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MEASUREMENT OF TRANSPORT NUMBERS IN AQUEOUS SOLUTIONS OF ELECTROLYTES

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I. INTRODUCTION

Problems arising in the measurement of the transport numbers and mobilities of ions in electrolyte solutions have been the object of many experimental and theoretical investigations[1-4]. The development of experimental techniques was particularly vigorous at the beginning of the present century, when the moving boundary method and the e.m.f. method achieved a popularity as wide as that of the Hittorf method. Since the late 1940's, several new procedures have been developed intensively, and have helped to provide many experimental data whose effect has been to increase our understanding of the transport numbers and mobilities of ions in solutions of various chemical compounds.

The most important characteristic of the motion of ions in solutions is ionic mobility. The mobility is a function of all the parameters of the solution, and is defined as the velocity of the ions under the influence of a unit potential gradient (1 V cm^{-1}). The ability of an electrolyte to carry an electric current, *i.e.* the electrical conductivity of the electrolyte, is determined by the total charge and by the mobility of the ions. The total current passing through a unit cross-section of a solution containing a mixture of various ions is given by

$$j = F \sum_i c_i z_i u_i , \qquad (1)$$

where c_i, z_i, and u_i are the concentration, the charge, and the mobility of the ions of the i-th kind, respectively, and F is Faraday's constant.

The fraction of the current carried by ions of the i-th kind is called the transport number of those ions, and can be expressed in the form

$$T_i = \frac{u_i z_i c_i}{\sum_i u_i z_i c_i} . \qquad (2)$$

Obviously, the sum of the transport numbers of all kinds of ion present in solution is

$$\sum_i T_i = 1 . \qquad (3)$$

In the simplest case of a binary electrolyte, dissociating into two ions ($MA \rightleftharpoons M^+ + A^-$), of mobility u_{M^+} and u_{A^-} respectively, the transport numbers are

$$T_{M+} = \frac{u_{M+}}{u_{M+} + u_{A-}}, \quad T_{A-} = \frac{u_{A-}}{u_{M+} + u_{A-}}, \qquad (4)$$

since the equivalent concentrations of the ions are equal. Ionic mobilities can be determined experimentally by measuring the velocity of the ions and the electrical potential gradient. Lodge[5] and Whethem[6] were the first to attempt this measurement, but they experienced great difficulty in measuring the electric field (and therefore also the mobility) with adequate precision. Later workers determined mobility values by calculation, from measured transport numbers, and from the electrical conductivity of the solutions. Electrical conductivity data are now available for a large number of electrolytes, but data relating to transport numbers are far less plentiful. This is because transport number measurements present more serious experimental difficulties.

All existing methods for measuring transport numbers rely on the displacement of atoms of a given kind as a means of monitoring the motion of charges. In fully dissociated solutions, which includes most dilute solutions, the displacements of atoms and charges are identical, and existing methods of measurement give a correct assessment of the motion of ions in solutions. A more complicated situation exists when a given substance can contribute to the composition of both the anions and the cations. There is ample experimental evidence for the formation of ion pairs in solution, and also of groups of three ions (ion triplets)[7,8]. Complex formation very often takes place in electrolyte solutions[9-11]. All these effects cause the experimentally measured transport numbers to differ from the values given by Eqn. (4). If the M atoms in a solution of MA can enter into the composition of both the cations and the anions, the value of the transport numbers obtained experimentally can be expressed as

$$T_M = \frac{\sum_i^n z_i u_{ci} c_{ci} p_{cMi} - \sum_i^m z_i u_{ai} c_{ai} p_{aMi}}{\sum_i^n z_i u_{ci} c_{ci} + \sum_i^m z_i u_{ai} c_{ai}}, \qquad (5)$$

where u_{ci} and c_{ci} are the mobility and the concentration of cations of the i-th kind, u_{ai} and c_{ai} the mobility and the concentration of anions of the i-th kind, p_{cMi} is the number of M atoms included in the composition of the i-th cationic component, and p_{aMi} the number of M atoms included in the composition of the i-th anionic component.

