THE ACTIVITIES OF THE IONS OF STRONG ELECTROLYTES.

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1. The Conductances and Mobilities of the Separate Ions.

Lewis,[1] in his paper on "The Activities of Ions and the Degree of Dissociation of Strong Electrolytes" concludes that hydrochloric acid and the alkali chlorides have the same degree of dissociation at like concentrations. The evidence is based on the following relation:

$$\gamma_1/\gamma_2 = \Lambda_1 n_1/\Lambda_2 n_2 \tag{1}$$

This expression was derived by R. C. Tolman with the aid of the assumption that the chloride ion has, at any given concentration, the same mobility in solutions of the chlorides of the univalent elements. In this expression Λ_1, Λ_2, γ_1, γ_2, n_1, n_2, denote, respectively, the equivalent conductances, the degrees of dissociation of the two different chlorides, and the transference numbers of the chloride ion in the two solutions. Table I contains data for 0.1 N solutions, at 18°, taken from Lewis' article. I have prepared Table II for 0.01 N solutions, also at 18°, from data given in Noyes and Falk's[2] compilations. In the sixth column of both tables the product Λn_{Cl} for the several chlorides is divided by the corresponding product for potassium chloride. As this ratio is equal to 1.000 within 0.5%, Lewis concludes that the ionization values are also equal within this limit, although the conductivity ratios, Λ/Λ_0 (given in Col. 3) vary widely, that of hydrochloric acid being about 7% higher than the mean value for the other chlorides. However, in this article mentioned, and in

TABLE I.
Data for 0.1 N Solutions of Chlorides.

	$\Lambda_{0.1}$	$\Lambda_{0.1}/\Lambda_0$	n_{Cl}	$n_{Cl}\Lambda_{0.01}$	$n_{Cl}\Lambda/(n_{Cl}\Lambda)_{KCl}$
HCl	351.4	0.925	0.1612	56.7	0.996
KCl	112.0	0.862	0.508	56.9	1.000
NaCl	92.0	0.844	0.617	56.8	0.998
LiCl	82.3	0.833	0.685	56.4	0.992
CsCl	113.4	0.850	0.500	56.7	0.996

TABLE II.
Data for 0.01 N Solutions of Chlorides.

	$\Lambda_{0.01}$	$\Lambda_{0.01}/\Lambda_0$	n_{Cl}	$n_{Cl}\Lambda_{0.01}$	$n_{Cl}\Lambda/(n_{Cl}\Lambda)_{KCl}$
HCl	369.3	0.972	0.167	61.67	1.004
KCl	122.4	0.942	0.502	61.44	1.000
NaCl	101.98	0.936	0.603	61.44	1.000
LiCl	91.97	0.931	0.668	61.43	0.9998

[1] THIS JOURNAL, 34, 1640 (1912).

[2] Ibid., 33, 1436 (1911) and 34, 454 (1912).

a later paper,[1] Lewis decides that the "corrected degree of dissociation" of hydrochloric acid is higher than that of potassium chloride; at $0.1\ N$, for instance, the values given are 81.6 and 78.0, respectively. These "corrected degrees of dissociation" will be discussed in Section 2 of this paper.

The small variation in the values in the last two columns of the two tables shows that the equivalent conductance Λn_{Cl} of the chloride-ion-constituent is, at any given concentration up to $0.1\ N$, substantially the same, whether the other ion-constituent associated with it is hydrogen ion or any of the alkali element ions. This fact makes it very probable that the two factors which determine the equivalent conductance of the chloride-ion-constituent—namely, the degree of ionization γ of the chloride and the equivalent conductance, or mobility, of the chloride ion itself,— must have the same value in the case of the several univalent chlorides at any given concentration, at any rate up to $0.1\ N$, for otherwise we would have to assume that any variation in the value of one of these factors is just balanced by an equal variation of the other factor in the opposite direction. This constancy of the equivalent conductance of the chloride-ion-constituent at any given concentration does not, however, show whether the decrease of it with increasing concentration is due to decrease in the ionization of the chloride, or to decrease in the mobility of the chloride ion, or to simultaneous variation in both these factors. Now, since it is very possible, as already shown, that the ionization is the same in the different chloride solutions, at any given concentration, it is almost certain that the divergence of the conductance ratio Λ/Λ_0 of hydrochloric acid from that of the other chlorides, and the corresponding divergence in the change of the equivalent conductance of the hydrogen-ion-constituent with the concentration from that of the other constituents, are really due to a considerable change with the concentration of the equivalent conductance or mobility of the hydrogen ion itself. And, also, since differences in the variation of the mobilities of the ions are thus demonstrated, it is very probable that actual variations of larger magnitude than these differences occur, with increasing concentrations, in the mobilities of all the ions.

