wire. He has described these experiments in another place.[1] He found no difference (beyond the range of experimental error) in the conductivity of the 2 kinds of lead nor in the effect of pressure or temperature upon their conductivity.

We are glad to acknowledge our indebtedness to the Carnegie Institution of Washington for much of the apparatus used in this research.

Summary.

In this paper experiments are described which show that the difference in the melting points of 2 specimens of lead differing 0.8 in atomic weight is, if appreciable, not over 0.05°. From this outcome, it is fairly safe to assume that the kinds of lead not only have very nearly the same melting point but also (since the sample consisting chiefly of the lighter isotope doubtless contained ordinary lead) they mix (or rather mutually dissolve) without affecting the melting point.

The Seebeck thermoelectric effect produced at a junction of the two kinds of lead is also shown to be nil.

CAMBRIDGE, MASS.

THE ACTIVITIES OF THE IONS IN AQUEOUS SOLUTIONS OF SOME "STRONG" ELECTROLYTES.

BY FREDERICK H. GETMAN.

Received May 3, 1920.

In a recent number of THIS JOURNAL, Noyes and MacInnes[2] gave an interesting summary of a series of investigations which have been carried out under their direction with a view to determining the activity of several electrolytes which are known to be largely ionized in solution.

The appearance of this paper has made it seem worth while to the author to publish a brief account of some studies made by him along similar lines which not only confirm the experimental results of Noyes and MacInnes but also furnish additional evidence in support of the validity of the formula developed by MacInnes[3] for the calculation of the electromotive force developed at a liquid junction.

The term "activity," which was first introduced by Lewis[4] to express the effective concentration of a dissolved substance may be defined as the quantity which must be introduced into the mass action equation to express correctly the effect of concentration in determining the equilibrium.

Apparently the first to derive activity coefficients from measurements

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[1] Bridgman, *Proc. Nat. Acad. Sci.*, **5**, 351–3 (1919).

[2] THIS JOURNAL, **42**, 239 (1920).

[3] *Ibid.*, **37**, 2301 (1915).

[4] *Proc. Am. Acad. Arts Sci.*, **43**, 259 (1907); *Z. physik. Chem.*, **61**, 129 (1908).

of electromotive force was Linhart,[1] who, by making use of a method recommended by Lewis, calculated the so-called "thermodynamic" degree of dissociation of potassium chloride from existing experimental data. Shortly afterward he published the results of similar calculations on hydrochloric acid[2] and at a later date, employing the silver-silver chloride electrode, he determined the activity coefficients of hydrochloric acid in extremely dilute solutions.[3]

In the present investigation 3 typical uni-univalent electrolytes, hydrochloric acid, sodium chloride, and potassium chloride, were studied in both dilute and concentrated solutions, making use of cells involving transference as indicated in the following scheme.

$$\mathrm{Hg} - \mathrm{HgCl} - \mathrm{MCl}(c_1) \,||\, \mathrm{MCl}(c_2) - \mathrm{HgCl} - \mathrm{Hg}$$

After correcting the observed electromotive forces for liquid potentials at the junctions of the 2 solutions, the activity coefficients were calculated in the usual manner. All measurements were made at a temperature of 25°.

Preparation of Materials and Solutions.

The mercury used was first sprayed through a column of 5% nitric acid 60 cm. in length and then further purified by distillation in a current of air at diminished pressure as recommended by Hulett.[4]

The calomel employed was prepared from pure mercury by dissolving in distilled nitric acid and precipitating with pure hydrochloric acid according to the directions of Loomis and Acree.[5]

The potassium chloride was obtained from a high-grade sample by 5 recrystallizations. The well-drained crystals were first dried at 110° and then heated to incipient fusion, after which they were pulverized in a mortar and preserved in a desiccator over phosphorus pentoxide. The purified salt, when tested spectroscopically, failed to reveal the presence of any sodium.

The sodium chloride used was prepared by 2 successive precipitations of a saturated solution of a good commercial sample of salt with hydrogen chloride followed by washing and thorough draining of the resulting crystals. The remaining treatment was similar to that employed in the preparation of pure potassium chloride. The hydrochloric acid used was obtained by redistillation of a good grade of commercial acid.

The water used in the purification of the above substances, as well as that employed in making up all solutions, was obtained by the usual procedure in the preparation of so-called "conductivity" water.

[1] THIS JOURNAL, 39, 618 (1917).

[2] *Ibid.*, 39, 2601 (1917).

[3] *Ibid.*, 41, 1175 (1919).

[4] *Phys. Rev.*, 21, 388 (1905).

