inhibits the reduction of palladium oxide at 100° and retards the completion of the reduction at 156°.

3. Oxygen in small amounts has been found to accelerate the reaction, causing complete reduction at 76°.

4. Palladium previously reduced from the oxide is only slightly autocatalytic toward the reduction. However, it is possible to consider that the reaction occurs at the interface and is retarded by strong adsorption of the product carbon dioxide on the oxide.

New Brunswick, New Jersey

THE FREE ENERGIES AND HEATS OF FORMATION OF TETRAHYDRATE AND ANHYDROUS FORMS OF CADMIUM BROMIDE AND THEIR TRANSITION TEMPERATURES

By Hugh M. Spencer and Robert F. Selden[1]

Introduction

In order that thermodynamic quantities may be fixed with the greatest possible exactness, it is necessary that they be determined by as many independent methods as are available. Spencer and Randall[2] in their theoretical treatment of cells involving the halides of silver, mercury, lead and cadmium tested the consistency of the various combinations involved by expressing the standard electromotive force of formation of the cadmium halides as determined through measurements of the electromotive force of formation of each of the other metallic salts of the same halogen and the metathetical relation of the halide and the corresponding cadmium halide. The standard electromotive force of formation[3] is that of the reaction by which the compound is formed from the elements and water in their standard states.

The standard electromotive force of formation of cadmium bromide may be calculated through those of mercurous and silver bromides. At the time when the experimental work of the present paper was completed there existed the measurements of Oeholm[4] on the cell
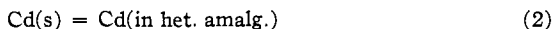
[1] Du Pont Fellow in Chemistry 1929–1930.
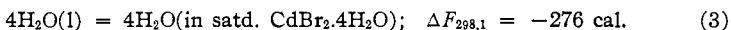
[2] H. M. Spencer and M. Randall, unpublished.

[3] The use of this quantity rather than the electromotive force of formation from the elements in their standard states and water in the saturated solution is open to the objection that with the data available interpolations or extrapolations are required for obtaining the free energy of transfer of water from the standard state to the saturated solution in question, and uncertain quantities subject to revision are inserted. However, the same quantity is introduced in all summations for a given halide.

[4] L. W. Oeholm, Acta Soc. Sci. Fennicae, 41, 1 (1913).

Cd(in het. amalg.), CdBr$_2$·4H$_2$O(s), satd. CdBr$_2$·4H$_2$O + HgBr, HgBr(s), Hg(l)   (1)

for which $E = 0.55916 - 0.000366$ (t-18) $- 0.0000046(t$-18$)^2$, or $E_{298.1} =$ 0.55637 v.   Ishikawa and Ueda[5] have since found for the same cell, $E =$ $0.55614 - 0.0004237(t - 25) - 0.00000589(t - 25)^2$ or $E_{298.1} = 0.55614$ v. From a reinterpretation of the bromine electrode and measurements of Gerke and Geddes[6a] and of Ishikawa and Ueda[6b] on the hydrogen–mercurous bromide cell, Spencer and Randall[7] find the electromotive force of formation of mercurous bromide to be 0.9259$_2$ (through Ishikawa and Ueda) or 0.92620 v. (through Gerke and Geddes).   They accept $E_{298.1} =$ 0.0505 v. as the best value of the electromotive force for the reaction
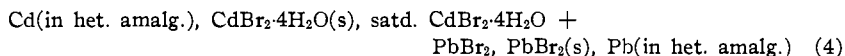
$$Cd(s) = Cd(\text{in het. amalg.}) \tag{2}$$

Ishikawa and Ueda[5] have shown that for

$$4H_2O(l) = 4H_2O(\text{in satd. } CdBr_2.4H_2O); \quad \Delta F_{298.1} = -276 \text{ cal.} \tag{3}$$
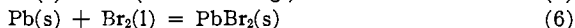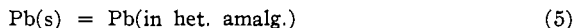
Thus the standard electromotive force of formation of the tetrahydrate of cadmium bromide is 1.53854 v. using the results of Ishikawa and Ueda, or 1.53906 v. through the results of Oeholm and of Gerke and Geddes.
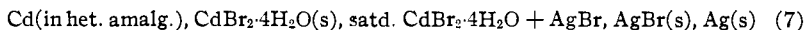
Obata[8] studied the cell

Cd(in het. amalg.), CdBr$_2$·4H$_2$O(s), satd. CdBr$_2$·4H$_2$O +

PbBr$_2$, PbBr$_2$(s), Pb(in het. amalg.)   (4)

and found $E = 0.14505 - 0.00037(t - 20) - 0.000005(t - 20)^2$ or $E_{298.1} =$ 0.14307.   Spencer and Randall have taken $E_{298.1}$ for the cells

$$Pb(s) = Pb(\text{in het. amalg.}) \tag{5}$$
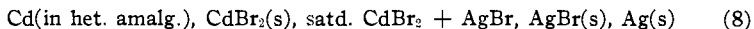$$Pb(s) + Br_2(l) = PbBr_2(s) \tag{6}$$

to be 0.00586 and 1.34560 (through the results of Ishikawa and Ueda or 1.3458 as best average of results).   Combining the reaction of Cell 4 with Reactions 2, 3, 5 and 6, the standard electromotive force of formation of the tetrahydrate of cadmium bromide is 1.53929 or 1.53949 v., respectively. The difference is thus 0.2–1.0 m. v., too great to be attributed to experimental error.

