ACTIVITY COEFFICIENTS AND TRANSFERENCE NUMBERS OF THE ALKALINE EARTH CHLORIDES

BY WALTER W. LUCASSE

The activity coefficient and transference numbers of a salt may readily be calculated from the results of measurements of the electromotive force of cells of the proper type without and with liquid junction. The present paper gives values for these quantities resulting from measurements of cells of the type,

$$Ag \mid AgCl \mid MeCl_2 \ (c) \mid Me(Hg)x \mid MeCl_2 \ (0.01 \ M) \mid AgCl \mid Ag$$

and of the type,

$$Ag \mid AgCl \mid MeCl_2(c) \mid MeCl_2 \ (0.01)M \mid AgCl \mid Ag$$
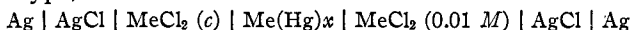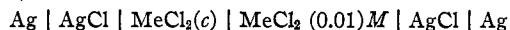
where Me represents barium, strontium and calcium, successively. All measurements were made at $25° \pm 0.01$.

The Activity Coefficients

The activity coefficients of aqueous solutions of barium chloride have been calculated up to 0.1 M by Lewis and Linhart[1] from the freezing-point data of Hall and Harkins.[2] These values are valid only at the freezing points of the solutions. The activity coefficients can also be calculated from measurements of the electromotive force of cells without liquid junction. No data are available, however, relative to such measurements for the alkaline-earth chlorides nor have the values of the activity coefficients for strontium and calcium chlorides been calculated from other types of measurement. The electromotive force of cells without liquid junction have been measured in the present study up to concentrations of 1.65, 3.015 and 3.502 M, respectively, and from the results the activity coefficients have been calculated.

Apparatus, Materials and Method.—The apparatus used and method of procedure for the cells without liquid junction were, in general, similar to those described by Mac-Innes and Beattie.[3] In the present case, however, due to the nature of the amalgam, it was found necessary to make certain changes in the amalgam droppers. It would appear that the amalgams of the alkaline-earth metals are somewhat more viscous than those of the alkali metals. It seemed also that they more readily decomposed upon coming in contact with stopcock grease and other foreign matter in the arms of the droppers and at surfaces of contact with the glass and solution such as the tip of the dropper. Thus, it was found impossible to obtain a continuous electrical contact through the dropper while using capillary tubing in the arms of the droppers. Tubing of about 2mm. bore was therefore used in place of the capillary and in order to prevent the mercury from being drawn out, under the vacuum, the ends of the arms were bent up for about

[1] Lewis and Linhart, THIS JOURNAL, 41, 1952 (1919).

[2] Hall and Harkins, ibid., 38, 2658 (1916).

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

1 cm. Thus the amalgam fell through the solution in drops rather than as a jet or fine spray. In order to prevent initial decomposition of the amalgam in the arms of the dropper and that the latter might be kept dry, they were filled in each case, prior to being introduced into the cell, with pure mercury which was, of course, displaced as the amalgam in the upper part of the dropper was allowed to flow.

The barium amalgam was made by electrolyzing a solution of barium hydroxide over a mercury cathode. After electrolysis the amalgam, which contained about 0.2% of barium, was immediately drawn into an evacuated flask, traces of oxide and other impurities being allowed to rise over a period of several days to the top of the liquid. Finally, the lower portion of the amalgam was allowed to flow into an evacuated flask containing such an amount of mercury that the final concentration of barium in the amalgam was about 0.02%. This diluted amalgam was kept for several days before the lower portions were withdrawn, always under vacuum, into the droppers of the cell a few hours before actual use. An attempt was made to produce the strontium amalgam in the same manner, that is, by electrolyzing a saturated solution of the hydroxide over a mercury cathode. Although the solution was maintained saturated it was found that the solubility of the hydroxide is too small to permit this method of preparation. The strontium and calcium amalgams were made, therefore, by electrolyzing a solution of the chloride over a mercury cathode, the anode being of graphite and held in a semi-porous clay cup. The amalgam was dried, purified, diluted to about 0.02% and kept for use, always under vacuum, in the same manner as described above. The mercury used in the preparation of each of these amalgams was first washed with dil. nitric acid and four times distilled.