2. The Activities of the Separate Ions.

The preceding considerations, which are based on the kinetic phenomenon of conductance, cannot, from their very nature, lead directly to a determination of the "activity" or "effective concentration" of ions, that is, to a determination of the concentrations which must be assigned to the ions in order that their actual mass action and other thermodynamic effects may be expressed by the familiar laws of perfect solutes. The
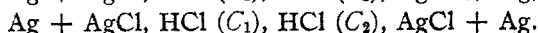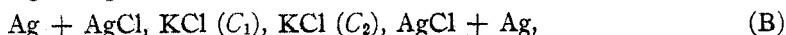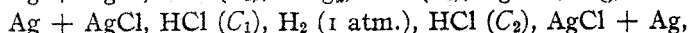
[1] THIS JOURNAL, **39**, 2258 (1917).

conclusions reached in the preceding paragraphs do, however, much increase the probability of a simple hypothesis which greatly assists in determining the probable values of the activities of the separate ions. Namely, the fact demonstrated above 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 choride ion, at any given concentration, is also independent of the cation associated with it.

This hypothesis differs from that employed, up to the present time, in computing activities. It has been commonly assumed that the cation and anion of the substance have equal activities in the same solution, even in the case of hydrogen ion and chloride ion in hydrochloric acid.

It is the purpose of this section of the article to show how the activities of hydrogen ion can be obtained from existing electromotive force data, with the aid of this hypothesis, and with the further assumption that the usual hypothesis is valid in the case of potassium chloride; that is, that its two ions, which have nearly the same weight and mobility, have the same activity in a solution of the salt.

We will consider cells of the types A and B, *i. e.*, cells without and with liquid junction:

Ag + AgCl, KCl (C_1), KHg$_x$, KCl (C_2), AgCl + Ag,   (A)
Ag + AgCl, HCl (C_1), H$_2$ (1 atm.), HCl (C_2), AgCl + Ag,
Ag + AgCl, KCl (C_1), KCl (C_2), AgCl + Ag,   (B)
Ag + AgCl, HCl (C_1), HCl (C_2), AgCl + Ag.

The electromotive forces E_A and E_B of cells of these two types are given by the following expressions,[1] in which a_1^+, a_1^-, a_2^+ and a_2^- denote, respectively, the activities of the positive and negative ions at the two concentrations C_1 and C_2, and n is the transference number of the cation:

$$E_A = \frac{RT}{F} \log \frac{a_1^+ a_1^-}{a_2^+ a_2^-} \quad \text{and} \quad E_B = \frac{nRT}{F} \log \frac{a_1^+ a_1^-}{a_2^+ a_2^-}.$$

From the electromotive force measurements available for potassium chloride cells of either of these types, by putting $a_1^+ = a_1^-$ and $a_2^+ = a_2^-$, we can find the ratio a_1^-/a_2^- for chloride ion at concentrations C_1 and C_2. Then from the electromotive force data for hydrochloric acid cells, containing acid at the same concentrations C_1 and C_2, we can find, by substituting this value of a_1^-/a_2^- in the appropriate equation, the value of a_1^+/a_2^+ for hydrogen ion.

Table III, which is self-explanatory, contains the available data and

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[1] Lewis, *Proc. Am. Acad.*, **43**, 259 (1907) and MacInnes and Parker, THIS JOURNAL, **37**, 1445 (1915).

the results of the computations just decribed. The electromotive forces in the lines marked J are the measurements of Jahn;[1] in the lines indicated by N. and E. the potentials were interpolated from the work of Noyes and Ellis,[2] by plotting, on a large scale, the logarithms of the ob-

TABLE III.

Sub-stance.	Type of cell.	Temp.	Concentrations. C_1.	C_2.	E. M. F. of cell.	Transference number of cation.	Activity ratios. a_1/a_2 for Cl−.	H+.	
HCl......	B	18°	0.006686	0.001665	—0.05614	0.833			J.
							3.82	3.84	
KCl......	B		0.006700	0.001670	—0.03330	0.495			J.
HCl......	B	18°	0.008315	0.001665	—0.06487	0.833			J.
							4.70	4.74	
KCl......	B		0.008329	0.001670	—0.03844	0.495			J.
HCl......	B	18°	0.01665	0.001665	—0.09235	0.833			J.
							8.86	9.38	
KCl......	B		0.01670	0.001674	—0.05434	0.496			J.
HCl......	B	18°	0.03330	0.003329	—0.09162	0.833			J.
							8.76	9.14	
KCl......	B		0.03347	0.003347	—0.05403	0.496			J.
HCl......	A	25°	0.05	0.005	—0.11234	...			N. and E.
							8.64	9.16	
KCl......	A		0.05	0.005	—0.11085	...			M. and P.
HCl......	A	25°	0.1	0.01	—0.1116	...			N. and E.
HCl......	A		0.1	0.01	—0.1117	...			L. B. S.
							8.33	9.23	
KCl......	A	25°	0.1	0.01	—0.1089	...			M. and P.
KCl........B			0.1	0.01	—0.0540	0.495			M. and P.

