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obtained graphically by Knowles¹⁴ from the same data, as well as previous data by Miles⁴ and by Kubo⁵ are shown. If the present points are weighted statistically, a least squares solution for the best straight line through them gives:

$$(K-1)RT/(K+2)p' \\ = (13.06 \pm 0.20) + (17,725 \pm 78)/T.$$

This yields an electric moment $(1.7056 \pm 0.0052) \times 10^{-18}$ for the ethyl alcohol molecule. Giving equal weights to all points leads to constants (13.35 ± 0.23) and $(17,610 \pm 85)$ in the above equation, thus yielding a moment $(1.7000 \pm 0.0058) \times 10^{-18}$. The probable errors of calibration in Knowles work probably approximated those estimated in the present work on methyl alcohol. If the same allowance is made for them, we obtain from a statistical weighting of points:

$$(K-1)RT/(K+2)p' \\ = (13.06 \pm 0.20) + (17,725 \pm 87)/T$$

from which $u = (1.7056 \pm 0.0059) \times 10^{-18}$. These results are compared with other extended works on the vapor in Table II.

The constant term $A = (13.06 \pm 0.20)$ is again

slightly smaller than the value $(1.05 \times 12.93) = 13.6$ which we might reasonably expect. Taking $A = 13.6$, statistical weighting of data at the various temperatures leads to values $B = (17,517 \pm 8)$ and $u = (1.6956 \pm 0.00055) \times 10^{-18}$. If allowance is made for probable errors of calibration, together with a 2 percent probable error in the value chosen for A , then $B = (17,517 \pm 110)$ and $u = (1.6956 \pm 0.0076) \times 10^{-18}$. This moment is smaller than that found entirely from dielectric data by somewhat less than the sum of the probable error. The mean $(1.702 \pm 0.007) \times 10^{-18}$ may be taken as the most probable value for the moment of the ethyl alcohol molecule. Results of similar calculations from data of other workers are shown in Table II.

Judging from the general agreement of results of various workers, together with the probable errors associated with these, it appears that little real improvement can be made in the moments of the methyl and ethyl alcohol molecules until several possible sources of error are eliminated. The author is attempting several improvements in this direction before proceeding to a study of other moments.

The Transference Numbers of Potassium Acetate in Aqueous Solution

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The transference numbers for aqueous solutions of potassium acetate at 25°C have been determined by the moving boundary method for the concentration range 0.01 *N* to 0.25 *N*. Two different types of cell and two different methods of measuring the number of coulombs were employed. Up to 0.16 *N* the transference numbers can be represented by the Shedlovsky-Longworth equation within ± 0.05 percent, and lead to a transference number for the cation at infinite dilution of 0.6428, in close agreement with that obtained from the limiting ionic mobilities.

IN recent years the determination of the transference numbers of ions in solution by the moving boundary method has been developed (thanks primarily to the work of MacInnes, Longworth and their associates) until it will yield results of the highest precision; combined with accurate conductivity data, such numbers permit the calculation of limiting ionic mobilities

with an accuracy of a part in several thousand. In the course of a study of the transference numbers for several electrolytes, Longworth¹ has determined the transference numbers for solutions of sodium acetate; in this paper we report the numbers for solutions of potassium acetate.

¹ Longworth, J. Am. Chem. Soc. **57**, 1185 (1935).

