[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

The Activity Coefficients of Cadmium Iodide[1]

BY ROGER G. BATES AND WARREN C. VOSBURGH

Cadmium iodide is of special interest as an electrolyte because its activity in solution as determined by electromotive force measurements is much less than that of the typical electrolytes of its type. Since any theory of the state of cadmium iodide in solution must take account of the activities of the cadmium and iodide ions, the stoichiometrical activity coefficients of cadmium iodide are of importance. Getman[2] has determined the activity coefficients by an electromotive force method, and this investigation was undertaken to check Getman's results by means of a different cell, namely, the cell

$$Cd(Hg)/CdI_2(m)/CdI_2(m), Hg_2I_2/Hg \qquad (1)$$
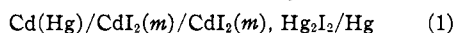
and to extend the measurements to more concentrated and more dilute solutions.

Preparation of Materials.—Mercury was distilled three times in a current of air. Cadmium amalgam containing 10% cadmium was prepared by electrolysis of a solution of recrystallized cadmium sulfate with a mercury cathode and an anode of c. p. stick cadmium. Mercurous iodide was prepared by precipitation as described by Vosburgh[3] from recrystallized mercurous nitrate and potassium iodide. The mercurous iodide was digested under water in the dark at a temperature near the boiling point for four days. It was preserved under water and used in the form of a paste. Cadmium iodide of c. p. quality was recrystallized twice. It was found that a pure white product was obtained if the water was boiled to remove dissolved gases before the cadmium iodide was dissolved and the solution not heated above 85°. A sample of the purified material

dried over phosphorus pentoxide was analyzed by an electrolytic determination of the cadmium content and also by a determination of the iodide content by the Volhard method. The two methods gave closely agreeing results, indicating that the salt had the correct composition. The results also indicated a high degree of purity.

Nitrogen gas was purified by passing through an ammoniacal cuprous salt solution[4] and two sulfuric acid solutions.

Cadmium–Mercurous Iodide Cell.—Cadmium iodide solutions a little more concentrated than desired were prepared, and weighed samples of the solutions were analyzed by the Volhard method. The solutions were then diluted to the desired molality by weight.
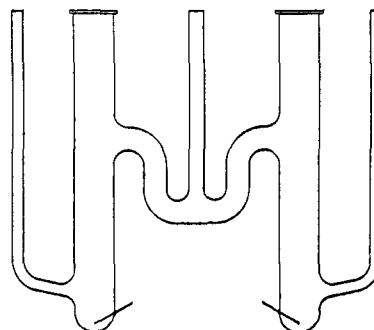

Fig. 1.—Cell vessel used in later cells.

Two types of cell vessels were used, H-shaped vessels and vessels of the type shown in Fig. 1. The latter were made of Pyrex glass with tungsten wires sealed in. Their advantage was that most of the operations in setting up the cell could be carried out entirely in an atmosphere of nitrogen, and also that mercurous iodide was prevented by the shape of the vessel from being carried over mechanically to the amalgam side of the cell.

Mercury and amalgam were placed in the cell vessel, a

(1) Part of a thesis submitted by Roger G. Bates in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University.

(2) Getman, *J. Phys. Chem.*, **32**, 940 (1928).

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

(4) Van Brunt, *ibid.*, **36**, 1448 (1914).

