

definit pressures, hence values for the vapor pressures at temperatures below the melting points are not given.

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THE CONDUCTANCE OF AQUEOUS SOLUTIONS OF SODIUM CHLORIDE, HYDROCHLORIC ACID AND THEIR MIXTURES.

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Introduction.

The object of this investigation was to study, for two salts of widely different conductances, the validity of the present method of calculating the specific conductance of mixtures of salts with a common ion. It has been concluded, from a consideration of existing conductance data,¹ that the degree of ionization of each salt in such a mixture is the same as in a solution of the pure salt at the same total ion concentration. By means of this "ionization rule," and with the additional assumption that the conductances of the ions are constant, values have been calculated for the specific conductances of mixtures which agree well with those determined experimentally.

In any method of calculating the specific conductance L of a binary mixture, this quantity may be divided into two parts, L' and L'' , the *individual specific conductances* of the separate salts, when $L = L' + L''$. Each of these may be calculated by means of a relation of the form:

$$1000 L' = (C'\gamma')(A'_k + A'_a), \quad (1)$$

where C' is the concentration, γ' the degree of ionization, $(A'_k + A'_a)$ the sum of the equivalent conductances of the ions of one of the salts in the mixture. According to the above rule γ' has the same value as in a solution of the single salt at the same total ion concentration, and has hitherto been calculated by a method of approximation on the assumption that $A'_k + A'_a$ is constant and equal to A'_0 , the conductance of the salt at zero concentration. This assumption is, of course, an uncertain one in any case, and especially when the transference number is known to change with the concentration. For this reason it must be admitted that the values of ion concentrations calculated by the above method may be considerably in error and it will be shown later that this may be the case even when the calculated and measured conductances agree perfectly.

If in the above formula stress is laid on the idea of equivalent conductance, instead of ion concentration ($C'\gamma'$), then we may write:

¹ For references see Sherrill, THIS JOURNAL, 32, 74 (1910); Mackay, *Ibid.*, 33, 308 (1911).

$$1000 L' = C'(\gamma' A'_k + \gamma' A'_a) = C' A', \quad (2)$$

where A' is the *individual equivalent conductance* of one of the salts in the mixture. The above rule may now be restated as a purely empirical principle: In a mixture of two salts with a common ion, the equivalent conductance of each in the mixture is the same as the equivalent conductance of the pure salt when present alone at the same total ion concentration. Since, moreover, the equivalent conductance of a salt changes only very slowly with its concentration, it is evident that in a given mixture the value of the specific conductance of one salt (L'), and therefore that of the specific conductance of the mixture, (L) must remain almost constant for different values of $A'_k + A'_a$, and also even when A'_k and A'_a are allowed to vary independently. This result will be illustrated later in connection with the discussion of our experimental results.

Whenever in a given series of mixtures, in which the specific conductance of one substance (L') remains nearly constant, the calculated values of L differ from the experimental, then the absolute differences must tend towards zero as the ratio of the individual conductances L''/L' becomes very small. The test of the ionization rule by comparing calculated and experimental conductances will evidently cease to be of value when the ratio L''/L' becomes less than some small number, say 1 : 10 for ordinary experimental conditions, and will in general be most satisfactory when $L' = L''$. Since in the case of existing measurements the equivalent conductances of the two separate salts do not differ greatly, equal individual conductances correspond to approximately equal concentrations, and the maximum range of concentrations (which has however not been covered in practice) lies between the ratios 10 : 1 and 1 : 10. In the present instance the method of calculating receives its most severe test when the concentration of the hydrochloric acid is about one-third that of sodium chloride, and the effective range of concentrations lies between approximately 30 : 1 and 1 : 3.

Experimental Details.—The sodium chloride was precipitated from a nearly saturated solution of Kahlbaum's C. P. salt by leading into it washed hydrogen chloride gas. The crystals were collected upon a Büchner funnel, washed with a little water, and ignited in a platinum dish. A stock solution was prepared, and from it nearly all the other solutions were made by diluting weighed amounts to known volumes. This solution was standardized by measuring the conductances of three approximately 0.01 normal solutions prepared in this way, and comparing these values with those of similar solutions made up by weighing out the solid salt. A less reliable preliminary standardization from two gravimetric silver chloride determinations gave a 0.1 per cent. higher normality for the stock solution.

The absence of an appreciable amount of acid in the stock sodium

chloride solution was proved by experiments with the indicators, methyl orange and para-nitrophenol, from which it was concluded¹ that the concentration of acid was in the neighborhood of 10^{-6} and certainly was not as great as 10^{-5} normal.

The stock hydrochloric acid solution was prepared by dissolving in conductivity water washed hydrogen chloride gas, liberated by dropping concentrated sulfuric acid into pure concentrated hydrochloric acid. The concentration of this solution, as determined from two probably inaccurate gravimetric silver chloride determinations, was 0.2006 mol HCl per 1000 grams solution. A somewhat lower concentration, 0.2004 mol, was obtained by titrating the chloride (after first neutralizing the acid) with a silver nitrate solution which had been standardized against the stock sodium chloride solution by an exactly similar titration. A still lower value 0.2001 was obtained at a later date from two very accurate gravimetric silver chloride determinations made by Dr. W. D. Harkins. The value finally adopted was 0.2003 mol. HCl per 1000 g. solution.

The potassium chloride used in determining cell constants was prepared by twice recrystallizing the C. P. salt from conductivity water.

Many of the solutions used in making the conductance measurements were prepared by weighing out the required amounts of one or both of the stock solutions, and diluting at 25° to a known volume. The remaining solutions were prepared from these by dilution by means of calibrated measuring flasks.

