[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

THE TRANSFERENCE NUMBERS OF CADMIUM CHLORIDE AND BROMIDE

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The transference numbers of an electrolyte can be calculated from the results of measurements of concentration cells with liquid junction if the activity coefficient of the electrolyte is known as a function of the concentration. In the present paper are given values of the electromotive force of cells of the type

$$\mathrm{Ag} \mid \mathrm{AgX} \mid \mathrm{CdX_2}\ (0.1\ M) \mid \mathrm{CdX_2}\ (m) \mid \mathrm{AgX} \mid \mathrm{Ag}$$

in which X represents the chloride or bromide ion, and m is varied from 0.01 to 6 M and from 0.01 to 3 M, respectively. The preceding paper gives values of the activity coefficient over these concentration ranges.

The solutions were the same as those used in measuring the cells without liquid junction and the electrodes were made up in the same manner. The cells used were the same as those in a previous study[1] and consisted of three parts, the middle compartment containing an approximately one-to-one mixture of the solutions surrounding the electrodes in the end compartments. In each case about four hours were allowed to elapse between the time the cell was introduced into the thermostat and the time of taking the first reading. From four to six readings were then taken at half-hour intervals, the mean of which was accepted as the value of the cell. The variation in these readings was always very slight, seldom more than a few hundredths of a millivolt. All measurements were made at 25 ± 0.01°.

In Col. 3 of Table I are given the values of the electromotive force of the above cell at the molality (moles of salt per 1000 g. of water) given in the first column. To facilitate comparison the corresponding normal concentrations (equivalents per liter of solution) are given in the second column.

The method used in calculating the transference numbers was the same as that for the alkaline earth chlorides[2] which, although a somewhat disadvantageous modification of the method of MacInnes and Beattie,[3] was

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[1] Lucasse, *J. Phys. Chem.*, **30**, 562 (1926).

[2] Lucasse, THIS JOURNAL, **47**, 743 (1925). See, however, Jones and Dole, *ibid.*, **51**, 1073 (1929). In the present case a method depending upon algebraic analysis, although highly desirable, would be more difficult of application than in the case of barium chloride, in part because of the failure to find a suitable relationship between the concentration and the activity. The dangers inherent in the graphical method have been reduced to some extent by taking into account also the ratios of the electromotive force values of the two types of cells between each concentration interval. The form of the curve and the accuracy of the values, especially below 1 M, are as nearly true, it would seem, as can be obtained from the data at the present time.

[3] MacInnes and Beattie, *ibid.*, **42**, 1117 (1920).

TABLE I

THE TRANSFERENCE NUMBERS OF CADMIUM CHLORIDE

m	N	E_t	Log A	t_+
(0.01)	0.0199	+(0.02670)	0.90227	0.486
.01010	.0201	+ .02652	0.90655	.485
.02015	.0401	+ .01766	1.11461	.466
.03030	.0603	+ .01290	1.22994	.460
.05056	.101	+ .00729	1.36847	.463
.06968	.139	+ .00382	1.45025	.472
.08145	.162	+ .00214	1.48996	.479
.1000	.199	.00000	1.54108	.487
.2014	.399	− .00697	1.70062	.498
.3027	.599	− .01067	1.78895	.494
.5101	1.00	− .01523	1.89059	.471
.6908	1.35	− .01747	1.94315	.445
.7962	1.55	− .01859	1.97095	.425
.9999	1.93	− .02033	2.01368	.386
2.045	3.82	− .02459	2.13450	.241
4.227	7.32	− .02736	2.27393	.002
5.133	8.62	− .02712	2.32613	−.104
6.146	10.0	− .02653	2.36940	−.192

here employed for the same reasons as given in the earlier paper. For a bi-univalent electrolyte the transference number of the cation is related to the electromotive force of a cell of the above type and the activity by the equation

$$\mathrm{d}E_t = -t_+ \frac{3RT}{2F} \mathrm{d} \ln a_\pm$$

The values of E_t were therefore plotted on a large scale as ordinates against the values of log A, at the corresponding concentrations, given in Col. 4. These latter (log A = 1000 log $a_\pm$) were obtained from the preceding paper. The slope of the curve ($\mathrm{d}E_t/\mathrm{d}$ log A) at each value of log A was then determined graphically and divided by the constant factor $3RT/2F$ (*i. e.*, 0.088733). Finally, the values of the transference number thus obtained were plotted against log A and the values given in the last column of the table read directly from the smooth curve passing through the points.

In Table II are given the results obtained from the cells containing cadmium bromide. The column headings have the same significance as in the previous table.

Data at 25° with which to compare these results are very meager. However, Jahn and his associates have made a number of measurements of the transference numbers of cadmium chloride, bromide and iodide at 18° in solutions from about 0.005 to about 1 N by gravimetric methods.[4] His highest concentration for the bromide is about 1.1 N and up to this point the agreement is very satisfactory. Beyond this point the values continue to decrease, passing through zero at about 2.7 N to negative

[4] Jahn, *Z. physik. Chem.*, **37**, 673 (1901).