The summation is carried out over all kinds of cation (n) and of anion (m). It is evident that the case where $\sum_{i=1}^{m}$ is greater than $\sum_{i=1}^{n}$ corresponds to anomalous values of the transport number.

Thus, the experimentally measured transport numbers are a measure of the ratio of the resulting flux of atoms of the substance M to the total flux of charged species[12].

The interactions between ions and the solvent lead to the formation of solvation (hydration) shells around the ions, which move in the electric field together with the ions[13-15]. The difference in degree of solvation and in mobility between cations and anions results in a net transfer of solvent in one direction, which has given rise to the concept of apparent and true transport numbers. Existing methods of measuring transport numbers use the solvent as the system of coordinates, and do not take account of the motion of solvent with the ions. Transport numbers measured in this way are the apparent (or, as they are often called, Hittorf) transport numbers. To measure true transport numbers, the system of coordinates is based on the solution as a whole[16,17], so that the preferential motion of the solvent is automatically compensated.

Experimental methods for measuring apparent transport numbers can be divided into three groups: (a) Hittorf's method; (b) methods based on the measurement of the e.m.f. of galvanic cells; (c) methods based on the observation of ionic boundaries.

The present review deals with existing methods of measuring apparent transport numbers of ions in aqueous solutions of electrolytes, the main emphasis being on methods developed relatively recently. Generalised experimental data on transport numbers in aqueous solutions of electrolytes are presented. Problems arising in the determination of true transport numbers and in measurements in non-aqueous electrolytes are not considered.

II. HITTORF'S METHOD

The principle of the method was first proposed by Hittorf[18-25] in 1853. It is most conveniently discussed by considering a binary electrolyte which dissociates by the reaction $MA \rightleftharpoons M^+ + A^-$. Fig. 1 shows an electrolytic cell for transport number measurements. If no secondary chemical reactions occur at the electrodes during electrolysis, and ions disappear from the cathodic compartment V_c by being discharged, after time t the loss of M^+ cations from the volume V_c will be

$$P_{M+} = \frac{It}{F}, \qquad (6)$$

where I is the current passing through the cell.

From the direction of the anode, a flow of M^+ cations enters V_c through the cross-section S:

$$I = \frac{T_{M+}}{F} \cdot \frac{\partial q}{\partial t} + DS\frac{\partial c}{\partial x}, \qquad (7)$$

where T_{M^+} is the transport number of the M^+ ions, q the quantity of electricity carried by the cations, t the time,

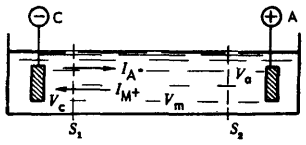


Fig. 1. Schematic diagram of an electrolytic cell for the measurement of transport numbers by the Hittorf method. C and A are the cathode and anode respectively; I_{M^+} and I_{A^-} are the cation and anion currents; S_1 and S_2 are arbitrary cross-sections defining the middle compartment of the cell; V_c and V_a are the cathodic and anodic compartments.

D the diffusion coefficient, and S the cross-sectional area of the cell.

The conditions are usually chosen so that the concentration of the solution in the middle compartment of the cell (V_m) does not change during the time (t) of the experiment. In this case the diffusional term $DS(\partial c/\partial x)$ vanishes, and

$$I_{M+} = \frac{IT_{M+}}{F}. \quad (8)$$

The overall cation balance in the compartment V_c is

$$\Delta P_{M+} = \frac{It}{F}(1 - T_{M+}) = \frac{It}{F} T_{A-}. \quad (9)$$

The quantity of anions moving out of V_c in time t is

$$\Delta P_{A-} = \frac{It}{F} T_{A-}. \quad (10)$$

The total change in the amount of the salt present in the cathodic compartment is

$$\Delta P_{MA} = \frac{It}{F} T_{A-} \quad \text{(equiv.)} \quad (11)$$

The same considerations can be applied to the anodic compartment. The values of ΔP_{MA} are obtained from the differences in concentration of the experimental solution before and after the experiment. The concentration differences produced by the passage of current are expressed in terms of the weight of solvent present in the solution at the end of the experiment. This allows for density changes, and therefore also volume changes, caused by changes in the amount of electrolyte.

