

quent paper with A. S. O'Brien^{5b} it will be shown that the speed of exchange between freshly precipitated, air-dried silver bromide and gaseous radioactive bromine is very great as a result of this thermal mobility. This thermal mobility should also be great when dealing with a freshly flocculated precipitate, but the speed of exchange with the solution decreases rapidly as a result of the decrease of the specific surface.

The coprecipitation of chloride with silver bromide decreases with decreasing temperature during the precipitation, as the distribution coefficient of the bromide between solid and solution decreases. This fact can be made use of to analytical advantage in the potentiometric titration of bromide in the presence of chloride with silver nitrate. It is expected that the errors will be smaller when the titration is carried out at the temperature of melting ice than at room temperature.

Acknowledgment.—We express our appreciation to the Graduate School of the University of Minnesota for the assignment of a grant which enabled us to carry out the present study.

Summary

1. Upon addition of silver nitrate to a mixture of bromide and chloride under such conditions that

the particles remain in colloidal solution, a homogeneous distribution of the halides between solid and solution has been found. The presence of nitrobenzene during precipitation did not affect the time of attainment of equilibrium in a measurable way.

2. When the precipitant is added under such conditions that the precipitate is flocculated instantaneously, heterogeneous mixed crystals are formed. Upon very slow addition of silver the distribution approaches that calculated on the basis of the Doerner and Hoskins equation, but does not equal it as a result of aging and of the effect of a local excess of precipitant. Homogeneous equilibrium is attained only after long periods of shaking of the precipitate with the supernatant liquid.

3. When the particles are aged in the colloidal state for several hours and the composition of the liquid phase is changed after this time, the solid comes to equilibrium with the liquid almost instantaneously. This great speed of exchange has been attributed to a great thermal mobility of the silver and bromide ions in the colloidal particles.

4. The coprecipitation of chloride with silver bromide decreases with decreasing temperature during the precipitation.

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

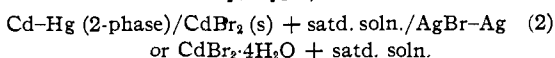
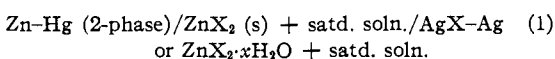
The Thermodynamics of Bi-univalent Electrolytes. V. The Heats of Formation and Entropies of Certain Zinc and Cadmium Halides

BY ROGER G. BATES¹

The free energy of a given chemical system and its change with change of temperature, as measured by the electromotive forces of suitable reversible cells, have been used successfully to obtain heats of reaction with accuracy comparable with that of the direct calorimetric method used in the classical researches of Thomsen.² This indirect procedure is limited in its application to those cases in which the cell reaction is known to be free from side reactions. Unfortunately, the difficulties attendant upon the use of halogen electrodes prevent the application of the electromotive force method to the study of the reac-

tion in which halide salts are formed directly from their elements. A survey of the literature, however, shows many instances of poor agreement between the results of calorimetry and electromotive force, even when a pure cell reaction may reasonably be assumed.

In this investigation measurements were made of the cells



where X represents Cl, Br or I, over the temperature range, 10–45°, except as limited by the stability of the particular solid phase present.

(1) Sterling Fellow in Chemistry, 1937–1939.

(2) J. Thomsen, "Thermochemische Untersuchungen," Vols. I–IV, Barth, Leipzig, 1882, 1882, 1883, 1886.