This paper presents the measurements on the cells

Cd(in het. amalg.), CdBr$_2$·4H$_2$O(s), satd. CdBr$_2$·4H$_2$O + AgBr, AgBr(s), Ag(s)   (7)

and

Cd(in het. amalg.), CdBr$_2$(s), satd. CdBr$_2$ + AgBr, AgBr(s), Ag(s)   (8)

through the ranges 25–35° and 35–45°, respectively.   Cell 7, along with the standard electromotive force of formation of silver bromide, and Reactions 2 and 3, permits a determination of the standard electromotive

[5] F. Ishikawa and Y. Ueda, *J. Chem. Soc. Japan*, **51**, 634 (1930), translated by Dr. K. Kitsuta.

[6] (a) R. H. Gerke and J. R. Geddes, *J. Phys. Chem.*, **31**, 886 (1927); (b) F. Ishikawa and Y. Ueda, *J. Chem. Soc. Japan*, **51**, 59 (1930).

[7] The present value differs from their value in the "International Critical Tables," McGraw-Hill Book Co., New York, 1930, Vol. VII, p. 260.

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

force of formation of the tetrahydrate of cadmium bromide partially independent (*i. e.*, except that Reactions 2 and 3 are involved) of the two mentioned above. Measurements were made over a range of temperatures and Cell 8 was investigated in order that the heats of reaction and transition temperature might be obtained.

Preparation of Materials

Mercury after the usual washing with mercurous nitrate was distilled three times at low pressure, the last in a stream of oxygen-free nitrogen. This last distillate was caught in a receiving vessel, illustrated in Fig. 1, in the following manner. The tip of the exit tube from the mercury still was placed within the tube (T) of the receiving vessel. The vessel was continuously swept out with dry oxygen-free electrolytic hydrogen during the entire distillation process. Hydrogen was admitted through the stopcock (S) and escaped through the tube (T). The flow of hydrogen was continued throughout the interim between cessation of distillation and the closing of the mercury trap (D) by cap (C). The mercury was stored under hydrogen in the receiving vessel.
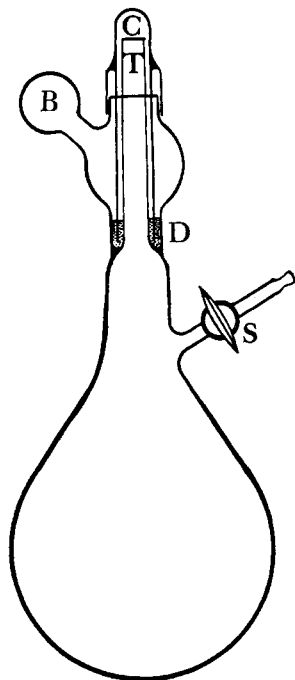

Fig. 1.

Conductivity water was used in the preparation of the cell solutions and in recrystallizations (except in the first steps of some purifications).

Cadmium bromide (Baker's C. P.) was thrice recrystallized by vacuum desiccation at temperatures below its transition point of 35.8°. The crystallizing dish containing the solution with its cover glass in place was placed within a glass cylinder (made from a bottle) and both rested on a large watch glass. The glass cylinder was covered with another large watch glass and the whole rested upon the plate of the desiccator. This arrangement prevented contamination due to evolution of bromine gas which would have resulted from the solution bumping and coming into contact with the sulfuric acid desiccating solution.

Cadmium sulfate and potassium bromide were twice recrystallized.

Silver nitrate was recrystallized twice from conductivity water in the dark room. Neither the final crystals nor the solutions made from them were ever exposed to other than red light for any period of time.

The cadmium bromide solution intended for use in the cells was saturated with respect to cadmium bromide and silver bromide. It was protected at all times from actinic light. The silver bromide was prepared in the dark room by adding very slowly about 200 cc. of 0.05 M silver nitrate to 285 cc. of 0.006 M potassium bromide kept at 80°. To facilitate rapid settling of the finely divided silver bromide, about 1.0 cc. of concentrated perchloric acid was added. After twelve washings by decantation the silver bromide was added to the cadmium bromide solution.

Silver oxide was prepared by adding slowly through a separatory funnel a silver nitrate solution (20 g. in 350 cc. of water) to a dilute solution of barium hydroxide (excess) at 50°. The barium hydroxide solution was made by adding about 400 cc. of a

saturated stock solution to about 1150 cc. of boiling distilled water through a siphon loosely inserted in the stopper of the flask holding the water. The separatory funnel containing the silver nitrate solution was fitted into this stopper just as the boiling was stopped so that precipitation was effected in the absence of carbon dioxide. The first few of the many washings of the precipitate were made with hot boiled conductivity water.

Preparation of Electrodes

Carmody[9] has shown that silver deposited from a $KAg(CN)_2$ solution must be washed free of cyanide with extreme care if reproducible electrodes are to be had. The necessity of this was avoided in the present investigation by using as the base a spiral of pure silver, instead of silver-plated platinum. From this point the silver–silver bromide electrodes were prepared in the same manner as Noyes and Ellis'[10] silver–silver chloride electrodes. The silver bromide was deposited from 0.5 M potassium bromide solution with a current of 4 milliamperes for five hours. These were never exposed to actinic light.

