\text{Zn(Hg)} \mid \text{ZnI}_2 \mid \text{ZnI}_2 + \text{AgI} \mid \text{Ag};\ E_{25} = 0.3987 \text{ v.}^9 \qquad (6)$$

the value $E_{25} = 0.0245$ v. is found for Cell 1, which is in poor agreement with the other values.

The purpose of this investigation was to measure accurately the electromotive force at various temperatures of the cell

$$\text{Pb(Hg)} \mid \text{PbI}_2 \mid \text{PbI}_2 + \text{Hg}_2\text{I}_2 \mid \text{Hg} \qquad (7)$$

Preparation of Materials

Mercury.—The mercury was purified by passing commercial redistilled mercury through a column of mercurous nitrate solution and redistilling at least once under reduced pressure in a current of air.

Lead Amalgam.—The lead amalgam was made electrolytically from purified mercury and either twice recrystallized lead nitrate or lead chloride made from recrystallized lead nitrate. Four different preparations were used. One contained 12.7% of lead and the other three contained 10% of lead.

Cadmium Amalgam.—The cadmium amalgam was prepared electrolytically from purified mercury and thrice recrystallized cadmium sulfate. It contained 10% of cadmium.

Lead Iodide.—The lead iodide was made by adding slowly a solution of recrystallized potassium iodide to a hot solution of twice recrystallized lead nitrate. The lead iodide so obtained was washed by decantation and preserved under water. Several different preparations were made in the course of the work, all by the same method.

Cadmium Iodide.—Two lots of cadmium iodide were prepared. No. 1 was prepared by recrystallizing C. P. cadmium iodide twice, the second time from redistilled water.

---

[5] The measurements of Cohen and Bruins were made at temperatures between 16 and 24°. The value $E_{25} = 0.41712$ v. was obtained by an extrapolation which, however. introduces an uncertainty of less than 0.1 mv.

[6] Obata, *Proc. Phys. Math. Soc. Japan,* [3] **3,** 64, 136 (1921).

[7] Vosburgh, This Journal, **49,** 2228 (1927).

[8] Ishikawa and Shibata, *Bull. Chem. Soc. Japan,* **1,** 169 (1926).

[9] Webb, *J. Phys. Chem.,* **27,** 448 (1923).

No. 2 was prepared by allowing c. p. cadmium metal to react with a solution of c. p. iodine.[10] The solution was stirred continuously and iodine was added occasionally. The cadmium iodide so prepared was recrystallized twice, the second time from redistilled water.

The cadmium iodide to be introduced into the cells in the solid form was heated for five days at 150° to convert it into the stable form.[11]

Mercurous Iodide.—The mercurous iodide was prepared by precipitation. A solution of recrystallized potassium iodide was added slowly with mechanical stirring to a solution of twice or thrice recrystallized mercurous nitrate containing nitric acid. It was washed by decantation with either water or a very dilute potassium iodide solution and was preserved under water. Some of the preparations stood for several months under water before being used. The concentrations of the reacting substances varied in the different preparations but were of the order of 0.1 *M*.

Preparation 1 was made as described, redistilled water being used. It was digested on a hot-plate for two hours with water. Air was excluded during the precipitation by a current of nitrogen.

Preparation 2 was made similarly but without exclusion of air. Toward the end of the precipitation some orange-colored precipitate presumably containing mercuric iodide was formed. The addition of more mercurous nitrate converted it into the yellow mercurous iodide. In the subsequent preparations care was taken to keep the mercurous nitrate present in excess throughout the precipitation. The mercurous iodide was washed by decantation, first with mercurous nitrate solution and then with very dilute potassium iodide solution.

Preparation 3 was a portion of No. 2 which was digested on a hot-plate at nearly boiling temperature for about seven hours under a very dilute potassium iodide solution.

Preparations 4, 5 and 6 were precipitated in the cold, the first from solutions more concentrated than usual and the second from solutions more dilute. During the precipitation of No. 4 air was excluded and the solution was stirred with a current of carbon dioxide. Preparations 4, 5 and 6 were not digested.

Preparation 7 was a portion of No. 6 which was digested for three days on a steam-bath in the dark.

