Simplified Procedure for the Preparation of [Cr(NH₂·-CH₂·CH₂·NH₂)₃]Br₃·3H₂O.—A one-liter flask is equipped with a mercury sealed stirrer, a dropping funnel, an inlet for nitrogen and an outlet for escaping gases. Twenty grams of chromium in small pieces and 400 cc. of water are placed in the flask and the water is boiled to expel dissolved oxygen. Air is swept from the flask by a current of nitrogen. One hundred cubic centimeters of concentrated hydrobromic acid is added over a period of five minutes, followed immediately by 70 cc. of ethylenediamine monohydrate. The solution is allowed to stand with occasional stirring until oxidation is complete (eight to ten hours), is filtered and evaporated. The bromide crystallizes as orange needles. The yield in a typical run was 47 g. or 81% based upon the fact that 5.8 g. of chromium dissolved.

Preparation of 2,3-Butylenediamine.—Angeli[9] has described the preparation of 2,3-butylenediamine by reduction of an alcoholic solution of dimethylglyoxime. This method gives very poor yields, apparently because the sodium salt of dimethylglyoxime is insoluble in alcohol. The substance has been prepared also by the action of ammonia on 2,3-dibromobutane[10] and by the catalytic reduction of dimethylglyoxime dissolved in alcohol.[11] The catalytic reduction gives excellent yields of the base when very dilute solutions are used. Under these conditions it is difficult to obtain the material in large amounts. We have found that it is possible to obtain 2,3-butylenediamine readily by the following modification of Angeli's directions: dimethylglyoxime is acetylated by the method of Biltz.[12] Seventy grams of the diacetate is dissolved in two liters of anhydrous alcohol in a flask fitted with a stirrer and an efficient reflux condenser. One hundred and sixty grams of sodium in lumps the size of marbles is introduced

rapidly. When the sodium has dissolved 200 cc. of water is added and the mixture is steam distilled. Most of the amine is obtained in the first three liters of distillate. Addition of a saturated solution of oxalic acid precipitates the oxalate. More of the oxalate can be obtained by concentrating the solution and adding alcohol and ether. The total yield is 27 g. or 40% of the theoretical. This material is pure enough for preparation of the free base. A sample, after recrystallization from water and drying over phosphorus pentoxide, melted at 235°. Angeli[9] reported 238°.

The base is liberated by mixing the oxalate with its own weight of sodium hydroxide in a small amount of water. Distillation gives a nearly quantitative yield of a fuming, somewhat viscous liquid with an odor similar to that of ethylenediamine. The hydrated base boils at 130°.

The major portion of the dimethylglyoxime not accounted for in the yield of diamine may be recovered from the original reaction mixture.

Summary

The stability of chromous ammines has been studied. Ammines containing ethylenediamine, 1,2-propylenediamine and 2,3-butylenediamine could not be isolated from water solution because of rapid oxidation to the chromic state by the water. On the other hand, when the chromous ion is coördinated with dipyridyl, pyridine or quinoline it is stable toward water, and in the case of the dipyridyl at least is somewhat stabilized to atmospheric oxidation.

A new and simple method for the preparation of triethylenediamino chromic salts and similar compounds has been presented.

An improved synthesis of 2,3-butylenediamine is described.

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(9) Angeli, *Ber.*, **23**, 1357 (1890).

(10) Morgan and Hickinbottom, *J. Soc. Chem. Ind.*, **43**, 307T (1924).

(11) Frejka and Zahlova, *Spisy vydávané Prírodovedeckou Fakultou Masarykovy Univ.*, No. **73**, 3 (1926); Strach and Schwaneberg, *Ber.*, **67**, 1006 (1934).

(12) Biltz, *Ber.*, **41**, 1883 (1908).

The Transference Number of Lanthanum Chloride as a Function of the Concentration

BY GRINNELL JONES AND LAURENCE T. PRENDERGAST

Introduction

The purpose of this paper is to test the general validity of several equations which have been proposed for the variation of the transference numbers of electrolytes with the concentration by the use of new data on lanthanum chloride covering a wide range of concentration. Although the old classical theory predicts that transference numbers should be independent of the concentration, it has long been known that variations do occur, especially among salts of polyvalent ions.

