49. *Transport Numbers of Zinc Halides.*

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The transport numbers of zinc chloride, bromide, and iodide, over the following ranges of molar concentration: zinc chloride 0·01—0·33, zinc bromide 0·01—0·33, zinc iodide 0·01—0·21, have been measured by the Hittorf method. The results indicate that zinc chloride behaves as a typical 2, 1 type electrolyte over the range of molarity studied and there is no indication of the presence of complex ions. Zinc bromide behaves similarly up to 0·25M., but at higher concentrations there are indications of the presence of small quantities of complex ions. Zinc iodide has an abnormally low cation transport number even at low concentrations, and the rapid decrease of cation transport number with increase of concentration suggests that a complex ion, such as ZnI_3^-, is present.

In a previous research (J., 1943, 157) it was found that the activity coefficients of zinc iodide are those of a typical 2, 1 type electrolyte up to 0·05M., but at higher concentrations they increase rapidly with concentration. This suggests that complex ions are present in the more concentrated solutions. Further evidence of the presence of complex ions could be obtained from transport number measurements. Although much information is available for cadmium salts, few determinations of transport numbers have been made with zinc halides (Hittorf, *Ann. Physik*, 1859, **106**, 513; *Z. physikal. Chem.*, 1901, **39**, 613; 1903, **43**, 239; Bein, *Ann. Physik*, 1892, **46**, 29; *Z. physikal. Chem.*, 1898, **27**, 1; 1899, **28**, 439; Kümmell, *Ann. Physik*, 1898, **64**, 655; Drucker, *Z. Elektrochem.*, 1913, **19**, 797). The present paper deals with the transport numbers of zinc chloride, bromide, and iodide as determined by the Hittorf method.

EXPERIMENTAL.

Solutions.—Zinc chloride, bromide, and iodide solutions were prepared as previously described (J., 1943, 159). The zinc and halogen contents of all newly prepared solutions were determined gravimetrically; in subsequent experiments only the halogen was determined, except in concentrated solutions, for which both the zinc and the halogen contents were determined to confirm the absence of basic salt. In the analyses 10, 20, or 40 ml. of solution (according to the concentration) were weighed, and the halogen content determined as silver halide. Corresponding analyses agreed to within 0·0004 g. of silver halide.

Electrodes.—The anode, which was of the same pure (99·99%) zinc as was previously used, was in the form of a rod, 3·5 cm. long and 0·7 cm. in diameter, fitted with sealing wax into a glass tube which was filled with mercury; contact with the external circuit was made by a copper wire dipping into the mercury. With fairly dilute solutions unamalgamated zinc was satisfactory, but above 0·1M. a white deposit of basic salt was formed. In order to prevent this, the zinc electrodes were amalgamated by placing them in mercurous nitrate solutions containing 5% of nitric acid for half an hour. All solutions were kept air-free by storage in completely filled stoppered bottles. No deposit formed on the amalgamated electrodes within the concentration range studied, and they were used throughout this research.

Pure mercury was used as the cathode. In dilute solutions (below 0·1M.), the zinc was deposited on the mercury in a sparingly soluble form, whilst that from more concentrated solutions was much more soluble. A similar phenomenon was noticed by Hittorf (*loc. cit.*) with cadmium salts.

Cells.—The electrolytic cell was a slight modification of that described by Findlay (*Chem. News*, 1909, **100**, 185; "Practical Physical Chemistry," 1941, p. 189). It consisted of similar anode and cathode compartments joined to a central U-tube (middle compartment) by rubber tubing. Each limb had a bulb at the lower end to reduce the resistance, and the anode and middle compartments each had an exit tube at the bottom, fitted with rubber tubing and a screw clip. The open end of this rubber tubing was closed by a piece of glass rod to prevent ingress of water from the thermostat. The cathode compartment was without an exit tube at the bottom. This form of the apparatus can be used in a water thermostat, and so has an advantage over one with glass stopcocks. The side arms and U-tube were 1·8 cm. in diameter, and were joined by pieces of soft black rubber tubing, which was previously boiled in distilled water for 15 minutes. If the side arms or rubber tubing are too narrow, heating occurs at these points owing to the increased resistance.

Current from the mains (220 or 110 volts) was passed through a suitable resistance.

