235. *Mechanism of Substitution at a Saturated Carbon Atom. Part LIII.** *Conductances of Some Quaternary Ammonium Salts in Benzene, as a Preliminary to the Study of Unimolecular Nucleophilic Substitution in that Solvent.*

By E. D. Hughes, C. K. Ingold, S. Patai, and Y. Pocker.

A revised plan for investigation of unimolecular nucleophilic substitution in polar and non-polar aprotic media is indicated. In preparation for a kinetic study in the non-polar medium, benzene, in which salts would be used as reagents, sometimes with other salts present to change the reaction rate, or to divert reaction, a study is undertaken of the conductance in benzene of the salts of interest, both singly and as mixtures, for the purpose of elucidating the involved electrolytic equilibria. The salts employed were tetra-*n*-butylammonium chloride, azide, nitrate, and perchlorate, alone and in pairs. The dissociation constants and concentrations are derived for all species up to triple ions, including the unsymmetrical triple ions given by the mixtures. A less quantitative study was made of mixtures of single salts with hydrogen chloride, and it is shown that the anions $(ClHCl)^-$ and $(ClHNO_3)^-$ are stable in benzene. Thus the conditions have been found in which interpretable kinetics can be expected in reactions in benzene involving salts, and a control has been provided on the interpretation of kinetic results.

(1) *Introduction to a Group of Papers.*—The nature of the unimolecular mechanism of nucleophilic substitution and elimination has long been a subject of controversy, because the first investigations of it (1933—1940) related to solvolytic substitution, for which the most elementary kinetic criterion of mechanism is unavailable. The circumstance that kinetically unimolecular non-solvolytic substitutions, as by azide ions acting on benzhydryl halides (diphenylmethyl halides) in aqueous acetone, could be arranged to accompany unimolecular solvolysis, seems to have made little impression on discussions of this mechanism. Therefore considerable interest attaches to unimolecular substitutions in conditions in which solvolysis is excluded by the use of aprotic media. The first experiments of this kind were made in solvent sulphur dioxide; [1] but it was subsequently decided that progress would be faster with a more manageable polar solvent, such as nitromethane, and a series of kinetic studies in this medium was commenced.[2] At that stage our idea was to investigate this solvent thoroughly, and then to use the knowledge gained in studies with successively less polar solvents, ending with the non-polar solvent, benzene. However, so many difficult questions have been raised by others on the basis of their kinetic experiments in benzene, that we have now decided to shorten this programme by conducting investigations in nitromethane and in benzene concurrently, and, giving up the progressive method, to try to establish the main phenomena at the two ends of the aprotic solvent series independently, leaving to the future the task of interpolating between them.

The following four papers present our first experimental kinetic studies of nucleophilic substitution in benzene, and to them the present paper is introductory. We must explain why its mood is predominantly electrochemical.

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* Part LII, *J.*, 1956, 855.

[1] Bateman, Hughes, and Ingold, *J.*, 1940, 1011, 1017; Bird, Hughes, and Ingold, *J.*, 1954, 634; Bunton, Greenstreet, Hughes, and Ingold, *J.*, 1954, 642, 647.

[2] Gelles, Hughes, and Ingold, *J.*, 1954, 2918; de la Mare, Hughes, Ingold, and Pocker, *J.*, 1954, 2930.

(2) *Purpose of the Present Paper.*—When facing the problem of what happens to a reaction, normally depending on ions, when it is transferred to a hydrocarbon solvent, the first thing to be clear about is the condition of undoubted ions in such a solvent. We know already that they will exist largely as ion-pairs, but that there may be present also a certain concentration of simple ions, as well as of more complex ionic aggregates.

We picture the problem of these nucleophilic substitutions in benzene as one to be approached in two successive stages. The first, and simpler, is that of substitution by reagent anions, particularly monatomic or symmetrical anions, such as chloride or azide, and this involves the use of salts. In problems of mechanism, illumination often follows from the kinetic effect of salts, such as perchlorates, which do not stoicheiometrically participate in reaction; and also from the forms of competition shown by simultaneous reagents which both participate. We therefore felt it necessary to familiarise ourselves with the electrochemistry of the principal salts which were to be used in the kinetic work, and to study them, not only alone, but also as mixtures.

The second, and more complicated, part of the mechanistic problem is that which concerns nucleophilic substitution with neutral dipolar molecules, such as alcohols or amines, as substituting agents. Even here, a knowledge of the electrochemistry of salts in the benzene medium must help, because it will necessarily include a study of ion-pairs. Such saline dipoles can be considered as a highly simplified model for molecular dipoles, and hence, if we can follow the associating properties of ion-pairs, and distinguish their function in reaction from those of other saline species, we shall have a reasonable basis on which to consider the behaviour of molecular reagents.

(3) *Ion–Ion and Ion–Dipole Interaction in Benzene.*—The mass law of chemical kinetics depends on the chance encounters of particles, which, for nearly the whole of their lives, are out of each other's force range, *i.e.*, at such separations that their mutual potential energy is negligible compared with their thermal kinetic energies. It is not altogether easy so to arrange kinetic experiments involving ions that this condition is fulfilled in a solvent, such as benzene, in which electrostatic forces extend over great distances. Two ions of unit charge in benzene will have a mutual electrostatic energy equal to the mean kinetic energy of either along a line, at a separation of about 500 Å. A cubic lattice of univalent ions with this spacing would correspond to a salt concentration of about 10^{-5}M. From well below this concentration to a long way above it, most of the ions must fall into pairs or other groups of shorter force range, leaving free ions only in much smaller concentration. Bjerrum[3] has defined an ion-pair as two counter-ions at any separation less than the statistically least prevalent one, down to contact. In solvents of higher dielectric constant an ion-pair can only be quite a compact assembly, but for univalent ions in benzene the maximum length of a pair is about 120 Å, though shorter pairs are much more prevalent.

These ideas have been extended by Fuoss and Kraus,[4] who have shown that in solvents of sufficiently low dielectric constants, simple ions will associate with pairs to form triple ions, which they analogously define as having an energy less than that of a most stable pair with a simple ion at the statistically least prevalent collinear distance from its attracting pole. In some solvents triple ions can only be close assemblies, but in those made from univalent ions in benzene, the maximum separation of unlike charges may amount to 40 Å, though most triple ions will be considerably more compact. Since they carry a net charge, triple ions, like simple ions, can appear only in very low concentration in benzene. The same authors have extended the theory to the next stage of association, in which the net charge is lost again in the formation of coupled pairs, or quadrupoles. At suitable salt concentrations, in a solvent such as benzene, quadrupoles can arise in appreciable proportions.

Fuoss and Kraus, whose methods we have followed, showed how to calculate, from the

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[3] Bjerrum, *Kgl. danske Vidensk. Selskab, Mat.-fys. Medd.*, 1926, **7**, No. 9.