In 1924 Drucker and Riethof[1] found that the data for the transference numbers for the chloride ion in hydrochloric acid between 0.01 and 0.1 normal, inclusive, could be expressed by the two parameter equation: $t_- = 0.172(1 - 1/N^{0.51})$; where t_- is the transference number of the anion and N is the moles of water per mole of salt. The figures 0.172 and 0.51 were selected to fit the data, but the figure 0.172 obviously must be the limiting value of t as the concentration approaches

(1) C. Drucker and G. Riethof, *Z. physik. Chem.*, **111**, 20 (1924).

zero. No general validity for this form of equation was claimed and it aroused little interest but has been revived by Drucker[2] in his recent book "Elektrochemie" in the form

$$t_- = t^0_- (1 - 1/\sqrt{N})$$

which differs from the original only in the change of the exponent from 0.51 to 0.50. This change was perhaps influenced by the development of the Debye–Hückel theory in the meantime.

Soon after the original proposal of Drucker's equation Scatchard[3] used an equation for potassium chloride which is readily transformable into the form, $t_+ = 0.4975 - 0.014\sqrt{m}$, where m is the molality (moles of salt per 1000 grams of water) and the figure 0.4975 must be the limiting value at zero concentration if this equation is valid. This equation is of essentially the same form as Drucker's revised equation, except that it contains one more arbitrary parameter, namely, the coefficient of the last term. Scatchard regarded this equation as valid for potassium chloride up to 1.25 normal but makes no claim that it has general validity.

In 1929 Jones and Dole[4] found that an equation of the form $t_+ = A/(1 + B\sqrt{c}) - 1$ (where c is moles of salt per liter and A and B are parameters chosen to fit the data) held for barium chlorides solutions over the range of concentration from 0.001 to 1.0. It is evident from the form that if this equation is valid for extrapolation down to zero concentration then $t^0_+ = A - 1$.

In 1931 Jones and Bradshaw[5] found that this equation could be applied to lithium chloride from $c = 0.001$ to 3.0 normal.

Dole[6] has pointed out that the Jones and Dole equation has the same form as the limiting law derivable from the Onsager conductance equation but that the numerical coefficients are different.

Longsworth[7] has proposed and tested a two parameter equation for the variation of the transference number of uni-univalent salts with the concentration

$$t_+ = t^0_+ - \frac{(1 - 2t^0_+)\,\beta\sqrt{c}}{\Lambda_0 - (\alpha\Lambda_0 + 2\beta)\,\sqrt{c}} + Ac\left(1 + \frac{2\beta\sqrt{c}}{\Lambda_0 - (\alpha\Lambda_0 + 2\beta)\,\sqrt{c}}\right)$$

where α and β have a definite known numerical value from the Onsager conductance theory and Λ_0 must be estimated from the data on conductance so that only the limiting value of the transference number and the constant A are selected to fit the data. This equation was shown to be valid for potassium chloride between 0.001 to 0.1 normal and for sodium chloride and lithium chloride and hydrochloric acid between 0.01 and 0.1 normal.

The interionic attraction theory predicts that the variation of ionic mobilities with concentration should be greater for trivalent ions than for univalent or bivalent ions and therefore that the variation of the transference numbers of the ions with the concentration should be larger for a tri-univalent salt than for the simpler types of salts. This is supported by the fragmentary available data.

As Onsager[8] has pointed out, a qualitative prediction as to the sign of the change can be made from the Onsager theory beyond the range of concentration for which the conductance equation is valid. The interionic electric forces decrease the mobilities of the two ions in equal ratios and, therefore, do not affect the transference numbers. On the other hand, the absolute effect of electrophoresis in diminishing the mobility of an ion is proportional to its valence and independent of its mobility. For a 3-1 salt, this means that if the transference number of the trivalent ion at infinite dilution is more than 0.75, the theory predicts that it will increase with increasing concentration; and if it is less than 0.75 it will decrease with increasing concentration.