Coulometer.—The quantity of electricity passing was measured by a silver coulometer. The cathode of this consisted of a platinum dish of 80 ml. capacity, cleaned with nitric acid, washed with water, and dried at 140°. The anode was a thick wire of pure silver, wound in a horizontal coil, and enclosed in a bag of filter-paper secured by sewing-cotton which had been boiled for some time in distilled water. The function of the filter paper is to retain the anode slime. The use of filter-paper was recommended by Rayleigh and Sidgwick (*Phil. Trans.*, 1884, **175**, 411), but disapproved by Richards, Collins, and Heimrod (*Z. physikal. Chem.*, 1900, **32**, 321), who used a small porous pot. The influence of good, unsized paper on the results is probably quite negligible. Pure silver nitrate was recrystallised from a solution slightly acidified with nitric acid, and a 15% solution was stored in a dark bottle. The platinum dish stood on a glass plate, and the coulometer was enclosed in a box to exclude light during the experiment. After the experiment the dish with the silver deposit was washed with distilled water, filled with water and left overnight, and finally rinsed with alcohol and dried at 140°.

Experimental Procedure.—The silver coulometer and a milliammeter (to give an approximate measure of the current strength) were joined in series with the cell. The thermostat stirrer must operate rather slowly so as not to cause vibration of the transport apparatus. All measurements were made at 25°. The cell was filled with zinc halide solution of known concentration, and a current of 0·01—0·04 amp. was passed through the circuit for 1½—3 hours, the current strength and duration of the experiment depending on the concentration of the solution. If the current strength is too high, heating and convection currents are produced, causing mixing in the solution, and if the experiment is continued too long the middle solution will have changed in composition. At the end of the experiment the screw clips on the U-tube rubber were closed, the apparatus removed from the thermostat, and the liquid in the anode compartment run into a weighed flask; the compartment was rinsed with some of the original solution, and the total amount of liquid weighed and analysed. The solution in the middle compartment was withdrawn and analysed, and if it had changed in composition the experiment was rejected. In several cases the cathode solution was also analysed, but this did not give satisfactory results, probably owing to the difficulty of washing the mercury and zinc deposit to remove all the solution.

Experimental Results.—The cation transport number is given by

$$n_c = \frac{\text{No. of equivalents of zinc lost from anode compartment}}{\text{No. of equivalents of silver deposited in coulometer}}$$

The analyses of the solutions are given in Tables I, III, and V. Col. 1 gives the molarity of the solution, cols. 3 and 2 the weight of silver halide produced from x g. of zinc halide solution before the experiment, and col. 4 the weight of zinc associated with 1 g. of water. Cols. 5, 6, and 7 give similar analytical data for the anode solution after electrolysis, and 8 and 9 the middle solution analyses. Details of the experiments, and the transport numbers obtained, are given in Tables II, IV, and VI, in which col. 1 gives the molarity, cols. 2 and 3 the mean current strength and the duration of the experiment (in minutes), respectively, 4 the weight of silver deposited in the coulometer, 5 the weight of the anode solution, and 6 and 7 the zinc contents of the anode solution before and after electrolysis, respectively. The cation transport number is given in the last column, and a graph of n_c against molarity is given in the figure.

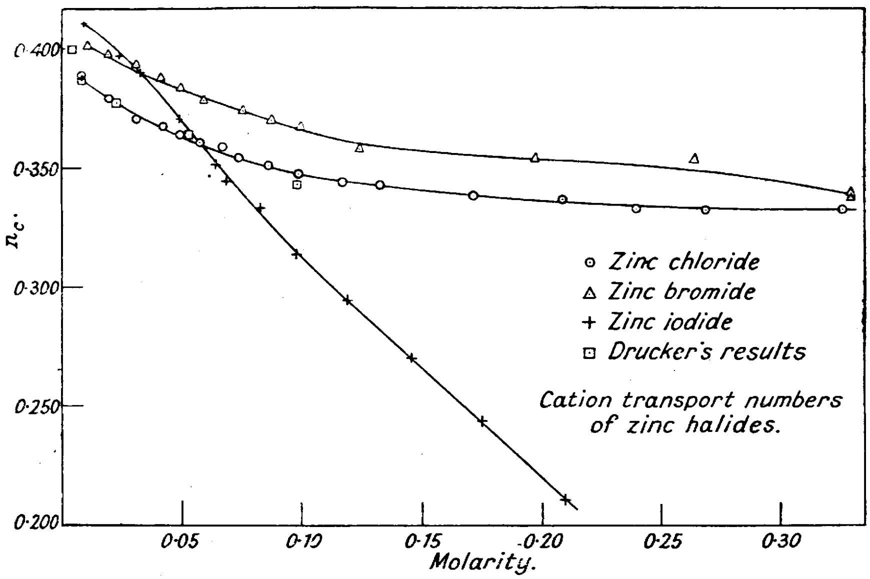

TABLE I.