The concentrations are usually found analytically by weighing the portion of the solution adjacent to the electrode. This method is therefore often referred to as the analytical or gravimetric method. Zhitomirskii and coworkers[286] have used a tracer method of analysis.

Many different types of measuring apparatus have been described. All of them have a cathodic, an anodic, and a central (intermediate) compartment[26-33]. In some designs porous diaphragms are used, including diaphragms made of ion-exchange resins[27,34-37]. However, different values of the transport numbers are usually obtained with diaphragms.

The application of Hittorf's method is limited by a number of factors:

(a) The need to choose reversible electrodes, or to make allowance for secondary electrode processes[27,38]. In the absence of an exact knowledge of the secondary products of the reaction, the results may be seriously in error[39].

(b) Analytical precision of a high order is needed[27,30,33].

(c) The thermal operating regime of the measuring apparatus must be optimised[38,40-44].

Most experimenters have confined their measurements to relatively small concentration changes: increasing the duration of electrolysis or the current enhances the effect of mixing (whether diffusional or convectional) on the results.

The accuracy of the results is also significantly influenced by the electrolyte concentration, since the relative concentration changes decrease, other things being equal, with increase in the concentration of the solutions. With dilute solutions different workers[38,45] have obtained results agreeing to 0.2% using Hittorf's method. However, the achievement of high precision presents real difficulties, and the moving boundary method is now used instead for accurate measurements of transport numbers.

III. METHODS BASED ON MEASUREMENTS OF THE E. M. F. OF GALVANIC CELLS

Measurements of the electromotive force (e.m.f.) of galvanic cells form the basis of two methods for measuring transport numbers. The first of these (the e.m.f. method) makes use of electromotive force measurements on concentration cells[46-49]. In the second method one measures the electromotive force of galvanic cells subjected to an external gravitational field[50-60].

The processes occurring in galvanic cells can be classified as thermodynamically reversible processes, and therefore thermodynamic methods are used to study them[61,62].

The electrical work done by a cell, excluding the mechanical work associated with any volume change, is equal to the change in the free energy G attending the process in the cell. At constant temperature and pressure dG can be expressed in terms of the change in the chemical potential μ_i of the individual components:

$$dG = Fd\mathcal{E} = \sum_i d\mu_i. \quad (12)$$

The quantity μ_i can itself be written in the form

$$\mu_i = \mu_i^0 + RT \ln a_i, \quad (13)$$

where μ_i^0 is the chemical potential in the standard state, R is the gas constant, T the temperature, and a_i the activity of the i-th component. These considerations are applied in calculating the e.m.f. of cells.

Concentration cells are a particular type of galvanic cell. Unlike the cells used as a source of e.m.f., whose electrical energy is derived from an overall chemical reaction, concentration cells derive their electrical energy from the tendency of the concentrations in different parts of the cell to reach a common level. According to the nature of the processes accompanying the equilibration of concentration, concentration cells can be divided into two types.

(a) Concentration cells without transport, of the type $\ominus$ reversible A electrode | $MA(c_1)$ | reversible M electrode $MA(c_2)$ | reversible A electrode $\oplus$. In such a cell there is no direct transport of electrolyte from one solution to the other. The solutions are separated by an additional reversible electrode. Transport takes place indirectly, as a result of chemical reactions. If the activities of the solutions differ by an amount da, the electromotive force of a cell without transport can be expressed, in general, by

$$d\mathcal{E} = \pm \frac{\nu}{\nu_\pm} \cdot \frac{RT}{z_\pm F} d\ln a, \quad (14)$$

where ν is the total number of ions formed when a solute molecule dissociates, and $\nu_\pm$ and $z_\pm$ are the number and the electrovalence, respectively, of ions of one sign. The $\pm$ signs refer to the ions with respect to which the external electrodes are reversible.