[5] *Am. Chem. J.*, 46, 596 (1911).

Solutions of the 2 salts were made up by direct weighing of the solutes and diluting to the mark in calibrated flasks, while solutions of the acid were standardized by precipitating with silver nitrate and weighing as silver chloride. The more dilute solutions were prepared by dilution from a solution of known concentration.

Cells.

Two different types of cells were used: (*a*) cells similar to those described by Gibbons and Getman[1] and (*b*) cells which were essentially the same as those employed by MacInnes and Parker[2] in their study of potassium chloride concentration cells. The latter type of cell proved to be very satisfactory provided care was taken when assembling to separate the mouths of the siphon tubes in the intermediate vessel as far as possible. The statement of MacInnes and Parker, that the "time change," which is apparently always present where a liquid junction is involved, was "less than 1 millivolt per hour" was more than corroborated; in fact, in a large number of cases the change in 24 hours did not exceed 0.1 millivolt when the boundary remained unchanged.

Method of Procedure.

In setting up the different cells studied in this investigation, the concentration of the electrolyte on one side was varied over a wide range, while that on the other side was maintained uniformly at 0.1 molar concentration. In the preparation of the electrodes, attention was paid to the precautions pointed out by Loomis and Acree[3] and also by Ellis[4] and special care was taken to compare the electrodes with each other at frequent intervals. Not only were similar electrodes intercompared, but the electromotive forces of the following combinations were also measured.

(*a*) $\mathrm{Hg} - \mathrm{HgCl} - 0.1\,N\ \mathrm{KCl} \,\|\, 0.1\,N\ \mathrm{NaCl} - \mathrm{HgCl} - \mathrm{Hg}$,

(*b*) $\mathrm{Hg} - \mathrm{HgCl} - 0.1\,N\ \mathrm{KCl} \,\|\, 0.1\,N\ \mathrm{HCl} - \mathrm{HgCl} - \mathrm{Hg}$,

and compared with the values calculated by means of the formula of Lewis and Sargent[5] for the electromotive force at the junction of 2 uni-univalent electrolytes having an ion in common. The measured electromotive forces were as follows. (*a*) 0.00469 volt and (*b*) 0.02838 volt, while the calculated values were 0.00434 volt and 0.02840 volt, respectively.[6] The maximum values of the electromotive force were taken in each case as a correct measure of the free energy attending the transfer of the solute from one concentration to the other. All measurements were made with a Leeds and Northrup potentiometer in conjunction with

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[1] THIS JOURNAL, 36, 1645 (1914).

[2] *Ibid.*, 37, 1455 (1915).

[3] *Loc. cit.*

[4] THIS JOURNAL, 38, 745 (1916).

[5] *Ibid.*, 31, 363 (1909).

[6] See also Lewis, Brighton and Sebastian, *Ibid.*, 39, 2255 (1917).

a sensitive galvanometer and a Weston standard cell, the latter having been recently certified by the Bureau of Standards.

Experimental Data.

Before giving the summarized data of the entire series of observations, it may be of interest to give a typical series of measurements of the electromotive force, *E*, of a single combination extending over a period of 5 days.

TABLE I.—OBSERVED VALUES OF THE E. M. F. OF THE CELL.

Hg-HgCl-0.1 *N* KCl || 0.0298 *N* KCl-HgCl-Hg.

Date.	*E.*	Date.	*E.*
Dec. 10, 10.25 A.M.	—0.02796	Dec. 12, 4.50 P.M.	—0.02791
4.05 P.M.	—0.02793	13, 12.00 M.	—0.02790
11, 11.00 A.M.	—0.02792	4.55 P.M.	—0.02794
5.00 P.M.	—0.02791	15, 11.00 A.M.	—0.02785
12, 12.20 P.M.	—0.02796	Mean	—0.02792

Average deviation from the mean, 0.02 millivolt.

The negative sign prefixed to the electromotive force indicates that the current tends to flow from left to right through the cell, this convention being in accord with the scheme adopted by Abegg, Auerbach and Luther.[1]

A complete summary of the measurements of potassium chloride cells is given in Table II.

TABLE II.—SUMMARY OF E. M. F. DATA ON KCL CELLS.