Zinc Chloride.

Analyses of solutions.

	Anode solution before expt. Weight of AgCl from x g. of solution.			Anode solution after expt. Weight of AgCl from x g. of solution.			Middle solution. Weight of AgCl from x g. of solution.	
Molarity.	x.	AgCl.	Wt. of Zn ≡ 1 g. of H_2O.	x.	AgCl.	Wt. of Zn ≡ 1 g. of H_2O.	x.	AgCl.
0·3271	20·74	1·8753	0·021545	10·40	0·9870	0·022667	10·38	0·9379
				10·39	0·9875	0·022697	10·37	0·9375
0·2800	20·62	1·6056	0·18463	10·33	0·8389	0·019264	10·32	0·8033
				10·33	0·8389	0·019264	10·31	0·8027
0·2102	20·46	1·2052	0·013817	10·24	0·62875	0·14424	10·23	0·6030
				10·25	0·6310	0·14459	10·22	0·6021
0·1724	20·35	0·9886	0·011340	20·37	1·0403	0·011938	20·36	0·9889
				20·36	1·0390	0·011928	20·35	0·9880
0·1500	20·29	0·86025	0·0098682	20·30	0·90305	0·010364	20·28	0·8607
				20·31	0·9000	0·010323	20·28	0·86025
0·1344	20·26	0·77065	0·0088359	20·27	0·8089	0·0092797	20·27	0·7704
				20·27	0·80915	0·0092797	20·26	0·7709
0·0986	20·18	0·5654	0·0064764	20·22	0·59665	0·0068256	20·17	0·5658
				20·23	0·59655	0·0068203	20·18	0·5651
0·0862	20·15	0·4943	0·0056590	20·18	0·5218	0·0059707	20·16	0·4950
				20·19	0·5214	0·0059634	20·16	0·4950
0·0750	20·125	0·4300	0·0049229	20·17	0·4568	0·0052211	20·13	0·4304
				20·16	0·4582	0·0052400	20·14	0·4296
0·0672	20·104	0·3853	0·0044088	20·15	0·4103	0·0046903	20·12	0·3849
				20·14	0·4115	0·0047599	20·11	0·3852
0·0581	20·07	0·3332	0·0038167	20·13	0·3590	0·0041020	20·09	0·3336
				20·125	0·35965	0·0041105	20·08	0·3329
0·0500	20·06	0·2867	0·0032817	20·16	0·31225	0·0035585	20·11	0·2865
				20·155	0·3121	0·0035578	20·14	0·2872
0·0431	20·05	0·24715	0·0028282	20·14	0·27045	0·0030819	20·05	0·2469
				20·14	0·2719	0·0030987	20·045	0·2470
0·0327	20·02	0·1876	0·0021467	20·10	0·2073	0·0023637	20·03	0·1877
				20·09	0·20835	0·0023772	20·03	0·1881
0·0210	39·98	0·24085	0·0013777	40·02	0·27445	0·0015692	39·99	0·2406
				40·03	0·27225	0·0015562	40·00	0·2410
0·0097	39·92	0·11065	0·0006328	40·01	0·13862	0·0007914	39·92	0·1108
				39·99	0·14065	0·0008030	39·92	0·1105

TABLE II.—*Zinc Chloride.*

Transport experiment results.