In order to test the various equations which have been proposed it seemed desirable to secure reliable data on some tri-univalent salt covering a wide range of concentration. Lanthanum chloride was selected because it is less hydrolyzed than any other chloride of a trivalent metal, is sufficiently soluble, and so far as is known does not form complex ions in solution. Moreover, conductance data on this salt have been obtained in this Laboratory.

The only published data known to us on the transference numbers of the ions of lanthanum chloride are by Proskauer.[9] His results are only given to two significant figures and show variations between the results obtained at the anode

(2) C. Drucker in Teil IV of "Elektrochemie," edited by K. Fajans and E. Schwarz, Akad. Verlagsgesellschaft, Leipzig, 1933, p. 24.

(3) G. Scatchard, THIS JOURNAL, 47, 705 (1925).

(4) Grinnell Jones and M. Dole, ibid., 51, 1073 (1929).

(5) Grinnell Jones and B. C. Bradshaw, ibid., 54, 138 (1932).

(6) M. Dole, J. Phys. Chem., 35, 3647 (1931).

(7) L. G. Longsworth, THIS JOURNAL, 54, 2741 (1932); B. B. Owen, ibid., 57, 2441 (1935).

(8) L. Onsager, Physik. Z., 28, 277 (1927).

(9) E. Proskauer, Diss., Frankfort am Main, 1933.

and at the cathode of about 5% on the average. A few unpublished measurements have been made in this Laboratory by B. C. Bradshaw which agree well with the new data given below.

Experimental

The lanthanum chloride used in the early part of the work was originally separated from other rare earths by Professor Charles James and purified and dried by C. F. Bickford[10] as described in an earlier paper from this Laboratory. After this supply was used up the material was recovered from the used solutions by precipitation as the oxalate, ignition to the oxide and conversion into the chloride by the procedure used by Bickford. A concentrated solution of the salt gave a pH of 6.2 as determined by Phenol Red indicator, showing that the hydrolysis was so slight that even for the most dilute solution investigated the correction to the transference number due to hydrolysis was less than the experimental error.
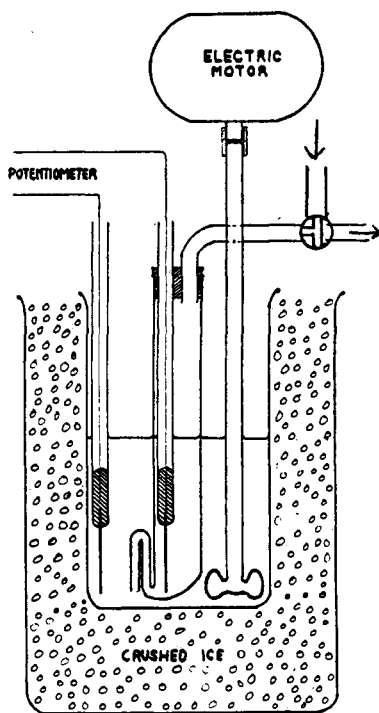

Fig. 1.

The transference numbers were determined by the analytical method using an apparatus of the type devised by Washburn.[11] The other details of the procedure were similar to those used by Jones and Dole, and Jones and Bradshaw with some modifications. The anode for solutions more concentrated than 0.01 normal was a roll of silver gauze, coated with spongy silver. This was made by covering the gauze with a paste of silver oxide in water, drying and heating to a low red heat. For very dilute solutions (0.01 molar and below), a roll of silver gauze without the spongy silver was used. This type of anode

(10) Grinnell Jones and C. F. Bickford, THIS JOURNAL, **56**, 604 (1934).
(11) E. W. Washburn, *ibid.*, **31**, 322 (1909).

was more easily cleaned than the spongy silver type. During electrolysis these electrodes became covered with adherent silver chloride which could be easily washed, dried and weighed without loss. There was no evolution of oxygen or formation of acid at the anode in any of the experiments reported. These electrodes gave entire satisfaction, except that with dilute solutions there is a tendency for the silver chloride to be formed in colloidal suspension instead of adhering to the anode. This limits the current density which can be used and the total permissible transference. The formation of colloidal silver chloride in dilute solution is probably due to the fact that the chloride ions become depleted in the immediate vicinity of the anode so that silver ions may be formed and migrate away from the electrode before they meet a chloride ion and are precipitated. If the potential gradient in the solution is too high (more than 1 volt per centimeter) there may be evolution of oxygen and formation of acid. The anodes after being used could be prepared for reuse by cathodic reduction, followed by washing and drying.