TABLE I

The Cell: Cd(Hg)/CdI₂(m)/CdI₂(m), Hg₂I₂/Hg

The Cell: $Cd(Hg)/CdI_2(m)/CdI_2(m), Hg_2I_2/Hg$

m	E_{25}, v.	E_{30}, v.	E_{35}, v.	$-Log\ \gamma_{25}$	$-Log\ \gamma_{30}$	$-Log\ \gamma_{35}$
0.001025[a]	0.5695	...	...	0.1217	...	...
.002043[a]	.5491	...	...	.1916	...	...
.005000	.5252	0.5296	0.5341	.3099	0.3092	0.3086
.01000	.5083	.5123	.5165	.4215	.4190	.4176
.01023[a]	.5076	...	...	.4226	...	...
.02015	.4932	.4969	.5006	.5545	.5520	.5485
.03708	.4826	.4859	.4892	.6998	.6950	.6891
.05000[a]	.4779	.4811	.4846	.7775	.7714	.7688
.1000	.46794	.47094	.47394	.9658	.9598	.9530
.1500	.46271	.46557	.46847	1.0829	1.0775	1.0698
.2500[a]	.45572	.45836	.46113	1.2260	1.2193	1.2114
.4843	.44665	.44926	.45188	1.4109	1.4054	1.3980
1.000	.43506	.43751	.44000	1.5959	1.5893	1.5834
1.448	.42792	.43032	.43276	1.6760	1.6703	1.6650
1.983	.42098	.42334	.42576	1.7342	1.7290	1.7262
2.366[a,b]	.41702	...	...	1.7668	...	...
2.404[b]	...	.41882[c]	...	...	1.7636	...
2.453[b]	...	...	.42062[c]	...	...	1.7612

[a] Cells were measured initially at 25°. [b] Saturated solutions. Solubility data for 30 and 35° taken from "International Critical Tables," Vol. IV, p. 222. [c] Electromotive forces of the saturated cell at 30 and 35° are those of Vosburgh (ref. 3).

stream of nitrogen passed through to displace the air, and the amalgam washed with several portions of oxygen-free cadmium iodide solution.[5] Mercurous iodide paste was freed of excess water on a suction filter and then washed five times by decantation with 5- to 10-ml. portions of oxygen-free electrolyte and placed above the mercury. The cadmium iodide solution was swept free of dissolved oxygen by means of a stream of nitrogen in a flask similar to the one described by MacInnes and Dole[6] and forced into the cell vessel without contact with the air. Some of the vessels were stoppered with paraffined corks and some with rubber stoppers.

The cells were placed in a constant-temperature oil-bath at 25 or 30 ± 0.02° and their electromotive forces measured frequently until constancy was assured. Constancy of electromotive force within 0.1 mv. was attained within twenty-four hours in the cells with electrolytes with a molality of 0.1 or more. In most of the cells with the more dilute electrolytes the electromotive force changed during the first two days, but remained constant within 0.2 mv. for three to seven days. The cells that were measured first at 30° were measured again at 25 and 35° but not until some of them had decreased in electromotive force appreciably. As a test of whether or not the temperature coefficients had changed, the change in electromotive force with temperature was plotted against the electromotive force at 30°. Most of the points, including some for cells that had not changed, fell on a smooth curve, and the curve was considered to give the correct relation between electromotive force and temperature. By means of this curve the electromotive forces at 25 and 35° were calculated from the accepted values at 30°. A few of the cells

were measured first at 25°. The results are given in Table I. Most of the cells were made in duplicate and the values given are the mean values. Duplicate cells with electrolytes above 0.1 m agreed within 0.05 mv. and those with more dilute electrolytes agreed within 0.2 to 0.3 mv. The cells with saturated electrolytes agreed excellently with the results of Vosburgh.[3] Two of the saturated cells prepared by Vosburgh in the earlier investigation, Nos. 525 and 526, had been preserved, and these when measured at 25° gave an electromotive force 0.02 mv. lower than their original value.

The solubility of cadmium iodide in water was determined by saturating a solution in an air-bath at 25 ± 0.05° and analyzing by the Volhard method. The solubility was found to be 2.366 moles per 1000 g. of water, this being the mean of four analyses on two saturated solutions. "International Critical Tables" gives 2.356 m at 25°.

Discussion

It is not practical to determine E^0 for the cadmium–mercurous iodide cell by extrapolation to infinite dilution, because too little is known about the composition of cadmium iodide solutions. Therefore, E^0 was calculated from the normal potentials of the cadmium amalgam and mercury–mercurous iodide electrodes. For the former 0.3518 v. at 25° was taken. This is the mean of 0.3519 v. given by Shrawder, Cowperthwaite and La Mer,[7] 0.3521 v. by Quintin[8] and 0.3515 v. by Harned and Fitzgerald.[9] For 30 and 35° the values 0.3529 and 0.3542 v. were cal-

(5) In the last few cells the evacuation procedure of Clayton and Vosburgh, THIS JOURNAL, **58**, 2095 (1936), was used in the introduction and treatment of the amalgam. These cells were somewhat more satisfactory than the others.

(6) MacInnes and Dole, ibid., **51**, 1125 (1929).