Preparation 8 was prepared by the usual method but using redistilled water and with concentrations of about 0.2 *M*. It was digested for four days on a steam-bath in the dark.

Preparation of the Cells

The cells were set up in glass H-vessels. For the earlier cells[12] vessels of the type used by Vosburgh and Eppley[13] or that used by the author[14] for portable Weston cells were used. These vessels were hermetically sealed when the cells were made. For Cells 511–526[15] vessels of the same type but of different dimensions were used. They were about 18 cm. long and 5.5 cm. wide. The inside diameter of the tubes was 12–15 mm. The cells set up in these vessels were closed by means of paraffined corks.

---

[10] See Ref. 4 a, p. 49.

[11] Cohen, "Physico-Chemical Metamorphosis and Some Problems in Piezochemistry," McGraw-Hill Book Co., Inc., New York, **1926**, p. 70; Cohen and Moesveld, *Z. physik. Chem.*, **94**, 471 (1920).

[12] Made at the Eppley Laboratory.

[13] Vosburgh and Eppley, This Journal, **45**, 2269 (1923).

[14] Vosburgh, *J. Optical Soc. Am.*, **9**, 66 (1924).

[15] Made at the State University of Iowa.

A paraffined cork disk was pushed into the top of each leg of the vessel to a distance of 2 or 3 cm. and then covered with a layer of paraffin about 1 cm. thick. Finally, the openings of the tubes were closed by corks shellacked on the outside.

In setting up the mercurous iodide electrodes the procedure was that used by the author for setting up the mercurous sulfate electrodes of Weston Cells.[16] The mercurous iodide, with which was mixed lead iodide and in Cells 511–522 ground cadmium iodide crystals also, was washed first in a Gooch crucible and then by decantation in an atmosphere of nitrogen or carbon dioxide with the solution to be used in the cells. It was then transferred to the cell vessels out of contact with air. The mercurous iodide layer was at least 1 cm. deep. On top of it was placed some lead iodide and in Cells 511–522 some cadmium iodide crystals also.

The lead iodide electrodes were made by introducing first lead amalgam and then a paste of the electrolyte and either lead iodide or a mixture of lead iodide and cadmium iodide. In setting up Cells 511–522, in which the latter mixture was used, special precautions were taken to prevent oxidation of the lead amalgam.

In a number of cells a saturated solution of lead iodide in redistilled water was the electrolyte. This gave sufficient conductance so that the electromotive force could be measured accurately within a tenth of a millivolt. However, most of the cells so made were less constant and less reproducible than the others. In other cells a 0.01 *M* or 0.02 *M* potassium iodide solution was used as the electrolyte. An iodide solution has the advantage of dissolving mercuric iodide, so when the mercurous iodide mixture is washed with an iodide solution, any mercuric iodide present tends to be washed out. The most reproducible cells were made with cadmium iodide solution as the electrolyte.

The cells were nearly always made in duplicate. Duplicates usually agreed within a few hundredths of a millivolt. In the best cells made, Cells 517–522, the difference between duplicates was within 0.01 mv.

The cells were mounted on wooden racks and the platinum wires leading from the cell electrodes were connected to copper terminals by means of fine copper wire which was soldered to both. Usually the negative electrodes were connected to a common terminal, while the positive electrodes were connected to separate terminals insulated from each other and from the wood by hard rubber or glass. In measuring the cells, copper lead wires from the potentiometer were clipped to the terminals of the rack by copper test clips. The racks of cells were immersed in an oil thermostat capable of being regulated to within 0.01° of the desired temperature.

Electromotive Force Measurements

Apparatus.—The electromotive forces were measured by means of a Leeds and Northrup Type K potentiometer. Two different potentiometers were used in the course of the work. The first was used only with the less reproducible cells with the very dilute solutions for electrolytes. The second, used for the measurement of the more reproducible cells with cadmium iodide electrolytes, was calibrated by the method described by the manufacturers.[17]

The standards used in the measurements recorded in Tables I and IV were those used in previous investigations.[16] The standards used in the measurements recorded in Tables II, III and V were nine others of equal quality, seven of which had been directly compared with the first stand-

---

[16] Vosburgh, This Journal, **47**, 1258 (1925).