The measurements were made at 25° in a large thermostat, whose temperature remained constant within 0.02° . This temperature was determined by means of a Baudin thermometer which had been certified by the Bureau of Standards at Washington.

The conductivity measurements were made in the usual way with a slide wire bridge of the Kohlrausch roller pattern. The bridge resistances were standardized to an accuracy of about 0.02 per cent. The slide wire was calibrated by the method of Strouhal and Barus, and in addition the middle point of the wire was checked in an independent determination by means of two equal resistances. The heavy copper lead wires had a resistance of 0.05 ohm. This was subtracted from the measured resistance, which was in no case less than 20 ohms. The specific conductance of the water used was determined before making up a solution, and was subtracted from the measured conductance. The value was always between the limits 0.5 and 1.0×10^{-6} .

Two glass cells of the pipet form,² with platinized platinum electrodes, were used in making the conductance measurements. Cell A had horizontal circular electrodes 2 cm. in diameter and 5.5 cm. apart; B had

¹ Cf. Salm, *Z. physik. Chem.*, 57, 500 (1906).

² THIS JOURNAL, 31, 732 (1909).

vertical electrodes 2.5 cm. square, and about 1 cm. apart. The 0.01 normal solutions were measured in both cells, while cell A was used for the more concentrated solutions and B for the more dilute.

The conductance capacities of the cells (*i. e.*, the ratios of specific conductance to measured conductance), which remained constant throughout the investigation, were derived by measuring the conductance of solutions of sodium chloride and of potassium chloride which were 0.01 normal at 25° (1910 atomic weights). The specific conductances 0.0011873 and 0.0014142, respectively, were derived, as explained below, from the corresponding values of Kohlrausch and Maltby at 18° by means of the temperature coefficients given in the following section.

The ratio of the specific conductances at 18° and 25°, L_{25}/L_{18} , was determined for a number of solutions by measuring at each temperature in separate thermostats the conductance of portions of each solution with the same cell on the same day. In this and in the later work each conductance is based on a series of concordant measurements in which two portions of the same solution were used and the solution in the cell was renewed at least three times.

The experimental values of L_{25}/L_{18} are given in Table I in the fifth column. The "final values" in the sixth column were derived by drawing

TABLE I.—RATIO OF SPECIFIC CONDUCTANCES AT 18° AND 25°.

| Solution. | | | Cell used. | Values of L_{25}/L_{18} . | | |
|------------|-------|-------------|------------|-----------------------------|--------|-----------|
| Substance. | Conc. | Made from | | Measured. | Final. | Déguisne. |
| NaCl | 0.1 | Stock soln. | A | 1.1618 | | |
| | | Salt | A | 1.1615 | | |
| | | Salt | M | 1.1609 | | |
| | | Salt | M | 1.1622 | 1.1616 | .. |
| NaCl | 0.05 | | .. | .. | 1.1624 | 1.1606 |
| NaCl | 0.02 | Salt | A | 1.1631 | 1.1632 | .. |
| NaCl | 0.01 | Stock soln. | B | 1.1636 | | |
| | | Salt | B | 1.1635 | | |
| | | Salt | A | 1.1637 | | |
| | | Salt | A | 1.1635 | | |
| | | Salt | C | 1.1632 | | |
| | | Salt | M | 1.1638 | 1.1636 | 1.1620 |
| NaCl | 0.005 | | .. | .. | 1.1638 | .. |
| NaCl | 0.002 | Salt | B | 1.1639 | 1.1639 | .. |
| NaCl | 0.001 | Salt | B | 1.1644 | | |
| | | Stock soln. | B | 1.1631 | | |
| | | Stock soln. | B | 1.1629 | 1.1639 | 1.1630 |
| | | Salt | A | 1.1543 | | |
| KCl | 0.01 | Salt | B | 1.1536 | | |
| | | Salt | M | 1.1535 | 1.1538 | 1.1536 |
| | | Salt | M | 1.1535 | 1.1538 | 1.1536 |
| HCl | 0.05 | Stock soln. | A | 1.1141 | | |
| | | Stock soln. | A | 1.1134 | 1.1136 | 1.1140 |
| | | Stock soln. | A | 1.1134 | | |

a smooth curve through the points obtained by plotting the separate values against the concentration. The corresponding values derived from Déguisne's temperature coefficients¹ are given in the last column for comparison. Some results obtained independently by Mr. A. C. Melcher of this laboratory are also included in the table, and are designated by the letter M in the fourth column: The cells A and B were described above. The cell C used in one series of measurements was similar to A.

An inspection of the table shows the striking agreement of our values of L_{25}/L_{18} with those of Mr. Melcher, and also with those of Déguisne for 0.01 N KCl and 0.05 N HCl. Déguisne's values for NaCl solutions, however, seem to be about 0.1 per cent. too small.

The specific conductances of 0.01 N NaCl and KCl solutions at 25°, which were used in determining the cell constants, were then calculated from the values of Kohlrausch and Maltby² at 18° as follows:

| Specific conductance $\times 10^3$. | NaCl. | KCl. |
|---|--------|--------|
| At 18° of soln. 0.01 N at 18° (Kohlrausch at. wts.)..... | 1.0195 | 1.2243 |
| At 18° of soln. 0.01 N at 18° (1910 at. wts.)..... | 0.0188 | 1.2237 |
| At 25° of soln. 0.01 N at 18° (1910 at. wts.)..... | 1.1855 | 1.4120 |
| At 25° of soln. 0.01 N at 25° (1910 at. wts.) (assuming the same coefficient of expansion as for pure water)..... | 1.1873 | 1.4142 |

Conductance Data.—The values of the equivalent conductance Λ of sodium chloride and of hydrochloric acid solutions are given in Tables II and III. The equivalent conductances are given for round concentrations³ but the actual concentrations never differed from these by more than a few tenths of a per cent. The concentrations given in the tables are millimols per liter, 1000 C.