TABLE I

OBSERVED ELECTROMOTIVE FORCES.				CONSTANTS OF EQUATION (3)			
<i>t</i>	$\frac{E}{\text{ZnCl}_2 \text{ (s)}}$	$\frac{E}{\text{ZnBr}_2 \cdot 2\text{H}_2\text{O}}$	$\frac{E}{\text{ZnBr}_2 \text{ (s)}}$	$\frac{E}{\text{ZnI}_2 \text{ (s)}}$	$\frac{E}{\text{CdBr}_2 \cdot 4\text{H}_2\text{O}}$	$\frac{E}{\text{CdBr}_2 \text{ (s)}}$	
25	0.77612 ^a	10 0.62840	36 0.61091	5 0.39887	10 0.49850	38	0.47928
30	.77513	15 .62556	38 .61048	10 .39842	15 .49528	40	.47920
35	.77404	20 .62236	40 .61003	15 .39792	20 .49190	42	.47914
40	.77301	25 .61867	42 .60956	20 .39736	25 .48833	45	.47900
		30 .61443	44 .60907	25 .39667	30 .48451	47	.47892
			46 .60858	30 .39595	33 .48191		
			48 .60812	35 .39515			
				40 .39433			
<i>a</i>	0.78133	0.63253	0.61599	0.39934	0.50373	0.48080	
<i>b</i> × 10 ⁵	-20.8	-32.1	-6.90	-8.15	-47.5	-4.00	
<i>c</i> × 10 ⁶	-0.004	-9.40	-2.00	-1.07	-5.61	0	
Δ <i>E</i> , mv.	0.01	0.03	0.01	0.03	0.06	0.004	

^a Metastable.

Values for the heats of formation of the anhydrous forms of zinc chloride, zinc bromide, zinc iodide and cadmium bromide have been obtained which are in satisfactory agreement with earlier calorimetric results. The entropies of these four salts have likewise been computed.

Experimental

Two-phase amalgams, containing 5% zinc or 10% cadmium by weight, were prepared from thrice-distilled mercury and the best grade of Kahlbaum zinc and cadmium. Amalgams of these compositions are known to be heterogeneous between 5 and 50°. In the construction of the cells, the amalgam was melted under an atmosphere of hydrogen and was drawn into the evacuated vessel in quantity sufficient to cover the tungsten contact. The surfaces of electrodes prepared in this way were never dulled by oxide.

Silver chloride electrodes of the electrolytic type were employed. Silver bromide electrodes were prepared by the thermal decomposition of a mixture of silver oxide and silver bromate. Silver iodide electrodes were made, as in a previous investigation,³ by the thermal decomposition of a mixture of silver oxide and silver iodide at 450°.

Zinc and cadmium bromides were studied in the hydrated as well as the anhydrous condition. According to "International Critical Tables,"⁴ cadmium bromide changes at about 35.8° from the tetrahydrate to the monohydrate. The hydration and dehydration studies of Ishikawa and Ueda⁵ and of Spencer and Selden,⁶ however, indicate that the anhydrous salt is the stable form above this transition temperature.

Extreme care was exercised to ensure that the salts present in the cells as solid phases should be in their most stable hydrated (or completely anhydrous) state. The crystalline dihydrated zinc bromide and the tetrahydrate of cadmium bromide were ground to a fine powder and stirred vigorously under their saturated solutions at a temperature

(3) Bates, *THIS JOURNAL*, **60**, 2983 (1938).

(4) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. IV, p. 222.

(5) Ishikawa and Ueda, *Sci. Repts., Tôhoku Imp. Univ.*, **22**, 285 (1933).

(6) Spencer and Selden, *THIS JOURNAL*, **54**, 4504 (1932).

near 0° to hasten the hydration of any anhydrous salt that may have been present. A portion of the salt used had been recrystallized below the transition temperature. The anhydrous forms of these salts and of zinc chloride were prepared by maintaining the finely powdered salt at a temperature of about 60° under saturated solution for at least two days, with occasional stirring. The point of transition between the anhydrous and hydrated forms of zinc chloride lies at about 28°. The continuity of the electromotive force-temperature plot between 25 and 40°, however, indicated that the solid phase remained unhydrated down to 25°. Zinc iodide is anhydrous between 5 and 40°.

It seemed unwise to attempt to effect the transition from hydrated to anhydrous salt (or *vice versa*) within the cell, as a small quantity of unchanged solid has been found to cause erratic results, particularly in the temperature coefficient. Separate groups of cells accordingly were prepared for the high- and low-temperature runs. The cells containing hydrated zinc and cadmium bromides and zinc iodide were constructed at room temperature, whereas those containing anhydrous salt (with the exception of zinc iodide) were kept at a temperature of 50° during the process by immersing vessels and solution flasks in hot water-baths.