(b) Concentration cells with transport, of the type $\ominus$ reversible A electrode | $MA(c_1)$ | $MA(c_2)$ | reversible A

electrode ⊕ , have a liquid boundary between the solutions of different concentration. A diffusion potential, determined by the mobility difference between cations and anions, arises at the liquid junction. The value of the diffusion potential depends on the difference between the work needed to transfer anions from the more concentrated to the more dilute solution and the work needed to transfer cations from the more dilute to the more concentrated solution. The e.m.f. of a concentration cell with transport (ϵ_t) can be expressed as

$$d\varepsilon_+ = \pm T_\pm \cdot \frac{\nu}{\nu_\pm} \cdot \frac{RT}{z_\pm F} d\ln a, \qquad (15)$$

where $T_\pm$ is the transport number of the ion with respect to which the electrodes are irreversible. Eqns. (14) and (15) are used in the e.m.f. method.

Two modifications of the e.m.f. method are used to measure transport numbers. In one of these electromotive forces are measured in cells with and without transport containing the same electrolyte. The concentration of one of the solutions is kept constant, whilst the concentration of the other is varied. Transport numbers are obtained from the slope of plots of $\epsilon = f(\ln a)$, according to the expression

$$\frac{d\varepsilon_+/d\ln a}{d\varepsilon/d\ln a} = T_\pm, \qquad (16)$$

where a is the activity of the solution whose concentration is varied.

The activities of the solutions of different concentrations should be determined independently. The activity is sometimes calculated from the concentration of the solution [$a = f(c)$] by means of the extended Debye–Hückel formula[63].

In the second modification of the e.m.f. method one measures the electromotive force of two concentration cells with transport, in one of which the diffusion potential is reduced to a minimum by introducing an intermediate electrolyte in which the cations and the anions have very similar mobilities[47,48,64]. Solutions of KCl or NH_4NO_3, which have been fully characterised, are commonly used as the intermediate electrolyte.

Many designs of cell have been used for the measurement of transport numbers[47,48,65–68]. A great deal of attention has been paid to the choice of electrodes[69–78] and to the formation of the liquid junction[79–84]. The use of this method is often limited by the difficulty of setting up satisfactory concentration cells. The need to establish the relation $a = f(c)$ complicates the procedure and introduces further errors.

The earliest report of the appearance of an electromotive force in a galvanic cell under the influence of external forces is due to Collie[50,51]. A thermodynamic discussion of the effect can be found in many monographs[2,3,8,52,57–61]. The essential features of the measurement are shown in Fig. 2. Vessel *1*, containing the reversible electrodes *2* and *3*, is filled with a solution of the experimental electrolyte MA and is subjected to the field of gravitational forces f. The cations and the anions, having different masses m_i and volumes V_i, move with different speeds in the gravitational field. The faster ions charge the electrode *3* to a potential ϵ. The charge on the electrode in equivalent to a definite internal electric field $E = \epsilon/h$, whose effect is to equalise the velocities of the ions. Allowing for the repulsive forces which act on the ions in

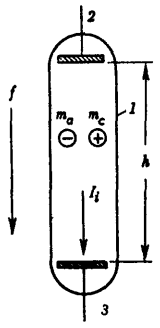


Fig. 2. Measurement of the electromotive force of a galvanic cell in a gravitational force field: 1) solution; 2) and 3) electrodes; h — interelectrode distance; f — external force; I_i — flux of the ith component; m_c and m_a — masses of the cation and anion.

the solution, the expression for the fluxes of cations and anions takes the form

$$I = c_i(u_i m_i g - u_i V_i \rho g \pm u_i \frac{\varepsilon F}{h}), \qquad (17)$$

where c_i is the concentration of ions of the i-th kind, ρ the density of the solution, and g the acceleration due to the gravitational force.

