the number of quanta of 2537 radiation incident on the vessel. This, at least, does not indicate any effect of the nature of that found by Moore and Noyes[11] in which the number of molecules reacting was roughly 10^8 times as great as the number of incident quanta.

Summary

1. Gaseous hydrogen and nitrogen combine to form ammonia in the presence of mercury vapor and the first resonance radiation of mercury at the boiling point of mercury, 630.4°K.

2. Hydrazine, if formed at all, is formed only in traces.

3. It is considered probable that the dissociation of hydrogen is the important factor in the reaction as here carried out, since the nitrogen would be little if at all affected by mercury vapor under the conditions of the experiments described.

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THE MOVING-BOUNDARY METHOD FOR DETERMINING TRANSFERENCE NUMBERS. IV. THE TRANSFERENCE NUMBERS OF SOME CHLORIDE SOLUTIONS

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In the earlier articles of this series[1] two forms of apparatus for measuring transference numbers by the method of moving boundaries were described, neither of which was entirely satisfactory. In the first form the electrodes were apparently too near the calibrated tube through which the boundary sweeps. The second form, which was otherwise properly designed, was constructed on too large a scale, and gave difficulty due to the heating effects of the current passing through the apparatus. In this article an apparatus is described which is satisfactory both in design and dimensions. Also, results are given of measurements, made with the new apparatus, of the transference numbers of solutions of potassium chloride, sodium chloride and of hydrochloric acid.

The equation for the transference number from the movement of a single boundary[1] and the correction, first pointed out by G. N. Lewis,[2] can be conveniently combined into the formula

$$T = \frac{1}{\Phi}\left(\frac{VF}{Q} \pm \Delta v\right) \qquad (1)$$

In this expression Φ is the volume of solution which contains one equivalent of solute, F is equal to 96,500 coulombs, Q is the number of coulombs

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[1] (a) MacInnes and Smith, THIS JOURNAL, **45**, 2246 (1923). (b) Smith and MacInnes, *ibid.*, **46**, 1398 (1924).

[2] Lewis, *ibid.*, **32**, 862 (1910).

passed during the time that the boundary sweeps through the volume V, Δv is a correction term for the change in volume per faraday, at the electrode in the closed side of the apparatus, due to the electrode reaction and to the concentration changes resulting from ionic migration.

The apparatus, which is shown to scale in Fig. 1, differs only in size, and the relative proportions of its separate parts, from that described in a previous article, so that a further description of its design and manipulation is unnecessary. The calibrated tube C has a length of about 28.5 cm., and an internal diameter of 0.3 cm.; thus it contains a volume (V of Equation 1) of about 2 cc. With a measuring tube of this size the heat generated by the current is conducted away by the thermostat water rapidly enough to prevent an appreciable rise of temperature inside the tube, at least at the current densities employed.

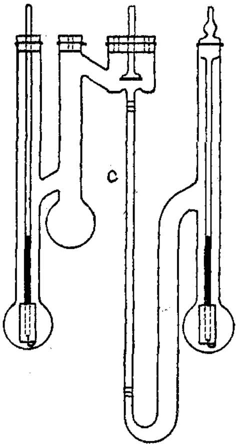

Fig. 1.

The number of coulombs passed (Q of Equation 1) was determined by measuring the time and the current, as described in the first article of this series. Since the current steadily tends to decrease due to the replacing of the measured solution by the less conductive indicator solution, a constantly increasing potential is necessary to keep the current through the apparatus constant. This increasing potential was conveniently obtained by hand operation of the sliding contact of a rheostat across which a battery of small storage cells was connected. (An automatic device for making this adjustment has, however, been developed and will be used in future work.)

As explained in the previous articles, the correct value of a transference number cannot be obtained by the moving-boundary method unless the concentrations of the measured and indicator solutions are adjusted, fairly closely, to the relation

$$C/T = C'/T' \tag{2}$$

in which C and T are the concentrations and the transference number of the solution being measured and C' and T' are the corresponding values for the indicator solution. This means that unless both transference numbers are known in advance it is necessary to make a series of determinations with varying values of the concentration of the indicator solution. Fortunately, the shape of the curve connecting values of the "transference number" thus determined and the concentration of the indicator solution give sufficient indication that adjustment to the condition of Equation 2 has been reached. This is due to the fact that a certain limited amount of adjustment to that condition takes place automatically during the passage of the current.