Molarity.	Current (amps.).	Time (mins.).	Ag deposited in coulometer, g.	Wt. of anode solution, g.	Wt. of Zn, g., in anode solution, before expt.	after expt.	n_c.	
0·3271	0·05	150	0·50115	92·38	1·9004	1·9995	0·3222	0·333
	0·05	155	0·51760	95·02	1·9548	2·0593	0·3337	
0·2800	0·045	120	0·3621	95·02	1·6867	1·7597	0·3348	0·333
	0·045	120	0·35445	93·39	1·6577	1·7295	0·3315	
0·2102	0·04	105	0·27215	92·72	1·2437	1·2984	0·3368	0·337
	0·04	115	0·2805	89·86	1·2053	1·2616	0·3376	
0·1724	0·03	125	0·25165	86·33	0·95519	1·0055	0·3392	0·338
	0·03	130	0·2519	86·33	0·97742	1·0281	0·3360	
0·1500	0·03	105	0·21035	86·755	0·83802	0·88016	0·3389	0·341
	0·03	105	0·2029	90·79	0·87708	0·91751	0·3423	
0·1344	0·025	110	0·1927	88·89	0·77050	0·80903	0·3417	0·342
	0·025	110	0·19385	88·70	0·76890	0·80754	0·3422	
0·0986	0·02	115	0·1487	85·41	0·54537	0·57478	0·3473	0·347
	0·02	120	0·1521	89·35	0·57056	0·60088	0·3462	
0·0862	0·02	105	0·13425	85·835	0·47975	0·50618	0·3503	0·351
	0·02	105	0·1368	89·32	0·49922	0·52609	0·3518	
0·0750	0·02	105	0·1347	89·28	0·43479	0·46114	0·3545	0·355
	0·02	100	0·13555	84·42	0·41111	0·43759	0·3560	
0·0672	0·02	100	0·1308	90·99	0·39728	0·42264	0·3601	0·361
	0·02	100	0·1298	85·50	0·37331	0·39842	0·3616	
0·0581	0·015	135	0·1279	86·94	0·32899	0·35359	0·3653	0·363
	0·015	135	0·12855	85·27	0·32269	0·34756	0·3616	
0·0500	0·02	100	0·1225	85·93	0·27993	0·30353	0·3641	0·365
	0·02	100	0·1297	90·90	0·29611	0·32102	0·3662	
0·0431	0·015	120	0·1178	89·50	0·25151	0·27407	0·3680	0·369
	0·015	120	0·1193	84·76	0·23817	0·26098	0·3691	
0·0327	0·015	100	0·10155	89·54	0·19127	0·21060	0·3718	0·372
	0·015	105	0·1047	86·78	0·18536	0·20528	0·3722	
0·0210	0·01	135	0·0899	88·54	0·12159	0·13847	0·3804	0·379
	0·01	135	0·09125	85·65	0·11763	0·13285	0·3772	
0·0097	0·015	80	0·0791	92·26	0·058290	0·072895	0·3907	0·390
	0·010	105	0·0823	89·48	0·056532	0·071767	0·3891	

TABLE III.—*Zinc Bromide.*

Analyses of solutions.

	Anode solution before expt.			Anode solution after expt.			Middle solution.	
	Weight of AgBr from *x* g. of solution.			Weight of AgBr from *x* g. of solution.			Weight of AgBr from *x* of solution.	
Molarity.	*x*.	AgBr.	Wt. of Zn ≡ 1 g. of H_2O.	*x*.	AgBr.	Wt. of Zn ≡ 1 g. of H_2O.	*x*.	AgBr.
0·3291	10·64	1·2359	0·021727	10·66	1·2771	0·022468	10·64	1·23585
				10·645	1·2702	0·022390	10·635	1·2360
0·3268	10·62	1·2272	0·021611	10·66	1·2901	0·022718	10·615	1·2266
				10·665	1·3017	0·022924	10·62	1·2278
0·2650	10·51	0·9950	0·017454	10·53	1·0377	0·018234	10·51	0·9945
0·1984	10·38	0·7446	0·013049	10·39	0·7806	0·013690	10·39	0·7446
				10·415	0·8003	0·014022	10·39	0·7450
0·1251	10·245	0·4689	0·0081919	10·245	0·4955	0·0086702	10·23	0·4689
				10·25	0·4940	0·0087226	10·24	0·4687
				10·235	0·4928	0·0086137	10·23	0·4683
0·1016	20·33	0·7628	0·0066823	20·34	0·8313	0·0072932	10·17	0·3812
				20·36	0·7904	0·0069193	10·17	0·3814
				20·33	0·7930	0·0069522	10·165	0·3814
0·0872	20·225	0·6552	0·0057120	20·25	0·6968	0·0061174	20·23	0·6558
				20·25	0·6918	0·0060716	20·23	0·6552
0·0760	10·12	0·2855	0·0049945	20·24	0·6020	0·0052715	20·23	0·5714
				20·22	0·6054	0·0053068	20·22	0·5713
0·0601	20·11	0·4513	0·0039595	20·16	0·4795	0·0042005	20·12	0·4513
				20·14	0·4812	0·0042195	20·12	0·4513
0·0499	20·13	0·3749	0·0032786	20·13	0·3987	0·0034893	20·13	0·3747
				20·13	0·4071	0·0035555	20·12	0·3754
0·0410	20·07	0·3081	0·0026969	20·09	0·3311	0·0028977	20·07	0·30825
				20·08	0·3343	0·0029277	20·06	0·3070
0·0310	20·04	0·2326	0·0020342	20·06	0·2543	0·0022238	20·04	0·2330
				20·06	0·2532	0·0022139	20·05	0·2328
0·0201	40·02	0·3011	0·0013186	40·06	0·3408	0·0014884	20·00	0·1506
				40·00	0·3345	0·0014303	20·00	0·1507
0·0119	19·97	0·0891	0·0007786	19·96	0·1005	0·0008790	19·96	0·0890
				19·93	0·0969	0·0008488	19·96	0·0887

