suspension, and part of the alkali neutralizes the zinc hydroxide giving the acid zincate. That there is no very great distinction between these processes is evident when we consider that zinc hydroxide, like aluminum hydroxide, silicic acid, etc., is colloidal, so that its formula really is $(H_2ZnO_2)_n.xH_2O$. It is hard to see any great distinction between the adsorption of OH^- by such a molecule, considered as a colloidal particle, on the one hand, and its gradual neutralization, considered as a polyacid, on the other hand. As the neutralization by OH^- (or adsorption of OH^-) proceeds, the molecule (or colloidal particle) becomes progressively smaller, until finally the acid zincate ion is produced. The solid polyzincate, $Na_2Zn_3O_5.18H_2O$, reported by Comey and Jackson, is evidence in favor of this point of view. A similar relation undoubtedly exists between silicic acid and the silicates.

Summary.

There exists in solutions of zinc chloride, bromide and iodide, each containing an excess of the corresponding acid, a weak acid of the type $HZnCl_3$.

Zinc hydroxide acts towards alkali essentially as a monobasic acid.

BERKELEY, CAL.

THE EXTRAPOLATION OF CONDUCTANCE VALUES.

BY MERLE RANDALL.

In connection with researches upon the electrical conductivity of aqueous solutions, a function of the form $1/\Lambda = 1/\Lambda_0 + K(c\Lambda)^{n-1}$ has been very largely used in order to obtain the equivalent conductance, Λ_0, at infinite dilution. In the above function Λ is the equivalent conductance at the concentration c, K is a constant, and n is a number which, for aqueous solutions, lies between 1.3 and 1.7. The value of n is so chosen that the graph obtained by plotting the values of $1/\Lambda$ against $(c\Lambda)^{n-1}$ is nearly a straight line, and two other graphs corresponding to neighboring values of n, on opposite sides of the first line, are also drawn so as to aid in determining the most probable point $(1/\Lambda_0)$ at which the graphs cut the $1/\Lambda$ axis.[1]

While the method outlined above enables one to obtain the best value for the equivalent conductance at zero concentration, the calculations are quite laborious, and unless the data are quite accurate and complete for the very dilute solutions, the result is somewhat uncertain.

[1] A. A. Noyes, THIS JOURNAL, 30, 335 (1908); J. Johnston, *Ibid.*, 31, 1010 (1909) discusses the use of the function and gives a plot which shows the general shape of the graphs obtained.

Noyes and Falk[1] have recently given accurate calculations of the Λ_0 value and percentage ionization[2] for a large number of salts by the above method. Abbott and Bray[3] have shown that, if percentage ionization of a salt is plotted against its ion concentration, the ionization curves of salts of the same valence type do not intersect. The relation is more obvious if the percentage ionization is plotted, not against the ion concentration but against the square root of the ion concentration as in Fig. 1.
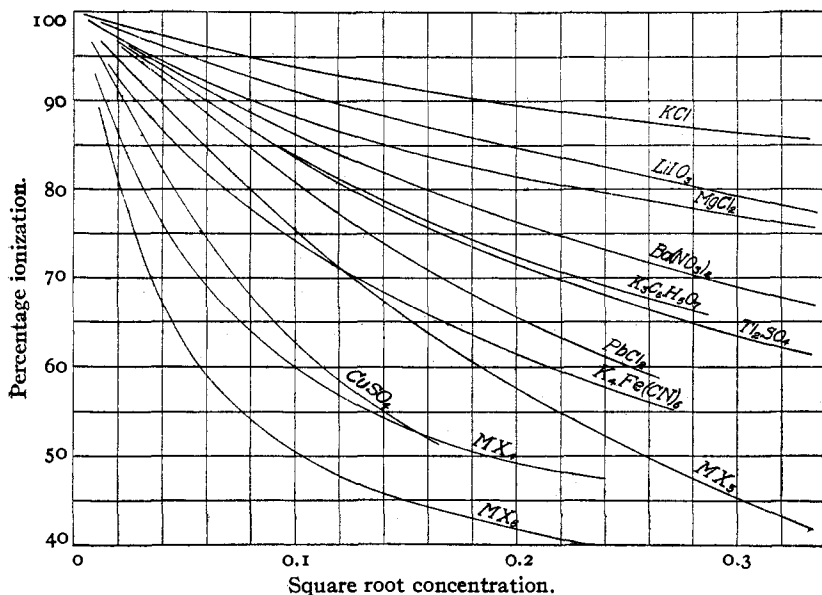