Two-phase cadmium amalgams of 10 to 14 weight per cent. cadmium were used. Amalgams of these compositions remain heterogeneous over the range 25–45°. Moesveld and de Meester[11] have shown that below 13.5% Cd equilibrium is attained at 25° at least within a few hours. The amalgams were prepared by electrolyzing a solution containing the desired amount of cadmium sulfate with a platinum anode and a given amount of mercury as cathode. The amalgam was thus obtained with an acid solution above it which prevented oxide formation on the surface of the amalgam. When once freed from the acid solution, oxidation of the liquid amalgam occurred so rapidly that a special procedure had to be developed whereby the amalgam was not only washed in but kept in an inert atmosphere until needed. This procedure will be described in some detail, because an amalgam free from all oxide contamination was an essential component of the cells to be described.

The amalgam was melted if it had been allowed to cool and transferred along with some of the sulfuric acid solution to the container shown in Fig. 2. This apparatus was a modification of one used by Carmody, details of which were obt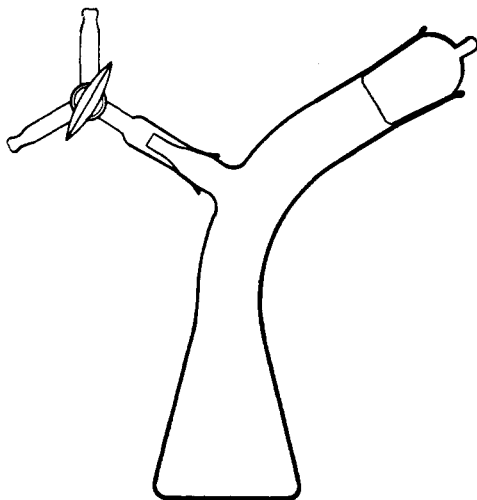ained by private communication. It was clamped loosely with its bottom resting on a wire gauze. The gauze was strongly heated while the solution above the amalgam was periodically poured off through the side arm by tilting the vessel, and replaced by boiling distilled water. By repetition of this process the amalgam was not only washed free of all acid but the air in the container was displaced by escaping steam as well. When washing was complete, the cap to the side arm

Fig. 2.

[9] W. R. Carmody, THIS JOURNAL, **51**, 2901 (1929).

[10] A. A. Noyes and J. H. Ellis, *ibid.*, **39**, 2532 (1917).

[11] A. L. Th. Moesveld and W. A. T. de Meester, *Z. physik. Chem.*, **130**, 146 (1927).

and the stopper were put into place and the container removed from the heat immediately. Because of the high temperature involved, a very stiff stopcock grease was necessary on both ground glass joints. The amalgam was then cooled in an ice box until it was completely solid. The water remaining in the vessel was then drawn off through the stopcock attached to the cap on the side arm. To prevent any slow oxidation of the solid amalgam the vessel was repeatedly evacuated and filled with an inert gas, $i. e.$, nitrogen.

Preparation of Cells and Experimental Method.—Most of the measurements were made with cells containing two electrodes of each kind, shown in Fig. 3, a modification of the H-cell with an upper cross arm and outlet and side arms for convenience in assembling the cell with the exclusion of oxygen. The silver bromide electrodes were supported in ground-glass stopp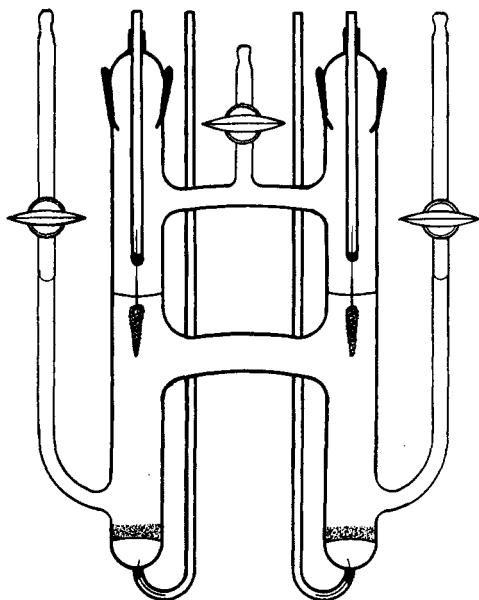ers closing the main arms. In these cells four combinations of the two kinds of electrodes were measured. Later single cells each containing one electrode of each kind were made up and measured in sets of six. In these cells the silver bromide electrode was supported by a tube which closed a mercury seal over the main tube. The earliest measurements, which proved to be valueless, were made in double cells in which the silver bromide electrodes were supported by cork stoppers coated with cement, and the side arms were closed by screw-clamps on rubber tubes rather than by stopcocks.

Fig. 3.