TABLE IV.—*Zinc Bromide.*

Transport experiment results.

Molarity.	Current (amps.).	Time (mins.).	Ag deposited in coulometer, g.	Wt. of anode solution, g.	Wt. of Zn, g., in anode solution, before electrolysis.	Wt. of Zn, g., in anode solution, after electrolysis.	n_e.	
0·3291	0·03	160	0·3191	92·62	1·8679	1·9315	0·3422	0·341
	0·03	140	0·28955	94·17	1·8996	1·9575	0·3401	
0·3268	0·05	150	0·4974	96·81	1·9402	2·0395	0·3412	0·339
	0·05	150	0·4986	82·41	1·6507	1·7508	0·3375	
0·2650	0·035	145	0·34375	91·75	1·5068	1·5741	0·3539	0·354
0·1984	0·025	150	0·2618	83·02	1·0346	1·0856	0·3571	0·356
	0·04	143	0·38575	81·36	1·0127	1·0882	0·3541	
0·1251	0·022	135	0·19885	83·15	0·66142	0·70003	0·3593	0·358
	0·022	130	0·1896	85·17	0·67756	0·71453	0·3565	
	0·022	125	0·1881	89·43	0·71146	0·74809	0·3573	
0·1016	0·04	95	0·2542	81·95	0·53417	0·58301	0·3675	0·368
	0·02	90	0·11665	94·49	0·62973	0·65206	0·3682	
	0·02	95	0·12385	90·03	0·58750	0·61126	0·3669	
0·0872	0·025	100	0·1612	85·87	0·48368	0·51448	0·3694	0·371
	0·02	100	0·13475	81·84	0·46101	0·48669	0·3716	
0·0760	0·02	100	0·1299	90·38	0·44336	0·46795	0·3754	0·375
	0·02	100	0·13655	84·33	0·41366	0·43951	0·3753	
0·0601	0·02	85	0·1137	90·33	0·35255	0·37401	0·3772	0·377
	0·02	85	0·1130	83·14	0·32448	0·34580	0·3774	
0·0499	0·015	95	0·0950	84·98	0·27529	0·29299	0·3851	0·384
	0·02	100	0·1348	89·57	0·29008	0·31530	0·3826	
0·0410	0·017	80	0·0887	82·80	0·22109	0·23757	0·3868	0·388
	0·017	90	0·10185	82·63	0·22061	0·23948	0·3886	
0·0310	0·018	75	0·0897	87·46	0·17658	0·19300	0·3959	0·393
	0·015	80	0·0783	81·06	0·16368	0·17811	0·3919	
0·0201	0·015	85	0·08625	93·365	0·12248	0·13826	0·3963	0·398
	0·015	55	0·0543	86·85	0·11656	0·12646	0·3988	
0·0119	0·01	65	0·04425	80·05	0·06214	0·07015	0·4026	0·402
	0·01	45	0·03095	82·32	0·06236	0·06998	0·4010	

TABLE V.—*Zinc Iodide.*

Analyses of solutions.