[4] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 2387, 3614; 1935, **57**, 1.

curve of equivalent conductance, Λ, *versus* the salt concentration, c, an equilibrium constant, K_2, for the dissociation of pairs to simple ions,

$$M^+X^- \rightleftharpoons M^+ + X^- \qquad K_2 = [M^+][X^-]/[M^+X^-]$$

and also an average equilibrium constant, K_3, averaged by an assumed equality, for the dissociation of triple cations and anions, each to an ion-pair plus a simple ion :

$$\begin{array}{l} M^+X^-M^+ \rightleftharpoons M^+X^- + M^+ \\ X^-M^+X^- \rightleftharpoons X^- + M^+X^- \end{array} \qquad K_3 = \frac{[M^+X^-][M^+]}{[M^+X^-M^+]} = \frac{[X^-][M^+X^-]}{[X^-M^+X^-]}$$

In solvents of low dielectric constant these Λ–c curves go through a minimum, $\Lambda_{\text{min.}}$, at some salt concentration, $c_{\text{min.}}$, usually between 10^{-5} and 10^{-3}M. At very low concentration, when the curve has a negative gradient, simple ions carry most of the current, and at the lowest concentrations, when they are almost the only carriers, Ostwald's law for weak electrolytes is obeyed. Immediately on the high-concentration side of the minimum, the main carriers are the triple ions. Further on, the gradient of the now rising conductance curve slackens, as quadrupoles begin to be formed, and further on still it steepens again, often somewhat irregularly, as higher charged complexes are produced. So long as the proportions of all species other than ion-pairs are small, the equation which takes account of all species up to quadrupoles is :

$$\Lambda = Ac^{-\frac{1}{2}} + Bc^{\frac{1}{2}} - Cc$$

Thus if we plot $\Lambda\sqrt{c}$ against c, a line is obtained, the initial straight part of which gives A and B, as intercept and slope, respectively, which are related to K_2 and K_3; whilst, when the curve begins to reduce its positive gradient, we know that quadrupoles are beginning to be formed. The equations [5] giving K_2 and K_3 are :

$$\begin{array}{ll} c_{\text{min.}} = A/B & \Lambda_{\text{min.}} = 2\sqrt{AB} \\ K_2 = c_{\text{min.}}(\Lambda_{\text{min.}}/2\Lambda_1^{\circ})^2 & K_3 = c_{\text{min.}}(\Lambda_3^{\circ}/\Lambda_1^{\circ}) \end{array}$$

Fuoss and Kraus's equilibrium constants are on a somewhat conventional scale, to which we have adhered : a value for the limiting conductance, Λ_1°, of simple ions in standard conditions, benzene at 25°, is adopted, and therefrom values are derived for other conditions by means of Walden's rule. It is assumed that the mean mobility of triple ions, and therefore their limiting conductance, Λ_3°, is one-third of that of simple ions.

The equilibrium constants K_2 and K_3 having been determined, the electrostatic theory developed by Bjerrum and by Fuoss and Kraus permits calculation, not only of the maximum separation, q_2 and q_3, of counter-ions, but also the nominal minimum, or most stable, separation, a_2 and a_3, of their charge centres in an ion-pair and in a triple ion, respectively. For the pair, the equations,[6] between which b_2 must be eliminated, to give q_2 and a_2 are :

$$q_2 = e^2/2DkT \qquad a_2b_2 = 2q_2 \qquad 32\pi Nq_2^{\,3}K_2Q(b_2) = 10^3$$

$$\left[Q(b_2) = \int_0^{b_2} x^4e^{-x}dx \text{ is tabulated}\right]$$

For the triple ion, b_3 and r_3 must be eliminated between the equations,

$$q_3 = a_3r_3 \qquad a_3b_3 = 2q_2 \qquad 2\pi Na_3^{\,3}K_3I(b_3) = 10^3 \qquad b_3(1 + 2r_3) = 2r_3(1 + r_3)^2$$

with the aid of tables for

$$I(b_3) = \int_1^{r_3} dx \int_{-1}^{+1} dy \left[x^2 \exp\left\{\frac{b_3}{x(x+1)}\right\} \exp\left\{\frac{b_3}{(x+1)} \cdot \left(1 - \frac{x+1}{\sqrt{(x^2+2xy+1)}}\right)\right\}\right]$$

in order to obtain q_3 and a_3.

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[5] Robinson and Stokes, " Electrolyte Solutions," Butterworths, London, 1955, p. 390.

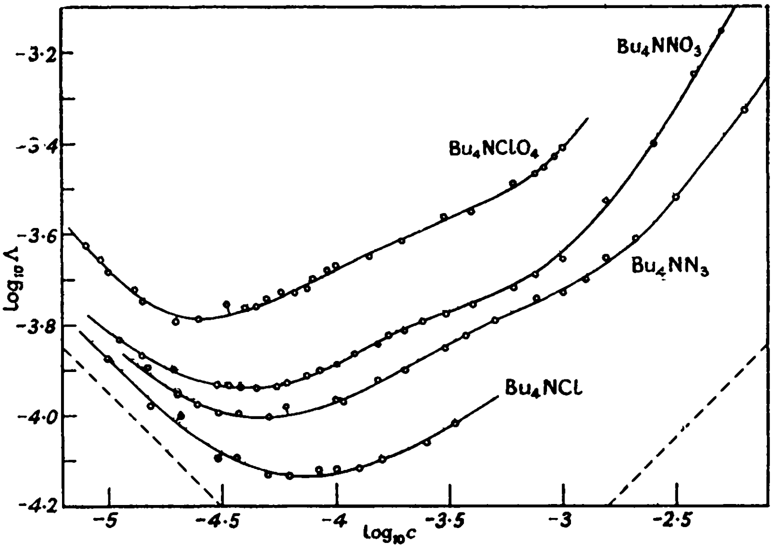
[6] Harned and Owen, " Electrolytic Solutions," Reinhold Publ. Corp., New York, 1950, pp. 42—47.

(4) *Conductances of Single Tetra*-n-*butylammonium Salts.*—We have measured the conductances, in benzene at 30°, of tetra-*n*-butylammonium chloride, azide, nitrate, and perchlorate. The perchlorate has been measured before,[7] but at 25°, these measurements, according to our estimate of the solubility of the salt, having been carried into considerably supersaturated solutions, a condition which we avoided, fearing the danger of crystallisation, which can be practically invisible.

The general form of our results for the four single salts is shown in Fig. 1, as a plot of $\log_{10} \Lambda$ *versus* $\log_{10} c$. The broken line on the left has the Ostwald-law slope $-\frac{1}{2}$, which should apply when simple ions are the only carriers of the current, whilst the broken line on the right shows the slope $+\frac{1}{2}$, which should obtain if triple ions alone carried the current, provided, in either case, that nearly the whole of the salt consists of ion-pairs.

The minima all occur within the concentration range 10^{-5}—10^{-4}M : at these minima, simple and triple ions each carry one-half of the current. The magnitude of the conductances in this region shows that almost the whole of the salts consists of ion-pairs : a fraction of the order of a few millionths at most exists as simple ions, and a similarly small fraction as triple ions. As the concentration rises towards 10^{-3}M and beyond, the pairs begin to associate to give quadrupoles. As it continues to rise towards 10^{-2}M, charged higher aggregates appear in sufficient amount to render them important carriers of the current.