In Table II the measured values of Λ_{25} are given in the second column, while the third column contains final values from measurements made independently by Mr. A. C. Melcher. The corresponding values in the fourth column are derived from the data of Kohlrausch and Maltby at 18° and our own values of L_{25}/L_{18} , the corrections for the expansion of the solutions and the change of atomic weights being made as explained above. The values of Λ_{25} finally chosen (column five) were shown to be concordant by plotting the values of $1/\Lambda$ against $(CA)^{n-1}$ in the usual way.⁴ The value of the exponent n which gave a straight line in a given concentration interval gradually increased with decreasing concentration. Between 0.2 and 0.2 N n was 1.40, and between 0.05 and 0.001 N 1.45. In a similar plot of the data of Kohlrausch and Maltby at 18° the line corresponding to $n = 1.50$ was chosen in extrapolating to zero concentration. The value of Λ_0 corresponding to this line was found

¹ Landolt-Börnstein-Meyerhoffer, Tabellen (1905), p. 744.

² *Ibid.*, p. 755.

³ Noyes and Johnston, THIS JOURNAL, 31, 996 (1909).

⁴ THIS JOURNAL, 31, 735 1010 (1909). Cf. the following article.

to be 109.0 at 18° and 127.0 at 25°. The corresponding percentage ionizations 100 γ , and equivalent ion concentrations in millimols per liter 1000 γ C, are given in the last two columns of the table.

TABLE II.—CONDUCTANCE AND IONIZATION OF NaCl SOLUTIONS AT 25°.

| Conc. 1000 C. | Equiv. cond. Λ at 25°. | | | | 100 γ . | 1000 γ C. |
|------------------|--------------------------------|----------|---------------------------|--------|----------------|-------------------|
| | Measured. | Melcher. | From Δ_{18} (K&M). | Final. | | |
| 200 | 101.70 | 101.7 | .. | 101.7 | 80.1 | 160.2 |
| 100 | 106.79 | | | | | |
| | 106.79 | | | | | |
| | 106.80 | 106.8 | 106.99 | 106.8 | 84.1 | 84.1 |
| 50 | 111.18 | 111.15 | 111.36 | 111.2 | 87.55 | 43.78 |
| 20 | 115.86 | .. | .. | .. | .. | .. |
| | 115.84 | 115.9 | 115.88 | 115.9 | 91.25 | 18.25 |
| 10 | 118.68 ¹ | | | | | |
| | 118.72 ¹ | | | | | |
| | 118.74 | 118.7 | 118.73 | 118.73 | 93.5 | 9.35 |
| 5 | 120.96 | 121.0 | 120.88 | 120.95 | 95.25 | 4.76 ₂ |
| | 122.99 | | | | | |
| 2 | 122.94 | | | | | |
| | 123.06 | 123.1 | 122.96 | 123.0 | 96.85 | 1.937 |
| | 124.03 | | | | | |
| | 124.17 | | | | | |
| 1 | 124.19 | .. | 124.05 | 124.1 | 97.7 | 0.977 |
| | .. | .. | .. | 127.0 | 100.0 | .. |

It is evident that our conductance results agree almost exactly with the values obtained independently by Mr. Melcher at all concentrations, and also with those derived from the data of Kohlrausch and Maltby at 18° at all concentrations except 0.05 and 0.1 *N*. In these two cases, moreover, the difference is only about 0.2 per cent.²

The conductance results for hydrochloric acid solutions are given in the second column of Table III. The final values given in the third column were shown to be concordant by means of the $1/\Lambda$, $(C\Lambda)^{n-1}$ plot. The error in the case of the 0.001 normal solution corresponds to that observed by other investigators in measuring the conductance of dilute solutions of acid in water.³ A fairly satisfactory straight line was obtained between the concentrations 0.005 and 0.2 normal with the exponent $n = 1.40$, but, as a result of a comparison with a similar plot of the results of Goodwin and Haskell³ at 18°, a higher exponent $n = 1.52$ was used in extrapolating to zero concentration. The value $\Lambda_0 = 424$

¹ This value was obtained in three independent measurements.

² This 0.2 per cent. difference indicates a real discrepancy between our results and those of Kohlrausch and Maltby, and for this we are unable to offer an explanation. It is worth noting, however, that the method used in obtaining our results in these solutions was identical in every detail with that employed with the 0.02 and 0.01 *N* solutions, in which cases there is no such discrepancy.

³ Goodwin and Haskell, *Proc. Am. Acad.*, 40, 415 (1904).

at 25° therefore corresponds to Goodwin and Haskell's value $\Lambda_0 = 380$ at 18°. The percentage ionizations and ion concentrations are given in the last two columns of the table.

TABLE III.—CONDUCTANCE AND IONIZATION OF HCl SOLUTIONS AT 25°.

| Conc. 1000 C. | Equivalent conductance. | | 100 γ . | 1000 Cr. |
|------------------|-------------------------|--------|----------------|----------|
| | Measured. | Final. | | |
| 200 | 380.2 | 380.2 | 86.7 | 179.4 |
| 100 | 390.4 | 390.4 | 92.1 | 92.1 |
| 50 | 398.6 | | | |
| | 398.2 | | | |
| | 398.5 ¹ | 398.4 | 94.0 | 47.0 |
| 20 | 406.5 | 406.7 | 95.9 | 19.18 |
| 10 | 411.4 | | | |
| | 411.8 | 411.6 | 97.1 | 9.71 |
| 5 | 415.3 | | | |
| | 415.8 | 415.3 | 98.0 | 4.90 |
| 2 | 418.4 | 418.6 | 98.7 | 1.974 |
| 1 | 419.0(?) | 420.4 | 99.1 | 0.991 |
| 0 | .. | 424.0 | 100.0 | .. |

The conductance of hydrochloric acid has been measured at 18° by several investigators, and our results may be compared with these at the concentration 0.05 normal by dividing $\Lambda = 398.4$, first by the conductance ratio $L_{25}/L_{18} = 1.1136$ obtained above, and then by the volume ratio 1.00156 to correct for the change in concentration of the solution. The equivalent conductance thus obtained for a 0.05 *N* solution at 18° is 357.2; Goodwin and Haskell found 358.4; interpolation from the results of Noyes and Cooper² gives 357.5; an early and probably inaccurate result³ of Kohlrausch⁴ is 360. It is seen that our result agrees with that of Noyes and Cooper and is only 0.3 per cent. less⁵ than that of Goodwin and Haskell.