The cells were rendered opaque with a thick black paint made by mixing carbon black with varnish. Preparation of the cells was carried out in the presence of red light and as far as possible the cell was swept out continuously with nitrogen while all the components were being put in place. The proper amount of cadmium bromide solution, removed by a pipet from the supernatant stock solutions, was added to the cell and at the same time filtered to remove any silver bromide which might be suspended in it. After nitrogen had been bubbled through for several minutes, molten cadmium amalgam and finally the tetrahydrate or anhydrous form of cadmium bromide in amount sufficient to ensure presence of crystals at the highest temperature used were added through funnels made of glass tubing. Finally the silver bromide electrodes were put into place and nitrogen was bubbled alternately through first one limb and then the other of the cell for twenty to thirty minutes.

An oil thermostat with a temperature regulator capable of keeping temperature constant within plus or minus 0.015° of any desired temperature over the range 25 to 45° was used. The temperatures were obtained with a thermometer which had been compared with another thermometer certified by the Bureau of Standards. Temperature intervals were also obtained with a Beckmann thermometer. Measurements of potential were made with a Leeds and Northrup Type K potentiometer and Type R (2500-C) galvanometer. The potentiometer, galvanometer, standard cell and the

switch box through which electrical corrections were completed with the cells in the thermostat, were all placed on interconnected metal plates. The shield system was not grounded.[12]

Though there were instances where the cells gave values which proved to be constant with an hour of immersion and also when twelve hours were necessary, five or six hours were generally sufficient, though possibly not requisite, as it was often convenient to leave the experiment for that period after adjustment of temperature. Except in cases where the solid phase underwent a change of form, adjustment of potential to a new temperature was generally complete within that time and frequently by the time the thermostat had been adjusted. Readings were taken at intervals of two to four hours until constancy was proved. As a rule, the bath temperature was successively fixed at 25, 30, 35, 37.5, 40 and 45°, and then lowered to 25° again. After this it was fixed at any value that was of immediate interest. In some cases the results obtained upon lowering the temperature appeared to represent better equilibrium values than those obtained initially. Measurements were made at every temperature after both lowering and raising the temperature but not in each series of measurements.

In spite of all precautions to make the cell function properly, some of the cells "aged" before the whole series of measurements were complete, in which case the results obtained after this phenomenon made its appearance have been omitted from the tables. This "aging" made itself evident by a gradual but steadily increasing deviation between the various pairs of electrodes. All cells, given sufficient time, showed this phenomenon.

Results and Discussion

Tables I and II summarize the average potentials for the cells in which the tetrahydrate and the anhydrous form, respectively, of cadmium bromide were the saturating solids. The values marked with one asterisk were made after measurements at lower and higher temperatures. Those marked with two asterisks were approached twice in one direction. The values for Cells 5 to 10 represent the average of the four combinations of two electrodes except in a few cases where real divergences appear. In Cell 5 the silver electrodes had become different when measurements at 37.50° were made the third time and ones at 40° for the second time. Here one pair of values coincided with all four of an earlier set. In Cell 7 one cadmium amalgam electrode appeared to be sluggish in response to changes of temperature. The temperatures indicate the true values with an uncertainty of 0.02°.

What appears to be an equilibrium value of the electromotive force for a metastable condition was obtained with Cell 6 by lowering the temperature from 37.5 to 35°. In Cell 3, though all the values appeared to be too low, there existed the same difference in readings at 37.5 and 35°. The metastable condition persisted at 35° for six hours. The thermostat was then allowed to cool to 28.3° for several hours and on readjustment to 35° the cells gave values different from the earlier ones by approximately the same amount as for the stable and metastable conditions in Cell 6.

The values of Tables I and II have been plotted and the data obtained from these curves are tabulated in Table III. The slopes of these curves.

[12] W. P. White, THIS JOURNAL, **36**, 2011 (1914).

TABLE I

ELECTROMOTIVE FORCES OF THE CELLS

Cd(in het. amalg.), CdBr$_2$·4H$_2$O(s), satd. CdBr$_2$·4H$_2$O + AgBr, AgBr(s), Ag(s)

Cell no.	E 25°	E 27°	E 30°	E 33°	E 35°
2	0.48833*				
5	.48837**		0.48415		0.47889*
6	.48838		.48366		.47840
7	.48839		.48347		.47846
8	.48814		.48333		.47805*
9	.48819		.48337		.47831
12–1			.48436*	0.48149	
12–2			.48408*	.48147	a
12–4			.48431	.48174	
12–6			.4844^b	.48180	
13–1		0.48686	.48439		
13–2		.48685	.48445		
13–3		.48685	.48409		
13–4		.48685	.48446		
13–5		.48685	.48429		
13–6		.48684	.48422		
13–1^c	.48821	.48661		.48144	
13–2	.48824	.48666		.48141	
13–3	.48832	.48682		.48130	
13–4	.48833	.48685		.48194	
13–5	.48829	.48679		.48147	
13–6	.48828	.48676		.48156	

^{a} At 35° Cells 12–1, –2, –4 and –6 were divergent and higher than was expected, indicating that they were not saturated.

^{b} Cell 12–6 became insensitive in the middle of the run and later recovered.

^{c} The order of temperature changes for Cell 13 was 27, 30, 35 (for a period insufficient for attainment of constancy), 27, 25 and 33°.