TABLE II

THE TRANSFERENCE NUMBERS OF CADMIUM BROMIDE

m	N	E_t	Log A	t_+
0.01000	0.0199	+0.02294	0.87829	0.434
.01386	.0276	+ .01943	0.97493	.434
.01993	.0397	+ .01538	1.07555	.434
.02801	.0558	+ .01188	1.16909	.433
.03997	.0796	+ .00832	1.26174	.430
.05629	.112	+ .00508	1.34733	.424
.08114	.161	+ .00176	1.43632	.415
.1000	.199	.00000	1.48173	.408
.1378	.273	− .00264	1.55206	.395
.2026	.401	− .00529	1.63114	.371
.2724	.537	− .00714	1.68895	.343
.4069	.798	− .00915	1.75959	.290
.5444	1.06	− .01031	1.81164	.222
.8056	1.55	− .01132	1.88497	.115
.9996	1.91	− .01169	1.92480	.066
1.314	2.48	− .01178	1.97248	.015
1.896	3.49	− .01164	2.05843	− .068
3.0815	5.38	− .01000	2.18070	− .185

values. This is not surprising in view of the tendency of these salts to form complex ions. The values for cadmium iodide pass through zero at a concentration of about one-half normal.

The agreement for cadmium chloride is less satisfactory. Jahn's results for this salt cover the range from about 0.006 to 0.12 N and vary irregularly between 0.427 and 0.432, from which Noyes and Falk[5] give the constant value over this range of 0.430 in their table of "best values." Throughout this range the values here determined are much higher and, furthermore, pass through a minimum. Beyond 0.12 N they rise to a maximum, after which they fall continuously, passing through zero at about 7.4 N to negative values. If these inflection points are erroneous the values of the cation transference number from these results remain practically constant at about 0.480 up to about normal concentration, after which they decrease continuously. Although the deviation of the E_t-log A curve from a straight line is very slight, it seems nevertheless too great in view of the number of points determined in this region to attribute to experimental error. The peculiar variation of the transference numbers of cadmium chloride in dilute solutions may perhaps better be assigned to changes in the nature of the ionic complexes in this region.

It would appear from Jahn's values for cadmium bromide that at concentrations below those compared here the transference numbers may have had smaller values, indicating a minimum at low concentrations.

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[5] Noyes and Falk, THIS JOURNAL, **33**, 1436 (1911).

Of this however it is impossible to be certain because of the small number of points and the experimental difficulties at high dilutions. In addition to this possible peculiarity of the transference numbers of the cadmium halides is the fact that all, as indicated above, pass to negative values at high concentrations. Again, while it is the general rule that values below 0.5 approach this quantity with increasing temperature, the results of Bein[6] on cadmium chloride would indicate that here too we find exceptional behavior, the values rising to markedly greater than 0.5.

Summary

Measurements at 25° of cadmium chloride and bromide concentration cells with liquid junction have been given at concentration ranges from 0.01 to 6 *M* and from 0.01 to 3 *M*, respectively.

From these data and the results from cells without liquid junction, the cation transference numbers of the salts have been calculated.

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THE HEAT OF ADSORPTION OF GASES BY SOLIDS

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Recently a number of measurements have been published for the heat of adsorption of gases by solids, showing a marked change of the heat with the amount of gas adsorbed. This change can be either a decrease[1] or an increase.[2] The first case can easily be explained by assuming the presence of spots with different affinity in the solid.[3] The spots with the higher affinity will adsorb the first part of the gas, and will in general give off larger amounts of heat. To give a more detailed description of these sensitive spots Taylor[2,4] has pointed out that the surface of metals used in adsorption experiments is very rough. The atoms lying on the top of a small hill will be bound less strongly to their surroundings than the atoms in a flat surface. Accordingly they will have more of their chemical affinity left free to bind the atoms of the adsorbed gas in analogy to an idea familiar in organic chemistry. In the case of heteropolar salts as adsorbing substance, Kossel[5] has shown by direct calculation that the

[6] Bein, *Z. physik. Chem.*, **27**, 1 (1898).

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[1] See F. Goldmann and M. Polanyi, *ibid.*, **132**, 321 (1927).

[2] H. S. Taylor, *J. Phys. Chem.*, **30**, 145 (1926); G. B. Kistiakowsky, E. W. Flosdorf and H. S. Taylor, THIS JOURNAL, **49**, 2200 (1927); W. E. Garner and D. McKie, *J. Chem. Soc.*, 2451 (1927).

[3] I. Langmuir, THIS JOURNAL, **38**, 221 (1916); **39**, 1848 (1917); **40**, 1361 (1918).

[4] H. S. Taylor and G. B. Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927).

[5] W. Kossel, *Gott. Nach.*, 135 (1927).