The results obtained with mixtures of sodium chloride and hydrochloric acid are given in Table IV, the number of the experiments in the first column; concentrations in the next three columns, and measured specific conductance (*L*) in the fifth. The last three columns contain values of *L* calculated as described below.

¹ This value 398.5 at 0.05 *N* was obtained with a solution prepared by dilution from a more concentrated solution which had been carefully standardized by Dr. W. D. Harkins.

² A. A. Noyes, *Car. Pub. Inst.*, 63, 139 (1907); *THIS JOURNAL*, 30, 388 (1908).

³ Noyes and Sammet, *Z. physik. Chem.*, 43, 70 (1903).

⁴ Kohlrausch, *Leitvermögen* (1898), p. 160.

⁵ On account of this discrepancy it is evident that the value $\Lambda = 425$ at 25° corresponds more closely to that of Goodwin and Haskell at 18° than does the value 424 adopted in our calculations.

TABLE IV.—SPECIFIC CONDUCTANCE OF MIXTURES OF NaCl AND HCl.

| Expt. No. | Conc. 1000 C. | | | 1000 L. measured. | 1000 L. calculated. | | |
|-----------|---------------|-------|--------|-------------------|---------------------|-------|--------|
| | NaCl. | HCl. | Total. | | I. | II. | III. |
| 1.... | 100.0 | 99.94 | 199.9 | 47.25 | 48.21 | 48.17 | 47.35 |
| 2.... | 99.92 | 49.94 | 149.9 | 29.14 | 29.62 | 29.60 | 29.00 |
| 3.... | 99.93 | 19.98 | 119.9 | 18.06 | 18.31 | 18.30 | 17.95 |
| 4.... | 99.91 | 9.984 | 109.9 | 14.36 | 14.50 | 14.49 | 14.28 |
| 5.... | 99.98 | 4.998 | 105.0 | 12.52 | 12.59 | 12.60 | 12.47 |
| 6.... | 99.98 | 2.006 | 102.0 | 11.41 | 11.45 | 11.45 | 11.40 |
| 7.... | 19.98 | 49.91 | 69.89 | 21.75 | 21.89 | 21.88 | 21.71 |
| 8.... | 20.00 | 19.99 | 39.99 | 10.157 | 10.27 | 10.26 | 10.143 |
| 9.... | 19.98 | 9.988 | 29.97 | 6.253 | 6.307 | 6.306 | 6.225 |
| 10.... | 19.98 | 3.996 | 23.98 | 3.889 | 3.919 | 3.919 | 3.876 |
| 11.... | 19.98 | 1.997 | 21.98 | 3.101 | 3.118 | 3.118 | 3.092 |
| 12.... | 20.00 | 1.000 | 21.00 | 2.709 | 2.721 | 2.720 | 2.705 |
| 13.... | 4.995 | 12.50 | 17.495 | 5.651 | 5.678 | 5.678 | 5.648 |
| 14.... | 5.000 | 4.996 | 9.996 | 2.632 | 2.650 | 2.650 | 2.635 |
| 15.... | 4.996 | 2.697 | 7.493 | 1.621 | 1.630 | 1.630 | 1.618 |
| 16.... | 4.997 | 0.999 | 5.996 | 1.011 | 1.016 | 1.016 | 1.009 |

Calculation of the Specific Conductance of the Mixtures.—The first method of calculation is based on the principle given in the introduction, that the equivalent conductance of each substance in the mixture is the same as in a solution of the pure substance at the same ion concentration. In order to calculate the ion concentration in the mixture (*i. e.*, the concentration of the common ion) definite values were assigned to the conductance of sodium, hydrogen and chloride ions in the mixture, *viz.*: $\Lambda_{\text{Na}^+} = 51.2$, $\Lambda_{\text{H}^+} = 348.2$, $\Lambda_{\text{Cl}^-} = 75.8$, and a method of approximation was used. (The calculated specific conductance, however, will be shown to be practically independent of these numbers.) The degrees of ionization, γ , given in Tables II and III for the single salts were first plotted against ion concentration, Σi . For each mixture the method of approximation consisted in choosing a provisional value of Σi , reading off the corresponding values of γ_{NaCl} and γ_{HCl} from the plot, calculating a new value of $\Sigma i = (C\gamma)_{\text{NaCl}^+} + (C\gamma)_{\text{HCl}}$, choosing a new value of Σi (which is usually found to be the correct one), and repeating the calculation until the assumed and calculated values of Σi agreed. The specific conductance,

$$1000 \text{ L} = 127.0 (C\gamma)_{\text{NaCl}} + 424.0 (C\gamma)_{\text{HCl}} \quad (3)^1$$

was then calculated. This result was also checked by plotting the equivalent conductances given in Table II and III against Σi , reading off the values of the equivalent conductances Λ_{NaCl} and Λ_{HCl} corresponding to the value of Σi , in the mixture and calculating L by means of the equation:

$$1000 \text{ L} = C_{\text{NaCl}} \Lambda_{\text{NaCl}} + C_{\text{HCl}} \Lambda_{\text{HCl}} \quad (4)^2$$

¹ Compare Equation 1.