FIG. 1. *Plot of log* Λ versus log *c for single salts; and theoretical slopes for simple and triple ions singly in equilibrium with ion-pairs constituting almost the whole of the salt.*



(In order to reduce the number of points, only those of Series A, Table 6, are shown.)

Some of these conclusions can be made quantitative on the basis of the electrostatic theory outlined. When we replot the conductance curves in the form $\Lambda\sqrt{c}$ *versus* c, we obtain good straight lines to about $c = 10^{-3\cdot5}$M. Two such lines for single salts appear in each of Figs. 2 and 3. From the intercepts A and slopes B of the lines, we can compute $\Lambda_{\text{min.}}$ and $c_{\text{min.}}$, the latter more accurately than it could be read from the curves of Fig. 1. Using Fuoss and Kraus's standard and procedure, we take as the limiting equivalent conductances in benzene at 30°, $\Lambda_1° = 107$, and $\Lambda_3° = 35{\cdot}6$ ohm^{-1} cm.^{2} mole^{-1}. Hence we can compute the ion-pair and triple-ion dissociation constants, K_2 and K_3, and then the maximum and minimum counter-ion distances, q_2 and a_2 for the pairs, and q_3 and a_3 for the triple ions. All these values are in Table 1.

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[7] Luder, Kraus, Kraus, and Fuoss, *J. Amer. Chem. Soc.*, 1936, **58**, 255.

TABLE 1. *Electrolytic constants of single tetra-*n*-butylammonium salts in benzene at* 30°.

	Chloride	Azide	Nitrate	Perchlorate
10^7A (A in ohm^{-1} cm.^{2} mole$^{-0 \cdot 5}$ l.$^{-0 \cdot 5}$)	3·4	3·8	3·7	5·0
10^3B (B in ohm^{-1} cm.^{2} mole$^{-1 \cdot 5}$ l.$^{0 \cdot 5}$)	4·2	7·0	9·3	15·5
$10^5\Lambda_{\text{min.}}$ (Λ in ohm^{-1} cm.^{2} mole^{-1})	7·55	10·3	11·7	17·6
$10^5c_{\text{min.}}$ (mole l.$^{-1}$)	8·1	5·4	4·0	3·2
$10^{18}K_2$ (mole l.$^{-1}$)	10·1	12·5	11·95	21·85
10^5K_3 (mole l.$^{-1}$)	2·70	1·80	1·33	1·08
q_2 (Å)	122	122	122	122
a_2 (Å)	5·8	5·8	5·8	5·8
q_3 (Å)	39	39	39	39
a_3 (Å)	8·9	8·5	8·3	8·1

It is to be observed that the power of a salt to give simple ions increases with its K_2, but that its power to give triple ions increases with decreasing K_3. Thus for the formation of simple ions, the salts become stronger in the order $Cl^- < N_3^- \sim NO_3^- < ClO_4^-$, and, for the formation of triple ions, they stand in the nearly similar order $Cl^- < N_3^- < NO_3^- < ClO_4^-$.

By the method of calculation used, q_2 is in principle the same for all uni-univalent salts; but the same is not true for a_2, q_3, and a_3. However, for the four salts treated, a_2 and q_3 come out constant to the accuracy with which they are quoted, whilst a_3 varies a little, and, as regards the two salts with isotropic anions, not in the direction one might naïvely expect. Without doubt, this is because the electrostatic theory is not a very good approximation at the short end of the distance range.

It is instructive to calculate the actual fractions of the salts, which are present as simple ions, and as triple ions, at various concentrations. This has been done, and the results are included with similar values for mixed salts in Table 3.

(5) *Conductances of Mixed Tetra-*n*-butylammonium Salts.*—In preparation for our mechanistic problem, we had to have some idea of the extent to which an ion-pair form of one salt could provide a stable seat for the simple anion of another, thereby possibly removing a chemically active species, or creating a chemically important new species, the unsymmetrical triple anion, whose properties could probably not be interpolated between those of the symmetrical triple anions given by the separate salts. This required a study of the conductances of mixed salts, and a solution of the problem of extracting from such results the dissociation constants of unsymmetrical triple ions. Studies of this kind seem not to have been made before.

We have set up the problem in a form, which is not only the simplest possible, but also probably the most accurate for the purpose in view, by measuring the conductances of binary mixtures, which are equimolar, and remain so with changing total salt concentration. We shall set down the method of deriving the new equilibrium constants from conductance data for this especially simple case.

The following eight equilibria require to be considered:

$$\begin{array}{rlrl}
M^+X^- & \rightleftharpoons M^+ + X^- & K_{2x} & = [M^+][X^-]/[M^+X^-] \\
M^+Y^- & \rightleftharpoons M^+ + Y^- & K_{2y} & = [M^+][Y^-]/[M^+Y^-] \\
M^+X^- + M^+ & \rightleftharpoons M^+X^-M^+ & K_{3x} & = [M^+X^-][M^+]/[M^+X^-M^+] \\
M^+X^- + X^- & \rightleftharpoons X^-M^+X^- & & = [M^+X^-][X^-]/[X^-M^+X^-] \\
M^+Y^- + M^+ & \rightleftharpoons M^+Y^-M^+ & K_{3y} & = [M^+Y^-][M^+]/[M^+Y^-M^+] \\
M^+Y^- + Y^- & \rightleftharpoons Y^-M^+Y^- & & = [M^+Y^-][Y^-]/[Y^-M^+Y^-] \\
M^+X^- + Y^- & \rightleftharpoons X^-M^+Y^- & K_{3xy} & = [M^+X^-][Y^-]/[X^-M^+Y^-] \\
M^+Y^- + X^- & \rightleftharpoons X^-M^+Y^- & K_{3yx} & = [M^+Y^-][X^-]/[X^-M^+Y^-]
\end{array}$$

There is one relation between the six equilibrium constants thus defined, *viz.*:

$$K_{3yx}/K_{2x} = K_{3xy}/K_{2y}$$

We have therefore five independent equilibrium constants, of which four can be evaluated from the conductances of the pure salt, leaving the fifth to be derived from the conductance of the mixture. The above relation also means that we have set down so far, not eight, but seven independent relations between the concentrations of the chemical species. However, charge balance provides the additional relation,

$$[M^+] + [M^+X^-M^+] + [M^+Y^-M^+] = [X^-] + [Y^-] + [X^-M^+X^-] + [Y^-M^+Y^-] + [X^-M^+Y^-]$$

and material balance two further relations, which can be simplified to

$$[M^+X^-] = [M^+Y^-] = c/2$$

because the fractional extent to which current-carrying ions are present is very small. Thus we have $8 - 1 + 1 + 2 = 10$ independent relations, of which 2 directly express the ion-pair concentrations, whilst the other 8 permit us to calculate the concentrations of the three simple ions and five triple ions.