An air-free technique was used in all instances, but it is believed that exclusion of traces of air from the cells was not as complete as is ordinarily the case when unsaturated solutions are used.

Results

The observed electromotive forces for cells (1) and (2) are listed in Table I. At least four cells of each type (*i. e.*, with the same solid phase) were prepared, except in the case of cadmium bromide, when the first two cells constructed gave particularly satisfactory results. The recorded results in general represent the average of those values believed to be most reliable.

At the bottom of Table I are listed the constants of the equation

$$E = a + bt + ct^2 \quad (3)$$

(7) Ishikawa, Kimura and Murooka, *Sci. Repts., Tôhoku Imp. Univ.*, **21**, 455 (1932).

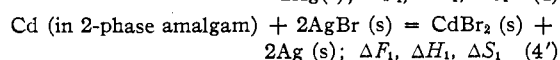
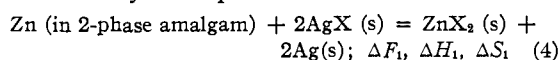
where E represents the electromotive force in volts and t is the temperature in degrees C . The average deviation, ΔE , of the experimental results from equation (3) is also listed at the end of the table. All data were fitted to the equation by the method of least squares with the exception of those relating to zinc iodide and anhydrous cadmium bromide cells. In these two instances a graphical method was employed.

Calculations and Discussion

Experience has shown that cells (1) and (2) are in all probability free from side reactions when silver halide is prevented from reaching the amalgam electrode. In a cell of this type, the presence of the silver salt at only one electrode leads to a small liquid junction potential, usually negligible when the solubility of the silver salt in the electrolyte is small and the electrolyte concentration is not too low. As the solution concentration is increased, the relative contribution from solubility ordinarily is lessened, and the liquid junction potential decreases. When the cell solution is in equilibrium with solid salt at each electrode, this potential may become quite unimportant.

Measurements similar to those described here have been made upon a number of inorganic salts in Japan by Ishikawa and his co-workers. Mercurous halide electrodes were employed for the most part, and, in the studies of salts having a hydrated low-temperature form, the same cells were measured above and below the transition point. Since transition may well be incomplete under these conditions, their procedure is occasionally the source of some uncertainty. Furthermore, the solubility of mercurous bromide and mercurous iodide in strong bromide and iodide solutions is not always inappreciable. The silver halide electrodes used in the present work contained, on the average, forty to sixty mg. of silver salt. The constancy of electromotive force over a reasonable period of time may be taken as evidence that the solubility of the silver halides was not large in the saturated halide solutions.

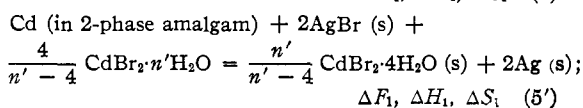
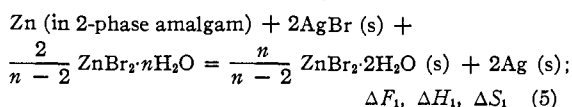
In the cells containing anhydrous solid phases, the chemical processes may most simply be represented by the equations



in which ΔF_1 , ΔH_1 and ΔS_1 represent the changes

in free energy, heat content and entropy resulting from the formation of a mole of anhydrous salt according to reactions (4) or (4'). The subscript 1 will be used to denote quantities computed directly from the experimental results. For the sake of brevity, likewise, cells will be referred to in terms of their solid salts.

A change of water activity in the formation of the solid hydrated salts complicates the representation of the reactions taking place in the hydrated zinc bromide and cadmium bromide cells. The total cell reactions may, however, be written



where n and n' are the numbers of moles of water to each mole of zinc bromide and cadmium bromide, respectively, in the saturated solutions.