² Compare Equation 2.

TABLE V.—CALCULATION OF THE SPECIFIC CONDUCTANCES OF THE MIXTURES I.¹

| 1 No. | 2 | | 3 | | 4 | | 5 Ion concs. | | 6 | | 7 | | 8 | | 9 | | 10 | | 11 | | 12 | | 13 | | 14 | |
|----------|--------|-------|---------------------|--------------------|---------------------|-------|-----------------------|-------|---------------------|---------|-------------|----------|-------------------------|--|---|--|----|--|----|--|----|--|----|--|----|--|
| | 100 r. | | 1,000 C. | | Σi | | Equiv. cond. in mixt. | | Spec. cond. × 1000. | | Difference. | | Percentage differences. | | | | | | | | | | | | | |
| | NaCl. | HCl. | (Na ⁺). | (H ⁺). | (Cl ⁻). | NaCl. | HCl. | NaCl. | HCl. | 1000 L. | 1000 δ. | 100 δ/L. | 100 δ/LHCl. | | | | | | | | | | | | | |
| 1..... | 79.7 | 89.9 | 79.7 | 89.8 | 169.5 | 101.2 | 381.1 | 10.12 | 38.09 | 48.21 | 0.76 | 1.6 | 2.0 | | | | | | | | | | | | | |
| 2..... | 81.63 | 91.0 | 81.55 | 45.45 | 127.0 | 103.7 | 385.7 | 10.36 | 19.26 | 29.62 | 0.48 | 1.6 | 2.5 | | | | | | | | | | | | | |
| 3..... | 83.05 | 91.76 | 82.98 | 18.32 | 101.3 | 105.4 | 389.1 | 10.54 | 7.774 | 18.31 | 0.25 | 1.4 | 3.2 | | | | | | | | | | | | | |
| 4..... | 83.54 | 92.05 | 83.46 | 9.19 | 92.65 | 106.1 | 390.3 | 10.60 | 3.897 | 14.50 | 0.14 | 1.0 | 3.6 | | | | | | | | | | | | | |
| 5..... | 83.81 | 92.20 | 83.79 | 4.61 | 88.39 | 106.4 | 390.9 | 10.64 | 1.954 | 12.59 | 0.07 | 0.6 | 3.6 | | | | | | | | | | | | | |
| 6..... | 83.96 | 92.30 | 83.94 | 1.852 | 85.79 | 106.7 | 391.4 | 10.66 | 0.785 | 11.45 | 0.04 | 0.3 | 5.1 | | | | | | | | | | | | | |
| 7..... | 85.64 | 93.19 | 17.11 | 46.51 | 63.62 | 108.8 | 395.1 | 2.173 | 19.72 | 21.89 | 0.14 | 0.7 | 0.7 | | | | | | | | | | | | | |
| 8..... | 88.50 | 94.60 | 17.70 | 18.91 | 36.61 | 112.4 | 401.0 | 2.248 | 8.018 | 10.27 | 0.11 | 1.1 | 1.4 | | | | | | | | | | | | | |
| 9..... | 89.70 | 95.20 | 17.92 | 9.51 | 27.43 | 113.9 | 403.7 | 2.277 | 4.030 | 6.307 | 0.054 | 0.9 | 1.3 | | | | | | | | | | | | | |
| 10..... | 90.57 | 95.66 | 18.10 | 3.823 | 21.92 | 115.1 | 405.6 | 2.299 | 1.620 | 3.919 | 0.020 | 0.5 | 1.2 | | | | | | | | | | | | | |
| 11..... | 90.80 | 95.80 | 18.14 | 1.913 | 20.05 | 115.4 | 406.2 | 2.306 | 0.812 | 3.118 | 0.017 | 0.5 | 2.1 | | | | | | | | | | | | | |
| 12..... | 91.10 | 95.90 | 18.22 | 0.959 | 19.18 | 115.7 | 406.7 | 2.314 | 0.4067 | 2.721 | 0.012 | 0.4 | 3.0 | | | | | | | | | | | | | |
| 13..... | 91.6 | 96.2 | 4.58 | 12.02 | 16.60 | 116.4 | 407.9 | 0.581 | 5.098 | 5.679 | 0.028 | 0.5 | 0.5 | | | | | | | | | | | | | |
| 14..... | 93.4 | 97.1 | 4.67 | 4.85 | 9.52 | 118.6 | 411.7 | 0.593 | 2.057 | 2.650 | 0.018 | 0.7 | 0.9 | | | | | | | | | | | | | |
| 15..... | 94.3 | 97.5 | 4.71 | 2.43 | 7.14 | 119.6 | 413.3 | 0.598 | 1.032 | 1.630 | 0.009 | 0.6 | 0.9 | | | | | | | | | | | | | |
| 16..... | 94.8 | 97.8 | 4.74 | 0.977 | 5.71 | 120.4 | 414.5 | 0.602 | 0.414 | 1.016 | 0.005 | 0.5 | 1.2 | | | | | | | | | | | | | |

¹ The equivalent conductance and degree of ionization of each substance is assumed to depend on the ion concentration alone;
 $\Lambda_{\text{Na}^+} + \Lambda_{\text{Cl}^-} = 127.0$, $\Lambda_{\text{H}^+} + \Lambda_{\text{Cl}^-} = 424.0$.