The result of this calculation can be the more conveniently expressed if we first introduce some auxillary quantities. First, we define certain combinations of the equilibrium constants, *viz.*, the arithmetic K_2 mean, a harmonic K_3 mean, and three K_2/K_3 ratios, and their sum :

$$K_{2m} = \tfrac{1}{2}(K_{2x} + K_{2y}) \qquad K_{3M}{}^{-1} = \tfrac{1}{2}(K_{3x}{}^{-1} + K_{3y}{}^{-1})$$

$$\rho_x = K_{2x}/K_{3x} \qquad \rho_y = K_{2y}/K_{3y} \qquad \rho_{xy} = K_{2x}/K_{2yx} = K_{2y}/K_{3xy}$$

$$S = \rho_x + \rho_y + \rho_{xy}$$

All K's have the dimensions of concentration. We now define a pure number F in terms of the above K combinations, and of the concentration c :

$$F = \left\{1 + \frac{cS}{4K_{2m}}\right\}^{\frac{1}{2}} \cdot \left\{1 + \frac{c}{K_{3M}}\right\}^{-\frac{1}{2}}$$

Finally, we define a concentration R in terms of F :

$$R = (cK_{2m})^{\frac{1}{2}} \, . \, F$$

The concentrations of the simple and triple ions can now be expressed as follows :

$$\begin{aligned}
[M^+] &= R \\
[X^-] &= cK_{2x}/2R \\
[Y^-] &= cK_{2y}/2R \\
[M^+X^-M^+] &= cR/2K_{3x} \\
[M^+Y^-M^+] &= cR/2K_{3y} \\
[X^-M^+X^-] &= c^2K_{2x}/4RK_{3x} \\
[Y^-M^+Y^-] &= c^2K_{2y}/4RK_{3y} \\
[X^-M^+Y^-] &= c^2K_{2x}/4RK_{3yx} = c^2K_{2y}/4RK_{3xy}
\end{aligned}$$

This allows us to derive the equation for the curve of the equivalent conductance of the mixed salts, taking into account all species up to triple ions. Basically the equation is :

$$\overline{\Lambda} = \Lambda_1{}^\circ\phi_1 + \tfrac{1}{3}\Lambda_3{}^\circ\phi_3$$

when ϕ_1 is the fraction of total salt present as simple ions, and ϕ_3 is the fraction present as triple ions. (The coefficient $\frac{1}{3}$ arises because complete conversion of the pairs could make only $\frac{1}{3}$ as many triple ions as it could make of simple ions, whereas the limiting conductances $\Lambda_1{}^\circ$ and $\Lambda_3{}^\circ$ are each reckoned for 1 mole of cation and 1 mole of anion.)

We have above the concentrations required for computing ϕ_1 and ϕ_3. The result of this calculation is again most simply expressed with the help of the function F :

$$\phi_1 = \left(\frac{K_{2m}}{c}\right)^{\frac{1}{2}} \cdot \frac{F^2 + 1}{2F}$$

$$\tfrac{1}{3}\phi_3 = \left(\frac{cK_{2m}}{K_3}\right)^{\frac{1}{2}} \cdot F + \left(\frac{K_{2m}}{c}\right)^{\frac{1}{2}} \cdot \frac{F^2 - 1}{2F}$$

In order to isolate, from the above equation for $\overline{\Lambda}$, the relatively simple part of it which is practically useful, we first expand the three involved F-factors in ascending powers of c. We then find that :

$(F^2 + 1)/2F$ gives terms in c^0, –, c^2, c^3, ...
F ,, ,, ,, c^0, c^1, c^2, c^3, ...
$(F^2 - 1)/2F$,, ,, ,, –, c^1, c^2, c^3, ...

and therefore that

$\Lambda_1{}^\circ\phi_1$ contains terms in $c^{-\frac{1}{2}}$, –, $c^{\frac{3}{2}}$, $c^{\frac{5}{2}}$, . . .
$\tfrac{1}{3}\Lambda_3{}^\circ\phi_3$,, ,, ,, –, $c^{\frac{1}{2}}$, $c^{\frac{3}{2}}$, $c^{\frac{5}{2}}$, . . .

Since the equation for $\overline{\Lambda}$ contains a negative power, as well as positive powers, of c, the $\overline{\Lambda}$–c curves for mixtures will, like the Λ–c curves for pure salts, pass through a minimum. Furthermore, with mixtures, as with pure salts, the term in $c^{-\frac{1}{2}}$ is controlled exclusively by the simple ions, and that in $c^{\frac{1}{2}}$ exclusively by the triple ions. The new feature of the conductance equation of mixed salts is that the interplay of simple with triple ions now produces terms in $c^{\frac{3}{2}}$ and higher powers, which do not come into the equation for pure salts, until we take account of complexes higher than quadrupoles.

Clearly then, the practically useful equation for $\overline{\Lambda}$ is

$$\overline{\Lambda} = \bar{A}c^{-\frac{1}{2}} + \bar{B}c^{\frac{1}{2}} + \dots$$

where $\bar{A}$ and $\bar{B}$ are to be calculated by evaluating the necessary coefficients in the above-mentioned expansions. The results of this calculation are

$$\bar{A} = \Lambda_1{}^\circ\sqrt{K_{2m}}$$

$$\bar{B} = \Lambda_3{}^\circ\left(\frac{\sqrt{K_{2m}}}{2K_{3M}} + \frac{S}{8\sqrt{K_{2m}}}\right)$$

When, from our observations, we plot $\Lambda\sqrt{c}$ against c we should get an initially straight line, characterised by an intercept $\bar{A}$ and a slope $\bar{B}$. The mean constants K_{2m} and K_{3M} being known from experiments with pure salts, $\bar{A}$ gives no new information, but $\bar{B}$ allows us to calculate the sum of ratios S; and since two of these ratios ρ_x and ρ_y are similarly known, we can deduce the remaining one, ρ_{xy}, and therefore the equilibrium constants, K_{3xy} and K_{3yx}, for the mixed triple anion.

For the equimolar salt-pairs which have been experimentally examined, the results are of the general form required by theory. We get linear plots of $\overline{\Lambda}\sqrt{c}$ versus c over nearly as wide a range as in the plots of $\Lambda\sqrt{c}$ against c for pure salts.

One such plot, apparently one of the commoner kind, is shown in Fig. 2. It is true of three of the four mixtures we have studied, of the chloride–nitrate, nitrate–perchlorate, and chloride–perchlorate mixtures, that the $\Lambda\sqrt{c}$ curve for the mixture lies much nearer the more steeply sloping of the curves for the pure components. This tells us qualitatively that the mixtures are making a better-than-statistical use of their additional opportunities of forming triple ions, and are therefore probably generating a more-than-statistical proportion of the mixed triple anion.

The exceptional mixture is chloride–azide, the plot for which is shown in Fig. 3. The curve for this mixture lies almost midway between the curves for the pure components. This means that total triple ions, and therefore probably mixed triple anions, are being produced only in roughly the statistical amounts, *i.e.*, that there is no large specific tendency to the formation of this particular mixed triple anion. Of course, any such specific tendency must depend in some way on a chemical difference between the constituent simple anions, since it disappears when they become identical. With respect to this form of difference, it would seem that chloride and azide are more alike, than are chloride and either of the oxy-anions, or than are the oxy-anions themselves.