Square root concentration.
Fig. 1.—Percentage ionization of type salts.

It is also found that the salts of a single valence type divide themselves into several distinct groups. Thus, of the salts of the uni-univalent type in tenth molal solution, the chlorides, bromides and iodides of lithium, sodium, potassium, rubidium, caesium and ammonium are all ionized to about the same extent.[4] The ionization of the nitrates, bromates and chlorates of the alkali metals, and of the halides of silver and thallium is several per cent. lower, and the ionization of silver nitrate and thallium nitrate is still several per cent. lower.

As the zero of concentration is approached the difference in the percentage ionization becomes smaller. If we may provisionally assume that the ionization of a salt such as thallous chloride is the same as that of a

[1] Noyes and Falk, THIS JOURNAL, 34, 454 (1912).

[2] The ionization is here defined by the conductance ratio Λ/Λ_0. This definition is made for convenience. The validity of the extrapolation is independent of the assumption that the conductance ratio gives the true ionization.

[3] Abbott and Bray, THIS JOURNAL, 31, 729 (1909).

[4] Lewis, Ibid., 34, 1631 (1912).

salt such as potassium chloride, the conductance of which has been carefully measured, and the Λ_0 value determined by any reliable method, as that mentioned above, the equivalent conductance at zero concentration is given by the usual equation

$$\Lambda_0 = \Lambda/\alpha$$

in which α is the degree of ionization.[1]   Thus in Col. 2 of Table I is given the percentage ionization of potassium chloride at 18°, in Col. 3 the conductance of thallous chloride, and in Col. 4 the value of $\Lambda TlCl/\alpha KCl$.

TABLE I.

Millimols per liter.	100 $\alpha_{18}°$ KCl.	$\Lambda_{18}°$ TlCl.	$\dfrac{\Lambda TlCl}{\alpha KCl}$.
0.1	99.2	130.3	131.4
0.2	99.0	130.0	131.3
0.5	98.5	129.2	131.2
1.0	97.9	128.2	131.0
2.0	97.1	126.8	130.6
5.0	95.6	123.7	129.4
10.0	94.1	120.2	127.8

If the actual values for the conductivity ratio of thallous chloride, instead of those for KCl, had been used, Col. 4 would have been constant, and equal to Λ_0 for TlCl.   We have seen that, as the dilution is increased, the ionization of TlCl approaches that of KCl more closely, becoming

TABLE II.

Ionization Values of Typical Salts of Various Valence Types at 18° (Λ/Λ_0).