The results of these calculations are given in detail in Table V. The percentage ionizations of sodium chloride and of hydrochloric acid are given in the second and third columns, and the corresponding concentrations of the ions Na^+ , H^+ and Cl^- in the next three columns. The individual specific conductances calculated for sodium chloride and hydrochloric acid are given in the ninth and tenth columns, and their sum, the calculated specific conductance of the mixture (1000 L), in the eleventh column. The individual equivalent conductances used in checking these calculations are given in the seventh and eighth column. The calculated specific conductances exceed the measured ones by the amounts given in the twelfth column, 1000 δ . In the last two columns these differences are expressed as the percentage differences with reference to (1) and calculated specific conductance and (2) the specific conductance of the acid alone.

The calculated specific conductances are always greater than the experimentally determined values, which indicates that the values calculated for one or both of the individual specific conductances are too large. The small percentage deviations from the total specific conductance obtained in some cases (column 13) have little significance, since these deviations necessarily tend towards zero as the ratio of the individual conductances $L_{\text{NaCl}}/L_{\text{HCl}}$ becomes very large or very small. On the other hand, the rough proportionality between δ and L_{HCl} in the first five experiments (column 14) indicates that the observed deviations are due mainly to errors in the specific conductance of hydrochloric acid. Finally a comparison of the three groups of experiments, Nos. 1-6, 7-12 and 13-16, indicates that the percentage deviations decrease with decreasing ion concentration.

In the second method of calculation, the equivalent conductance of each substance in the mixture was assumed to depend on the total salt concentration, instead of on ion concentration. The equivalent conductance of each substance was plotted against salt concentration, and the individual equivalent conductances corresponding to the total salt concentration in a mixture were read off from this plot. The specific conductance of the mixture was then calculated by means of equation 4. The results are given in Table VI in column 11. The individual equivalent conductances are in columns 7 and 8, and the individual specific conductances in 9 and 10. It is of interest to note that these calculations are much more direct and less time-consuming than those which involve the determination by trial of the total ion concentration.

This method of calculation may be brought into accord with the original "ionization rule" by assuming that hydrochloric acid has the same degree of ionization as sodium chloride at the same concentration. The solutions of the separate substances at equal concentrations must have the same

TABLE VI.—CALCULATION OF THE SPECIFIC CONDUCTANCES OF THE MIXTURES II.¹

| 1 No. | 2 100 γ . | 3 $\Lambda_{H^+} + \Lambda_{Cl^-}$ | 4 Ion concentration. | | | 7 Individual equiv. cond. | | 9 Spec. cond. $\times 1000$. | | 11 1000 L. | 12 Difference 1000 δ . |
|----------|---------------------|---------------------------------------|-------------------------|-------------------|--------------------------------|------------------------------|-------|----------------------------------|--------|---------------|-------------------------------------|
| | | | (Na ⁺) | (H ⁺) | (Cl ⁻) Σ i. | NaCl. | HCl. | NaCl. | HCl. | | |
| 1..... | 80.1 | 474.8 | 80.1 | 80.1 | 160.2 | 101.7 | 380.2 | 10.17 | 38.00 | 48.17 | 0.72 |
| 2..... | 81.9 | 469.8 | 81.8 | 40.9 | 122.7 | 104.0 | 384.7 | 10.39 | 19.21 | 29.60 | 0.46 |
| 3..... | 83.11 | 466.7 | 83.05 | 16.61 | 99.66 | 105.5 | 387.9 | 10.55 | 7.75 | 18.30 | 0.24 |
| 4..... | 83.61 | 465.4 | 83.53 | 8.35 | 91.88 | 106.2 | 389.1 | 10.61 | 3.885 | 14.49 | 0.13 |
| 5..... | 83.85 | 464.9 | 83.83 | 4.19 | 88.02 | 106.5 | 389.7 | 10.65 | 1.947 | 12.59 | 0.07 |
| 6..... | 84.0 | 464.3 | 84.0 | 1.685 | 85.69 | 106.7 | 390.1 | 10.67 | 0.783 | 11.45 | 0.04 |
| 7..... | 85.98 | 459.2 | 17.18 | 42.92 | 60.10 | 109.2 | 394.8 | 2.182 | 19.70 | 21.88 | 0.13 |
| 8..... | 88.58 | 452.2 | 17.72 | 17.71 | 35.43 | 112.5 | 400.6 | 2.250 | 8.008 | 10.26 | 0.10 |
| 9..... | 89.76 | 449.3 | 17.93 | 8.97 | 26.90 | 114.0 | 403.3 | 2.278 | 4.028 | 6.306 | 0.053 |
| 10..... | 90.63 | 447.1 | 18.11 | 3.62 | 21.73 | 115.1 | 405.2 | 2.300 | 1.619 | 3.919 | 0.030 |
| 11..... | 90.91 | 446.5 | 18.16 | 1.815 | 19.98 | 115.5 | 405.9 | 2.307 | 0.8106 | 3.118 | 0.017 |
| 12..... | 91.10 | 446.0 | 18.22 | 0.911 | 19.13 | 115.7 | 406.3 | 2.314 | 0.4063 | 2.720 | 0.011 |
| 13..... | 91.72 | 444.5 | 4.581 | 11.47 | 16.05 | 116.5 | 407.7 | 0.582 | 5.096 | 5.678 | 0.027 |
| 14..... | 93.49 | 440.3 | 4.674 | 4.671 | 9.345 | 118.7 | 411.6 | 0.594 | 2.056 | 2.650 | 0.018 |
| 15..... | 94.28 | 438.4 | 4.710 | 2.354 | 7.064 | 119.7 | 413.3 | 0.598 | 1.032 | 1.630 | 0.009 |
| 16..... | 94.83 | 437.1 | 4.739 | 0.947 | 5.686 | 120.4 | 414.5 | 0.602 | 0.414 | 1.016 | 0.005 |