The + sign corresponds to the slow ion, the - sign to the fast ion. In the gravitational field the movement of the ions causes transport of the solute as a whole, and the cell becomes a concentration cell. In time, the e.m.f. of the concentration cell opposes its gravitational electromotive force. Time changes of the e.m.f. have been observed experimentally[85,87]. The resulting e.m.f. can be calculated by imposing the condition of equal cation and anion fluxes:

$$\varepsilon = -\frac{gh}{F}[T_c(m_c - V_c\rho) - T_a(m_a - V_a\rho)] + \varepsilon_1,$$

where

$$\varepsilon_1 = (T_a - T_c + 1)\frac{RT}{F}\ln\frac{\gamma_2\left[c_1 + \int_0^t AI_i(t)\,dt\right]}{\gamma_1 c_1},$$

c_1 is the initial concentration, $\gamma_{1,2}$ are the activity coefficients, and A is a parameter describing the distribution of the solution in the cell.

In the particular case of systems consiting of iodide solutions (such as KI with a small amount of free iodine) the transport number is calculated by the formula

$$T_{K+} = \frac{\varepsilon F\left|gh + \frac{1}{2}(M_{I_2} - V_{I_2}\rho)\right.}{M_{KI} - \overline{V}_{KI}\rho}, \qquad (19)$$

where M_{KI} and $\overline{V}_{KI}$ are the molecular weight and the partial volume of the salt and M_{I_2} and V_{I_2} the molecular weight and partial volume of the free iodine.

A considerable enhancement of the effect has been achieved by placing the galvanic cell in a centrifuge[55,56,85,86]. An e.m.f. generated by the centrifugal acceleration arises at the electrodes of the cell, located at distances r_1 and r_2

from the centre of rotation. To calculate the transport numbers, one uses formula (19) with the substitution

$$gh = 2\pi^2 n^2 (r_2^2 - r_1^2), \qquad (20)$$

where n is the number of revolutions per second.

As in the e.m.f. method, reversibility of the electrodes is an essential requirement in measurements of transport numbers by the gravitational method. Radial temperature gradients must also be carefully avoided[58].

Measurements of transport numbers by the e.m.f. method and by the method based on e.m.f. measurements on a galvanic cell in a gravitational force field are inferior in accuracy to measurements by the moving boundary method. In all these methods serious difficulties arise in the treatment of results for multicomponent systems: these require a knowledge of the relationship between the e.m.f.'s of the galvanic cells and the transport numbers of the individual components[68,88-90].

IV. METHODS BASED ON OBSERVATIONS OF IONIC BOUNDARIES

1. General Considerations and Stability Conditions of Ionic Boundaries

The existence of stable ionic boundaries between electrolytes[5,6,91] has been used as the basis for several methods of measuring transport numbers. The conditions under which such boundaries can exist, and their main features, arise from the following considerations. An ionic boundary can be formed between two electrolytes M_1A and M_2A whenever the mobilities of the non-common ions ($u_{M_1^+}$ and $u_{M_2^+}$) differ by a sufficient amount. To this end, the electrolytes are positioned so that $u_{M_1^+}$ and $u_{M_2^+}$ increase in the direction in which the ions move in the electric field (Fig. 3). The passage of an electric current through the electrolytes generates a stable boundary between the electrolytes, arising from the difference in mobility between the cations. When the electrolytes on either side of the boundary have reached a steady state, i.e. when their concentrations cease to change, the velocities v_1 and v_2 of the ions M_1^+ and M_2^+ become identical and equal to the velocity of the boundary (v_b):

$$v_1 = v_2 = v_b. \qquad (21)$$

If the solution as a whole does not move, we have

$$v_b = u_{M_1^+} \cdot E_1 = u_{M_2^+} \cdot E_2, \qquad (22)$$

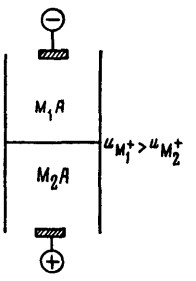


Fig. 3. Measurements by the moving boundary method.

where E_1 and E_2 are the electric field strengths in the electrolytes M_1A and M_2A respectively. Expressing E in terms of the current density j, we can write

$$v_b = jT_{M_1^+}/Fc_1 = jT_{M_2^+}/Fc_2, \qquad (23)$$

for the velocity of the boundary, where $T_{M_1^+}$ and $T_{M_2^+}$ are the transport numbers of the cations and c_1 and c_2 the concentrations of the solutions M_1A and M_2A.