Since the moving boundary method has been adequately discussed in the literature,² no general description is needed here. The cells used were of two types; the first (referred to as I) is essentially that of Smith³ and is similar to that used by Reevely and Gordon;⁴ here a lithium acetate solution serves as indicator solution with a descending boundary. The electrode on the closed side (the cathode) was a platinum wire covered with fused silver chloride, and the general technique of filling the cell and forming the boundary was essentially theirs. In our measurements, the graduated tube (*A* in their Fig. 1) had an internal diameter of 4.3 mm. The second type (II) was a simplified autogenic boundary cell with rising boundary, illustrated in Fig. 1. The anode (of chemically pure cadmium) was carefully machined to fit the lower end of the graduated Pyrex tube, and before each experiment was sealed in the tube with De Khotinsky cement. To do this the lower end of the tube was heated by a small wire resistance bound around it, and the anode, whose sides had been covered with melted cement, was pressed into place; the lowest graduation on the tube is far enough from the heater so that there is no appreciable rise in temperature of the graduated part of the tube during the brief heating. The tube *B* was of sufficient length to ensure that none of the products of electrolysis at the cathode (a platinum wire covered with fused silver chloride) could reach the graduated tube during a run. In filling the cell, solution was added at *C*, any air that might be trapped in the graduated tube being allowed to escape through a narrow capillary inserted at *A*, the capillary being removed after filling. Two cells of type II were used (internal diameter of the graduated tube 3.4 and 2.5 mm). The volumes between graduations in all three cells were determined by mercury weighings as recommended by MacInnes, Cowperthwaite and Huang.⁵ The cells were mounted in a glass-sided water bath, electrically controlled to $\pm 0.01^\circ\text{C}$, and the

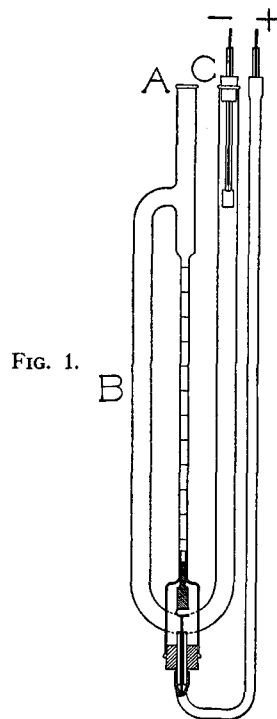


FIG. 1.

movement of the boundary was followed by the illuminated slit method recommended by MacInnes and Longworth.²

To determine the number of coulombs necessary to displace the boundary through a known volume, two entirely different methods of measurement were employed. The first of these involved the use of microcoulometers as described by Reevely and Gordon.⁴ The cathodes were small platinum crucibles, and the anodes were silver wires surrounded by glass shields perforated at the sides to permit the passage of the current; each coulometer contained 5 cc of a 10 percent silver nitrate solution tested as recommended by Rosa and Vinal.⁶ The only change in the technique from that of Reevely and Gordon was that the removal of the electrolyte and wash water from the crucible after the experiment was effected by suction using a small filter stick of a type familiar in microchemical work; the stick was always weighed with its coulometer, and thus there was no chance of loss of minute silver crystals. Duplicate determinations of the number of coulombs by this method as a rule are self-consistent to 0.03

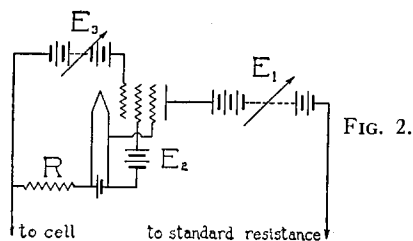
² MacInnes and Longworth, *Chem. Rev.* **11**, 171 (1932).

³ Smith, *Nat. Bur. Stand. J. Research* **6**, 917 (1931).

⁴ Reevely and Gordon, *Trans. Electrochem. Soc.* **26**, 261 (1933).

⁵ MacInnes, Cowperthwaite and Huang, *J. Am. Chem. Soc.* **49**, 1710 (1927).

⁶ Rosa and Vinal, *Nat. Bur. Stand. Bull.* **13**, 479 (1916).



percent or better when the total weight of silver deposited is from 10 to 40 mg; numerous trials have shown that such determinations agree within the same limit of accuracy with the result of current-time measurements.

The second method is what might be called a semi-constant current device, which permits the number of coulombs to be measured from current time readings without employing the elaborate apparatus developed by MacInnes, Cowperthwaite and Blanchard.⁷ The significant features are shown in Fig. 2; a somewhat similar circuit has been reported by Hartley and Donaldson.⁸ The 1 B 4 vacuum tube has the characteristic that the plate current is almost independent of the plate voltage; consequently when the tube is connected as shown, the current is practically independent of the internal resistance of the cell, which may increase by as much as 100 percent during the course of a run. The potential E_1 is supplied by 45-volt B batteries, and the filament current by a 2-volt storage cell; for satisfactory operation E_1 can be varied up to 630 volts depending on the resistance to be expected in the cell. The screen voltage E_2 is kept at $62\frac{1}{2}$ volts, and the grid bias resistance R is about 20,000 ohms; small C batteries E_3 are used to bring the grid back to 2.5–4.0 volts negative. During an experiment, there is a slight but steady fall in current,⁹ but this can be followed without difficulty by readings at 5- or 10-minute intervals; a simple graphical integration then gives the mean effective current during any part of the run. The current was measured by means of a 500-