¹ The assumptions are (1) the equivalent conductances depend on total salt concentration, or (2) in each mixture $\gamma_{HCl} = \gamma_{NaCl}$; the values of γ and of $(\Lambda_{H^+} + \Lambda_{Cl^-})$ depend on the total ion (or salt) concentration; $\Lambda_{Na^+} = 51.2$ and $\Lambda_{Cl^-} = 75.8$.

ion concentration, and it is immaterial whether the individual equivalent conductances and degrees of ionization in the mixtures are considered to depend on the ion concentration or on the salt concentration. For the sake of simplicity in the calculations it was assumed that Λ_{Na^+} and Λ_{Cl^-} remained constant, with the same values as before and that Λ_{H^+} increased with increasing salt concentration.¹ The value of $\Lambda_{\text{H}^+} + \Lambda_{\text{Cl}^-}$ at each concentration was calculated by dividing the observed conductance (Table III) by the degree of ionization of sodium chloride. From a plot against salt concentration the values corresponding to the total salt concentrations in the mixtures were then determined, and are given in column 3 of Table VI. The specific conductance L of each mixture was next calculated as follows: The degree of ionization of sodium chloride was plotted against its concentration, the value $\gamma_{\text{NaCl}} = \gamma_{\text{HCl}}$ for each mixture corresponding to the total salt concentration was read off from this plot, the ion concentration calculated, and the value of L obtained from the relation $1000 L = 127 (C\gamma)_{\text{NaCl}} + (\Lambda_{\text{H}^+} + \Lambda_{\text{Cl}^-}) (C\gamma)_{\text{HCl}}$. These values of L were of course identical with those obtained as described in the preceding paragraph. It is evident that the results would have been the same if any other assumptions had been made with regard to the conductances of the ions. For example, if Λ_{Na^+} increased slightly with increasing concentration in accordance with existing transference data,² and Λ_{Cl^-} decreased or remained constant, then somewhat larger values would have been obtained for $\gamma_{\text{NaCl}} = \gamma_{\text{HCl}}$, and smaller values for $(\Lambda_{\text{H}^+} + \Lambda_{\text{Cl}^-})$, but the calculated specific conductances would have been exactly the same.

The specific conductances given in this table are seen to be nearly the same as those in Table V. The individual specific conductances of sodium chloride are, it is true, distinctly larger and those of hydrochloric acid smaller than in Table V, but their sums are practically identical. The small differences in the individual specific conductances correspond to the differences in the individual equivalent conductances, not to the differences in the degrees of ionization given in the tables. These results substantiate the conclusion anticipated in the introduction, that when the equivalent conductances in the mixture are assumed to depend on the ion concentration, the value calculated for the specific conductance

¹ That the cation transference number of hydrochloric acid, and therefore the ratio of Λ_{H^+} to Λ_{Cl^-} , increases with the concentration is a well known fact (A. A. Noyes, *Pub. Car. Inst.*, 63, 313; *THIS JOURNAL*, 25, 167 (1903); 30, 318 (1908)). Lewis and Sargent (*THIS JOURNAL*, 31, 364 (1909)) in connection with measurements of diffusion potentials between liquids assumed that the degrees of ionization of potassium chloride and hydrochloric acid are equal, and the satisfactory nature of their results furnishes an indication of the correctness of the assumption.

² See the summary of transference data by A. A. Noyes and K. G. Falk which will soon be published in *THIS JOURNAL*.

of a mixture must be practically independent of the degrees of ionization assumed. Since finally these calculated specific conductances are always too large it follows that the specific conductance of mixtures of sodium chloride and hydrochloric acid cannot be calculated by assuming the equivalent conductances in the mixture to depend on total ion or total salt concentration. The familiar "ionization rule," stated in the first paragraph of this article, evidently does not apply either, as long as the conductances of the ions are assumed to be constant, or to depend on total ion (or salt) concentration.

Whether or not there are other cases which show similar deviations from this rule cannot be decided without a more critical examination of existing data than has been made by us. This we hope will soon be undertaken in this laboratory.

In interpreting conductance data one of the important factors to be considered is the effect of viscosity.¹ In the present instance, however, the effect of viscosity on the calculated values of specific conductance is negligible, since the viscosities of sodium chloride and hydrochloric acid solutions differ but slightly. Thus in 0.2 normal solutions at 25° the viscosities compared with water are 1.0190 and 1.0135 respectively² and that of a mixture 0.1 normal with respect to each substance would be about 1.0162.³ On assuming this value in Expt. I, and correcting for viscosity, L was calculated to be 0.04810 instead of 0.4817, as given in Table VI. The difference was smaller in the other experiments.

In interpreting our results it has seemed best to seek some simple modification of the ionization rule which will apply in this case. This is not very difficult, since there are two variables which may be arbitrarily chosen, *viz.*: degrees of ionization and conductances of the ions. For the same reason, however, an agreement between calculated and observed conductances, when reached in this way, has little significance, and certainly does not prove the validity of the assumptions.

The following calculations are presented merely as an illustration of one of the possible methods of reaching the desired result. The degrees of ionization of sodium chloride and hydrochloric acid were assumed to be equal in each mixture and to have the same values as given in Table VI. Lower values for the specific conductance of hydrochloric acid were obtained by assuming that the conductance of the hydrogen ion depended on its own concentration, instead of on the total ion concentration. The conductances of sodium and chloride ions were assigned the same values as before. The results of the calculations are given in Table VII. The concentrations of the separate substances given in Table IV are repeated

¹ MacKay, *THIS JOURNAL*, 33, 308 (1911).

² Reyher, *Z. physik. Chem.*, 2, 744 (1888).