The substances chosen for investigation were hydrochloric acid and sodium and potassium chlorides, since it was desired to obtain data to test the relation

$$T\Lambda\eta^k = K \qquad (3)$$

for chloride ion at 25°. In this expression T is the transference number, Λ the equivalent conductance, η the relative viscosity, k an empirical constant, and K a constant which, physically interpreted, is the equivalent conductance of an ion constituent in a solution of unit relative viscosity. Equation 3 has been found to hold, at 18°, for a series of chlorides, as has been shown by MacInnes.[3]

Purification of Materials

The *potassium chloride,* a C. P. (American) product, was recrystallized twice, dried and fused. The *sodium chloride,* also a C. P. (American) product, was further purified by precipitation from a saturated solution, with hydrogen chloride gas, then dried and fused. The *hydrochloric acid* solution was prepared by diluting concentrated C. P. acid to about constant-boiling strength, distilling this solution, and retaining the middle portion of the distillate, which was analyzed gravimetrically for its chloride content. The *lithium chloride* which was used throughout in the indicator solutions, was prepared from a C. P. lithium carbonate of German origin, and pure hydrochloric acid, and the resulting chloride was twice recrystallized.

The Experimental Results

Sodium Chloride.—The results of a series of measurements on solutions of 0.1 N sodium chloride at 25° are given in Table I. A graph of these data is very similar in shape to that shown in Fig. 2, and has a break or flat space between the indicator concentrations 0.069 and 0.081 N. The computed "adjusted" concentration, according to Equation 2, is 0.081 N. The plot, Fig. 2, is representative of all the results obtained in this investigation in showing a flat space throughout the range of concentrations in which there is adjustment, and a sudden rise and a sudden fall when the concentration is too high and too low, respectively. The average value of the transference number at the concentrations where there is adjustment is 0.3873. The small correction term Δv in Equation 1

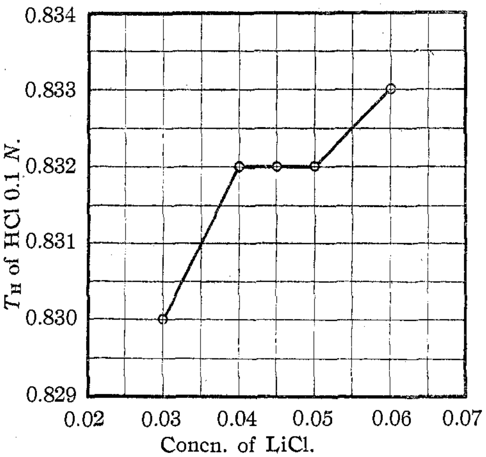

Fig. 2.

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[3] MacInnes, THIS JOURNAL, **43**, 1217 (1921).

changes this result by —0.0009 making the final value[4] *0.3865*. This constant is particularly interesting since it shows that the values obtained by Jahn and his associates,[5] (0.395 at 18°, and 0.403 at 30°) and on which Noyes and Falk's[6] "best values" are based, are both too high. Hopfgartner's value, 0.383 at 16°, is apparently more nearly correct. That Jahn's values are in error had already been suspected by MacInnes[3] after a study of the values of the transference numbers of other chlorides.

TABLE I

THE TRANSFERENCE NUMBER OF SODIUM ION IN 0.1 *N* SODIUM CHLORIDE, AT 25°

Current 0.01050 amperes

Concn. LiCl	0.065	0.069	0.081	0.086	0.091
Trans. No. Na$^+$	0.3859	0.3876	0.3876	0.3905	0.3939
	.3865	.3874	.3870	.3903	.3934
	.3862	.3872	.3872	.3902	.3932