I. *C.*	II. E_t.	III. E_l.	IV. *E.*	V. Δ.
0.001	—0.11101	+0.00089	—0.11190	0.17
0.005	—0.07240	+0.00058	—0.07298	0.08
0.010	—0.05438	+0.00044	—0.05482	0.15
0.01499	—0.04430	+0.00036	—0.04466	0.04
0.0298	—0.02792	+0.00023	—0.02815	0.02
0.03994	—0.02108	+0.00017	—0.02125	0.05
0.049	—0.01700	+0.00014	—0.01714	0.01
0.0800	—0.00523	+0.00004	—0.00527	0.03
0.100	0.00000	0.00000	0.00000	0.00
0.1599	+0.01059	—0.00008	+0.01067	0.09
0.490	+0.03526	—0.00028	+0.03454	0.20
1.000	+0.05241	—0.00042	+0.05283	0.05
1.4988	+0.06269	—0.00051	+0.06320	....
2.9985	+0.08077	—0.00065	+0.08142	....

Throughout the series the 0.1 *N* calomel electrode formed one-half of each cell; the concentration of the solution in the other half of each cell, expressed in mols per liter, had the respective values given in Col. I of the table. Col. II gives the observed electromotive force, E_t, while Col. III gives the value of the liquid junction potential, E_l, as calculated by the MacInnes formula,[2]

$$E_l = E_t\,(1 - {}^{1}/_{2n_c}),$$

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[1] "Messungen elektromotorischer Kräfte galvanischer Ketten," 1911, p. 114.

[2] *Loc. cit.*

where n_c is the transference number of the cation to which, in the case of potassium chloride, the value 0.496 has been assigned. It is of course quite improbable that the value of the transference number remains constant throughout the entire range of concentration included in the table, but it may be assumed to undergo little change up to 0.2 molar concentration. Column IV of the table contains the electrode potential, *E*, *i. e.*, the observed electromotive force of the cell minus the electromotive force developed at the liquid junction. The last column of the table contains the average deviation from the mean, Δ, of each series of measurements expressed in millivolts. The values of *E* were plotted as ordinates against the logarithms of the concentrations as abscissas and a smooth curve was then drawn through the resulting points. From this curve the activity coefficients at round concentrations were calculated as shown in Table III. In calculating the activity coefficients it has been assumed that at 0.001 molar concentration the numerical values of the activity coefficient and the conductance viscosity ratio are equal. The table also contains the conductance viscosity ratios, $\Lambda\eta/\Lambda_0\eta_0$, corresponding to the different activity coefficients.

TABLE III.—ACTIVITY COEFFICIENTS AND CONDUCTANCE-VISCOSITY RATIOS FOR POTASSIUM CHLORIDE.

I. *C.*	II. *E.*	III. α.	IV. $\Lambda\eta/\Lambda_0\eta_0$.
0.001	—0.11190	0.979	0.979
0.005	—0.07039	0.938	0.956
0.01	—0.05410	0.907	0.941
0.02	—0.03782	0.855	0.922
0.03	—0.02829	0.826	0.914
0.04	—0.02153	0.805	0.898
0.05	—0.01629	0.790	0.889
0.06	—0.01200	0.778	0.882
0.07	—0.00838	0.768	0.876
0.08	—0.00524	0.759	0.871
0.09	—0.00248	0.753	0.866
0.10	0.00000	0.745	0.860
0.20	+0.01629	0.703	0.827
0.50	+0.03782	0.650	0.779
1.00	+0.05410	0.613	0.742
2.00	+0.07039	0.577	...
3.00	+0.07991	0.557	...

The data of the preceding table are represented graphically in Fig. 1, together with the activity data determined by Noyes[1] and Harned.[2]

The corresponding data for sodium chloride and hydrochloric acid are contained in Tables IV and V, only the values at rounded concentrations being given.

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[1] *Loc. cit.*

[2] THIS JOURNAL, 38, 1990 (1916).

TABLE IV.—ACTIVITY COEFFICIENTS AND CONDUCTANCE-VISCOSITY RATIOS FOR SODIUM CHLORIDE.

I. C.	II. E.	III. α.	IV. $\Lambda\eta/\Lambda_0\eta_0$.
0.001	−0.11200	0.976	0.976
0.005	−0.07023	0.932	0.954
0.01	−0.05403	0.897	0.936
0.02	−0.03777	0.845	0.914
0.03	−0.02825	0.815	0.898
0.04	−0.02150	0.795	0.886
0.05	−0.01626	0.780	0.877
0.06	−0.01198	0.767	0.871
0.07	−0.00837	0.758	0.865
0.08	−0.00524	0.749	0.860
0.09	−0.00247	0.742	0.855
0.10	0.00000	0.735	0.848
0.20	+0.01626	0.692	0.816
0.50	+0.03776	0.639	0.772
1.00	+0.05403	0.602	0.738
2.00	+0.07029	0.567	...
3.00	+0.07981	0.548	...