³ Grüneisen, *Wiss. Abh. Phys. Tech. Reichsanstalt*, 4, 239 (1905).

in this table. The degrees of ionization and ion concentrations are the same as in Table VI.

TABLE VII.—CALCULATION OF THE SPECIFIC CONDUCTANCES OF THE MIXTURE III.¹

| 1 No. | 2 Conc. 1000 C. | | 4 $\Delta_{H^+} + \Delta_{Cl^-}$ | 5 Spec. cond. $\times 1000$. | | | 8 Difference. 1000 δ . |
|----------|--------------------|-------|-------------------------------------|----------------------------------|-------|---------|-------------------------------------|
| | NaCl. | HCl. | | NaCl. | HCl. | 1000 L. | |
| 1 | 100.0 | 99.94 | 464.2 | 10.17 | 38.00 | 47.35 | —0.10 |
| 2 | 99.92 | 49.94 | 455.0 | 10.39 | 18.61 | 29.00 | —0.14 |
| 3 | 99.93 | 19.98 | 445.7 | 10.55 | 7.40 | 17.95 | —0.11 |
| 4 | 99.91 | 9.984 | 440.2 | 10.61 | 3.674 | 14.28 | —0.08 |
| 5 | 99.98 | 4.998 | 436.0 | 10.65 | 1.827 | 12.48 | —0.05 |
| 6 | 99.98 | 2.006 | 432.2 | 10.67 | 0.729 | 11.40 | —0.01 |
| 7 | 19.98 | 49.91 | 455.0 | 2.182 | 19.53 | 21.71 | —0.04 |
| 8 | 20.00 | 19.99 | 445.7 | 2.250 | 7.893 | 10.143 | —0.014 |
| 9 | 19.98 | 9.988 | 440.2 | 2.278 | 3.947 | 6.225 | —0.028 |
| 10 | 19.98 | 3.996 | 435.0 | 2.300 | 1.576 | 3.876 | —0.013 |
| 11 | 20.00 | 1.997 | 432.2 | 2.307 | 0.785 | 3.092 | —0.009 |
| 12 | 20.00 | 1.000 | 430.3 | 2.314 | 0.391 | 2.705 | —0.004 |
| 13 | 4.995 | 12.50 | 441.9 | 0.582 | 5.066 | 5.648 | —0.003 |
| 14 | 5.000 | 4.996 | 436.0 | 0.594 | 2.038 | 2.635 | —0.003 |
| 15 | 4.996 | 2.497 | 433.1 | 0.598 | 1.020 | 1.618 | —0.003 |
| 16 | 4.997 | 0.999 | 430.3 | 0.602 | 0.407 | 1.009 | —0.002 |

The calculated specific conductances agree much more closely with the experimental than those previously obtained, but are in this case somewhat too small instead of much too large. It is evident that the agreement would, have been almost perfect if somewhat larger degrees of ionization had been assumed for hydrochloric acid, corresponding for example to potassium chloride rather than sodium chloride. This is true of course only when the assumption that the conductance of hydrogen ion depends upon its actual concentration is true, and other assumptions would lead to other values for the degrees of ionization of the acid. Different results would also be obtained if the conductances of sodium and chloride ions were allowed to vary with the concentration. Additional calculations have accordingly not seemed worth while at the present time, since no additional conclusions could be drawn from them.

Summary.

Measurements have been made at 25° of the conductance of 0.001 to 0.2 normal solutions of sodium chloride and of hydrochloric acid and of mixtures of them in which the concentrations were varied systematically.

The specific conductances of the mixtures have been calculated by

¹ γ_{NaCl} and Δ_{HCl} are equal in each mixture and depend on the total ion (or salt) concentration. $(\Delta_{H^+} + \Delta_{Cl^-})$ depends on the concentration of the acid in the mixture. $\Lambda_{Na^+} = 51.2$, $\Lambda_{Cl^-} = 75.8$

means of the familiar ionization rule for mixtures of salts with a common ion, *viz.*: that the degree of ionization of each salt in the mixture is the same as that of a solution of the pure salt at the same ion concentration.

It is shown that large variations in the degrees of ionization (which correspond to different assumptions with regard to the values of the ionic conductances and their change with concentration) produce practically no change in the calculated specific conductances, provided that the conductance of each ion is assumed to depend upon the total equivalent ion concentration. This assumption is identical with stating the equivalent conductance of each salt in a mixture to be equal to the equivalent conductance of a solution of the pure salt at the same ion concentration. The assumption usually made that ionic conductances are constant is included in this more general case.

In the present instance the specific conductances calculated in this way are always greater than the experimental values. The difference is about 1.6 per cent. of the actual specific conductance when the concentration of each substance is 0.1 normal in the mixture, and is less at smaller concentrations. The suggestion is made that the conductance of an ion may depend upon its actual concentration rather than upon the total ion concentration, and it is shown to be possible to obtain a satisfactory agreement between the measured and calculated values by assuming that this is true for hydrogen ion and that hydrochloric acid is ionized to about the same extent as potassium chloride.

The ratio of the specific conductances at 25° and 18° has also been determined for 0.01 normal potassium chloride, 0.05 normal hydrochloric acid, and a number of sodium chloride solutions. Déguisne's results are confirmed for the first two solutions, but seem to be about 0.15 per cent. too low in the case of the sodium chloride solutions.

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THE CONDUCTANCE AND IONIZATION OF CERTAIN SALTS AT 18° AND 25°.

BY FRANKLIN L. HUNT.

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This investigation is a continuation of earlier work¹ in this laboratory,

¹ A. A. Noyes, *et al.*, *Pub. Car. Inst.*, 63 (1907); *THIS JOURNAL*, 30, 335-53 (1908); A. A. Noyes and J. Johnston, *THIS JOURNAL*, 31, 987, 1010 (1909).