The cathodes were made similar to the anodes and then were thickly coated with silver chloride by electrolysis in hydrochloric acid, thoroughly washed and dried at 105°. The silver chloride and reduced silver formed therefrom by electrolysis were so adherent that there was no loss of weight in handling the electrodes. For the more concentrated solutions, it was necessary to use very large electrodes weighing 30 g.

In order to prevent the formation of hydroxyl ion at the cathode when using these electrodes, it is necessary to remove the oxygen dissolved in the solution. This was done by bubbling oxygen-free nitrogen through the solution before pumping it into the transference cell. Then the cell was sealed with paraffin to exclude oxygen.

The analysis was carried out by differential potentiometric titration, similar to the procedure used by MacInnes and Dole. Our experience confirms the advantages of this method claimed by these authors. For the titration we have used the device shown in Fig. 1 which we have found to be more rapid and positive in its action than the air lift device used by MacInnes and Dole. The solution to be analyzed was added from a weight buret to a beaker immersed in an ice-bath. The sharpness of the end-point is greatly increased by chilling. The electrodes were platinum wires covered with silver by electroplating from a cyanide-bath. One electrode was inside a tube connected with the bath by a narrow gooseneck. A standard solution of silver nitrate was added from a weight buret until the end-point was near and then the titration completed by means of a very dilute solution added from a volumetric buret. After each addition of a drop of silver nitrate the solution in the beaker was thoroughly stirred and the change in potential was observed. The solution around the inner electrode was then mixed with the main body of the solution by making alternate connections with a pressure bottle and the outer air by means of a three-way cock as shown in the diagram. This method of electrometric titration is far more rapid than the gravimetric method and is sufficiently accurate for the purpose. The error in the analysis is probably not more than 0.01% except when applied to solutions less than 0.01 molar when the error increases somewhat.

TABLE I

TRANSFERENCE NUMBER OF THE LANTHANUM ION IN LANTHANUM CHLORIDE SOLUTIONS AT 25°

c, molar	t_+, from anode	t_+, from cathode	t_+, ave.
0.003814	0.4703	0.4689	0.4696
.010407	.4587	.4582	.4585
.010414	.4587	.4581	.4584
.015614	.4514	.4513	.4514
.022803	.4438	.4428	.4433
.051602	.4266	.4262	.4264
.075659	.4181	.4173	.4177
.087366	.4142	.4139	.4140
.087387	.4141	.4132	.4137
.198411	.3873	.3866	.3869
.198441	.3869	.3863	.3866
.40426	.3580	.3571	.3575
.67725	.3268	.3263	.3266
1.01778	.3004	.2997	.3000

Discussion of the Data

The experimental data presented above show that the transference number of the lanthanum ion in lanthanum chloride solutions decreases with the concentration from 0.4696 in 0.0038 molar solution to 0.3000 in 1 molar solution. This is a greater variation than has been observed for any strong electrolyte of the uni-univalent or uni-bivalent types.[12] This case is, therefore, especially well suited to test the general validity of the various proposals which have been made for the variation of transference numbers with the concentration. An important part of the problem is the estimation of the limiting value of the transference number at infinite dilution which requires that some law be assumed to be valid in the dilute range where reliable experimental data are not obtainable.

The results confirm the predictions of the Onsager theory both in regard to the great variability of the transference number with the concentration and to the sign of this variation.