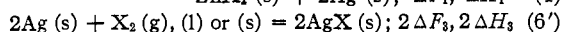
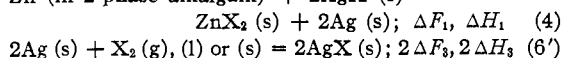
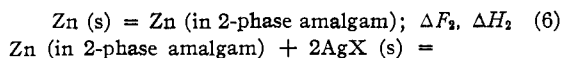
The thermodynamic quantities for reactions (4), (4'), (5) and (5') at 25° are given in Table II. These values have been computed from the constants of equation (3) in the usual way.

TABLE II
THERMODYNAMIC DATA FOR REACTIONS (4,4') AND (5,5') AT 25°

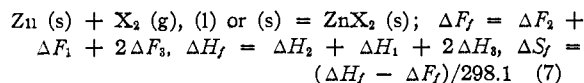
	ΔF_1	ΔH_1	ΔS_1
Reactions (4,4')			
ZnCl ₂ (s)	-35,816	-38,680	- 9.61
ZnBr ₂ (s)	-28,289	-30,614	- 7.80
ZnI ₂ (s)	-18,308	-20,165	- 6.23
CdBr ₂ (s)	-22,142	-22,692	- 1.85
Reactions (5,5')			
ZnBr ₂ ·2H ₂ O	-28,550	-39,432	-36.50
CdBr ₂ ·4H ₂ O	-22,535	-32,928	-34.87

The calculation of the free energy and heat content changes in the formation of a mole of anhydrous salt from its elements may be made most directly with the use of the anhydrous cell results. Zinc chloride and zinc iodide cells were measured at 25°, and the small deviations from equation (3) for cadmium bromide (0.004 mv. for five temperatures over a 9° range) and for zinc bromide (0.01 mv. for seven temperatures over a 12° range) justify the extension of the equations for these measurements down to 25°.

The thermochemical equations involved in the calculation of these quantities for the compound, ZnX₂ (s), are



By addition



where ΔF_f and ΔH_f refer to the free energy and heat content changes in the simple combination reaction, equation (7).

For reaction (6), $\Delta F_2 = 0$, $\Delta H_2 = 0$ and $\Delta S_2 = 0$, as pointed out by Clayton and Vosburgh.⁸ For the analogous process, Cd (s) = Cd (in 2-phase amalgam), Parks and La Mer⁹ found $\Delta F_2 = -2328$ cal., $\Delta H_2 = -5079$ cal. and $\Delta S_2 = -9.23$ cal./degree mole.

Latimer, in his recent book,¹⁰ has given a summary of free energies of formation of inorganic compounds. His values for the silver halides (ΔF_3) are probably the most reliable. For the heat of formation of silver chloride, the value of $-30,300$ cal. found by Rossini¹¹ was used. The results given by Ishikawa and Watanabe¹² and Eucken, Clusius and Voitinek¹³ are in close agreement with that of Rossini. For silver bromide, Webb's value of $-23,810$ cal.¹⁴ has been chosen. This value is in good agreement with $-23,760$ cal. (corrected to 25°) found by Roth and Bertram¹⁵ by direct synthesis. For silver iodide, the value of $-15,170$ cal. was adopted. This figure is the mean of the closely-agreeing values of Braune and Koref,¹⁶ Taylor,¹⁷ Krahmer¹⁸ and Gerth.¹⁹

In those cases in which the heats of reaction were measured at temperatures other than 25°, they have been corrected to this temperature with the use of approximate ΔC_p values computed from the specific heats of Kelley²⁰ and of Lewis

(8) Clayton and Vosburgh, *THIS JOURNAL*, **58**, 2093 (1936). See also Lindeck, *Wied. Ann.*, **35**, 311 (1888).

(9) Parks and La Mer, *THIS JOURNAL*, **56**, 90 (1934).

(10) W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 302-308.

(11) Rossini, *Bur. Standards J. Research*, **9**, 679 (1932).