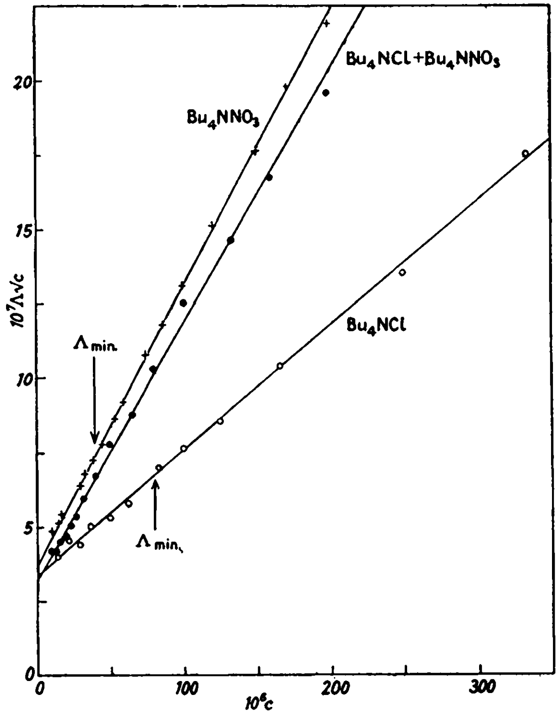

FIG. 2. *Plots of* $\Lambda\sqrt{c}$ versus c *for tetra*-n-*butylammonium chloride and nitrate and their equimolar mixture.*

(Points from Series A of Table 6.)

The values of $\overline{A}$ and $\overline{B}$ found in these experiments, and some of the intermediate figures obtained from them and from the data for pure salts, as well as the derived values of K_{3xy} and K_{3yx} (which are the objects of the exercise), are given in Table 2.

TABLE 2. *Electrolytic constants of equimolar binary mixtures of tetra*-n-*butylammonium salts in benzene at* 30°.

X^- Y^-	Cl^- N_3^-	Cl^- NO_3^-	Cl^- ClO_4^-	NO_3^- ClO_4^-
Observational results for mixed salts :				
$10^7\overline{A}$ (ohm^{-1} cm.^{2} mole$^{-0.5}$ l.$^{-0.5}$)	3·6	3·3	5·5	4·7
$10^3\overline{B}$ (ohm^{-1} cm.^{2} mole$^{-1.5}$ l.$^{0.5}$)	5·35	8·6	14·2	14·9
Calculated from data on pure salts :				
$10^{18} K_{2m}$ (mole l.$^{-1}$)	11·8	11·0	16·0	16·9
$10^{-5}/K_{3M}$ (mole l.$^{-1}$)	0·463	0·561	0·648	0·839
$10^7\overline{A}$ (ohm^{-1} cm.^{2} mole$^{-0.5}$ l.$^{-0.5}$)	3·6	3·5	4·3	4·4
Calculated from data on mixed salts :				
$10^{13}S$	19·6	39·4	86·1	81·1
10^5K_{3xy} (mole l.$^{-1}$)	1·405	0·447	0·349	0·421
10^5K_{3yx} (mole l.$^{-1}$)	1·135	0·378	0·161	0·230

The agreement between the found and the calculated $\bar{A}$ values is fair or good for three of the mixtures, though for one there is a marked discrepancy. However, $\bar{A}$ and A values depend on an extrapolation influenced mainly by conductance measurements at the dilute end of the concentration range, and, calculated in terms of equivalent conductance, these are the least accurate of the measurements. The slopes $\bar{B}$ and B are much more certain, and it is with these that we are now concerned.

When we compare the K_{3xy} and K_{3yx} values in Table 2 for the mixed triple anions chloride–nitrate, chloride–perchlorate, and nitrate–perchlorate, with the K_3 values for any of the four symmetrical triple anions, as given in Table 1, we see a general difference of about one order of magnitude: smallness of dissociation constant being taken as a measure of stability, these three unsymmetrical triple ions are roughly ten times more stable than the symmetrical triple ions. There are individual differences, which are consistent with the idea that an excess of stability in the mixed triple ion is connected with a stability difference in the component simple anions. The chloride–perchlorate triple anion is the most stable, then comes nitrate–perchlorate, and then the chloride–nitrate.

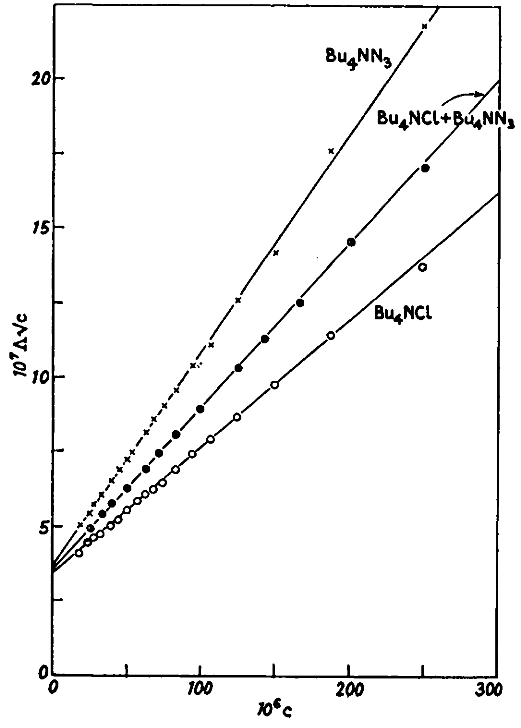

FIG. 3. *Plots of* $\Lambda\sqrt{c}$ versus *c for tetra*-n-*butylammonium chloride and azide and their equimolar mixture.*

(Points from Series B of Table 6.)

Last, by a long way, comes the chloride–azide anion, which is of the same order of stability as any of the four symmetrical triple ions, though it is actually somewhat more stable than either the chloride triple ion or the azide triple ion.

It is interesting to note in what directions the unsymmetrical triple ions prefer to break up. The chloride–perchlorate ion prefers to drop off a perchlorate ion, the nitrate–perchlorate a perchlorate, the chloride–nitrate a nitrate, and the chloride–azide an azide ion. Thus the competitive success in separation of simple anions from mixed triple anions stands in the order $ClO_4^- > NO_3^-, N_3^- > Cl^-$. We have seen that the ease of separation of simple anions from ion pairs has the order $ClO_4^- > NO_3^- \sim N_3^- > Cl^-$; and that their ease of splitting from symmetrical triple ions is in the order $ClO_4^- > NO_3^- > N_3^- > Cl^-$; and, finally, that if the stability of mixed triple anions depends on the difference in a property of the component simple anions, then that property places them in the order $ClO_4^- > NO_3^- > N_3^- \sim Cl^-$.