Hydrochloric Acid.—Since the "adjustment concentration" of the indicator solution is the concentration at which the leading and following ions at the boundary are moving with equal velocities, it follows that if lithium chloride is used as indicator for a hydrochloric acid solution, the solution of the lithium salt will have to be relatively much more dilute in order that the potential gradient in that solution will increase the velocity of the lithium ions to the required extent. This requirement of equal velocities is the basis of the derivation of Equation 2. Due to this high dilution the lithium chloride indicator solution can be used *over* the hydrochloric acid solution although it is, of course, heavier than the hydrochloric acid at equal concentrations. Measurements made at and near the adjustment concentration are given in Table II, and a plot of the results in Fig. 2. The curve shows that there is complete adjustment throughout the range of indicator concentrations, 0.040 to 0.050, and but small changes when these concentrations are raised and lowered. The correction for the volume change at the electrode is, in this case, negligible. An average value of the number at the adjusted concentrations is *0.8320*. There are no other measurements of this constant at this concentration and tempera-

TABLE II

THE TRANSFERENCE NUMBER OF HYDROGEN ION IN 0.1 *M* HYDROCHLORIC ACID, AT 25°

Current, 0.0055 amperes

Concn. LiCl	0.030	0.040	0.045	0.050	0.060
Trans. No. H$^+$	0.8300	0.8321	0.8325	0.8328	0.8338
	.8299	.8316	.8322	.8325	.8326
	.8298	.8315	.8322	.8319	.8323

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[4] Computations of these corrections are given by Lewis, Ref. 2, and by MacInnes and Smith, Ref. 1 a.

[5] Jahn and others, *Z. physik. Chem.*, **17**, 673 (1901); **58**, 641 (1907).

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

ture, the nearest being 0.834 at 0.05 N and 20° as determined by Noyes and Sammett[7] and the value 0.839 at 0.1 N and 18° by Riesenfeld and Reinhold.[8] Denison and Steele's[9] original work gives 0.835 at 0.1 N and 18°.

Potassium Chloride.—A single determination of the transference number of 0.1 N potassium chloride solution was made in the new apparatus using the adjusted concentration of the lithium chloride solution (0.064 N) determined in the other investigations of this series, the result being *0.492* for the potassium ion agreeing with the value given by MacInnes and Smith[1] and by MacInnes and Brighton.[10] A series of measurements were also carried out with 0.2 N potassium chloride solution, particularly as the number was desired in connection with another investigation carried out in this Laboratory. The results of these measurements are given in Table III. The break in the curve corresponding to Fig. 2, occurs between the lithium chloride concentrations 0.125 and 0.130 N, the computed value being 0.125 N. The average value of these determinations at the adjusted concentration is 0.4904 but the correction lowers the value to *0.4900.*

TABLE III

THE TRANSFERENCE NUMBER OF POTASSIUM ION IN 0.2 N POTASSIUM CHLORIDE, AT 25°

Current, 0.0095 amperes

Concn. LiCl	0.110	0.125	0.130	0.150
Trans. No. K^+	0.4872	0.4904	0.4905	0.4932
	.4875	.4904	.4906	.4932
	.4873	.4903	.4904	.4930

Discussion of Results

The apparatus used in this investigation possesses the advantage that correct values of transference numbers are obtained throughout wider ranges of indicator concentrations than with the previous forms. The shape of the curve shown in Fig. 2, which is typical of the results of this investigation, is different from that described in the first paper of this series in that there is no rise to a maximum on the dilute side of the indicator concentrations, and from the curve obtained in the second investigation, with a large apparatus, in that adjustment is not limited to a very narrow range of concentrations.

From the values of the transference numbers and the equivalent conductances, Λ, of the corresponding solutions the conductances of the chloride-ion constituent can be computed for each of the solutions. The results of this computation are given in Table IV.

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[7] Noyes and Sammett, THIS JOURNAL, **24**, 958 (1902).

[8] Riesenfeld and Reinhold, *Z. physik. Chem.*, **68**, 440 (1909).

[9] Denison and Steele, *ibid.*, **57**, 110 (1907).

[10] MacInnes and Brighton, THIS JOURNAL, **47**, 994 (1925).

TABLE IV

CONDUCTANCES OF CHLORIDE ION FROM 0.1 *N* SOLUTIONS OF DIFFERENT CHLORIDES, AT 25°

Soln.	Equiv. cond. Λ	Trans. No. T_{Cl}	$T_{Cl}\Lambda$
HCl	390.4	0.1680	65.58
KCl	129.0	.508	65.53
NaCl	106.8	.6137	65.52

It will be seen that the product $T_{Cl}\Lambda$ is the same for these solutions, well within the experimental error. The same constancy for this product is shown, at 18°, by these and other chlorides, as has been shown by Lewis[11] and more generally by MacInnes.[3] At the low concentration involved in the experiments described in this paper there is apparently no effect arising from differences in viscosities, which vary by about 1% in the different solutions, although, from analogy from the behavior at 18°, such an effect would be expected.