Figure 2 shows a plot of the transference numbers of the lanthanum ion in lanthanum chloride against the square root of the concentration $\sqrt{c}$. This curve, although approximately straight, shows unmistakable positive curvature which makes extrapolation to zero concentration hazardous. Therefore, an equation of the form $t_+ = t_+^0 - A\sqrt{c}$ can only be a rough approximation over the entire range. This curvature is most pro-

(12) Although relatively greater changes in transference numbers have been observed for cadmium bromide and cadmium iodide, there is independent evidence that in the cases of these salts the cadmium is present partly in the form of a complex anion. Since the fraction of the cadmium present in the complex ion varies with the concentration, the decrease in the transference number of the cadmium is due to this cause.

nounced in the middle range and tends to disappear in the dilute range and also in the concentrated range (0.2 to 1 molar). The four lowest points (0.0038 to 0.022) are on a straight line within the experimental error. There is no reason, either experimental or theoretical, to suspect that the curve could become more nearly horizontal as it approaches the axis which would require a change in the sign of the curvature at extreme dilution. Therefore, if we extrapolate the curve to zero concentration along the straight line determined by the last four points the result, $t_+^0 = 0.4881$, should be the minimum estimate of the transference number at zero concentration. The equation of this straight line is $t_+ = 0.4881 - 0.2946\sqrt{c}$, which agrees with the data within the experimental error up to $c = 0.022803$ but fails badly at the higher concentrations. This is shown in column 4 of Table II, which gives the difference between the experimental values and the values computed by this equation.
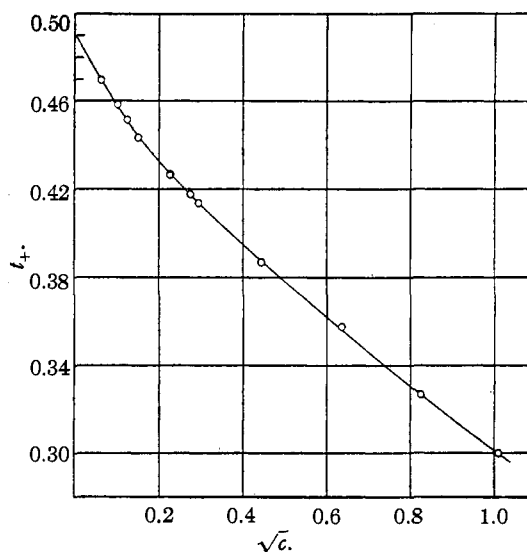

Fig. 2.

If the curve depicted by Fig. 2 has an appreciable curvature below the lowest concentration measured, then the limiting transference number would be higher than 0.4881.

We have tried the effect of adding a term proportional to the concentration, giving an equation of the form $t_+ = t_+^0 - A\sqrt{c} + Bc$, but the result was not satisfactory as it gives too great a curvature.

If we express the composition in terms of moles of salt per thousand grams of water (following Scatchard's suggestion) instead of concentrations,

the curvature of this plot is increased rather than decreased, so that there is no advantage for this purpose in this method of expressing the composition.

The Jones and Dole equation has been shown to hold for barium chloride and for lithium chloride over a wide range of concentration. This equation may be written $t_+ = A/(1 + B\sqrt{c}) - 1$; or $\dfrac{1}{1 + t_+} = \dfrac{1 + B\sqrt{c}}{A} = \dfrac{1}{A} + \dfrac{B\sqrt{c}}{A}$ where it is obvious that $t_+^0 = A - 1$. Figure 3 shows a plot of
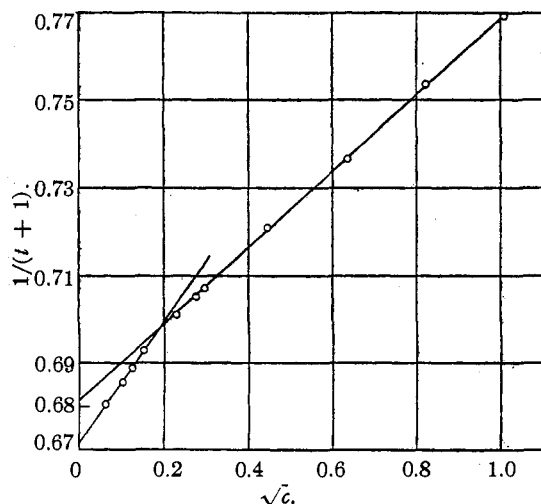

Fig. 3.