The solutions of barium chloride were made up by dissolving weighed amounts of high grade salt in conductivity water. These solutions were then boiled to remove oxygen and kept out of contact with air, correction of the concentration being made for the loss of the solvent in boiling. The 0.01 M solution was made up in amounts sufficient for several determinations by adding a weighed quantity of salt to enough freshly distilled, boiled, conductivity water to make the exact concentration. The solution was kept in an atmosphere of hydrogen and withdrawn as needed into an evacuated flask. The solutions of strontium and calcium chlorides were made by diluting in conductivity water portions of a strong solution which had been made up from a high-grade salt dissolved in conductivity water, the concentration of the strong solution having been determined by gravimetric analysis. As in the case of barium chloride the solutions were boiled to remove oxygen and the 0.01 M solutions which were made up in amounts sufficient for several determinations were kept in an atmosphere of hydrogen. Throughout the manipulation of the cell care was exercised to keep the system free from oxygen.

The electrodes used in both types of cells were made according to the method described by Noyes and Ellis,[4] the silver being formed from silver oxide as was done by Lewis.[5] The silver chloride was formed on the electrode by making it the anode in a 0.75 M hydrochloric acid solution for five hours with a current of 0.004 ampere. When completed, the electrodes were checked against each other to make sure that they introduced no vitiating source of electromotive force.

Results and Discussion.—In Table I are given the results of the cells without liquid junction. In the row headed m is given the concentration in moles of salt dissolved in 1000 g. of water and in the row headed E, the values of the electromotive force generated in a cell of this

[4] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).
[5] Lewis, *ibid.*, **28**, 166 (1906).

type when a 0.01 M solution flows through one side of the cell and a solution of the corresponding concentration through the other.

TABLE I

RESULTS FROM CELLS WITHOUT LIQUID JUNCTION

Ag | AgCl | MeCl₂(c) | Me(Hg)x | MeCl₂ (0.01 M) | AgCl | Ag

BARIUM CHLORIDE[a]

m	0.01	0.03016	0.1004	0.2978	0.9710	1.521	1.650
E	.0	.03548	.07420	.10921	.15322	.17183	.17713
γ	.716	.596	.489	.409	.393	.407	.430

STRONTIUM CHLORIDE[b]

m	0.01	0.02908	0.08996	0.1167	0.3458
E	.0	.03523	.07220	.07976	.11702
γ	.716	.614	.518	.486	.431

m	1.049	1.403	2.115	3.015
E	.16117	0.17670	0.20305	0.23557
γ	.447	.500	.658	1.073

CALCIUM CHLORIDE[c]

m	0.01	0.03504	0.06294	0.1032	0.2066	0.3713	0.4655
E	.0	.04106	.06062	.07717	.10136	.12347	.13349
γ	.716	.593	.549	.514	.481	.475	.491

m	.6622	.9608	1.003	1.606	1.960	3.167	3.502
E	.15426	.17499	.17731	.21050	.23130	.28557	.30047
γ	.592	.699	.711	1.051	1.48	3.74	4.98

[a] The last value of the activity coefficient lies about 2% above a smooth curve drawn through the points; the one immediately preceding lies below the curve by about the same amount. The remaining points fall upon the curve within less than a unit in the last place.

[b] The mean deviation of the values of γ from a smooth curve drawn through the series is about one unit in the last place.

[c] The mean deviation of the values of γ from a smooth curve drawn through the series is somewhat less than 2%. If the values at 0.6622 and 1.606 M be disregarded, the mean deviation is much less, being about three units in the last place.

For a concentration cell without liquid junction containing a bi-univalent salt the electromotive force, activity coefficient and concentration are related according to the equation

$$E = \frac{RT}{nF} \ln \left(\frac{\gamma_1 \, 2^{2/3}m_1}{\gamma_2 \, 2^{2/3}m_2} \right)^3 = \frac{3\,RT}{nF} \ln \left(\frac{\gamma_1 \, m_1}{\gamma_2 \, m_2} \right)$$

Thus if we have the value of the activity coefficient at some one concentration from some other type of measurement we can calculate its value at the various concentrations from the electromotive force. No such value is available at 25°. However, we may assume without introducing great error that the value, 0.716, calculated by Lewis and Linhart[1] for the 0.01 M solution of barium chloride at its freezing point holds also at 25°; and as has been done in the case of alkali chlorides, and the sulfates of mag-

nesium, cadmium, and copper,[6] we may because of their similarity assign the same value to the activity coefficient of all the alkaline earth chlorides at 0.01 M concentration. Introducing the numerical values, the equation above takes the form

$$E = \frac{3 \times 8.316 \times 298.1 \times 2.3026}{2 \times 96494} \log \frac{\gamma_1 \, m_1}{0.716 \times 0.01}$$

or for the present calculation, log $\gamma_1 = 11.270 \, E + (7.85491 - 10) - \log m_1$. The values given under γ in Table I were calculated from this equation and are obviously subject to revision should another reference value be chosen or determined at 25°.