The results given above show conclusively that at 25° as well as at 18° these chloride solutions have the *same* degree of dissociation. Due to the additivity of the properties of solutions of alkali halides and of the corresponding acids and bases, as well as the failure to discover evidences of an "escaping tendency" of the undissociated solute except at extremely high concentrations, and from similar facts, it has appeared desirable to the authors, and to many others, to consider these solutions as substantially completely dissociated. According to this conception, the variation of the equivalent conductances with the concentration is due to changes of mobilities rather than to changes in the number of ions. A proof that these solutions are *not* completely dissociated would be conclusively furnished by evidence of conduction of the chloride-ion constituent greater, at the corresponding temperature and concentration, than that given for the $T_{Cl}\Lambda$ product in Table IV. So far as has been investigated this product always has the same value at a given concentration and temperature, if allowance is made, at the higher concentrations, for differences in viscosity. The same generalization can be made for the other ions in the range of substances outlined above.[12]

Summary

The transference numbers of 0.1 *N* and 0.2 *N* potassium chloride, 0.1 *N* sodium chloride solutions and 0.1 *N* hydrochloric acid have been determined by the moving-boundary method at 25°, with a modified apparatus.

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[11] Lewis, THIS JOURNAL, **34**, 1631 (1912).

[12] Schneider and Braley [THIS JOURNAL, **45**, 1121 (1923)] present what they consider to be ample evidence that these solutions are not completely dissociated, based on transference measurements of mixtures of salt solutions. In a forthcoming paper their conclusions will be discussed on the basis of new measurements.

Using this apparatus, "adjustment" throughout a wider range of indicator concentrations and greater accuracy have been attained.

The product of the chloride-transference number and the corresponding equivalent conductance has been found to be constant for these substances within the experimental error. The bearing of this fact on the theory of the ionization of strong electrolytes is briefly outlined.

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[CONTRIBUTION FROM THE FIXED NITROGEN RESEARCH LABORATORY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CONCENTRATION OF AMMONIA IN A COMPRESSED MIXTURE OF HYDROGEN AND NITROGEN OVER LIQUID AMMONIA

BY ALFRED T. LARSON AND CHARLES A. BLACK

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In many of the technical adaptations of the direct synthetic ammonia process the ammonia formed is removed from the high pressure system by liquefaction and mechanical separation. It has been customary to assume that the concentration of uncondensed ammonia in the vapor phase is identical with the concentration of ammonia vapor over pure liquid ammonia at the temperature of the condenser. Harker,[1] for example, employs for this calculation the simple formula $X = (100/p)p_t$, in which X is the volume-per cent. of uncondensed ammonia, p the total pressure, and p_t the vapor pressure of pure liquid ammonia at the temperature of the condenser, t. In practice, however, the amount of uncondensed ammonia is much greater than that calculated by this expression. This excess may be due either to an incomplete adjustment of the equilibrium or to the operation of factors which the equation neglects, such for instance as the effect of total pressure and of the dissolved hydrogen and nitrogen upon the vapor pressure of the liquid ammonia and the effect of the hydrogen and nitrogen gas upon the partial pressure of the ammonia gas in the gas mixture.

With the exception of a single observation by Haber and Le Rossignol,[2] we have found no recorded measurement of the vapor concentration of ammonia in the presence of compressed nitrogen and hydrogen. These investigators found that the ammonia content of the gas phase at —79° and a total gas pressure of 190 atmospheres was about five times as great as corresponds to the vapor pressure of pure ammonia at this temperature. Accurate data of this sort are required for the design and operation of direct synthetic ammonia plants.

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[1] Harker, "Physical and Chemical Data of Nitrogen Fixation," M. I. D. Research Laboratory, University College, London.

[2] Haber and Le Rossignol, *Z. Elektrochem.*, 19, 53 (1913).