[17] Leeds and Northrup Company, Bulletin No. 755, **1923**, p. 22.

ards. Three saturated Weston Cells set up at the State University of Iowa agreed with these seven cells, which had been carefully carried from Newport to Iowa City, within 0.002%. Two years later a portable saturated Weston Cell obtained from the Eppley Laboratory agreed with the standards within 0.002%.

Measurements at 25°.—Measurements were made occasionally over a considerable period of time to show the constancy of the electromotive force before the values were accepted as final. Some of the cells had electromotive forces lower than the normal at first. Among these were Cells 511–522. The electromotive forces increased as time went on till finally a constant value was attained. Fig. 1 shows the change undergone by four of the cells. It is to be noted that constancy of electromotive force was not attained by Cells 511–512 until a month after they were set up. Thus, electromotive force measurements made soon after cells are set up cannot always be relied upon to give correct values.

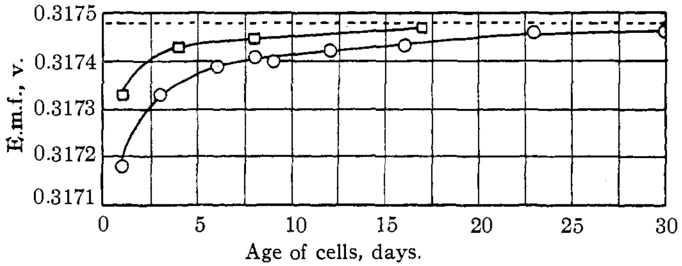

Fig. 1.

Tables I and II give the electromotive forces of the cells after constancy was attained. The time intervals are the periods of time which elapsed between the preparation of the cells and the measurements in question. Table I gives measurements of the cell

$$\mathrm{Pb(Hg)} \mid \mathrm{PbI_2, sat.} + \mathrm{x}\,M\,\mathrm{KI} \mid \mathrm{x}\,M\,\mathrm{KI} + \mathrm{PbI_2} + \mathrm{Hg_2I_2} \mid \mathrm{Hg} \qquad (8)$$

and Table II gives the results of measurements of the cell

$$\mathrm{Pb(Hg)} \mid \mathrm{PbI_2, sat.} + \mathrm{CdI_2, sat.} \mid \mathrm{CdI_2, sat.} + \mathrm{PbI_2\ sat.} + \mathrm{Hg_2I_2} \mid \mathrm{Hg} \qquad (9)$$

TABLE I

CELL: $\mathrm{Pb(Hg)} \mid \mathrm{PbI_2, SAT.} + \mathrm{x}\,M\,\mathrm{KI} \mid \mathrm{x}\,M\,\mathrm{KI} + \mathrm{PbI_2, SAT.} + \mathrm{Hg_2I_2} \mid \mathrm{Hg}$

Amalgam, cells	Concn. % Pb	Hg_2I_2 KI, M	No.	Electromotive force at 25° 1 month, v.	2, v.	3, v.	4, v.
410–411	10	0.01	1	0.31765	0.31765	0.31765	0.31770
431–432	10	.01	2	.31761	.31770	....	.31788
433–434	12.7	.02	3	.31761	.31786	.31778	....
436–437	12.7	.02	1	.31748	....	.31760	....
439–440	12.7	[a]	3	.31722	....	....	.31730

[a] The electrolyte for these cells was prepared by treating a 0.01 M sulfuric acid solution with an excess of solid lead iodide and filtering.