ohm certificated standard resistance and a Leeds and Northrup type K potentiometer, while time readings to the nearest half-second were effected by an electrical chronograph.

The potassium acetate solutions were made by essentially the method employed by MacInnes and Shedlovsky¹⁰ in preparing their sodium acetate solutions. B.D.H. "analar" potassium bicarbonate, recrystallized from conductivity water, was heated in a platinum crucible to constant weight at 350°C in an atmosphere of CO₂; a weighed amount of the resulting normal carbonate was dissolved in water, a weighed quantity of glacial acetic acid, prepared after the method of Bousfield and Lowry,¹¹ was added in slight excess of the amount needed to neutralize the carbonate, the solution was boiled to remove CO₂, and then diluted gravimetrically to form a stock solution of convenient strength. All solutions were prepared by gravimetric dilution of such stock solutions. It was found essential to evacuate any solution before placing it in the cell, but weighings before and after evacuation

TABLE I.

CELL	C	t_{+obs}	SOL. CORR.	VOL. CORR.	t_{+}	t_{+calc}
II	0.009963	0.6493 .6499 .6478	0.0007	−0.0000	0.6497	0.6498
II	0.02184 ₀	.6525 .6529	0.0003	−0.0001	.6529	.6527
II	0.03631 ₇	.6557 .6548	0.0003	−0.0002	.6554	.6552
I	0.05003	.6569 .6565 .6574	0.0002	−0.0002	.6569	.6569
II	0.06627	.6592 .6588	0.0001	−0.0003	.6588	.6585
I	0.09990	.6613 .6605	0.0000	−0.0003	.6606	.6609
II	0.10747	.6618 .6614	0.0000	−0.0006	.6610	.6614
I	0.16964	.6643 .6647	0.0000	−0.0004	.6641	.6639
I	0.2521	.6690 .6696	0.0000	−0.0006	.6687	.6652

⁷ MacInnes, Cowperthwaite and Blanchard, J. Am. Chem. Soc. **48**, 1909 (1926).

⁸ Hartley and Donaldson, Trans. Faraday Soc. **33**, 457 (1937).

⁹ For example, in one experiment with 0.06627 *N* solution, the current when the boundary crossed the first of the division marks was 1.4668 ma, while when it crossed the last, the current had fallen to 1.4639 ma.

¹⁰ MacInnes and Shedlovsky, J. Am. Chem. Soc. **54**, 1429 (1932).

¹¹ Bousfield and Lowry, J. Chem. Soc. **99**, 1432 (1911).

measured any loss in water from this cause. The lithium acetate solutions, required for cell I, were made by the same procedure, the lithium carbonate being twice recrystallized from hot conductivity water. The conductivity water used had a specific conductivity of from 0.4 to 1.0×10^{-6} .

The pH of the acetate solutions was always adjusted to 5.5–5.8 (by the addition of weighed amounts of acetic acid after dilution if necessary)

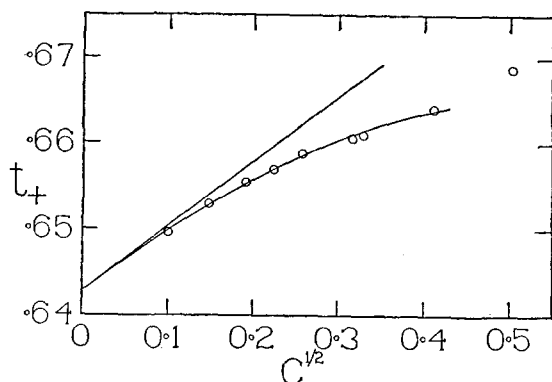


FIG. 3.

since by so doing the effect of dissolved carbon dioxide is minimized; the pH was determined colorimetrically with brom-cresol purple or by means of a quinhydrone electrode. The concentration of potassium acetate in the solution was calculated from its potassium content, and the effect of the slight excess of acetic acid was taken into account in computing the solvent correction; see below and also reference 10. In computing the volumetric concentration of the solutions from the gravimetric concentration, density data¹² from *International Critical Tables* were employed.