It will be noted that in the case of barium chloride all of the present values fall below those of Lewis and Linhart, the differences being about 2%, 3% and 2% at 0.02, 0.05 and 0.1 M, respectively. That there should be a difference is to be expected in view of the increasing difference in temperature and the neglect of the heat of dilution in the calculations from the freezing-point data. It will be seen that the values of the activity coefficient fall somewhat more rapidly than do those of the common uni-univalent electrolytes, passing through a rather flat minimum value of 0.388 at about 0.65 M, beyond which the value rises as the concentration approaches that of the saturated solution, 1.779 M. In the case of strontium chloride the values lie everywhere slightly above those of barium chloride, the difference being about 2.5% at 0.1 M and increasing to slightly over 10% at 1.0 M. The minimum value in this case is reached at a somewhat lower concentration, being 0.418 at about 0.60 M. The minimum value with calcium chloride is reached at a still lower concentration, being 0.473 at about 0.29 M.

The distribution of the curves of the activity coefficients of the alkaline earth chlorides may be seen in Fig. 1. Here the activity coefficients are given as ordinates and the square root of the molality as abscissas. It will be seen that up to about 0.1 M the curves for calcium and strontium chlorides lie somewhat closer than those of strontium and barium chlorides. Above this concentration the curves diverge much more rapidly than do those of the latter salts. As has been indicated, the minimum passes to higher concentrations with increasing molecular weight. In order to reduce the size of the plot, the values for calcium chloride are given only up to about 1.6 M, beyond which the curve rises very steeply as shown in Table I. It will be noticed that the order of the curves is the same as that for the alkali chlorides, the values for the salts of higher molecular weight lying successively lower. This is as we should expect from the theory, if the ionic hydration and consequently the ionic diameter decrease with increasing atomic weight.

While the cells without liquid junction were in operation both the amal-

Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., 1923.

gam and the solutions were flowing. During this interval a number of readings of the electromotive force, usually about ten, were taken, the means of which are given in the table. Though the individual results with calcium chloride are less concordant and vary more from a smooth curve than in the other cases it is believed that, due to the larger number of points taken, the final curve may be relied upon to almost the same extent. Although no results are given in any case for concentrations below 0.01 M, a sufficient number of such determinations were made to prove the accuracy of the cells at this concentration and justify its use as the reference in these measurements.
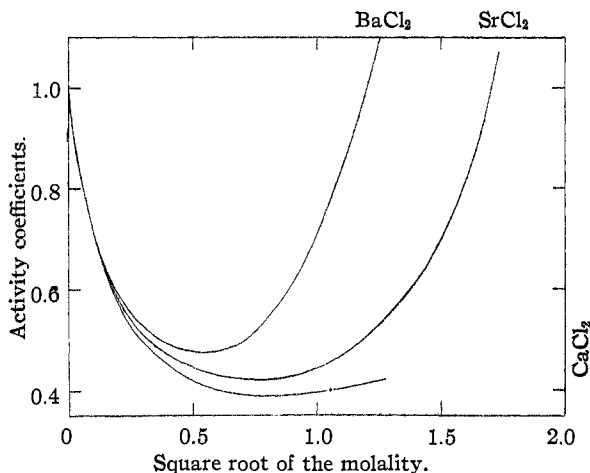

Fig. 1.—The activity coefficients of the alkaline earth chlorides.