A word should be said about the accuracy of the mixed-ion constants K_{3xy} and K_{3yx}, inasmuch as they are calculated by difference. For the three especially stable mixed anions, chloride–nitrate, chloride–perchlorate, and nitrate–perchlorate, the point scarcely arises; for ρ_{xy} is much the most important term in the sum S, and the S-term is the main term in the formula for $\overline{B}$. For the chloride–azide anion, ρ_{xy} supplies about one-half of S, and the S-term about one-half of $\overline{B}$; and so the difference character of the calculation multiplies the error by 4. On the other hand, the $\Lambda\sqrt{c}$ plots for chloride, for azide, and for the mixture were very good, and were, indeed, the best we had, and we therefore think that the constants for this particular mixed anion may be no worse than those for the others.

We have now all the equilibrium constants necessary for calculating the concentrations of any or all the ionic species present at any concentration of mixed salts below those at which quadrupoles and higher aggregates are formed in quantity. We can, of course, do the same calculation for the component pure salts, and so discover what happens to the various species when two salts are mixed. In Table 3, the results of such calculations are

TABLE 3. *Ionic fractions in millionths* (10^6f) *for simple and triple ions at various stoicheiometric concentrations* (c) *of tetra-*n*-butylammonium salts,* MX, MY, *and of their equimolar mixtures,* $\frac{1}{2}$(MX + MY), *in benzene at* 30°.

	$c = 10^{-6}$M			$c = 10^{-5}$M			$c = 10^{-4}$M			$c = 10^{-3}$M		
	X	$\frac{1}{2}$(X + Y)	Y	X	$\frac{1}{2}$(X + Y)	Y	X	$\frac{1}{2}$(X + Y)	Y	X	$\frac{1}{2}$(X + Y)	Y
(1) Chloride (X), azide (Y), mixture {$\frac{1}{2}$(X + Y)}.												
M^+	3·18	3·38	3·54	1·00	1·06	0·12	0·32	0·33	0·35	0·10	0·10	0·11
X^-	3·18	1·49	—	1·00	0·48	—	0·32	0·15	—	0·10	0·05	—
Y^-	—	1·86	3·54	—	0·59	0·12	—	0·19	0·35	—	0·06	0·11
M_2X^+	0·12	0·06	—	0·37	0·19	—	1·18	0·62	—	3·72	1·90	—
M_2Y^+	—	0·09	0·20	—	0·29	0·62	—	0·92	1·97	—	2·85	6·21
MX_2^-	0·12	0·03	—	0·37	0·09	—	1·18	0·29	—	3·72	0·91	—
MY_2^-	—	0·05	0·20	—	0·16	0·62	—	0·53	1·97	—	1·68	6·21
MXY^-	—	0·07	—	—	0·22	—	—	0·69	—	—	2·17	—
(2) Chloride (X), nitrate (Y), mixture {$\frac{1}{2}$(X + Y)}.												
M^+	3·18	3·37	3·46	1·00	1·16	1·09	0·32	0·41	0·35	0·10	0·13	0·11
X^-	3·18	1·50	—	1·00	0·44	—	0·32	0·12	—	0·10	0·04	—
Y^-	—	1·77	3·46	—	0·52	1·09	—	0·15	0·35	—	0·04	0·11
M_2X^+	0·12	0·06	—	0·37	0·21	—	1·18	0·75	—	3·72	2·45	—
M_2Y^+	—	0·13	0·26	—	0·44	0·82	—	1·53	2·60	—	4·96	8·23
MX_2^-	0·12	0·03	—	0·37	0·08	—	1·18	0·23	—	3·72	0·71	—
MY_2^-	—	0·07	0·26	—	0·19	0·82	—	0·55	2·60	—	1·70	8·23
MXY^-	—	0·20	—	—	0·58	—	—	1·64	—	—	5·06	—
(3) Chloride (X), perchlorate (Y), mixture {$\frac{1}{2}$(X + Y)}.												
M^+	3·18	4·13	4·67	1·00	1·51	1·48	0·32	0·56	0·47	0·10	0·18	0·15
X^-	3·18	1·22	—	1·00	0·33	—	0·32	0·09	—	0·10	0·03	—
Y^-	—	2·65	4·67	—	0·73	1·48	—	0·19	0·47	—	0·06	0·15
M_2X^+	0·12	0·08	—	0·37	0·28	—	1·18	1·03	—	3·72	3·37	—
M_2Y^+	—	0·19	0·43	—	0·70	1·37	—	2·58	4·32	—	8·43	13·70
MX_2^-	0·12	0·02	—	0·37	0·06	—	1·18	0·17	—	3·72	0·51	—
MY_2^-	—	0·12	0·43	—	0·33	1·37	—	0·91	4·32	—	2·78	13·70
MXY^-	—	0·38	—	—	1·04	—	—	2·82	—	—	8·62	—
(4) Nitrate (X), perchlorate (Y), mixture {$\frac{1}{2}$(X + Y}).												
M^+	3·46	4·18	4·67	1·09	1·42	1·48	0·35	0·48	0·47	0·11	0·16	0·15
X^-	3·46	1·43	—	1·09	0·42	—	0·35	0·12	—	0·11	0·04	—
Y^-	—	2·62	4·67	—	0·77	1·48	—	0·23	0·47	—	0·07	0·15
M_2X^+	0·26	0·16	—	0·82	0·53	—	2·60	1·82	—	8·23	5·84	—
M_2Y^+	—	0·19	0·43	—	0·66	1·37	—	2·24	4·32	—	7·19	13·70
MX_2^-	0·26	0·05	—	0·82	0·16	—	2·60	0·46	—	8·23	1·45	—
MY_2^-	—	0·12	0·43	—	0·36	1·37	—	1·05	4·32	—	3·26	13·70
MXY^-	—	0·31	—	—	0·91	—	—	2·69	—	—	8·37	—

given in a form in which the concentration of each kind of ion has been divided by c, the total salt concentration, to give an "ionic fraction" f. These ionic fractions, *viz.*:

$$f = \frac{\text{Concentration of one kind of ion which may be simple or triple}}{\text{Total stoicheiometric concentration of salt or salts}}$$

are small, and are conveniently expressed in millionths.

Two conclusions may be drawn from Table 3, which are significant for our kinetic studies. The first holds in all cases: it is that when two salts are mixed the simple anion of neither is unduly consumed; *e.g.*, when one-half of a salt is replaced by one with a different anion, the original simple anion is never reduced in concentration to as little as one-quarter. The second conclusion is that, when two salts are mixed, a far from complete consumption occurs of those triple anions that are formed by the separate salts, though in this there is a notable quantitative difference between the mixtures. In the chloride–nitrate, chloride–perchlorate, and nitrate–perchlorate mixtures, some 70—85% of the symmetrical triple anions may disappear to give a greatly preponderating amount of the unsymmetrical triple anion. In the chloride–azide mixture, the total of triple ions is about the mean of those given by the chloride and azide separately, and of that total, roughly one-half consists of the two symmetrical triple anions, leaving about one-half for the mixed triple anion.

(6) *Cursory Survey of Effects of Added Molecular Substances on Salt Conductances.*—Hydrogen chloride in benzene has a conductance, but it is smaller than that of any of the tetra-*n*-butylammonium salts. However, as will be seen from Table 4, the addition of hydrogen chloride raises the conductance of tetra-*n*-butylammonium chloride strongly, and of the corresponding nitrate moderately, but of the perchlorate not at all.