Table I summarizes the results; t_{+obs} is computed by the relation $t_{+obs} = 1000VC/f$ where C is the concentration of the solution in equivalents per liter and f is the number of faradays necessary to displace the boundary through V cc. When f was measured by means of current time readings, the number recorded in the table is obtained by averaging the results of at least 6 independent measurements of the number of coulombs required to displace the boundary between two of the division marks on the

¹² *International Critical Tables*, Vol. 3, p. 90.

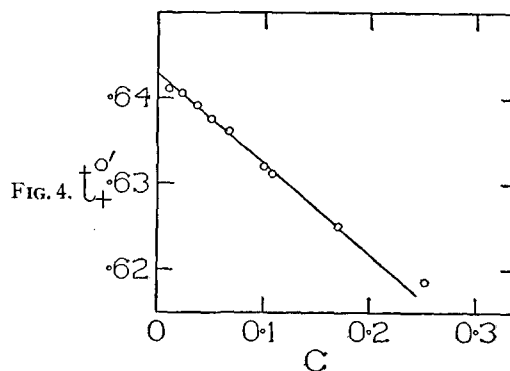


FIG. 4.

graduated tube; when f was measured by coulometer, the entry is the average of three independent measurements, each corresponding to the f obtained from one coulometer. In general, the values of t_{+obs} thus obtained from one experiment are self-consistent to 2 or 3 units in the fourth decimal place or better, although the variation from one experiment to the next is somewhat greater.

The numbers of column 3 are subject to two corrections. The first, the solvent correction, which must be added to t_{+obs} , has been shown¹³ to be $t_+ \cdot (\text{conductivity of solvent})/(\text{conductivity of solute})$. The conductivity of the solvent in our solutions is from two distinct causes, from the excess acetic acid added in making up the solution, and from residual impurities (apart from carbon dioxide) present in the conductivity water. We estimate the specific conductivity of the solvent due to this latter factor as 0.6×10^{-6} ; the correction due to the former can be calculated from the measured hydrogen ion concentration of the solution by using the limiting mobilities listed by MacInnes, Shedlovsky and Longworth¹⁴ for the ions involved. The resulting solvent corrections for the various solutions are given in the fourth column of the table.

The second, or volume correction is given by

$$t_+ = t_{+obs} \pm C\Delta V/1000$$

where ΔV is the change in volume in cc brought about at the electrode on the closed side by the passage of one faraday. The upper sign is

¹³ For a general discussion of the solvent correction, see reference 2, and for the special case of an acetate solution containing free acetic acid, see reference 10.

¹⁴ MacInnes, Shedlovsky and Longworth, *J. Am. Chem. Soc.* **54**, 2758 (1932).

appropriate for cell I and the lower for cell II; ΔV is given by

$$\Delta V = V_{Ag} - V_{AgCl} + \bar{V}_{KCl} - t_- \cdot \bar{V}_{KAc}, \quad (I)$$

$$\Delta V = \frac{1}{2} \bar{V}_{CdAc_2} - \frac{1}{2} V_{Cd} - t_+ \cdot \bar{V}_{KAc}. \quad (II)$$

Here t_+ and t_- are the transference numbers of potassium and acetate ion, V_{Ag} , V_{AgCl} and V_{Cd} are the molal volumes of silver, silver chloride and cadmium, and \bar{V}_{KCl} , \bar{V}_{KAc} and \bar{V}_{CdAc_2} are the partial molal volumes of potassium chloride, potassium acetate and cadmium acetate, respectively; from the numerical values of these quantities listed by Longworth,¹ the volume corrections of the fifth column are obtained. The resulting corrected values of the transference number for potassium ion are given in the sixth column, and are shown graphically in Fig. 3.