served electromotive forces against the logarithms of the corresponding concentrations. L. B. S. refers to the work of Lewis, Brighton and Sebastian,[3] and M. and P. to that of MacInnes and Parker.[4]

In Table IV the activities of the H+ and Cl− ions (Columns 2 and 3) are given at the hydrochloric acid concentrations shown in Col. 1. For the lowest concentration (0.00166 N) the activities of the two ions are assumed to be the same and equal to γC, in which γ is the conductance ratio, at this concentration, for potassium chloride. For the activities at 3 of the higher concentrations this figure has been multiplied by the appropriate ratios from Table III. The values corresponding to 0.0033, 0.005 and 0.01 N were next obtained by plotting the logarithms of the

[1] Z. physik. Chem., 33, 545 (1900).
[2] THIS JOURNAL, 39, 2532 (1917).
[3] Ibid., 39, 2245 (1917).
[4] Ibid., 37, 1445 (1915).

TABLE IV.

| Concentrations. | Activities. | | Activity coefficients. | |
	K+ or Cl⁻.	H+.	K+ or Cl⁻.	H+.
0.001665	(0.001627)	(0.001627)	0.976	0.976
0.003330	0.003140	0.003205	0.935	0.972
0.00500	0.004588	0.004750	0.918	0.949
0.00666	0.006215	0.006247	(0.932)	0.937
0.0100	0.008785	0.009257	0.878	0.925
0.01666	0.01441	0.01526	0.864	0.915
0.03333	0.02750	0.02945	0.825	0.883
0.0500	0.0396	0.0434	0.792	0.869
0.100	0.0732	0.0854	0.732	0.854

activities obtained as described above against the logarithms of the corresponding concentrations, the result being very nearly a straight line. These numbers were in turn multiplied by ratios from Table III for the activities at still higher concentrations. Cols. 4 and 5 of Table IV contain the activity coefficients, $i.\ e.$, the activities divided by the corresponding concentrations. The activity coefficients are based on the same considerations as Lewis' "corrected degrees of dissociations" for salts whose ions have the same activity at any concentration. If the ion activities of a substance are different the "corrected degree of dissociation" is the mean of the activity coefficients.

Since the activity coefficients in Table IV are obtained in part by interpolation and from electromotive force data at two different temperatures, the values given can hardly be final ones. More experimental work is needed in this field. In regard to the temperature, however, the effect on the activity ratios cannot be large since Ellis[1] has found that activity coefficients calculated from freezing-point measurements agree closely with those obtained from electromotive force data at 25°.

3. The Normal Hydrogen *versus* The Normal Calomel Electrode.

Lewis, Brighton and Sebastian[2] have calculated the potential of (hypothetical) molal solution, with respect to hydrogen ion, against the normal calomel electrode. This calculation is repeated below, using the activity coefficients of Table IV instead of the "corrected degrees of dissociations" of these authors.
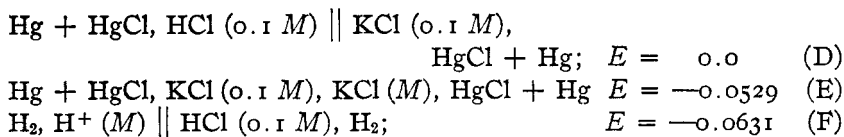
The potential in question, represented by the expression,[3]

$$H_2, H^+ (M) \parallel KCl (M), HgCl + Hg$$
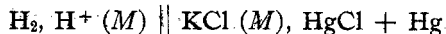
is the sum of the electromotive forces of the cells:

$$H_2, HCl (0.1\ M), HgCl + Hg; \qquad\qquad E = 0.3989 \quad (C)$$

[1] This Journal, 38, 761 (1916).

[2] *Loc. cit.*

[3] As in Lewis' papers, the symbol ‖ indicates that correction has been made for the liquid junction.