Molarity.	Anode solution before expt. Weight of AgI from *x* g. of solution. *x*.	AgI.	Wt. of Zn ≡ 1 g. of H_2O.	Anode solution after expt. Weight of AgI from *x* g. of solution. *x*.	AgI.	Wt. of Zn ≡ 1 g. of H_2O.	Middle solution. Weight of AgI from *x* g. of solution. *x*.	AgI.
0·2106	10·61	0·9889	0·014230	10·67	1·0732	0·0150310	10·615	0·9893
				10·665	1·0701	0·0149920	10·61	0·9887
0·1768	10·515	0·8302	0·0116130	10·54	0·88165	0·0123480	10·52	0·8306
				10·54	0·8801	0·0123260	10·515	0·8303
0·1467	10·42	0·6889	0·0096374	10·44	0·73465	0·0102890	10·42	0·6892
				10·445	0·7359	0·0103020	10·415	0·6888
0·1197	10·31	0·5620	0·0078819	10·35	0·60905	0·0085342	10·305	0·5617
				10·355	0·6121	0·0085740	10·31	0·5621
0·1020	10·265	0·4790	0·0067098	10·29	0·5163	0·0072324	10·27	0·4792
0·0998	10·259	0·4687	0·0065648	10·27	0·4917	0·0068902	10·26	0·4685
				10·27	0·5019	0·0070361	10·255	0·46855
0·0961	10·245	0·4513	0·0063225	10·27	0·4840	0·0067788	10·25	0·4519
0·0880	10·225	0·4134	0·005703	10·24	0·4422	0·0061940	10·22	0·4131
0·0831	10·22	0·3901	0·0054584	10·24	0·4370	0·0061185	10·225	0·3900
				10·24	0·4361	0·0061058	10·22	0·3896
0·0728	10·18	0·3417	0·0047809	10·20	0·3674	0·0051405	10·18	0·3421
0·0702	10·175	0·3294	0·0046089	10·19	0·3551	0·0049700	10·17	0·3291
				10·19	0·3544	0·0049601	10·18	0·3298
0·0648	10·17	0·3045	0·0042564	10·18	0·3299	0·0046140	10·17	0·30445
				10·18	0·3337	0·0050016	10·165	0·3047
0·0503	20·20	0·4724	0·0033081	20·225	0·5051	0·0035371	20·21	0·4726
				20·22	0·50965	0·0035704	20·20	0·4729
0·0397	10·094	0·1863	0·0026285	10·10	0·1999	0·0027932	10·09	0·1859
0·0331	20·10	0·3104	0·0021726	20·10	0·3352	0·0023482	20·09	0·3098
				20·12	0·33945	0·0023718	20·09	0·3105
0·0256	10·061	0·1205	0·0016808	10·075	0·1324	0·0018463	10·06	0·12055
0·0256	20·05	0·2405	0·0016833	20·075	0·2605	0·0018220	20·05	0·24115
				20·075	0·2615	0·0018298	20·10	0·2403
0·0109	20·00	0·1021	0·0007132	20·015	0·1143	0·0007981	20·00	0·1017
				20·015	0·1148	0·0008017	20·05	0·1020

TABLE VI.

Zinc Iodide.

Transport experiment results.

Molarity.	Current (amps.).	Time (mins.).	Ag deposited in coulometer, g.	Wt. of anode solution, g.	Wt. of Zn, g., in anode solution, before electrolysis.	after electrolysis.	n_c.	
0·2106	0·04	115	0·2785	89·36	1·1846	1·2514	0·2084	0·210
	0·04	105	0·2539	85·50	1·1337	1·1944	0·2110	
0·1768	0·04	105	0·2680	88·67	0·97120	1·0327	0·2427	0·244
	0·04	100	0·24045	81·72	0·89513	0·95007	0·2459	
0·1467	0·03	125	0·2377	84·775	0·77794	0·83048	0·2727	0·271
	0·03	125	0·23305	81·57	0·74841	0·80006	0·2686	
0·1197	0·03	125	0·2436	83·45	0·63142	0·68366	0·2925	0·294
	0·03	130	0·2537	81·57	0·61708	0·67125	0·2954	
0·1020	0·025	130	0·2132	88·22	0·57174	0·61626	0·3123	
0·0998	0·028	85	0·1569	103·20	0·65542	0·68791	0·3166	0·315
	0·028	115	0·1874	85·21	0·54080	0·57975	0·3140	
0·0961	0·03	90	0·1768	82·56	0·50523	0·5417	0·3192	0·323
0·0880	0·025	110	0·1839	95·70	0·53786	0·57536	0·3271	
0·0831	0·026	170	0·2664	84·23	0·44643	0·50043	0·3311	0·330
	0·026	160	0·2443	79·075	0·41915	0·46887	0·3284	
0·0728	0·02	115	0·1491	85·49	0·39875	0·42873	0·3365	
0·0702	0·025	95	0·15655	88·10	0·39641	0·42748	0·3449	0·344
	0·025	95	0·15960	92·765	0·41744	0·44925	0·3423	
0·0648	0·020	110	0·1435	80·85	0·33656	0·36482	0·3492	0·351
	0·022	115	0·1660	80·85	0·3347	0·36900	0·3533	
0·0503	0·022	75	0·10435	88·25	0·28698	0·30685	0·3716	0·371
	0·02	90	0·11455	84·92	0·27611	0·2980	0·3697	
0·0397	0·02	75	0·0835	96·54	0·25034	0·26603	0·3799	
0·0331	0·017	75	0·08085	85·82	0·18435	0·19925	0·3919	0·391
	0·02	70	0·0940	86·31	0·18536	0·20274	0·3902	
0·0256	0·01	110	0·0738	81·99	0·13659	0·15003	0·3990	
0·0256	0·016	65	0·0682	88·96	0·14842	0·16072	0·3956	0·397
	0·016	65	0·0673	84·43	0·14086	0·15313	0·3983	
0·0109	0·01	60	0·0401	84·55	0·060065	0·067217	0·4114	0·412
	0·01	60	0·0423	85·43	0·060695	0·068228	0·4123	