The relation known as Kohlrausch's "regulating function" [92] follows from condition (23). Since in a steady state the fluxes of solvent on either side of the boundary must be equal[93], the regulating function can be written in the form

$$\frac{T_i}{c_i'} = \text{const.}, \qquad (24)$$

where c_i' is the electrolyte concentration expressed in equiv. per kg of solvent.

If the concentration of the indicator electrolyte (the solution containing the slower M^+ ions) does not satisfy relation (24), a concentration readjustment takes place as electrolysis proceeds[4,94]. The concentration change during this readjustment[95-97] is described by the following differential equation:

$$-\frac{\partial c}{\partial t} = \frac{j}{F} \cdot \frac{\partial T(c)}{\partial c} \cdot \frac{\partial c}{\partial x} - D\frac{\partial^2 c}{\partial x^2}. \qquad (25)$$

Ignoring the diffusional term, we can write an expression for the rate of readjustment[94], i.e. for the velocity of the Kohlrausch concentration front relative to that of the boundary:

$$v_{readj} = v_b - \frac{j}{F}\frac{\Delta T(c)}{\Delta c}. \qquad (26)$$

In most solutions the change in transport number with concentration, $\Delta T(c)/\Delta c$, is not large, and to a first approximation the Kohlrausch concentration front moves away from the boundary with the speed of the ions. The time needed to establish a steady state is

$$\tau = \frac{l}{v_{readj}}, \qquad (27)$$

where l is the length of the region over which the concentrations adopt the Kohlrausch value.

For univalent ions, the concentration ratio of the solutions in the region of the boundary can be obtained from the relation

$$\frac{c_2}{c_1} = b \cdot e^{-\frac{u_1 - u_2}{u_1} \cdot \frac{e}{kT} \cdot \frac{v_b x}{u_2}}, \qquad (28)$$

where b is a constant, u_1 and u_2 are the mobilities of the non-common ions, k is Boltzmann's constant, T the absolute temperature, e the electronic charge, and x the distance measured from the origin of the system of coordinates.

This expression can be used to calculate the width of ionic boundaries.

The stability of the boundary and the rate of readjustment depend essentially on a correct choice of the operating conditions of the measuring tube, in particular the range of currents and electric fields. The evolution of Joule heat causes various effects, which can seriously affect methods based on ionic boundaries. The following are the most significant effects associated with the temperature conditions:

(a) Change in temperature of the solution. Due to the evolution of Joule heat, the motion of the boundary occurs at a temperature which is not the same as that of the surroundings. The change of transport with temperature will cause a change in the Kohlrausch concentration.

(b) Ionic convection. Since the mobility of the ions is a function of temperature, ions at different distances from the centre of the tube will have different velocities:

$$v_i = [u_0 + \beta\Delta T(\rho)]E, \qquad (29)$$

where β is the temperature coefficient of mobility and u_0 the mobility of the ions at temperature T_0.

Since the boundary moves at an average velocity v_b, the speed of the ions in some central region will exceed that of the boundary, whilst the speed of the ions close to the walls wil be somewhat less than the speed of the boundary. Thus, ionic convection will occur along the tube with a velocity $\Delta v_i = v_i - \bar{v}_b$. This motion of the ions is equivalent to an additional contribution to diffusional mixing[99-101]. The increase in the effective diffusion coefficient causes the boundary between the electrolytes to become diffuse.