$1/(t + 1)$ against $\sqrt{c}$ which should give a straight line if the equation is valid. An inspection of this curve shows that a good straight line can be put

through the points from $c = 0.05$ to 1.0, but that there appears to be a definite curvature in the more dilute range. The equation of this straight line is $1/(t_+ + 1) = 0.6815 + 0.08728\sqrt{c}$; or $t_+ = 1.4673/(1 + 0.128\sqrt{c}) - 1$.

The differences between the experimental data and the figures computed by this equation are shown in column 5 of Table II. This is a good interpolation formula for the stronger solutions between the limit $c = 0.05{-}1.0$, but this equation fails in the dilute range. This equation leads to a value of $t_+^0 = 0.4673$, which is obviously too low since it is less than the observed transference number at $c = 0.0038$.

As is also shown in Fig. 3, we may put a straight line through the four lowest concentrations which gives $\dfrac{1}{t_+ + 1} = 0.6717 + 0.1388\sqrt{c}$, or $t_+ = 1.4887/(1 + 0.2067\sqrt{c}) - 1$, and hence $t_+^0 = 0.4887$. As will be seen from column 6 of Table II, this equation agrees with the data over the lower range but fails badly in the upper range.

A modified form of the Jones and Dole equation containing one more parameter selected to fit the data would be $t_+ = A/(1 + B\sqrt{c}) - D$. For barium chloride and lithium chloride the constant D was equal to 1, but this might not be generally true of all types of salts. We tried, therefore, evaluating the constant D by the method of least squares but the result was $D = 0.9998$ and there was no significant improvement

TABLE II

SUMMARY OF DEVIATIONS BETWEEN EXPERIMENTAL DATA FOR TRANSFERENCE NUMBERS OF LANTHANUM CHLORIDE AND RESULTS COMPUTED BY VARIOUS EQUATIONS

1	2	3	4	5	6	7	8
c	$c^{1/2}$	t_+ obsd.			$\Delta t = t_{\text{obsd.}} - t_{\text{comp.}}$		
0.003814	0.06176	0.4696	-0.0003	$+0.0138$	-0.0003	-0.0011	$+0.0006$
.010414	.10205	.4584	$+ .0003$	$+ .0100$	$+ .0004$	$+ .0013$	$+ .0001$
.015614	.12496	.4514	$+ .0001$	$+ .0072$	$+ .0002$	$+ .0008$	$+ .0000$
.022803	.15101	.4433	$- .0003$	$+ .0038$	$- .0003$	$- .0009$	$- .0016$
.051602	.22716	.4264	$+ .0052$	$+ .0006$	$+ .0045$	$- .0001$	$- .0010$
.075659	.27506	.4177	$+ .0106$	$+ .0003$	$+ .0091$	$+ .0258$	$+ .0003$
.087377	.29559	.4138	$+ .0108$	.0000	$+ .0108$	$+ .1331$	$+ .0004$
.19843	.44545	.3868	$+ .0298$	$- .0013$	$+ .0236$	$- .1304$	$+ .0004$
.40426	.63581	.3575	$+ .0567$	$+ .0007$	$+ .0417$	$- .2778$	$+ .0011$
.67725	.82295	.3266	$+ .0809$	$- .0008$	$+ .0543$	$- .5047$	$- .0016$
1.01778	1.00885	.3000	$+ .1091$	$+ .0007$	$+ .0682$	$- .7261$	$- .0014$

Column 4: $t = 0.4881 - 0.2946\sqrt{c}$

Column 5: $t = 1.4673/(1 + 0.1281\sqrt{c}) - 1$ (Jones and Dole)

Column 6: $t = 1.4887/(1 + 0.2067\sqrt{c}) - 1$ (Jones and Dole)

Column 7: $t = \dfrac{(0.4972 + 2.5702c)(\Lambda' + 880.24\sqrt{c}) - 660.18\sqrt{c}}{\Lambda'}$ (Longsworth)

Column 8: $\dfrac{1}{t + 1} = \dfrac{1}{0.4893 + 1} + 0.16563\sqrt{c} - 0.06835c + 0.07457c\log c$

n the agreement between the observed and computed result by replacing the term -1 by -0.9998.