Salt.	Milliequivalents per liter.									
	0.1.	0.2.	0.5.	1.	2.	5.	10.	20.	50.	100.
KCl	99.2	99.0	98.5	97.9	97.1	95.6	94.1	92.2	88.9	86.0
LiIO$_3$	99.1	98.7	97.9	97.0	95.8	93.6	91.2	88.3	83.4	78.9
MgCl$_2$	98.4	97.8	96.7	95.5	93.9	91.0	88.3	85.1	80.3	76.5
Ba(NO$_3$)$_2$	98.4	97.8	96.7	95.3	93.4	89.8	86.1	81.8	74.4	67.9
Tl$_2$SO$_4$	..	..	(96.4)	94.8	92.4	88.2	83.7	78.0	69.4	62.5
PbCl$_2$	..	..	(96.0)	94.3	91.7	86.5	80.8	73.8	62.7	..
K$_3$C$_6$H$_5$O$_7$	..	..	96.4	94.8	92.6	88.2	81.7[2]	..	70.5	..
MX$_2$[3]	..	..	94.5	92.2	88.6	82.3	75.5	67.0	54.1	43.8
K$_4$Fe(CN)$_6$	..	..	..	..	85.9	..	71.2[2]	..	59.1	..
CuSO$_4$	96.1	94.4	90.5	86.2	80.4	70.9	62.9	55.0	..	..
MX$_4$[4]	..	90.1	83.9[5]	..	74.2	64.2[6]	..	54.3	48.1	..
MX$_5$[7]	..	85.2	77.2[5]	..	65.2	55.0[6]	..	45.6	40.3	..

[1] Noyes and Falk, THIS JOURNAL, 34, 455 (1912).

[2] 12.5 millinormal.

[3] No accurate determination of the conductance of salts of this type is available. Theoretical values in which $1 - \alpha$ for a salt of this type was considered equal to $3/2(1 - \alpha)$ for Tl$_2$SO$_4$ have been found very useful.

[4] Tetra sodium benzene pentacarboxylate.   Noyes and Lombard, THIS JOURNAL, 33, 1423 (1911).

[5] 0.6 millinormal.

[6] 6.0 millinormal.

[7] Penta sodium benzene pentacarboxylate.

equal at infinite dilution. If, then, we plot the values of $\Lambda TlCl/\alpha KCl$ against the ion concentration, or, better, against the square root of the ion concentration, and extrapolate this curve graphically to zero concentration we will obtain for TlCl $\Lambda_{0\,18°} = 131.4$. Noyes and Falk found 131.4. Even in the case of very accurate data a rough plot will suffice to give an accurate extrapolation.

The ionization values at 18° calculated by Noyes and Falk for a number of typical salts of the various valence types are given in Table II.

The examples given in Table III will illustrate the extreme simplicity of the method outlined above.

TABLE III.

Milliequivalents per liter.	$\Lambda_{18}°LiIO_3$ $\overline{\alpha_{18}°KCl}$	$\Lambda_{25}°Ba(BrO_3)_2$ $\overline{\alpha_{18}°Ba(NO_3)_2}$	$\Lambda_{25}°K_2SO_4$ $\overline{\alpha_{18}°Ba(NO_3)_2}$	$\Lambda_{25}°K_2SO_4$ $\overline{\alpha_{18}°MgCl_4}$	$\Lambda_{25}°Mg(NO_3)_2$ $\overline{\alpha_{18}°Ba(NO_3)_2}$	$\Lambda_{25}°Mg(NO_3)_2$ $\overline{\alpha_{18}°MgCl_2}$	$\Lambda_{25}°La(NO_3)_3$ $\overline{\alpha_{18}°K_2CaH_5O_7}$
1	66.7	119.3	.....	.....	125.4	125.3	.....
2	66.4	119.1	155.1	154.4	125.7	125.0	139.2
5	65.9	119.1	155.7	153.7	126.8	125.1	.....
10	65.2	119.3	156.3	152.3	128.1	125.0	.....
20	64.4	118.9	156.9	150.8	129.7	124.6	140.0
50	63.1	.....	159.3	147.5	134.1	124.3	141.4

The Λ_0 value calculated by this new method for $LiIO_3$, using KCl as the reference salt, was 67.3, in agreement with the value calculated by Noyes and Falk. For $Ba(BrO_3)_2$ Λ_0 is 119.2, while the longer method gives 120.0. When K_2SO_4 is compared with $Ba(NO_3)_2$ Λ_0 is 154.0, with $MgCl_2$ Λ_0 is 155.4, mean 154.7. Noyes and Falk found 154.8. Likewise, $Mg(NO_3)_2$ compared with $Ba(NO_3)_2$ gave $\Lambda_0 = 124.4$, and with $MgCl_2$ $\Lambda_0 = 125.4$. The last result is entitled to much greater weight, since the variation of the latter ratio is much smaller, hence Λ_0 is taken as 125.3. Noyes and Falk found $\Lambda_0 = 125.6$. In the case of $La(NO_3)_3$ the new value 138.6 is certainly much nearer the correct value than that of Noyes and Falk, namely, 142.6.