Table II

Cell: Pb(Hg) | PbI_2, Sat. + CdI_2, Sat. | CdI_2, Sat. + PbI_2, Sat. + Hg_2I_2 | Hg

Cells	Hg_2I_2 no.	Electromotive force at 25°			
		1 month, v.	2, v.	3, v.	4, v.
511–512	4	0.31746	0.31748	0.31749	0.31740
513–514	5	.31768	.31769	.31768	.31766
515–516	6	.31754	.31755	.31756	....
517–518	7	.31746	.31747	.31748	.31748
519–520	8	.31747	.31747	.31748	.31748
521–522	8	.31748	.31748	.31748	.31749

It is quite evident that the cells with the cadmium iodide electrolyte (Table II) were superior to the other cells both in reproducibility and constancy. Of the former the best were Cells 517–522. These were all made with mercurous iodide which had been digested on a steam-bath under water with the object of bringing it to a stable physical condition. This practice has been shown[18] to be of value also in the preparation of mercurous sulfate for standard cells. The good agreement of Cells 517–522 makes it probable that the materials used were in a stable physical state. Most of the materials used for Cells 521–522 were different preparations from those used for the other four cells and if anything were better purified. Cells 513–514 were 0.2 mv. higher in electromotive force than most of the others, and it is to be concluded that the mercurous iodide preparation used was not in its most stable physical form.

To check the values of Cohen and Bruins[4a] and Yoshida[4b] for Cell 2 and to compare the mercurous iodide which the former authors prepared from mercury and iodine with that prepared by precipitation, 4 cells like Cell 2 were set up. The procedure used was enough like that described above for the lead–mercurous iodide cells to need no further description. The electromotive forces are given in Table III. It is evident that the agreement with the cells of Cohen and Bruins and also those of Yoshida is very good.

Table III

Cell: Cd(Hg) | CdI_2, Sat. | CdI_2, Sat. + Hg_2I_2 | Hg

Cells	Hg_2I_2 no.	Electromotive force at 25°			
		1 month, v.	2, v.	3, v.	3.6, v.
520–524	7	0.41702	0.41701	0.41704	0.41704
525–526	8	.41701	.41698	.41700	.41700

Temperature Coefficients.—The cells of Table I were measured at 5° intervals of temperature between 15 and 40°. The measurements were made along with some measurements at the same temperatures of Weston standard cells and the details as to temperature regulation and general procedure have already been published.[19] The lead–lead iodide cells

---

[18] Ref. 16, p. 1267.

[19] Vosburgh, *J. Optical Soc. Am.*, **12,** 512 (1926).

did not show the hysteresis which the Weston cells showed, and so came to equilibrium more quickly, especially after a decrease in temperature. Table IV shows the differences between the electromotive forces at 25° and those at the other temperatures.

TABLE IV

VARIATION OF ELECTROMOTIVE FORCE WITH TEMPERATURE

		$E_t - E_{25}$				
Cells	E_{25}, v.	15°, mv.	20°, mv.	30°, mv.	35°, mv.	40°, mv.
410–411	0.31766	−1.25	−0.62	0.61	1.26	1.94
431–402	.31780	−1.22	−.57	.61	1.26	1.94
433–434	.31783	−1.44	−.73	.67	1.36	2.07
436–437	.31764	−1.42	−.70	.63	1.30	1.96
439–440	.31727	−1.29	−.65	.63	1.29	1.93

The effect of temperature changes on Cells 517–522 and 523–526 was also determined. The temperature was changed successively from 25 to 20, 30, 35, 40, 35, 30 and 25°, while the standards were maintained at 25° in a separate thermostat. Temperatures were measured by a thermometer certified by the Bureau of Standards, and are probably accurate to ± 0.03°. The results are given in Table V.

TABLE V

VARIATION OF ELECTROMOTIVE FORCE WITH TEMPERATURE

		$E_t - E_{25}$						
Cells	E_{25}, v.	20°, mv.	30°, mv.	35°, mv.	40°, mv.	35°, mv.	30°, mv.	25°, mv.
517–518	0.31748	−0.61	0.65	1.28	1.93	1.30	0.67	0.01
519–520	.31748	− .63	.66	1.28	1.93	1.29	.65	.00
521–522	.31749	− .66	.65	1.27	1.91	1.29	.64	.00
523–524	.41704	−1.93	1.79	3.60	5.41	3.57	1.74	−.10
525–526	.41700	−1.88	1.80	3.61	5.42	3.59	1.77	−.04

If E_{25} = 0.31748 v. is taken as the best value for Cell 7, the electromotive force between 15 and 40° is given by the equation

$$E_t = 0.31748 + 0.000129\ (t-25)$$

within the limits of error of measurement in the case of Cells 517–522 and within the limits of reproducibility in the case of the cells of Table IV.