(c) Convective entrainment of indicator electrolyte. This phenomenon occurs because some of the indicator electrolyte is carried into the overlying electrolyte by convective flow. Usually, the boundary remains fairly sharp, but the velocity of the boundary becomes a non-linear function of the current[101]. Convective entrainment of the indicator electrolyte is associated with the difference in temperature between the top solution and the indicator solution, and can be minimised by suitable choice of the thermal regime under which the tube is operated. Alternatively, the measuring tube can be packed with a porous filler[102].

Several procedures for forming the boundaries and observing their position are known. A sharp separation between solutions can be obtained by the following methods.

(a) The sheared boundary method[103]. The simplest form of this method is illustrated in Fig. 4*a*. Two carefully lapped plates *1* and *2* are provided with openings in which are located the tips of tubes *3* and *4*, filled with different solutions. By sliding the plates, the tips of the tubes are brought into contact, and the drops of solution protruding from the tips are sheared together and generate a sharp boundary.

(b) The air bubble (air lock) method[104]. Fig. 4*b* shows part of the measuring tube. Vessels *5* and *6* are initially filled with a solution of the top electrolyte; an air bubble which separates the solution into two parts is introduced into the capillary *8* through the side tube *7*. Vesel *6* is then filled with a solution of the indicator electrolyte. A sharp boundary is obtained when the air bubble is forced out of capillary *8* into tube *7*.

(c) The self-generated boundary method[105]. The method (Fig. 4*c*) makes use of a soluble electrode *9*, above which is located the solution of M_1A. The solution of indicator electrolyte M_2A is formed by electrolysis, and is separated from the top electrolyte by a sharp boundary. Cady and Longsworth have pointed out[106] that the automatic adjustment of the concentration of the indicator electrolyte is confined to the immediate vicinity of the boundary.

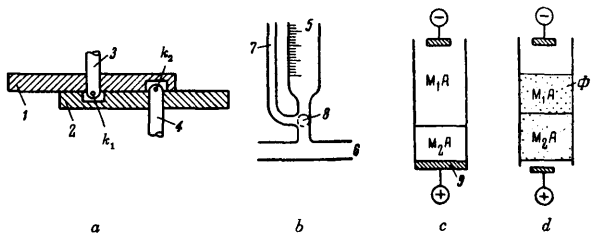


Fig. 4. Methods of forming ionic boundaries: *a*) sheared boundary method; *b*) air bubble method; *c*) self-generated boundary method; *d*) porous packing method; 1) and 2) lapped plates; 3), 4), 5), and 6) parts of the measuring tube; 7) and 8) capillaries; 9) a soluble electrode; k_1 and k_2 — drops of the solutions; Φ — the porous packing.

(d) The porous packing method[102,107]. The solutions of M_1A and M_2A are joined in the porous filter Φ (Fig. 4*d*). A boundary forms automatically when the current is switched on. The porous packing minimises mixing effects and eliminates convection of the solutions.

Various methods are used to observe the boundaries. The most important of these are as follows.

(a) Optical methods. Visual observation is used when one of the solutions contains coloured ions or when the refractive indices of the two solutions are very different. Occasionally, penumbra projections are photographed[44,95], or one observed the diffraction pattern produced on a screen behind the measuring tube by a narrow beam of light[98].

(b) Methods based on conductivity and temperature differences between the top and the indicator electrolyte. The position of the boundary is monitored either by auxiliary electrodes[35,108-112,287,288] or by miniature thermistors[113] located inside the tube.

(c) Methods involving radioactive tracers[107,114,115,289]. Small amounts of β- or γ-active isotopes of the same elements are added to one or both of the experimental solutions. The position of the boundary is detected by accurately collimated radiation counters.

The methods of measuring transport numbers which rely on ionic boundaries can be divided into two groups: the direct methods, including the moving boundary method and the method of simultaneous observation of the motion of the ions and of the solution, and the indirect methods, based on the use of Kohlrausch's regulating function.