In general, that salt is chosen for the reference salt which makes the provisional value of Λ_0 most nearly constant. In some cases it is advisable to choose several reference salts, and take the average. It is not necessary that the reference salt be chosen at the same temperature, for the ionization curves do not cross as the temperature is changed. It will often be possible by the aid of three or four points to determine a fairly accurate value of Λ_0, as in the case of $La(NO_3)_3$.

In a large number of papers published recently[1] the percentage dissociation has been calculated from the equation $100\,\alpha = 100\mu/\mu_\infty$ where μ_∞ is the highest value of μ (Siemen's units[2]) measured, obtained sometimes at

[1] Watkins and Jones, THIS JOURNAL, 37, 2626 (1915).

[2] The use of the obsolete Siemen's units for expressing conductance data leads to

1024, and sometimes at 2048 and 4096 liters. These "percentage ionizations" obviously have no significance since the values of μ_{∞} (reduced to mhos) are in no case as large as Λ_0 obtained by any method of extrapolation. The divergence is greatest in the case of polyionic salts. Moreover, conductivity measurements are in most cases unreliable at these extreme dilutions. In the papers cited the equivalent conductance at 2048 liters is often less than at 1024 liters. The method outlined in the present paper will enable one rapidly to extrapolate conductance values and in the case of inconsistent and incomplete data to obtain approximately correct percentage ionization values.

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A STUDY OF THE LEAD ELECTRODE.

BY FREDERICK H. GETMAN.

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The present paper contains a brief summary of the results of a series of experiments carried out with a view to determining the constancy and reproducibility of the lead electrode. The methods employed are essentially those described in previous papers dealing with the reproducibility of the copper electrode[1] and the reproducibility of the cadmium electrode.[2] In both of these papers it was pointed out that the variations observed in the potential of electrodes cast or drawn from the metals under investigation were most satisfactorily explained on the ground of allotropism. The recent studies of Cohen and his co-workers[3] on the metastability of the metals, has established the existence of metallic allotropes beyond any question.

Evidence of the allotropism of lead has been adduced by Heller[4] who observed that when a piece of freshly cast, pure lead was immersed in a solution of lead acetate, acidified with nitric acid, it gradually underwent transformation into a gray modification, the change being complete in about three weeks. This gray modification was found to be brittle

much confusion. Electrical measuring instruments as now manufactured are calibrated in international ohms and not in Siemen's ohms. In the paper of Watkins and Jones references are given to numerous other papers from the Johns Hopkins Laboratory in which Siemen's units are used. In the most recent article (Lloyd, Wiesel and Jones, THIS JOURNAL, 38, 121 (1916)) the conductances are presumably in Siemen's units although it is not so stated by the authors. In general, investigators both here and abroad use international ohms.

[1] Getman, Trans. Am. Electrochem. Soc., 26, 67 (1914).

[2] Getman and Gibbons, THIS JOURNAL, 37, 953 (1915).

[3] Cohen, Verslag Akad. Wetenschappen, 16, 485, 565, 628, 632, 807 (1913–14); 17, 54, 59, 60, 122, 200 (1914); 23, 754, 896 (1914); 23, 1220 (1915); 18, 91 (1915); Z. physik. Chem., 85, 419 (1913); 87, 409, 419, 426, 431 (1914); 89, 493, 728, 733, 742, 748, 757 (1915); Trans. Faraday Soc., 10, 216 (1915).

[4] Z. physik. Chem., 89, 761 (1915).