TABLE II

ELECTROMOTIVE FORCES OF THE CELLS

Cd(in het. amalg.), CdBr$_2$(s), satd. CdBr$_2$ + AgBr, AgBr(s), Ag(s)

Cell no.	35° (metastable)	37.5°	40°	45°
5		0.47807*	0.47797**	0.47774
6	0.47772	.47759*	.47749*	.47720
8		.47758		
9		.47766	.47760	
10		.47734	.47730	

i. e., $\partial E/\partial T$, at 25° are given in the second column, the slopes at the transition point for the tetrahydrate of cadmium bromide cells in the third column, and for the anhydrous form at this temperature in the fourth column. The transition temperatures in the fifth column were obtained from the intersections of the curves.

Ishikawa and Ueda[5] have shown that, contrary to facts hitherto accepted, the tetrahydrate of cadmium bromide changes at a temperature

TABLE III

TEMPERATURE COEFFICIENTS OF ELECTROMOTIVE FORCE AND THE TRANSITION
TEMPERATURE

Cell no.	25° $-(\partial E/\partial T) \times 10^6$	$-(\partial E/\partial T) \times 10^6$	$-(\partial E/\partial T) \times 10^6$	E at transi- tion temp.	Transi- tion temp.
5	787	1168	32	0.47814	35.63 °C.
6	882	1118	42	.47770	35.64
7	980	1036			
8	898	1100			
9	896	1032	26	.47770	35.61
Mean	890	1091	33		

near 36° to the anhydrous form rather than to CdBr$_2$·H$_2$O (or CdBr$_2$·1.5-H$_2$O).[13] With the Bremer-Frowein tensimeter they determined the vapor pressures of the systems (a) CdBr$_2$·4H$_2$O(s)–saturated solution, (b) CdBr$_2$·2.6H$_2$O, $i.\ e.$, CdBr$_2$·4H$_2$O(s)–CdBr$_2$(s), and found for the range 20–35°

(a) log $p_{\text{(mm.)}}$ = 1.32491 − 2095.4(1/T − 1/298.1); (p =0.07 mm.)   (9)

(b) log $p_{\text{(mm.)}}$ = 1.24102 − 2731.1(1/T − 1/298.1); (p =0.06 mm.)   (10)

For 37.5, 40 and 42.5° they found p in Series (a), 40.43 ± 0.10, 46.26 ± 0.06 and 52.68 ± 0.05, in Series (b), 40.23 ± 0.06, 46.03 ± 0.12 and 52.7 ± 0.05 mm., respectively. Moreover, measurements were made at 20 and 42.5° on a mixture of the tetrahydrate and anhydrous form corresponding to a solid of composition CdBr$_2$·0.348H$_2$O and the values checked Series (b).
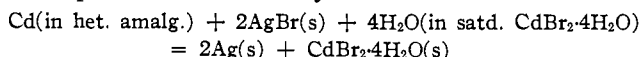
The direct determination of the water of crystallization of the solid prepared above the transition point, as given, is unconvincing. Their dehydration and hydration experiments at 25° with 34.3% and 24.8% sulfuric acid, the vapor pressures of which (16 and 19.6 mm.) are, respectively, lower and higher than 17.35 mm., the dissociation pressure, as measured are very interesting. The first solution changes mixtures of the tetrahydrate and water, of compositions, CdBr$_2$·4H$_2$O + 0.69H$_2$O and CdBr$_2$·4H$_2$O + 0.79H$_2$O to CdBr$_2$ in two to four hundred hours without any discontinuity in the water content–time curves and leaves the higher temperature form unchanged while the second solution takes the higher temperature form and the tetrahydrate plus 0.97 mole of water to the tetrahydrate also without any discontinuity. We have repeated the experiments in which an attempt was made to obtain an intermediate degree of hydration from the form prepared in the ordinary way slightly above the transition point, and have found from the analysis for bromide ion that the salt is anhydrous.

Whereas the transition temperature determined from our cells is 35.63° and that determined from the cadmium bromide–mercurous bromide cells is 36.0°, it seemed expedient to investigate the transition point by the usual

[13] (a) R. Dietz, $Z.\ anorg.\ Chem.$, **20**, 240 (1899); (b) M. Étard, $Ann,\ chim.\ phys.$, [7] **2**, 503 (1894).

thermal methods. This leads to $35.82°$, assuming the same deviation of the thermometer (i. e., $-0.02°$) at this temperature as at $32.38°$, the transition point for decahydrate–anhydrous forms of sodium sulfate.
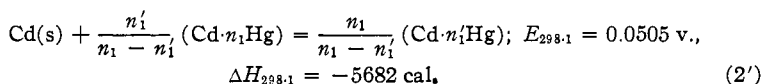
The mean value of the potential at $25°$, $E_{298.1} = 0.48829$ or 0.4883 v. from Table I, represents the tendency for the reaction

$$\text{Cd(in het. amalg.)} + 2\text{AgBr(s)} + 4\text{H}_2\text{O(in satd. CdBr}_2\cdot4\text{H}_2\text{O)}$$
$$= 2\text{Ag(s)} + \text{CdBr}_2\cdot4\text{H}_2\text{O(s)}$$