TABLE 4. *Reciprocal resistance* (ohm^{-1}) *of a cell containing solutions in benzene at* 30° *of tetra*-n-*butylammonium salts* (MX) *with added hydrogen chloride.*

10^4[HCl]	10^4[MX]	10^8 ohm^{-1} HCl only	10^8 ohm^{-1} Salt only	10^6 ohm^{-1} Mixture
Tetra-n-*butylammonium chloride.*				
0·40	1·92	0·02	0·17	0·33
3·0	4·55	0·10	0·55	2·08
3·3	3·84	0·10	0·41	2·00
3·4	3·57	0·11	0·38	1·87
3·6	3·33	0·11	0·36	1·74
3·8	3·12	0·11	0·34	1·60
4·0	2·00	0·12	0·18	0·93

10^4[HCl]	10^4[MX]	10^8 ohm^{-1} HCl only	10^8 ohm^{-1} Salt only	10^8 ohm^{-1} Mixture
Tetra-n-*butylammonium nitrate.*				
—	10·0	—	2·55	2·55
0·25	9·7	0·01	2·5	2·63
0·50	9·5	0·02	2·4	2·83
Tetra-n-*butylammonium perchlorate.*				
—	10·0	—	4·5	4·5
0·60	9·4	0·02	4·2	4·1
1·00	8·8	0·03	3·7	3·8

These results may be considered in conjunction with those of a preliminary survey by Dr. S. F. Mok of the effect of tetra-*n*-butylammonium chloride on the partial vapour pressure of hydrogen chloride in benzene. She found that, in concentrations of order 10^{-3}M, a strong depression of the vapour pressure occurs when the quantity of salt becomes comparable with that of the hydrogen chloride. She also found that the catalytic effect of hydrogen chloride on the methyl-alcoholysis of triphenylmethyl chloride in benzene is largely destroyed by an equivalent of added tetra-*n*-butylammonium chloride. All these results point to the conclusion that the hydrogen-dichloride ion, $(ClHCl)^-$, is very stable in benzene, and that its quaternary ammonium salts are stronger salts than are the simple chlorides. Herbrandson, Dickerson, and Weinstein have recently isolated tetramethyl- and tetraethyl-ammonium hydrogen-dichlorides from nitrobenzene solution.[8] It appears further from the conductance results that the ion $(ClHNO_3)^-$ must be moderately stable in benzene. Finally, it can be inferred that the anion $(ClHClO_4)^-$ does not exist in benzene. And this conclusion is likewise indicated by another finding of Dr. S. F. Mok, *viz.*, that

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[8] Herbrandson, Dickerson, and Weinstein, *J. Amer. Chem. Soc.*, 1954, **76**, 4046.

hydrogen chloride and tetra-*n*-butylammonium perchlorate act additively in their catalysis of the methyl-alcoholysis of triphenylmethyl chloride in benzene.

For the purposes of the associated kinetic investigation, we were concerned to determine whether the presence in benzene of hydroxylic compounds in concentrations of the order of 0·1M would make any great difference to the number of simple ions produced by the ammonium salts. We therefore measured the conductance of tetra-*n*-butylammonium chloride, and that of the corresponding perchlorate, over a range of salt concentrations, in a 0·1M-solution of methyl alcohol in benzene, and in a 0·1M-solution of phenol in benzene. From the plots of $\Lambda\sqrt{c}$ *versus* c, we obtained the intercepts A and slopes B, and thence the values of $\Lambda_{\text{min.}}$ and $c_{\text{min.}}$, given in Table 5.

TABLE 5. *Electrolytic constants of single tetra-*n*-butylammonium salts in solutions of hydroxylic compounds in benzene at* 30°. [Units: A in ohm^{-1} cm.^{2} mole$^{-0.5}$ l.$^{-0.5}$; B in ohm^{-1} cm.^{2} mole$^{-1.5}$ l.$^{0.5}$; $\Lambda_{\text{min.}}$ in ohm^{-1} cm.^{2} mole^{-1}; $c_{\text{min.}}$, M.]

	Chloride			Perchlorate		
	Pure C_6H_6	0·1M-MeOH in C_6H_6	0·1M-PhOH in C_6H_6	Pure C_6H_6	0·1M-MeOH in C_6H_6	0·1M-PhOH in C_6H_6
10^7A	3·4	2·7	2·0	5·0	6·0	3·2
10^3B	4·2	4·8	10·0	15·5	20·4	25·2
$10^5\Lambda_{\text{min.}}$	7·55	7·2	8·95	17·6	22·1	18·0
$10^5c_{\text{min.}}$	8·1	5·6	2·0	3·2	2·9	1·3

There is no evidence here of any very great change in the degree of dissociation of the ion-pairs. If we consider, as an example, the effect of methyl alcohol on tetra-*n*-butylammonium chloride, remembering that K_2, the equilibrium constant for the dissociation of ion-pairs to simple ions, is proportional, among other things, to A^2, it would at first sight appear that methyl alcohol slightly reduced the proportion of simple ions. This deduction would be valid only if ionic mobilities would remain the same: it is much more likely that methyl alcohol actually increases the proportion of simple ions, but solvates them, or at least solvates the chloride ion, thus decreasing ionic mobility, possibly several-fold, and at any rate in greater proportion than that in which it increases the number of the ions. Phenol, if it similarly solvated the dissociated ions, would produce a still larger electrokinetic entity, and hence a more reduced ionic mobility; and this may be the main reason why the intercept A, for both salts, drops appreciably in the presence of phenol. What we may conclude is that the proportions of simple ions are not increased very greatly by the presence of the hydroxylic compounds, probably not by more than a factor of 5 at most.

It can similarly be deduced from the figures, that the hydroxylic compounds increase the proportions of triple ions, but again by somewhat small factors.

EXPERIMENTAL

Materials.—The salts were made as described in the following paper. The benzene was dried by boiling it for one day with, and then fractionating it from, molten potassium. We found this material to be just as good as that prepared with the aid of the more recently suggested drying agent, calcium hydride.

Solubilities.—The solubilities of tetra-*n*-butylammonium chloride and perchlorate in benzene at 30° were estimated very roughly as 0·005 and 0·0005 mole/l., respectively. Tetra-*n*-butylammonium azide and nitrate are very much more soluble. The solubilities of all the salts in benzene are much increased in the presence of 0·05 or 0·1M-methyl alcohol or -benzyl alcohol.

Apparatus.—A cell was constructed by sealing, into the bottom of a 250 ml., conical flask, a cylindrical well 8 cm. deep and 2 cm. in diameter. The electrodes were two concentric platinum cylinders within the well. Measurements could then be conducted with a sample of 12 ml., which could be successively diluted up to 250 ml. In this cell, the resistance of a 0·001M-solution of potassium chloride at 25° was 59·3 ± 0·4 ohm, from which, with the aid of Shedlovsky's data,[9] the cell constant was calculated to be 0·00872. All glass apparatus was

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[9] Shedlovsky, *J. Amer. Chem. Soc.*, 1932, **54**, 1411; Shedlovsky, Brown, and McInnes, *Trans. Electrochem. Soc.*, 1934, **66**, 165.