$Hg + HgCl$, HCl (0.1 M) $\parallel$ KCl (0.1 M),
$$HgCl + Hg; \quad E = \quad 0.0 \qquad (D)$$
$Hg + HgCl$, KCl (0.1 M), KCl (M), $HgCl + Hg \quad E = -0.0529 \quad (E)$
H_2, H^+ (M) $\parallel$ HCl (0.1 M), H_2; $\qquad E = -0.0631 \quad (F)$
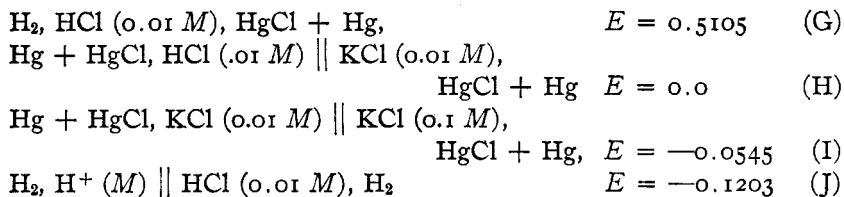
Of these (C) is the mean of the closely agreeing results of several observers; (D) is zero, since, according to the viewpoint of this article, the chloride ion has the same activity in both solutions; (E) is a direct measurement of Lewis and Randall; and (F) has been calculated by the usual logarithmic formula using 0.854 from Table IV as the activity coefficient of hydrogen ion in 0.1 M hydrochloric acid. Performing the addition, we obtain

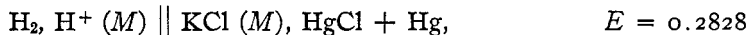$$H_2, \ H^+ \ (M) \parallel KCl \ (M), \ HgCl + Hg, \quad E = 0.2829.$$

Lewis and his collaborators found practically the same value (0.2828) for this constant.

Following, once more, the method of these authors, this constant can also be calculated by starting from measurements on 0.01 M hydrochloric acid. In this case the potential desired is the sum of the electromotive forces:

H_2, HCl (0.01 M), $HgCl + Hg$, $\qquad E = 0.5105 \qquad (G)$
$Hg + HgCl$, HCl (.01 M) $\parallel$ KCl (0.01 M),
$$HgCl + Hg \quad E = 0.0 \qquad (H)$$
$Hg + HgCl$, KCl (0.01 M) $\parallel$ KCl (0.1 M),
$$HgCl + Hg, \quad E = -0.0545 \quad (I)$$
H_2, H^+ (M) $\parallel$ HCl (0.01 M), $H_2 \qquad E = -0.1203 \quad (J)$

Adding these potentials, together with (E), we obtain

H_2, H^+ (M) $\parallel$ KCl (M), $HgCl + Hg$, $\qquad E = 0.2828$

agreeing exactly with the above workers. Potential (G) is from the article quoted; (H) is based on the same assumption as (D); and (I) and (J) were found by using activity coefficients from Table IV. Although, in this case, the same result is obtained as that found with the usual assumptions as to activities, some of the potentials making up the totals have quite different values. For instance, the article quoted gives 0.0012 for (D), the potential arising from the supposed difference in the activities of the chloride ions in the two solutions.

An example of the difference between the proposed system and the usual assumptions appears in the computation of the liquid junction

$$HCl \ (C_1), \ HCl \ (C_2).$$
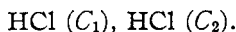
If the concentrations are, for instance, 0.01665 and 0.001665 N, the assumption of equal activities of the two ions leads to -0.03694 for the potential at this point of contact,[1] whereas the activity values given in

[1] THIS JOURNAL, **37**, 2305 (1915).

Table IV yield —0.03767. The latter figure also gives the same potential (0.05468) for the systems:

$$Ag + AgCl, HCl\ (0.01665)\ \|\ HCl\ (0.001665), AgCl + Ag$$

and

$$Ag + AgCl, KCl\ (0.01665)\ \|\ KCl\ (0.001665), AgCl + Ag$$

as would be expected if hydrochloric acid and potassium chloride are equally dissociated, since all the electrodes are reversible to the chloride ion. These computations will be discussed further in a forthcoming article.

I am indebted to Prof. A. A. Noyes for valuable criticism in the preparation of this paper.

4. Summary.

Since the product of the transference number of the chloride ion and the equivalent conductance $n\Lambda$ is a constant, at a given concentration and temperature, for the chlorides of the alkali metals and of hydrogen, it has been assumed that the "activity" of the chloride ion in these solutions is also independent of the nature of the (univalent) positive ion. On this basis the activity coefficients of both ions of hydrochloric acid have been calculated for a series of concentrations, and the potential of the normal hydrogen electrode against the normal calomel electrode has been computed.

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NOTE.

Corrections.—In the paper entitled "Notes on Neutral Salt Catalysis" (THIS JOURNAL, **40**, 1461 (1918)). On p. 1463, Equation 2 should read $H_2O_2 + IO' = H_2O + I' + O_2$, instead of $H_2O_2 + IO' = H_2O + IO_2'$; on p. 1477, in the middle of the page, for $E_t + E_l$ read $E_t - E_l$; in the last line, for $E_t + E_l$ read $E_t - E_l$; on p. 1478, in Table VII, all numbers in the column headed E_l should be positive instead of negative; the column headed $E_t + E_l$ should read $E_t - E_l$; and on p. 1479, in Table VIII, under the column headed $\dfrac{K \times 10^2}{a_1}$, read 14.14 for 13.14.

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