TABLE V.—ACTIVITY COEFFICIENTS AND CONDUCTANCE-VISCOSITY RATIOS FOR HYDROCHLORIC ACID.

I. C.	II. E.	III. α.	IV. $\Lambda\eta/\Lambda_0\eta_0$.
0.001	−0.11130	0.990	0.990
0.005	−0.07278	0.965	0.981
0.01	−0.05595	0.929	0.972
0.02	−0.03910	0.895	0.964
0.03	−0.02925	0.876	0.957
0.04	−0.02226	0.862	0.952
0.05	−0.01684	0.852	0.948
0.06	−0.01241	0.844	0.944
0.07	−0.00867	0.836	0.940
0.08	−0.00542	0.831	0.936
0.09	−0.00256	0.825	0.931
0.10	0.00000	0.821	0.925
0.20	+0.01684	0.791	0.909
0.50	+0.04000	0.776	0.890
1.00	+0.05900	0.829	0.845

The transference numbers used in calculating the electromotive forces at the junctions of the different solutions were taken from Noyes and Falk's compilation of transference data;[1] the values of n_c employed in the calculations were as follows: KCl, 0.496; NaCl, 0.396; HCl, 0.833 for all concentration below 0.2 molar, and 0.845 for the higher concentrations. The data contained in Tables IV and V are represented graphically in Fig. 1, together with Linhart's values for dil. hydrochloric acid.

Since the error in the measured values of the electromotive force of the

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[1] THIS JOURNAL, 33, 1449 (1911).

different cells may reasonably be assumed to be less than 0.0003 volt, it follows that the values of the activity coefficients given in the foregoing tables are probably accurate to within 1%. The agreement between the foregoing values and those obtained by Jahn,[1] Harned,[2] Linhart,[3] MacInnes and Parker,[2] Ellis[2] and Noyes and Ellis[4] is, in general, quite satisfactory; the average deviation from the mean values recently published by Noyes and MacInnes for potassium chloride and hydrochloric acid is approximately 5%.

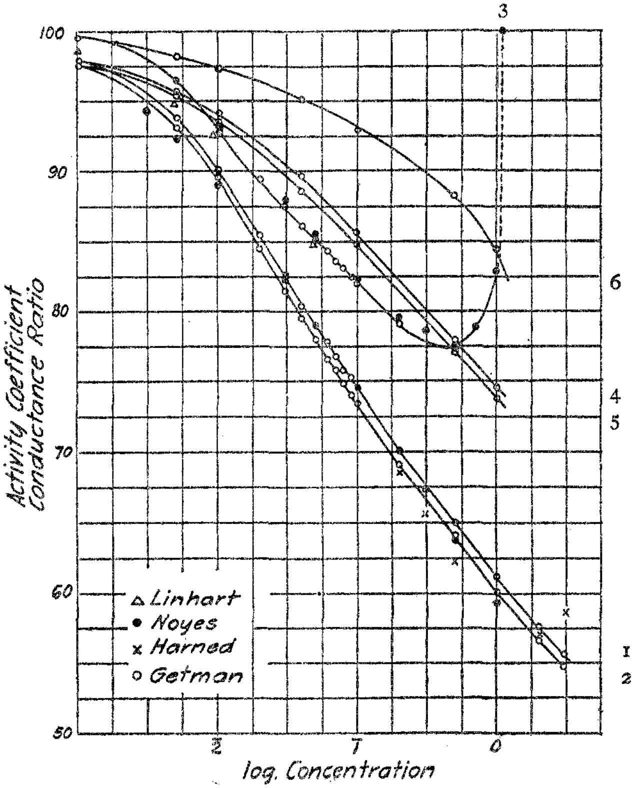

Fig. 1.—Curve 1, activity coefficients of KCl; Curve 2, activity coefficients of NaCl; Curve 3, activity coefficients of HCl; Curve 4, conductance-viscosity ratios of KCl; Curve 5, conductance-viscosity ratios of NaCl; Curve 6, conductance-viscosity ratios of HCl.

The results of this investigation may be briefly summarized as follows.

(1) It is apparent in the case of each of the substances studied, that the rate of decrease in the activity coefficient with increasing concentration,

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[1] *Z. physik. Chem.*, 33, 559 (1900).

[2] *Loc. cit.*

[3] THIS JOURNAL, 41, 1178 (1919).

[4] T *Ibid.*, 39, 2532 (1917).

is greater than the corresponding decrease in the conductance-viscosity ratio.

(2) The differences between the activity coefficients of the chlorides of potassium and sodium, at the same concentrations, are very slight, whereas the corresponding values of the activity coefficients of hydrochloric acid differ appreciably from those of either of the above 2 salts.