(12) Ishikawa and Watanabe, *Sci. Repts., Tohoku Imp. Univ.*, **22**, 401 (1933).

(13) Eucken, Clusius and Voitinek, *Z. anorg. Chem.*, **203**, 54 (1931).

(14) Webb, *J. Phys. Chem.*, **29**, 827 (1925).

(15) Roth and Bertram, unpublished result. See Landolt-Börnstein, "Physikalisch-chemische Tabellen," Verlag von Julius Springer, Berlin, 1936, Ergbd. III, 3, p. 2760.

(16) Braune and Koref, *Z. anorg. Chem.*, **87**, 186 (1914).

(17) Taylor, *THIS JOURNAL*, **38**, 2295 (1916).

(18) Krahmer, *Z. Elektrochem.*, **26**, 97 (1920).

(19) Gerth, *ibid.*, **27**, 287 (1921).

(20) K. K. Kelley, *Bur. Mines, Bull.* 371, U. S. Government Printing Office, Washington, D. C., 1934.

and Randall.²¹ Table III is a tabulation of the best values of these quantities.

The thermodynamic data relating to the formation of the anhydrous salts from their elements in the standard reference states were computed as indicated in equation (7). They are listed in Table IV.

TABLE III

FREE ENERGIES AND HEATS OF FORMATION OF THE SILVER HALIDES AT 25°

Reaction	ΔF_3	ΔH_3
Ag (s) + $\frac{1}{2}$ Cl ₂ (g) = AgCl (s)	-26,220	-30,300
Ag (s) + $\frac{1}{2}$ Br ₂ (l) = AgBr (s)	-22,900	-23,810
Ag (s) + $\frac{1}{2}$ I ₂ (s) = AgI (s)	-15,810	-15,170

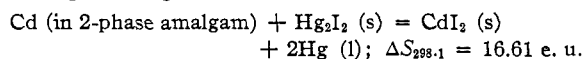
TABLE IV

FREE ENERGY, ENTROPY AND HEAT CONTENT CHANGES IN THE FORMATION OF THE ANHYDROUS SALTS FROM THEIR ELEMENTS

Reaction	ΔF_f	ΔH_f	ΔS_f
Zn (s) + Cl ₂ (g) = ZnCl ₂ (s)	-88,256	-99,280	-36.98
Zn (s) + Br ₂ (l) = ZnBr ₂ (s)	-74,089	-78,234	-13.90
Zn (s) + I ₂ (s) = ZnI ₂ (s)	-49,928	-50,505	-1.94
Cd (s) + Br ₂ (l) = CdBr ₂ (s)	-70,270	-75,390	-17.18

The vapor pressure and heat of solution measurements of Ishikawa and Ueda⁵ make possible the calculation of ΔF_f and ΔH_f for cadmium bromide from the electromotive forces of the hydrated cells. This procedure yields $\Delta F_f = -70,193$ and $\Delta H_f = -74,724$.

Table V is a summary of the entropies of the anhydrous zinc and cadmium halides. Values for the four salts studied in this investigation were derived from ΔS_1 , together with appropriate entropy data for the other reactants and products involved in equations (4) and (4'). The entropy of cadmium iodide was recalculated from the entropy change in the reaction



as measured by Vosburgh,²² and a value of 56.82 e. u. for the entropy of solid mercurous iodide.²³ Since cadmium chloride retains one molecule of water of crystallization in the highest temperature range in which cadmium chloride cells have been studied, existing electromotive force data may not be used in this simple way to obtain the

(21) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923.

(22) Vosburgh, *THIS JOURNAL*, **50**, 2386 (1928).