to occur. This represents in an abbreviated form the complete cell reaction

$$\frac{n_1}{n_1 - n_1'} (\text{Cd}\cdot n_1'\text{Hg}) + 2\text{AgBr(s)} + \frac{4}{A - 4} (\text{CdBr}_2\cdot A\text{H}_2\text{O})$$

$$= 2\text{Ag(s)} + \frac{4}{A - 4} \text{CdBr}_2\cdot4\text{H}_2\text{O(s)} + \frac{n_1'}{n_1 - n_1'} (\text{Cd}\cdot n_1\text{Hg});$$
$$E_{298.1} = 0.4883 \text{ v.}, \ (\partial E/\partial T)_{298.1} = -8.9 \times 10^{-4}$$
$$\Delta H_{298.1} = -34{,}777 \text{ cal.}, \ E_{308.73} = 0.4777 \text{ v.}, \ (\partial E/\partial T)_{308.73}$$
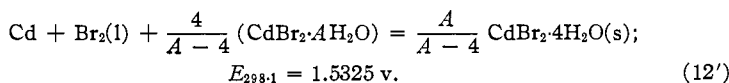$$= -1.091 \times 10^{-3}, \ \Delta H_{308.73} = -37{,}589 \text{ cal.} \tag{7'}$$

where n_1 and n_1' are, respectively, the moles of mercury per mole of cadmium in the liquidus and solidus and A is the number of moles of water per mole of cadmium bromide in the saturated solution. Combining with Reaction 2 or rather $2'$
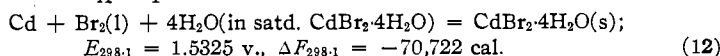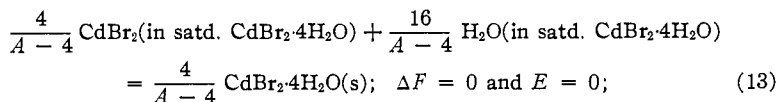
$$\text{Cd(s)} + \frac{n_1'}{n_1 - n_1'} (\text{Cd}\cdot n_1\text{Hg}) = \frac{n_1}{n_1 - n_1'} (\text{Cd}\cdot n_1'\text{Hg}); \ E_{298.1} = 0.0505 \text{ v.},$$
$$\Delta H_{298.1} = -5682 \text{ cal.} \tag{2'}$$

and that for the formation of silver bromide from its elements

$$2\text{Ag(s)} + \text{Br}_2(\text{l}) = 2\text{AgBr(s)}; \ E_{298.1} = 0.9937 \text{ v.}[14] \tag{11}$$
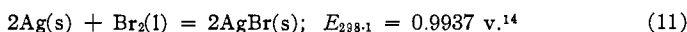
we have for the formation from the elements and the saturated solution

$$\text{Cd} + \text{Br}_2(\text{l}) + \frac{4}{A - 4} (\text{CdBr}_2\cdot A\text{H}_2\text{O}) = \frac{A}{A - 4} \text{CdBr}_2\cdot4\text{H}_2\text{O(s)};$$
$$E_{298.1} = 1.5325 \text{ v.} \tag{12'}$$

and since for

$$\frac{4}{A - 4} \text{CdBr}_2(\text{in satd. CdBr}_2\cdot4\text{H}_2\text{O}) + \frac{16}{A - 4} \text{H}_2\text{O(in satd. CdBr}_2\cdot4\text{H}_2\text{O)}$$

$$= \frac{4}{A - 4} \text{CdBr}_2\cdot4\text{H}_2\text{O(s)}; \ \Delta F = 0 \text{ and } E = 0; \tag{13}$$

$$\text{Cd} + \text{Br}_2(\text{l}) + 4\text{H}_2\text{O(in satd. CdBr}_2\cdot4\text{H}_2\text{O)} = \text{CdBr}_2\cdot4\text{H}_2\text{O(s)};$$
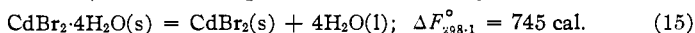$$E_{298.1} = 1.5325 \text{ v.}, \ \Delta F_{298.1} = -70{,}722 \text{ cal.} \tag{12}$$

Equation 3 follows from Ishikawa and Ueda's measurement[5] of the vapor pressure of the saturated solution of the tetrahydrate at $25°$, $p = 21.15$ mm. (Equation 9), and hence, adding Equations 3 and 12, we find for the standard free energy and electromotive force of formation of the tetrahydrate of cadmium bromide
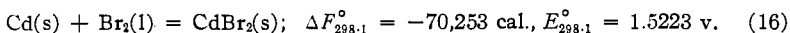
$$\text{Cd(s)} + \text{Br}_2(\text{l}) + 4\text{H}_2\text{O(l)} = \text{CdBr}_2\cdot4\text{H}_2\text{O(s)}; \ \Delta F^\circ_{298.1} = -70{,}722 \text{ cal.}, \ E^\circ_{298.1} = 1.5385 \text{ v.}$$
$$\tag{14}$$
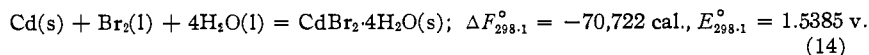
[14] Though this value of the electromotive force of formation of silver bromide was derived primarily for this paper, it has seemed best to present the basis for it in another paper by one of the authors and Professor Randall.[2]