The Transference Number

A few values for the transference numbers of the alkaline earth chlorides determined by gravimetric methods are recorded, as are also a few determinations by the moving-boundary method. From a knowledge of the electromotive force of cells without and with liquid junction of the types indicated in the first part of this paper, the cation transference numbers can immediately be calculated. In the above section have been given the results of measurements of concentration cells of these salts without liquid junction. Drucker[7] determined the electromotive force of cells of the type 1% Ba amalg. | $BaCl_2(c)$ | $KCl(2\ M')$ | $BaCl_2(0.005\ M')$ | 1% Ba amalg., in which c was varied from 0.01 to 0.103 M'. He also measured cells of the form, Hg | HgCl | $BaCl_2(c_1)$ | $BaCl_2(c_2)$ | HgCl | Hg, varying c_1 and c_2 from 0.001 to 0.05 M' and 0.005 to 0.1 M', respectively. While Drucker failed to state at what temperature his measurements were made, the work was presumably carried on at about 17°. The values obtained in

[7] Drucker, Z. Elektrochem., **19**, 804 (1913).

the present investigation agree well with those of Drucker in the case of the cells with liquid junction over the comparable concentration range.

Apparatus and Materials.—The cell with liquid junction which was found very convenient is shown diagrammatically in Fig. 2. A, B and C are tubes of about 2.5 cm. diameter and about 9 cm. in length. The connection between B and C is through a 5cm. tube of about 0.2cm. bore. The connection between A and B is through a tube of the same bore, passing through the stopper of B. Afte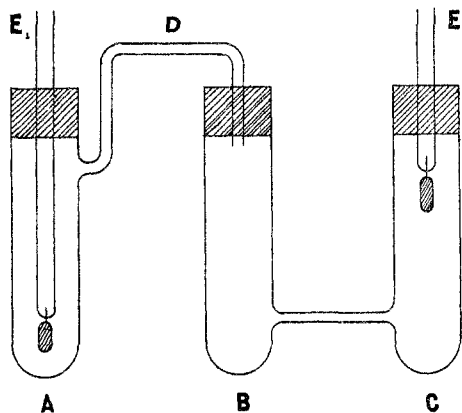r the entire volume of A, including the connecting tube, D, had been filled with the dilute solution, the rubber stopper carrying the silver-silver chloride electrode, E_1, was introduced. C and the connecting tube with B were filled with the concentrated solution and the electrode, E_2, was introduced. B was then filled with a solution intermediate between the two concentrations, being made up of an approximately 1:1 mixture of the two. Finally, the rubber stopper through which the end of D

Fig. 2.—The cell with liquid junction.

passes was introduced into B, a small hole passing through the stopper in order to allow for displacement of liquid by adjusting stoppers in any part of the cell.

The solutions were made up from the same materials as before and in the same manner except that in the present case they were not boiled.

Results and Discussion.—Under the column headed E in Table II

TABLE II

RESULTS FROM CELLS WITH LIQUID JUNCTION

Ag | AgCl | MeCl$_2$(c) | MeCl$_2$(0.01 M) | AgCl | Ag

BARIUM CHLORIDE[a]

m	E	Log A	t_+
0.01	0.0	1.0556	0.439
.01923	.00927	1.2949	.432
.3815	.01852	1.5415	.423
.07977	.02804	1.8092	.410
.1791	.03941	2.0997	.393
.2426	.04277	2.2099	.387
.3927	.04907	2.3936	.380
.5971	.05475	2.5662	.376
.8122	.05995	2.7009	.374
1.372	.06872	2.9498	.371
1.715	.07134	3.0624	.370

TABLE II   (*Concluded*)

STRONTIUM CHLORIDE[b]

m	E	Log A	t_+
0.01	0.0	1.0556	0.424
.01577	.00640	1.2281	.420
.03198	.01566	1.4866	.412
.04564	.02079	1.6160	.407
.07925	.02767	1.8170	.397
.1466	.03557	2.0440	.384
.3168	.04534	2.3400	.361
.6246	.05404	2.6180	.332
1.269	.06425	2.9836	.292
2.027	.07206	3.3100	.278
2.954	.08185	3.6860	.276

CALCIUM CHLORIDE[b]

m	E	Log A	t_+
0.01	0.0	1.0556	0.420
.01547	.00601	1.2218	.417
.02006	.00974	1.3192	.415
.03955	.01898	1.5691	.408
.04966	.02198	1.6522	.404
.08053	.02841	1.8318	.394
.1612	.03683	2.0974	.367
.3208	.04600	2.3827	.321
.6162	.05487	2.7151	.277
1.013	.06264	3.0612	.259
1.600	.07164	3.4558	.254
2.586	.08357	3.9903	.251

[a] For the last value of log A, given here, a slight extrapolation of the curve relating the quantities given in the first and last columns of Table I, from which the above values were obtained, was necessary. The mean deviation of the values of the electromotive force given in this table from a smooth curve drawn through the series is about 0.2 mv.