TABLE 6. *Equivalent conductances of single and mixed tetra*-n-*butylammonium salts in benzene at* 30°.

10^6c	$10^6\Lambda$	10^6c	$10^6\Lambda$	10^6c	$10^6\Lambda$	10^6c	$10^6\Lambda$
[Bu$^n_4$NCl] = *c*							
Series A							
10·0	135	37·5	82·0	83·0	76·2	166	80·0
15·0	105	50·0	74·5	100	76·5	250	87·5
21·0	101	62·0	73·5	125	76·5	330	96·5
30·0	80·0						
Series B							
18·5	94·0	44·2	78·6	75·0	74·3	125	78·0
24·2	90·0	50·0	78·3	83·3	75·2	150	80·0
27·8	87·7	57·7	76·9	94·5	76·4	187	83·5
32·6	82·8	62·5	76·6	107	76·5	250	87·0
39·5	79·3	68·2	75·3				
[Bu$^n_4$NN$_3$] = *c*							
Series A							
15·0	130	60·0	106	300	142	1250	199
20·0	112	100	110	375	150	1560	225
24·0	107	120	107	500	163	2080	243
30·0	103	150	119	750	183	3130	304
37·5	103	200	126	1000	187	6250	470
50·0	100						
Series B							
18·5	117·5	44·2	104·1	75·0	104·4	125	113·0
24·2	111·3	50·0	102·7	83·3	104·4	150	116·0
27·8	109·5	53·5	102·5	94·6	106·8	187	125·4
32·6	106·7	62·5	103·0	107	107·0	250	138·0
39·5	103·5	68·2	103·2				
[Bu$^n_4$NNO$_3$] = *c*							
Series A							
11·3	146	45·4	116	120	138	300	168
14·3	136	54·5	117	150	144	400	176
19·5	127	60·0	119	171	151	600	194
30·3	117	75·0	124	200	155	750	207
34·0	118	85·5	127	240	163	1000	224
39·0	116	100	131				
[Bu$^n_4$NClO$_4$] = *c*							
Series A							
8·0	236	20·0	161	50·0	181	100	216
9·4	220	22·8	153	53·3	187	133	227
13·3	190	25·8	159	60·0	189	150	226
10·0	209	28·6	173	75·0	191	200	244
14·3	177	32·0	168	80·0	202	300	271
16·0	171	33·3	176	91·0	203	400	282
17·8	166	42·2	177				
Series B							
23·7	165	62·5	188	100·0	205	200·0	254
36·5	176	71·5	192	125·0	218	250·0	275
50·0	181	83·3	198	166·7	240		
[Bu$^n_4$NCl] = *c*/2; [Bu$^n_4$NN$_3$] = *c*/2							
Series B							
25·0	99·2	62·5	87·8	100·0	89·6	166·6	97·3
33·3	94·0	71·5	88·8	125·0	92·5	200·0	103·5
40·0	91·4	83·3	88·8	142·8	94·5	250·0	108·0
50·0	88·8						
[Bu$^n_4$NCl] = *c*/2; [Bu$^n_4$NNO$_3$] = *c*/2							
Series A							
8·0	139	20·0	104	40·0	105	100	125
10·0	135	22·8	106	50·0	110	133	126
13·3	114	26·6	105	66·6	107	160	132
16·0	112	32·0	105	80·0	115	200	138

TABLE 6. (*Continued.*)

10^6c	$10^6\Lambda$	10^6c	$10^6\Lambda$	10^6c	$10^6\Lambda$	10^6c	$10^6\Lambda$
$[\mathrm{Bu^n{}_4NCl}] = c/2$; $[\mathrm{Bu^n{}_4NClO_4}] = c/2$ *Series A*							
10·7	226	40·0	173	66·6	181	115	207
20·0	186	44·4	178	80·0	188	133	213
22·8	182	50·0	175	89·0	190	160	217
26·6	186	57·2	181	100	200	200	225
32·0	185						
$[\mathrm{Bu^n{}_4NNO_3}] = c/2$; $[\mathrm{Bu^n{}_4NClO_4}] = c/2$ *Series A*							
4·0	290	16·0	176	40·0	163	133	203
5·3	261	17·8	182	53·4	171	200	215
7·1	214	20·0	172	64·0	176	266	230
8·5	218	22·8	185	80·0	182	320	241
10·0	224	26·6	168	100	192	400	251
13·0	183	32·0	162				
$[\mathrm{Bu^n{}_4NCl}] = c$; $[\mathrm{MeOH}] = 0{\cdot}1\mathrm{M}$. *Series B*							
25·0	76·5	62·5	72·5	100·0	74·0	200·0	87·0
40·0	71·8	71·5	73·2	125·0	78·0	250·0	92·4
50·0	71·4	83·3	73·1	166·7	81·0		
$[\mathrm{Bu^n{}_4NCl}] = c$; $[\mathrm{PhOH}] = 0{\cdot}1\mathrm{M}$ *Series B*							
22·0	97·0	50·0	101·0	83·3	111·8	166·7	144·0
28·6	91·4	62·5	105·8	100·0	117·5	200·0	155·0
41·6	96·3	71·5	107·0	125·0	129·0	250·0	172·2
$[\mathrm{Bu^n{}_4NClO_4}] = c$; $[\mathrm{MeOH}] = 0{\cdot}1\mathrm{M}$ *Series B*							
23·8	219	60·0	235	100·0	265	200·0	331
36·0	216	71·5	243	125·0	282	250·0	354
48·0	229	83·3	250·5	166·7	311		
$[\mathrm{Bu^n{}_4NClO_4}] = c$; $[\mathrm{PhOH}] = 0{\cdot}1\mathrm{M}$ *Series B*							
28·6	197·5	71·5	246	125·0	314	200·0	383
48·0	221	83·3	261	166·7	348	250·0	425
60·0	235	100·0	283				

given a prolonged baking at 150° before use with the benzene solutions. The bridge had the cell as one arm, a 4-dial box of resistance 10^4 ohms as the second, a 10^6 ohm resistance as the third, and a resistance of 10^4, 10^5, 10^6, or 10^7 ohms (usually 10^5 ohms) as the fourth. A 240-volt D.C. battery supplied the current, and the poles were reversed after each reading to minimise the polarisation. A Pye-Scalamp galvanometer was employed as the null-instrument. This arrangement gave self-consistent results, though we would make no claim as to their absolute accuracy. For all measurements in benzene solution, the temperature was 30°. Each reading was repeated three or four times, sometimes more often.

Results.—These are in Table 6, apart from those already given in Table 4. The two sets of measurements, called series *A* and *B*, were made at different times, with different materials, by different experimenters. Where there was repetition, the two series led to identical values of *A* and *B*, those already quoted, and hence to identical values of all other electrolytic constants of the substances concerned.

We thank the Humanitarian Trust and the Friends of the Hebrew University for a Fellowship (to S. P.) during the period of this work.

WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, GOWER ST., LONDON, W.C.1.

[*Received, October 5th,* 1956.]