From Ishikawa and Ueda's measurement of the vapor pressure of the system $CdBr_2·4H_2O(s)$–$CdBr_2(s)$, $p = 17.35$ mm. (Equation 10), at $25°$

$$CdBr_2·4H_2O(s) = CdBr_2(s) + 4H_2O(l); \quad \Delta F°_{298·1} = 745 \text{ cal.} \qquad (15)$$

and thence for

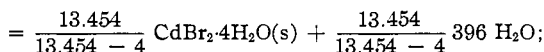$$Cd(s) + Br_2(l) = CdBr_2(s); \quad \Delta F°_{298·1} = -70{,}253 \text{ cal.}, E°_{298·1} = 1.5223 \text{ v.} \quad (16)$$
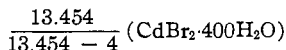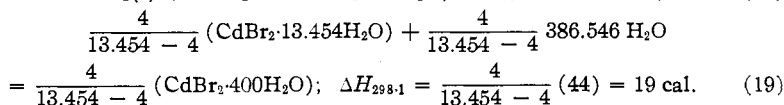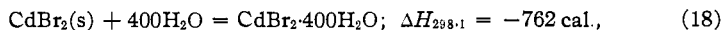
These values are in excellent agreement with the values determined through mercurous bromide by Ishikawa and Ueda.[15] We shall see that the heats of reactions calculated from the two sets of data do not agree satisfactorily.

The heat effect of the reaction

$$\frac{A}{A-4} CdBr_2·4H_2O(s) = CdBr_2(s) + \frac{4}{A-4} (CdBr_2·A H_2O) \qquad (17)$$
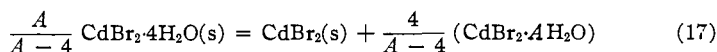
is required in the calculation of the heat of formation of cadmium bromide from the electromotive force measurements. It may be split into three parts, for each of which Ishikawa and Ueda[5] have determined calorimetrically the heat effects at $25°$, where $A = 13.454$

$$CdBr_2(s) + 400H_2O = CdBr_2·400H_2O; \quad \Delta H_{298·1} = -762 \text{ cal.}, \qquad (18)$$

$$\frac{4}{13.454-4} (CdBr_2·13.454H_2O) + \frac{4}{13.454-4} 386.546 \text{ H}_2O$$

$$= \frac{4}{13.454-4} (CdBr_2·400H_2O); \quad \Delta H_{298·1} = \frac{4}{13.454-4} (44) = 19 \text{ cal.} \qquad (19)$$

$$\frac{13.454}{13.454-4} (CdBr_2·400H_2O)$$

$$= \frac{13.454}{13.454-4} CdBr_2·4H_2O(s) + \frac{13.454}{13.454-4} 396 \text{ H}_2O;$$

$$\Delta H_{298·1} = \frac{13.454}{13.454-4} (-7139) = -10{,}160 \text{ cal.} \qquad (20)$$

$$\frac{13.454}{9.454} CdBr_2·4H_2O(s) = CdBr_2(s) + \frac{4}{9.454} (CdBr_2·13.454H_2O);$$
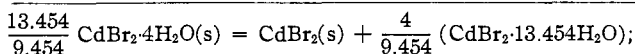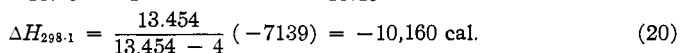
$$\Delta H_{298·1} = -10{,}903 \text{ cal.} \quad (17)$$

By addition of Reactions 7′, 2′, 17 and that for the formation of two moles of silver bromide,[16] for which $\Delta H = -47{,}620$, the ΔH of formation of cadmium bromide (Reaction 16) is $-77{,}176$ cal. From Ishikawa and Ueda's cells involving mercurous bromide, $\Delta H_{298·1}$ for the reaction corresponding to 7′ is $-31{,}494$ cal. Addition of this reaction to Reactions 2′, 17 and that for the formation of two moles of mercurous bromide, $-50{,}940$ (Thomsen), $-49{,}000$ (Nernst), $-49{,}100$ (Varet) or $-49{,}240$ cal. ("I. C. T."), gives for the ΔH of formation of cadmium bromide $-77{,}213$, $-75{,}$-273, $-75{,}373$ or $-75{,}513$ cal., respectively. Oeholm's mercurous bromide

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[15] In Ishikawa and Ueda's paper the free energies and potentials are referred to α-cadmium. The heat capacity data used in their calorimetric measurements are not very satisfactory. The results nominally given in $18°$ calories can probably be considered approximately correct.
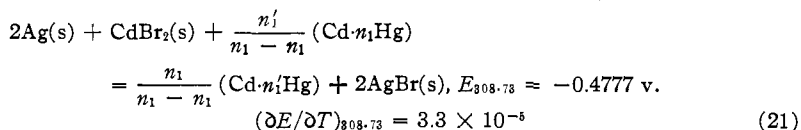
[16] T. J. Webb, *J. Phys. Chem.*, **29**, 816 (1925).

cells yield −31,590 cal., for the reaction corresponding to 7′. Similar treatment of Obata's cells involving lead bromide, for which $\Delta H_{298.1} =$ −12,380 cal., along with ΔH for Reactions 5 and 6, −82 and −66,350 cal., respectively, the latter by Braune and Koref, and Reactions 2′ and 17 gives for the ΔH of formation of cadmium bromide −73,427 cal.