A small lag in the attainment of equilibrium was noticed in the case of Cells 517–522. Usually two or three days were required for the attainment of constancy, although the electromotive force was usually within 0.04 mv. of its final value one day after an increase in temperature of 5°.

For Cell 2 the electromotive force between 25 and 40° is given by the equation

$$E_t = 0.41702 + 0.000360\ (t-25)$$

The agreement is not good at 20°, perhaps because sufficient time was not allowed for equilibrium. Equilibrium was attained rapidly after an increase in temperature, but rather slowly after a decrease, and the measurements made after a decrease in temperature are to be considered less reliable than those made after an increase.[20] Both Cohen and Bruins[4a] and Yoshida[4b] gave as the temperature formula for Cell 2 an equation for a curve instead of a straight line. However, the above formula agrees with the experimental values of Cohen and Bruins within 0.1 mv., and if the first term on the right-hand side of the equation (the value at 25°) were increased by 0.1 mv., the formula would agree with all but one of their experimental values within 0.01 mv.

Discussion

The difference between the electromotive forces of Cells 2 and 7 should give the electromotive force of the cell

$$\mathrm{Cd(Hg)} \mid \mathrm{CdI_2,\ sat.} \mid \mathrm{CdI_2,\ sat.} + \mathrm{PbI_2} \mid \mathrm{Pb(Hg)} \qquad (10)$$

Subtracting $E_{\mathrm{Cell}\ 7} = 0.31748 + 0.000129\ (t - 25)$ from $E_{\mathrm{Cell}\ 2} = 0.41702 + 0.000360\ (t - 25)$, the value

$$E_t = 0.09954 + 0.000231\ (t-25)$$

is obtained for Cell 10 as compared with

$$E_t = 0.0996 + 0.000235\ (t-25) - 0.0000002\ (t-25)^2$$

previously found by the author,[7] which is in good agreement with the results of Obata[6] for the same cell. The agreement between the two formulas is within the experimental error of the latter. Thus, the results for Cells 2, 7 and 10 are consistent among themselves, and as the values for Cells 2 and 10 agree with those of other observers, it is probable that the value given for Cell 7 is correct.

From the results for Cell 7 the free energy change, entropy change and heat of reaction can be calculated for the reaction

$$\mathrm{Pb(s)} + \mathrm{Hg_2I_2(s)} \longrightarrow \mathrm{PbI_2(s)} + 2\mathrm{Hg(l)}$$

If the electromotive force of Cell 7 is added to that of the cell[21]

$$\mathrm{Pb} \mid \mathrm{Pb^{++}} \mid \mathrm{Pb(Hg)};\ E_t = 0.0057 + 0.000016\ (t-25) \qquad (11)$$

the electromotive force of the cell

$$\mathrm{Pb} \mid \mathrm{PbI_2,\ sat.} \mid \mathrm{PbI_2,\ sat.} + \mathrm{Hg_2I_2} \mid \mathrm{Hg} \qquad (12)$$

is found to be $E_t = 0.3232 + 0.000145\ (t - 25)$. Therefore, for the above reaction $\Delta F_{25} = -14{,}915$ cal., $\Delta S = 6.69$ cal. per degree and $\Delta H = -12{,}920$ cal.

For the heat of formation of lead iodide Braune and Koref[22] found thermochemically $\Delta H_{20} = -41{,}850$ cal., and Gerke[21] found electrochemically $\Delta H_{25} = -41{,}859$ cal. From the latter value and from the heat of reaction of lead and mercurous iodide, the heat of formation of mercurous iodide is found to be

$$2\mathrm{Hg(l)} + \mathrm{I_2(s)} \longrightarrow \mathrm{Hg_2I_2(s)};\ \Delta\mathrm{H}_{25} = -28{,}939\ \text{cal.}$$

---

[20] In showing hysteresis only after a decrease in temperature these cells resemble Weston cells. The latter, however, have abnormally high values after a decrease in temperature while the former show abnormally low values.