Longsworth has recently proposed a method of extrapolating transference numbers to infinite dilution based on Onsager's limiting law for the variation of the conductance of ions with the concentration. Longsworth only claims that his method is valid for four univalent chlorides but it is of interest to test the method for salts of other valence types. Although Jones and Bickford have shown that Onsager's limiting law is not valid for lanthanum chloride even up to 0.001 molal, nevertheless if the influences which cause the failure of Onsager's law should affect the two ions proportionally a transference equation based on Onsager's law might be valid to much higher concentrations than Onsager's conductance equation. Longsworth's treatment may be readily generalized to apply to salts of any valence type. The mathematical details of this generalization are omitted to save space in printing. A plot prepared according to Longsworth's method was approximately straight up to 0.05 molar only. The corresponding equation is given in Table II and the difference between the experimental values and the values of t computed by this equation is given in column 7 of Table II. The deviations between the observed and computed values are not much greater than the experimental error up to $c = 0.051$, but the equation fails utterly at higher concentrations which indicates that it does not have the proper mathematical form to be regarded as generally valid. The values of t_{+}^{0} are higher than those given by other methods of extrapolation.

Onsager and Fuoss[13] have suggested, without giving detailed mathematical proof, that any property of a solution of an electrolyte can be expressed as a function of the concentration by an equation of the form

$$F(c) = F(o) + A\sqrt{c} + Bc + Dc \log c + \ldots$$

We have attempted to fit this equation to our transference data but the result was disappointing. The coefficient D of the $c \log c$ term came out nearly zero, thus reducing the equation to the form $t = t^{0} + A\sqrt{c} + Bc$ which had already been found to be unsatisfactory. The next step was to try an equation of the form

$$\frac{1}{t+1} = \frac{1}{t^{0}+1} + A\sqrt{c} + Bc + Dc \log c$$

(13) L. Onsager and R. M. Fuoss, *J. Phys. Chem.*, **36**, 2689 (1932).

which may be regarded as an extension of the Jones and Dole equation since it reduces to the Jones and Dole equation as c approaches zero or if B and D are placed equal to zero. The equation

$$\frac{1}{t+1} = \frac{1}{0.4893+1} + 0.16563\sqrt{c} - 0.06835c +$$
$$0.07456c \log c$$

agrees with our data over the entire range better than any other equation known to us. Since this equation contains four parameters, it is to be expected that it can be made to fit better than the simpler forms discussed above. The differences between the experimental values and the values computed from this equation are shown in column 8 of Table II.

The data throw light on the difficult problem of the extrapolation of conductance data discussed by Jones and Bickford. The foregoing discussion makes it seem probable that the limiting value of the transference number must be at least as high as 0.4881 and may be as high as 0.4893. If the limiting value of the conductance of the chloride ion is 76.34 and $t_{\pm}^{0} = 0.4881$, then the conductance of lanthanum chloride at infinite dilution would be 447.4, whereas if $t_{\pm}^{0} = 0.4893$ then Λ_0 would be 448.4.

Jones and Bickford have found that if the conductance data for lanthanum chloride are extrapolated by the method of Shedlovsky the value for Λ_0 obtained was 432.7, which is much below the estimates based on the transference numbers. If the value 432.7 is correct the value of t^{0} would be 0.4707. It seems clear from Fig. 2 that the curve would have to take an extremely improbable course to reach a value of t_{+}^{0} as low as this. The extrapolation of the conductance data by the Jones and Dole conductance equation gives $\Lambda_0 = 442.97$ corresponding to a value of t_{+}^{0} of 0.483. It is evident that these figures agree much better with the estimates based on the transference numbers. This evidence, therefore, indicates that for this case at least the Jones and Dole conductance equation is better than the Onsager or Shedlovsky equations for finding the limiting value of the conductance.