(7) Shrawder, Cowperthwaite and La Mer, ibid., **56**, 2348 (1934).

(8) Quintin, Compt. rend., **200**, 1754 (1935).

(9) Harned and Fitzgerald, THIS JOURNAL, **58**, 2627 (1936).

culated from the value at 25° with the aid of the data of Harned and Fitzgerald. For the mercurous iodide electrode the value[10] 0.0405 v. at 25° was used. For 30 and 35° the values 0.0407 and 0.0410 v. were calculated by means of the temperature coefficients of the hydrogen–silver iodide cell,[11] the lead–silver iodide cell[12] and the lead–mercurous iodide cell.[8] Combination of the two electrode potentials gives for the cadmium–mercurous iodide cell $E^0_{25} = 0.3113$ v., $E^0_{30} = 0.3122$ v. and $E^0_{35} = 0.3132$ v.

The activity coefficients were calculated by the relation

$$-k \log \gamma_t = E_t - E^0_t + k \log 4^{1/3} m$$

in which m is the stoichiometrical molality and $k = 3 \times 2.303 \, RT/2F$. The values of $-\log \gamma$ at the three temperatures are given in Table I. In Fig. 2, $\log \gamma_{25}$ is plotted against $m^{1/2}$. Curves for cadmium chloride[13] and barium chloride[14] are in-

cluded for comparison. In Table II, values of γ at even molalities are given. These were read from a large-scale graph similar to Fig. 1. The results of Getman[2] recalculated with the use of more recent electrode potential data[7,10,11] are given for comparison. Getman used two different iodide electrodes, and the agreement of the results of this investigation with those of Getman is as good as the agreement of Getman's two series of values, except in the most dilute solutions.

TABLE II

ACTIVITY COEFFICIENTS OF CADMIUM IODIDE

m	Getman (AgI) 25°	Getman (PbI₂) 25°	B. and V. (Hg₂I₂) 25°	B. and V. (Hg₂I₂) 30°	B. and V. (Hg₂I₂) 35°
0.001	...	...	0.759	....	....
.002	...	...	.649	....	....
.005	...	0.67	.490	0.491	0.491
.007	...	...	.441	.441	.442
.01	0.44	.46	.379	.381	.382
.02	.28	.30	.281	.281	.283
.05	.15	.17	.167	.169	.170
.07			.136	.138	.139
.1	.10	.11	.108	.110	.111
.2	.065	.067	.0685	.0695	.0705
.5	.037	.037	.0382	.0387	.0392
.7			.0310	.0315	.0320
1.0	.025	.025	.0254	.0257	.0261
1.3		.022	.0222	.0225	.0227
2.0			.0183	.0186	.0188
Satd.			.0171	.0172	.0173

(10) Bates and Vosburgh, THIS JOURNAL, 59, 1188 (1937).
(11) Owen, ibid., 57, 1527 (1935).
(12) Gerke, ibid., 44, 1702 (1922).
(13) Scatchard and Tefft. ibid., 52, 2272 (1930).
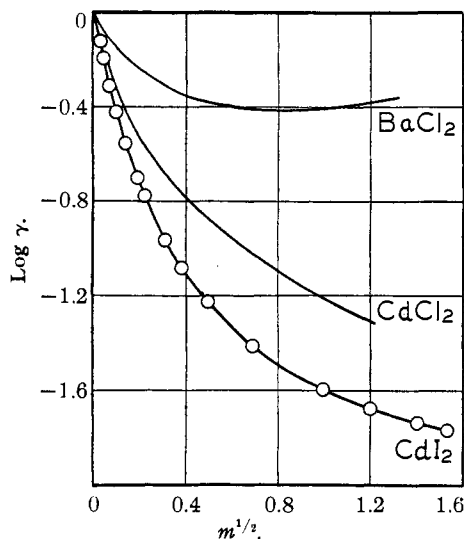(14) Tippetts and Newton, ibid., 56, 1675 (1934).

Fig. 2.—Logarithm of the activity coefficient as a function of the square root of the molality for cadmium iodide, cadmium chloride (ref. 13) and barium chloride (ref. 14).

Summary

The stoichiometrical activity coefficients of cadmium iodide in water solution have been determined from 0.001 m to saturation by means of the cadmium–mercurous iodide voltaic cell.

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