[b] The mean deviation of the values of the electromotive force from a smooth curve drawn through the series is about 0.1 mv.

are given the values of the electromotive force generated in a cell with liquid junction made up of a 0.01 M solution surrounding one electrode and a solution of the molal strength given in the column headed m surrounding the other.

If the electromotive force of a cell without liquid junction be plotted against the logarithm of the geometrical mean activity a straight line will result, while if the electromotive force of a cell with liquid junction be plotted against the same abscissa a line will result which curves slightly from a straight line, the amount of curvature depending upon the concentration. That the ratio of the slopes of these lines at any given activity and consequently at any corresponding concentration is equal to the transference number has been shown by MacInnes and Beattie.[3] In the present case the equation for the curve without liquid junction is of the form

$$dE = \frac{3\,RT}{2\,F} \, d \, ln \, a_\pm$$ (1)

and that of the curve with liquid junction

$$dE_t = t_+ \frac{3\,RT}{2\,F} \, d \, ln \, a_\pm.$$ (2)

In order to solve this latter equation it is necessary to know the values of the activity at the concentrations at which the electromotive forces of the cells of this type have been determined. To find these, since the determinations of the cells with and without liquid junction were not made at the same concentrations, a large plot was made of the square root of the molality against the activity coefficient determined from the cells without liquid junction. From this the activity coefficient could be read off directly at the concentrations at which the electromotive force had been determined in the cells with liquid junction. The logarithm of the activity was then found from the following relation: $\log a_\pm = \log \gamma + \log m + \log (2)^{3/2}$. A number of attempts were made to determine the equation relating the electromotive force and $\log A$ $(= \log 1000\ a_\pm)$, the values of which are given in Table II, by the method of least squares both using the entire curve and dividing it into parts. Differentiating such an equation with respect to log A and dividing by the constant slope of Equation 1 should give immediately a simple equation relating the transference number of the cation with log A. It was found,[8] however, that the curvature of the line relating the electromotive force of the cells with liquid junction with $\log A$ was too complex, starting as an almost straight line, increasing in curvature to a comparatively high maximum and again approaching a straight line, to permit of its determination either as a whole or in parts as a simple parabolic function. Any function which might fit part or all of the curve more closely but which would require $\log A$ to appear at a power higher than the second, or one which upon differentiation would lead to a complicated relation between the transference number and $\log A$ would be too cumbersome for ordinary use. It was found, too, that the ratio of the slopes of the curves (1 and 2) yielded transference numbers far too sensitive to permit any portion of Curve 2 to be forced into a predetermined type. It would appear that the method used so successfully by MacInnes and Beattie in the case of lithium chloride is inapplicable to salts of higher type where the change in the transference number with the concentration is less regular and usually much greater than in the case of uni-univalent salts.

In the present case, therefore, the slope of Curve 2 at the various values of log A was obtained directly from a large plot of this quantity against the electromotive force. Dividing this slope by the constant slope of Curve

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[8] These statements are especially true in the cases of strontium and calcium chlorides.

1, namely 0.088733, yielded values of the mean transference numbers over a small concentration range, the concentration range depending upon the interval of log A used in determining the slope.   Throughout, this interval was made as small as was consistent with accuracy in order that the values of the transference numbers might approach as nearly as possible those at single points.   A plot of these values against the logarithm of the molality led to the results given in Table II and elsewhere.

The agreement between the values of the cation transference numbers determined in the present investigation and previous values is satisfactory. In the case of barium chloride the present values lie slightly above those given by Kohlrausch and Holborn,[9] the differences being less than 1% in the concentration range between 0.01 and 0.25 M, and somewhat below the "best values" of Noyes and Falk.[10]   A single determination at 25° was made by Denison and Steele[11] by the moving-boundary method.   This result, 0.416, at 0.05 M compares well with the present value, 0.418 at 0.05 M. The result, 0.376, by this same method at 0.35 M' at 18° agrees well with that of the present investigation, 0.382, at 0.35 M at 25°.   The meager data with which the values for strontium chloride may be compared indicate, as in the case of barium chloride, a somewhat better agreement with the results of the moving-boundary method than with the results of the gravimetric method as given in the "best values."   In the case of cal-

Fig. 3.—The cation transference numbers of the alkaline earth chlorides.

cium chloride the single value by the moving-boundary method lies slightly below the curve of the present values: the "best values" of Noyes and Falk, as in the other two cases, lie slightly above the curve.