(23) This figure was arrived at by combining the heat of formation of mercurous iodide, found by Vosburgh,²² the free energy of formation of mercurous iodide computed from the results of Bates and Vosburgh, *ibid.*, **59**, 1188 (1937), and the entropies of iodine and mercury. It agrees well with 56.8 e. u. found by Ishikawa and Shibata, *Sci. Repts., Tohoku Imp. Univ.*, **17**, 107 (1928).

entropy of the anhydrous salt. Ishikawa, Kimura and Murooka²⁴ have computed the entropy of formation of cadmium chloride at 25° from vapor pressure, heats of solution and the best electromotive force data available. Their result, recalculated with the use of most recent measurements⁹ of the free energy and heat content changes in the amalgamation of cadmium, is -34.45 e. u. The entropy of cadmium chloride listed in Table V was computed from this result. Entropies of the elements and of the silver halides were taken from the excellent summary of Kelley.²⁵

TABLE V

ENTROPIES OF THE ZINC AND CADMIUM HALIDES AT 25°

ZnCl ₂ (s)	25.94	CdCl ₂ (s)	31.16
ZnBr ₂ (s)	32.95	CdBr ₂ (s)	32.02
ZnI ₂ (s)	38.52	CdI ₂ (s)	39.50

It is interesting to note that the electromotive force of cell (2) at 25° with hydrated cadmium bromide as the solid phase agrees exactly with the value of Spencer and Selden⁶ but that the temperature coefficient of the anhydrous cell differs sufficiently to yield a heat of formation for cadmium bromide of -75,390 cal., considerably different from -77,176 cal. found by these investigators, thus bringing the electromotive force and thermochemical measurements into agreement. The calorimetric value recommended by Bichowsky and Rossini,²⁶ corrected to conform with the most recent value for the heat of solution of cadmium bromide,⁶ is -75,480 cal.

For zinc chloride, Ishikawa, Kimura and Murooka⁷ obtained $\Delta H_f = -98,420$ cal. Bichowsky and Rossini²⁶ (p. 64) list a calorimetric result of -99,550, in reasonably good accord with -99,280

(24) Ishikawa, Kimura and Murooka, *Sci. Repts., Tôhoku Imp. Univ.*, **21**, 463 (1932).

(25) K. K. Kelley, *Bur. Mines. Bull.* 394, U. S. Government Printing Office, Washington, D. C., 1936.

(26) F. R. Bichowsky and F. D. Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corp., New York, N. Y., 1936, p. 67. The heats of formation quoted from this summary are at 18°.

computed from the cell electromotive forces of the present investigation.

Ishikawa and Yoshida²⁷ found -78,470 cal. for the heat of formation of zinc bromide, while the value calculated by Bichowsky and Rossini²⁶ (p. 269), using Thomsen's heat of solution, is -78,300 cal. Both results are in acceptable agreement with -78,234 cal. listed in Table IV. For zinc iodide, Ishikawa and Shibata²⁸ found -50,760 cal., and Webb²⁹ gives -49,900 cal. Both values were derived from electromotive force measurements.

By the simultaneous solution of the electromotive force-temperature equations for anhydrous and hydrated cadmium bromide, the transition temperature is found to be 36.00°. Spencer and Selden⁶ found 35.63° from their cells of type (2) and 35.82° by direct measurement. Ishikawa and Ueda⁵ studied the corresponding cell with mercurous bromide electrode. Their results indicate a change of solid phase composition at 36.0°. A similar solution of the equations for zinc bromide places the temperature of transition at 33.22°, in poor agreement with 35.04° obtained from the equations for the zinc-mercurous bromide cells of Ishikawa and Yoshida.²⁷

Summary

From electromotive force measurements of suitable reversible cells, the changes in free energy, heat content and entropy attendant upon the formation of anhydrous cadmium bromide, zinc chloride, zinc bromide and zinc iodide from their elements in the standard states have been computed. Satisfactory agreement with the best calorimetric results was obtained. The entropies of the cadmium and zinc halides have been evaluated.

NEW HAVEN, CONN.

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(27) Ishikawa and Yoshida, *Sci. Repts., Tôhoku Imp. Univ.*, **21**, 474 (1932).

(28) Ishikawa and Shibata, *ibid.*, **17**, 99 (1928).

(29) Webb, *J. Phys. Chem.*, **24**, 448 (1923).