Bichowsky[17] has recalculated the calorimetric value of the heat of formation of solid cadmium bromide and found −75,790 cal. This is based primarily on the values of Thomsen and of Nernst, −75,640 and −76,300, for the formation in solution. Thomsen's value results from the combination of four equations. Nernst[18] measured directly the heat effect of formation in solution (often quoted as heat of formation of the solid) in the presence of a small excess of bromine and found −76,400 ± 600 cal. (actual average of his data) which when corrected by reason of his use of 112.1 as the atomic weight of cadmium, yields −76,610 cal. This magnitude should be further increased to express the result in 15° calories. Ishikawa and Ueda's measurement of the heat of solution of cadmium bromide, $\Delta H = $ −762 cal. now supersedes −440 by Thomsen so that the −75,790 given by Bichowsky would now be changed to −75,570 cal.

Thus while the values derived from the silver and mercurous bromide cells do not agree well, the calorimetric values to which they are to be compared are in the same range and of the same order of variability.
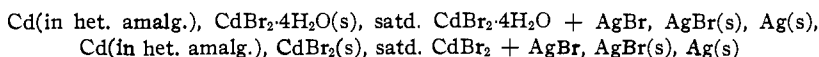
Comparison of the silver and mercurous bromide cells is disappointing in another respect, though the method is very sensitive to experimental error. Addition of Reaction 7′ and the reverse of the reaction in cells with anhydrous cadmium bromide as the solid phase

$$2Ag(s) + CdBr_2(s) + \frac{n_1'}{n_1 - n_1}(Cd \cdot n_1 Hg)$$

$$= \frac{n_1}{n_1 - n_1}(Cd \cdot n_1' Hg) + 2AgBr(s), \quad E_{308.73} = -0.4777 \text{ v.}$$

$$(\partial E/\partial T)_{308.73} = 3.3 \times 10^{-5} \tag{21}$$

yields Reaction 17, $\Delta H_{308.73} = $ 15,074 cal. The corresponding reactions in the mercurous bromide cells give $\Delta H_{308.73} = $ 12,094 cal. The difference of these values from the calorimetric one at 25°, 10,903 cal., is not surprising when one considers that not only the ratio A but also the heat effects of the three individual reactions are different at the higher temperature.

Summary

1.   The electromotive forces of the following cells

Cd(in het. amalg.), CdBr₂·4H₂O(s), satd. CdBr₂·4H₂O + AgBr, AgBr(s), Ag(s),
    Cd(in het. amalg.), CdBr₂(s), satd. CdBr₂ + AgBr, AgBr(s), Ag(s)

[17] F. R. Bichowsky, "International Critical Tables," McGraw-Hill Book Co., New York, 1929, Vol. V, p. 185.

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

prepared in the absence of oxygen have been measured over the ranges 25–35 and 35–45° respectively.

2. The transition temperature, $CdBr_2 \cdot 4H_2O(s)-CdBr_2(s)$–saturated solution, was found to be 35.63° by the cell measurements and 35.82 by the usual thermal method, and the hydration of the stable solid phases has been discussed.

3. The standard electromotive force and free energy of formation of cadmium bromide have been found to check those through mercurous bromide and not those through lead bromide. The heats of formation have been compared with the calorimetric values.

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SOME REACTIONS OF COMPLEX CHLORIDES OF TRIVALENT AND PENTAVALENT TUNGSTEN

BY RALPH C. YOUNG

When tripotassium ditungsti-chloride, $K_3W_2Cl_9$, prepared by the method of Olsson[1] was treated with a solution of potassium hydroxide at 5°, a vigorous evolution of hydrogen occurred as simultaneously a precipitate of an hydroxide or hydrous oxide formed. These same phenomena occurred also when $K_3W_2Cl_9$ was heated with water. An oxide of trivalent tungsten is not stable even at low temperatures when prepared in aqueous solutions. It is therefore to be expected that, if the mechanism of complex cyanide formation in the case of tungsten is similar to that of molybdenum,[2] with the intermediate formation of an hydroxide, a complex cyanide of tetravalent tungsten would form when $K_3W_2Cl_9$ is treated with potassium cyanide solution in an atmosphere of nitrogen. Such has proved to be the result even when the reaction is carried out at low temperatures. Hydrogen is not evolved in this reaction in which oxidation of the tungsten occurs but if the contents of the solution after reaction are made acid, the Schiff test for aldehyde is obtained. Hydrogen cyanide and ammonia are present in the solution, resulting from the hydrolysis of the potassium cyanide, and it is known that hydrogen cyanide is reduced in neutral solutions to formaldehyde and ammonia. These compounds are able to form certain condensation products, which may be the reason for not obtaining the test for aldehyde until the solution was made acid.

It seemed of interest to determine to what extent the tungsten in $K_3W_2Cl_9$ would be oxidized in an atmosphere of nitrogen by water alone, and by

[1] Olsson, Z. anorg. allgem. Chem., 88, 49 (1914).

[2] Young, THIS JOURNAL, 54, 1402 (1932).