In Fig. 3 are given the curves of the transference numbers of the alkaline earth chlorides found in this investigation plotted against the logarithm of the molality.   The uppermost curve is that of the barium ion, and below are those of strontium and calcium, the order being the same as with the cation transference numbers of the alkali chlorides.   The
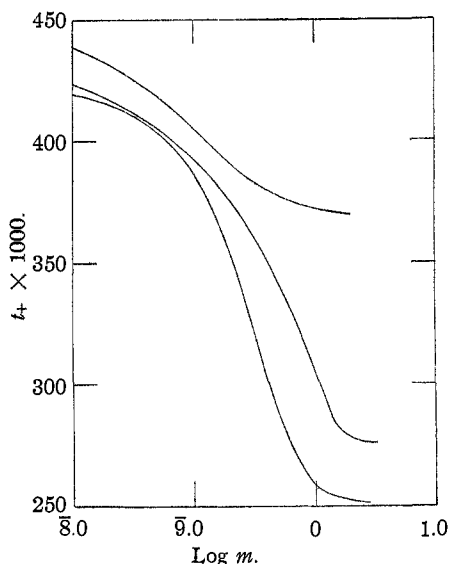
[9] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," Teubner, 1898.

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

[11] Denison and Steele, Z. physik. Chem., 57, 110 (1906).

large change in the transference numbers of salts of this type has often been attributed to the presence of complex intermediate ions.   In the very dilute solutions the ions are undoubtedly simple, except for hydration, but as the concentration is increased the formation of complex ions takes place. When the curve falls very rapidly we must assume, according to such a theory, a rapid change in the number or nature of the complex ions.   After a certain concentration is reached, it would appear from the present results that, in the case of the alkaline earth chlorides, there is relatively little change in the carriers of the current.

It may be of advantage to group into a single table the values of the activity coefficients and of the cation transference numbers at round molal concentrations which have been determined in this study.   The values of the former were taken from a large plot of this quantity against the square root of the molality, and of the latter from a plot against the logarithm of the molality.   These values are given in Table III which is self-explanatory.

TABLE III

THE ACTIVITY COEFFICIENTS AND TRANSFERENCE NUMBERS AT ROUND CONCENTRATIONS

Molality	Activity coefficients			Transference numbers		
	$CaCl_2$	$SrCl_2$	$BaCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
0.01	0.716	0.716	0.716	0.420	0.424	0.439
.02	.655	.651	.641	.416	.417	.431
.05	.569	.561	.549	.404	.405	.418
.07	.541	.531	.520	.397	.400	.412
.1	.516	.503	.490	.387	.393	.406
.2	.480	.457	.435	.355	.376	.390
.5	.499	.420	.391	.289	.343	.377
.7	.560	.420	.388	.271	.326	.375
1.0	.709	.441	.394	.259	.306	.372
2.0	1.521	.627	..	.252	.279	..
3.0	3.311	1.064	..	.251	.276	..

Lewis[12] has shown that the product of the equivalent conductance and the anion transference number in the case of five univalent chlorides at 0.1 N is a constant within 0.5%, although the conductivity ratio, Λ/Λ_0, of hydrochloric acid is about 7% higher than the mean of those of the other chlorides considered.   MacInnes[13] made a similar calculation at 0.01 N and concluded that the fact "that the equivalent conductance of the chloride-ion-constituent at a given concentration is independent of the cation constituent, and the strong presumption that the concentration and mobility of the chloride ion is the same at any given concentration in the solutions of univalent chlorides, raises the further presumption that the activity of the chloride ion, at any given concentration, is also independent

[12] Lewis, THIS JOURNAL, 34, 1640 (1912).
[13] MacInnes, ibid., 41, 1086 (1919).