(3) The activity coefficient curve of hydrochloric acid passes through a well-defined minimum in the neighborhood of 0.5 molar concentration and thereafter increases rapidly with the concentration. Inspection of Fig. 1 reveals the fact that a similar, though much less clearly defined, minimum was found by Harned to exist in the activity coefficient curve of potassium chloride at approximately 2 molar concentration. The present investigation, however, failed to confirm the existence of this minimum.

Discussion of Results.

The foregoing results furnish confirmatory evidence of the conclusion which has been reached in several recent investigations, that the conductance-viscosity ratio does not afford a trustworthy measure of the activity of the ions of "strong" electrolytes. Furthermore, the marked increase in the activity coefficient of hydrochloric acid, which occurs beyond 0.5 molar concentration, proves conclusively that this quantity cannot be proportional to the degree of ionization.

Recent investigations by Chow[1] on potassium hydroxide and by MacInnes and Beattie[2] on lithium chloride, have revealed the fact that a minimum occurs in the activity coefficient curves of each of these substances at the same concentration as that observed with hydrochloric acid. Inspection of the following table shows that a similar minimum occurs in the molar freezing point depression of solutions of hydrochloric acid, lithium chloride and potassium hydroxide in the neighborhood of 0.2 molar concentration, whereas no such minimum occurs in the freezing point depressions of the chlorides of sodium and potassium.

TABLE VI.—MOLAR FREEZING-POINT DEPRESSIONS.

Concentration.	Molar Freezing-Point Depression. Δ/C.				
C.	KCl.	NaCl.	HCl.	LiCl.	KOH.
0.005	3.648	3.629	3.700	3.612	3.706
0.01	3.610	3.600	3.669	3.598	3.684
0.02	3.564	3.568	3.637	3.582	3.655*
0.05	3.502	3.516	3.591	3.563	3.61*
0.10	3.451	3.478	3.555	3.546	3.56*
0.20	3.394	3.424	3.56*	3.525	3.51*
0.30	3.359	3.396	3.60*	3.57*	3.50*
0.40	3.334	3.375	...	3.65*	3.51*
0.50	3.314	3.358	3.66	3.73*	3.53*

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[1] THIS JOURNAL, 42, 488 (1920).

[2] *Ibid.*, 42, 1117 (1920).

With the exception of the values marked with an asterisk, the data contained in the foregoing table have been compiled from the valuable summary of freezing-point data published by Noyes and Falk;[1] the values marked with an asterisk were taken from the tables published by Jones.[2]

The hypothesis advanced by Jones and the author[3] in explanation of this minimum in the freezing-point curve of a large number of electrolytes was that a certain portion of the solvent was removed from functioning as such owing to solvation of the dissolved substance. Should solvation tend to occur in solutions of hydrochloric acid, it is apparent that in a cell such as that indicated by the following scheme,

$$\text{Hg} - \text{HgCl} - 0.1\,N\ \text{HCl}\ \|\ 1.0\,N\ \text{HCl} - \text{HgCl} - \text{Hg},$$

the removal of an increasing amount of water from the rôle of solvent, with increasing concentration, would tend to cause an increase in the observed values of the electromotive force above those calculated by the Nernst equation, and therefore a corresponding increase in the values of the activity coefficient would occur. If the minima are due to solvation, we might reasonably expect a shift in the direction of increasing concentration as the temperature is raised. Such is actually found to be the case; the minima in the freezing-point curves occur at 0.2 molar concentration while those in the activity curves, based on measurements of electromotive force at 25°, occur at 0.5 molar concentration. While it is not claimed that the existence of similar minima in the 2 sets of curves is to be ascribed to solvation, or to any other common cause, it is suggested that such an explanation is not without the range of probability.

The author hopes to continue the investigation of this question in the near future.

STAMFORD, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGICAL CHEMISTRY, MARQUETTE SCHOOL OF MEDICINE.]

A STUDY OF A DECOLORIZING CARBON.

BY JOSEPH C. BOCK.

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The use of finely divided carbon to decolorize solutions is universal. There are, however, comparatively few attempts recorded in the literature to use it for the removal of substances other than coloring matters. While working on the removal from blood of residual proteins (after heat coagulation) we tried a charcoal of vegetable origin. While this was found to remove proteins quantitatively, it also caused a lowering of the non-protein nitrogen. As there are numerous occasions where decolor-

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[1] THIS JOURNAL, 32, 1011 (1910).

[2] "Hydrates in Aqueous Solution," *Carnegie Inst. Publication* 60.

[3] *Z. physik. Chem.*, 46, 286 (1903).