Summary

1. The transference numbers of the lanthanum ion in lanthanum chloride solutions have been determined by the analytical method at 25° at eleven concentrations over a range of 0.0038

to 1.0 molar. The transference number varies from about 0.47 to 0.30 over this range.

2. Several equations purporting to express the transference number as a function of the con-

centration and the problem of extrapolation of transference numbers to infinite dilution are discussed.

Polarization and Dielectric Constant of Liquids

By Jeffries Wyman, Jr.

There is much evidence that the dielectric constant is a linear function of the polarization per unit volume in the case of the more polar liquids for which the Clausius–Mosotti relationship ceases to hold. This appears to be almost the only conceivable interpretation of the strikingly simple behavior of a variety of strongly polar molecules in solvents of high dielectric constant.[1] It is in accord with the temperature variation of the dielectric constant of polar liquids, and the change of dielectric constant with density, under pressure, at constant temperature (see below). If we suppose the linear function to approximate direct proportionality, it offers a ready explanation of such a simple empirical relationship as that submitted by Girard,[2] according to which for water and the aliphatic alcohols the product of molecular weight times the dielectric constant is nearly constant; for in these cases the electric moments and consequently the molecular polarizations are all about the same, and therefore the polarizations per cc. should be inversely proportional to the molecular volumes or, roughly, to the molecular weights.[3] Onsager, in the following paper in THIS JOURNAL, develops a theoretical argument for a linear relation between dielectric constant and polarization in strongly polar media.

The problem of determining the two constants of this inferred linear relationship between dielectric constant and polarization is of course of great interest and the present paper is an attempt to deal with it from a purely empirical point of view.[4] There are of course no cases of polar

liquids in which we have exact independent knowledge of the polarization with which to correlate the dielectric constant. We may, however, calculate ideal or hypothetical values of the polarizations per unit volume for such liquids by making use of the values of the electric moments and molar polarizations obtained from measurements on the vapor or on dilute solutions in non-polar solvents and by taking account of the density. Clearly, such ideal, calculated values of the polarization per unit volume cannot be supposed in general to be realized more than approximately, but, nevertheless, apart from special cases of strongly associated liquids such as those forming hydrogen bonds, they may be expected to be fairly representative of the actual values. We may then try the effect of comparing these calculated values of the polarization with the observed values of the dielectric constant, to see whether or not the linear relation shows up. If it does, there is justification of our procedure of making use of the calculated values of the polarization and we may then proceed to determine the magnitude of the two constants. This in fact is what has been done.

By reference to the section of the "International Critical Tables" (Vol. VI) devoted to the dielectric constant of liquids and to the recent extensive table of electric moments and polarizations given in the *Transactions of the Faraday Society*,[5] it was possible to pick out about 140 cases of liquids with a dielectric constant greater than 5 and for which the electric moments and polarizations had been determined. In most of these the dielectric constant is pretty well known, although in some, accompanied in Table I below by a question mark, it has been measured only at very high frequencies, several times 10^8 cycles per second, and the values may be too low, the more so in the case of the larger molecules, owing to anomalous dispersion. On the other hand the

(1) See J. Wyman, THIS JOURNAL, **56**, 536 (1934).

(2) P. Girard, *Trans. Faraday Soc.*, **30**, 763 (1934).

(3) As a matter of fact Cohn has pointed out that Girard's relationship is improved if we multiply the dielectric constant in each case not by the molecular weight but by the molecular volume. E. J. Cohn. "Annual Review of Biochemistry," Annual Review of Biochemistry, Ltd., Stanford University P. O., California, Vol. IV, 1935, p. 100.

(4) An attempted derivation of the relation based on a modification of the underlying assumptions of the classical theory with regard to the internal field has been suggested but appears far too special.[1]

(5) *Trans. Faraday Soc.*, **30** (1934).