TABLE IV

THE CONDUCTANCE OF THE CHLORIDE ION

Log m	$\bar{8}.0$	$\bar{8}.4$	$\bar{8}.8$	$\bar{9}.2$	$\bar{9}.6$	$\bar{9}.8$
			CALCIUM CHLORIDE			
$t-$	0.580	0.587	0.601	0.632	0.696	0.724
μ	227.3	213.3	197.2	178.4	157.2	146.1
$2t-\mu = x_1$	263.7	250.4	237.0	225.5	218.8	211.6
			STRONTIUM CHLORIDE			
$t-$	0.576	0.585	0.598	0.618	0.648	0.669
μ	231.7	217.0	199.8	179.9	157.3	145.0
$2t-\mu = x_2$	266.9	253.9	239.0	222.4	203.9	194.0
			BARIUM CHLORIDE			
$t-$	0.561	0.572	0.586	0.604	0.620	0.625
μ	235.7	221.7	204.4	185.7	165.1	154.4
$2t-\mu = x_3$	264.5	253.6	239.6	224.3	204.7	193.0
x_1/x_3	0.997	0.987	0.989	1.005	1.069	1.096
x_2/x_3	1.009	1.001	0.997	0.992	0.996	1.005
x_3/x_3	1.0	1.0	1.0	1.0	1.0	1.0

of the cation associated with it." In Table IV we have made a similar calculation using the conductance data of Jones and his associates[14] and the transference numbers determined in the present investigation. In the first row is given the logarithm of the molality. For each salt there is given the anion transference number at the given molality. Below this appears the molecular conductance of the salt at the same concentration. Since the conductance is given in molal rather than equivalent terms, we have considered the passage of two equivalents and multiplied the molecular conductance by twice the transference number. At the botton of the table are given the ratios of the conductance of the chloride-ion constituent at each concentration. Since these ratios vary only slightly from unity up to about 0.15 M, the variation being perhaps within the experimental error, we may draw conclusions relative to the chloride ion in solutions of the alkaline earth salts in this concentration range similar to those drawn by MacInnes from consideration of the univalent chlorides. It must be stated, however, that the evidence here is less conclusive due to the greater uncertainty of the combined experimental data and less striking in view of the fact that the conductance ratio varies less between these salts than between the univalent chlorides considered. It would appear that if complex intermediate ions are formed in these solutions they are present in only small amounts at concentrations below 0.15 M.

The results from the cells with liquid junction which are given in Table II are, in each case, the mean of about eight readings taken over an interval of several hours.

[14] *Carnegie Inst. Pub.*, **170**, 1912.

The writer wishes to acknowledge his indebtedness to Dr. Herbert S. Harned at whose suggestion this investigation was undertaken, for help and many valuable suggestions throughout its execution.

Summary

Values are given for the activity coefficient of barium chloride from 0.01 to 1.65 M, of strontium chloride from 0.01 to 3.015 M, and of calcium chloride from 0.01 to 3.5 M.

Values for the cation transference numbers of these salts over similar concentration ranges are also given.

Values for these two quantities for the alkaline earth chlorides are grouped at round concentrations into a single table.

The values of the electromotive forces of cells without and with liquid junction from which these quantities were calculated are also given.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, McGILL UNIVERSITY]

THE VISCOSITIES OF THE LIQUID HALOGENS

BY E. W. R. STEACIE AND F. M. G. JOHNSON

On account of the interesting relationships existing between viscosity and chemical constitution, a great many determinations of the viscosities of organic liquids have been made. Little attention, however, has been paid to inorganic compounds and to the elements themselves.

The viscosity of bromine has been measured over a wide range of temperature by Thorpe and Rodger,[1] and also, at one temperature only, by Kann[2] and by Beck.[3] Beck has also measured the viscosity of liquid iodine at the melting point only. We have been unable to find any previous measurement of the viscosity of liquid chlorine. It was therefore considered of interest to determine the viscosities of liquid chlorine, bromine and iodine.

Chlorine

Preparation.—The chlorine was prepared from hydrochloric acid and potassium permanganate. The gas was washed twice with water and dried by bubbling through concd. sulfuric acid. It was then liquefied with solid carbon dioxide and ether and fractionally distilled four times, the middle portion always being retained. It was finally liquefied in the viscosimeter. At no time during its preparation did the gas come into contact with rubber or grease.

[1] Thorpe and Rodger, *Phil. Trans.*, **185A**, 397 (1894).

[2] Kann, *Wien. Ber.*, **106**, 2a, 431 (1897).

[3] Beck, *Z. physik. Chem.*, **48**, 641 (1904).