DISCUSSION OF RESULTS.

The curves n_c–M for zinc chloride and bromide resemble those for calcium chloride (Longsworth, *J. Amer. Chem. Soc.*, 1934, **57**, 1185; cf. Drucker and Luft, *Z. physikal. Chem.*, 1926, **121**, 307), barium chloride (Jones and Dole, *J. Amer. Chem. Soc.*, 1929, **51**, 1073), and cadmium chloride (Jahn, *Z. physikal. Chem.*, 1901, **37**, 673). The cation transport number of the chloride from 0·01 to 0·1M. decreases; after 0·1M. the decrease is very small. The cation transport number of the bromide begins to decrease rather more rapidly at about 0·25M., and it is possible that complex ions are present in these concentrated solutions. In the case of zinc chloride up to 0·33M., and zinc bromide up to 0·25M., there is no indication of the presence of complex ions. The results for the chloride agree well with those of Drucker (*loc. cit.*). The cation transport number of zinc iodide, on the contrary, varies considerably with concentration, and the n_c–M curve resembles that for cadmium iodide (Jahn, *loc. cit.*). This result was expected from the activity coefficients reported in the previous paper, and indicates that complex ions are present in solutions of quite low concentration, probably down to 0·03M. The marked fall in cation transport number with increasing concentration indicates the formation of complex anions and a negative value may ultimately be reached. Hittorf (*loc. cit.*) found that the cation transport numbers in concentrated zinc and cadmium iodide solutions were negative, and concluded that complex ions $(ZnI_4)^{--}$, $(CdI_4)^{--}$, respectively, are present. Jahn (*loc. cit.*) found similar results with cadmium iodide. McBain (*Z. Elektrochem.*, 1905, **11**, 215) correlated the transport, conductivity, and freezing-point data of previous workers for cadmium iodide, and concluded that a complex anion, probably $(CdI_3)^-$, is present, except in rather dilute solutions. Later (*J. Physical Chem.*, 1931, **34**, 999), McBain made transport measurements with cadmium chloride, bromide, and iodide, and in the last case attempted to calculate the amounts of the various possible ions present.

In this research the cation transport numbers of zinc iodide show a marked decrease with increase of concentration, and this, when correlated with the E.M.F. results, makes probable the existence of $(ZnI_3)^-$ or $(ZnI_4)^{--}$, or perhaps both, but it is a matter of difficulty to distinguish between the two. Bates and Vosburgh (*J. Amer. Chem. Soc.*, 1938, **60**, 137) concluded from E.M.F. measurements with cadmium iodide that the complex anion is $(CdI_3)^-$, and McBain (*loc. cit.*) considered that $(CdI_3)^-$ is much more likely than $(CdI_4)^{--}$, since the latter would be a large ion which would have a correspondingly low velocity, and would not readily account for the observed conductivity and transference data. It seems probable that the complex anion in the case of zinc iodide is also $(ZnI_3)^-$, though the possibility of $(ZnI_4)^{--}$ cannot be ruled out.

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