Shedlovsky¹⁵ has shown that his semi-empirical extension to the limiting Onsager equation for conductivity fits the experimental data for many electrolytes remarkably closely, and Longworth¹⁶ has used an analogous equation to represent his transference numbers. For a 1-1 valent electrolyte, Longworth gives

$$t_+ = t_+^\circ - \frac{1 - 2t_+^\circ}{\Lambda'} \cdot \beta\sqrt{C} + AC \left(1 + \frac{2\beta\sqrt{C}}{\Lambda'} \right). \quad (1)$$

Here C is the concentration, t_+° is the transference number of the cation at infinite dilution, $\Lambda' = \Lambda_0 - (\alpha\Lambda_0 + 2\beta)\sqrt{C}$, Λ_0 is the equivalent conductance of the solution at infinite dilution (114.37 for potassium acetate at 25°), and α and β have their theoretical values for 1-1 electrolytes in aqueous solution at 25°C *viz.* 0.2274 and 29.90, respectively; A is a disposable constant. If $t_+^{\circ'}$ be written for $t_+^\circ + AC$, Eq. (1) is equivalent to

$$t_+^{\circ'} = (t_+ \cdot \Lambda' + \beta\sqrt{C}) / (\Lambda' + 2\beta\sqrt{C}). \quad (2)$$

Hence, a plot of $t_+^{\circ'}$ against C should be a straight line whose slope is A , and whose intercept at $C=0$ is t_+° . Fig. 4 shows the result of such a plot; except for the highest concentration,

the points lie on a straight line for which $A = -0.105_4$ and t_+° is 0.6428, as determined by the method of least squares. The last column of Table I and the continuous curve of Fig. 3 give the values of t_+ computed from Eq. (1) with these values of A and t_+° ; Table II gives values

TABLE II.

C	0.01	0.02	0.04	0.06	0.08	0.10	0.12	0.14	0.16
t_+	0.6498	0.6523	0.6556	0.6579	0.6596	0.6609	0.6620	0.6629	0.6636

of t_+ for a few round values of the concentration, and the straight line of Fig. 3 shows the limiting Debye slope. The discrepancy between the calculated and observed values of t_+ for the highest concentration is not surprising, since this concentration lies somewhat above the range where the Shedlovsky-Longworth equation would be expected to hold; on the other hand, with such a strong solution, a relatively high current must be used, and consequently part of this discrepancy may be simply experimental error due to heating of the solution.

MacInnes, Shedlovsky and Longworth¹⁴ give as the mobilities of potassium and acetate ion at infinite dilution at 25°, 73.50 and 40.87, values which they obtained from a consideration of the transference and conductance data for a number of electrolytes; the corresponding value of t_+° is 0.6427. The fact that the transference number obtained here is in such very close agreement is further evidence, if any were needed, of the essential correctness of their assignment of limiting ionic mobilities.¹⁷ In conclusion, we wish to express our thanks to Mr. R. W. Allgood for assistance in calibrating one of the cells.

¹⁷ MacInnes, Shedlovsky and Longworth's value for acetate ion was obtained by subtracting from MacInnes and Shedlovsky's limiting equivalent conductance for sodium acetate 90.97 (see reference 10) the limiting mobility of sodium ion, 50.10, which is known from their work to a high degree of precision; the extrapolation of the conductance to infinite dilution was effected by the Onsager-Shedlovsky equation. A recalculation of the disposable constants by the method of least squares from MacInnes and Shedlovsky's data shows, however, that the equation

$$\Lambda = 90.93_8 - 80.47C^{1/2} + 101.1C(1 - 0.2274C^{1/2})$$

fits their experimental values more closely than does the equation they employ. With $\Lambda_0 = 90.94$, the limiting ionic mobility for acetate ion will be 40.84, and the value of t_+° for potassium acetate 0.6428; this change in the transport number is of course quite insignificant.

¹⁵ Shedlovsky, J. Am. Chem. Soc. **54**, 1405 (1932).

¹⁶ Longworth, J. Am. Chem. Soc. **54**, 2741 (1932).