[21] Gerke, THIS JOURNAL, **44**, 1703 (1922).

[22] Braune and Koref, *Z. anorg. Chem.*, **87**, 180 (1914).

This agrees with the value of Varet,[23] $\Delta H = -28{,}850$ cal., and less well with the value of Nernst,[24] $\Delta H = -28{,}400$ cal., but does not agree with the value of Thomsen,[25] $\Delta H = -31{,}100$ cal.

The electromotive force of Cell 2 (Table V) can be combined with the electromotive force of the cell[26]

$$\text{Cd} \mid \text{Cd}^{++} \mid \text{Cd(Hg)};\ E_t = 0.0505 - 0.000244\,(t-25) \qquad (13)$$

to give the electromotive force of the cell

$$\text{Cd} \mid \text{CdI}_2\text{, sat.} \mid \text{CdI}_2\text{, sat.} + \text{Hg}_2\text{I}_2 \mid \text{Hg};\ E_t = 0.4675 + 0.000116\,(t-25) \qquad (14)$$

From this it can be calculated that for the reaction

$$\text{Cd(s)} + \text{Hg}_2\text{I}_2\text{(s)} \longrightarrow \text{CdI}_2\text{(s)} + 2\text{Hg(l)}$$

$\Delta F_{25} = -21{,}575$ cal., $\Delta S_{25} = 5.35$ cal. per degree and $\Delta H_{25} = -19{,}979$ cal. If the above value for the heat of formation of mercurous iodide is taken as correct, the heat of formation of cadmium iodide is found to be

$$\text{Cd(s)} + \text{I}_2\text{(s)} \longrightarrow \text{CdI}_2\text{(l)};\ \Delta\text{H}_{25} = -48{,}918 \text{ cal.}$$

Thomsen[27] found $\Delta H = -48{,}830$ cal.

Summary

The following cells were set up and their electromotive forces measured at 25° and at five degree intervals between 20 and 40°:

$$\text{Pb(Hg)} \mid \text{PbI}_2 + x\,M\,\text{KI} \mid x\,M\,\text{KI} + \text{PbI}_2 + \text{Hg}_2\text{I}_2 \mid \text{Hg}$$
$$\text{Pb(Hg)} \mid \text{PbI}_2 + \text{CdI}_2\text{, sat.} \mid \text{CdI}_2\text{, sat.} + \text{PbI}_2 + \text{Hg}_2\text{I}_2 \mid \text{Hg}$$
$$\text{Cd(Hg)} \mid \text{CdI}_2\text{, sat.} \mid \text{CdI}_2\text{, sat.} + \text{Hg}_2\text{I}_2 \mid \text{Hg}$$

The electromotive force of the first two was found to be $E_t = 0.31748 + 0.000129\,(t - 25)$ volts. The two cells agreed within the limits of reproducibility of the first, which was the less reproducible of the two.

The electromotive force of the third was found to be $E_t = 0.41702 + 0.000360\,(t - 25)$ volts, which is in good agreement with the results of Cohen and Bruins and Yoshida for the same cell.

From the electromotive forces of the cells the free energy and entropy changes and heats of reaction for the corresponding reactions were calculated. From the latter and a reliable value for the heat of formation of lead iodide the heats of formation of mercurous iodide and cadmium iodide were calculated to be

$$2\text{Hg(l)} + \text{I}_2\text{(s)} \longrightarrow \text{Hg}_2\text{I}_2\text{(s)};\ \Delta H_{25} = -28{,}939 \text{ cal.}$$
$$\text{Cd(s)} + \text{I}_2\text{(s)} \longrightarrow \text{CdI}_2\text{(s)};\ \Delta H_{25} = -48{,}918 \text{ cal.}$$

IOWA CITY, IOWA

---

[23] Varet, *Ann. chim. phys.*, [7] **8**, 91 (1896).

[24] Nernst, *Z. physik. Chem.*, **2**, 23 (1888).

[25] Thomsen, "Thermochemistry," Longmans, Green and Co., London, **1908**, p. 283.

[26] Ref. 1, p. 382.

[27] Ref. 25, p. 268; see also ref. 7.