2. The Moving Boundary Method

Expression (23), relating the transport number to the velocity of the boundary, forms the basis of the moving boundary method. The displacement of the boundary caused by the passage of a known quantity of electricity is measured experimentally[91,106,116,117]. A vertical cross-section through part of the measuring tube is shown in

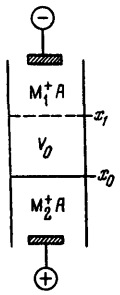


Fig. 5. Measurements by the moving boundary method: x_0 — initial position of the boundary; x_1 — final position of the boundary.

Fig. 5. The volume V_0, defined by the cross-sections with coordinates x_0 and x_1, is usually identified by fiducial marks and accurately measured before the experiment. By measuring the time t needed for the boundary to move between the marks, and knowing the current I and the concentration C_{M^+} of the electrolyte under study, the transport number can be calculated:

$$T_{M+} = \frac{V_0 C_{M+} F}{It}. \qquad (30)$$

Various corrections are usually applied to the formula. Miller[94] first drew attention to the fact that the volume change due to electrolysis and ion migration induces a drift of the solution relative to the measuring tube. An appropriate correction to the volume V_0 can either be determined experimentally[8,61,118-133] or calculated from data on the density of the solutions and of the electrode components[134]. At low concentrations of the experimental solutions another correction becomes necessary: it arises from the transport of current by the ions formed by dissociation of the solvent and of trace impurities[135]. Allowing for these effects, the expression for calculating the transport number takes the form

$$T_i = \frac{F}{It} c_i (V_0 - \Delta V) \frac{1}{1 - \frac{L_0}{L}}, \qquad (31)$$

where ΔV is Miller's correction, L the electrical conductivity of the solution, and L_0 the electrical conductivity arising from impurities.

Measurements by the moving boundary method are complicated by the need to choose the concentration of the indicator electrolyte, c_{ind}, in preliminary experiments. The velocities of the ions are equal to the velocity of the boundary if the state of the electrolytes is stationary ($\partial c/\partial t = \partial c_{ind}/\partial t = 0$), i.e. if Kohlrausch's regulating function is obeyed. It has been shown[106,109] that Kohlrausch conditions are established automatically and exactly only if the initial concentration of the indicator electrolyte, c_{ind}^{init}, is not very different from the Kohlrausch value c_{ind}^{K}. In practice, the difference between the two values should not be more than 5–10%. At larger deviations, the rearrangement process gives rise to an additional mode of transport of the solution as a whole. Since the value of c_{ind}^{K} is not known before the experiment, the normal procedure is to determine the relationship $T_i = f(c_{ind}^{init})$, whose form is shown in Fig. 6. The value of c_{ind}^{K} is taken

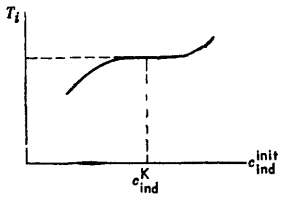


Fig. 6. Variation of the transport number with concentration of the indicator electrolyte during measurements by the moving boundary method.

to be the mid-point of the range over which the transport number remains constant.

The precision of transport number measurements decreases with increased concentration of the experimental electrolytes, because the correction for the transport of solution as a result of the motion of the boundary becomes larger.

The maximum concentration of the solutions which can be studied by the moving boundary method is no more than 0.1 N. The limitation arises from convective transport and convective entrainment effects. The use of a porous filler is not permissible, because the effect of electro-osmotic solution transport cannot be allowed for when using this method.

The analytical and the differential moving boundary methods are variants of this procedure.

The principle of the analytical method is as follows. The measuring tube, divided into two compartments by the porous diaphragm Φ (Fig. 7), is filled with the electrolytes M_1A and M_2A. When current is passed, the boundary emerges from the filter (position x_0) and reaches position x_1 after time t. The amount of M_2^+ ions above the filter is determined by a conventional analytical procedure, and hence the transport numbers in a solution of M_2A can be obtained. The calculation is based on a formula analogous to Eqn. (30):

$$T_{M_2^+} = \frac{V_0 C_{M_2^+} F}{It}. \qquad (32)$$

The shortcoming of this method is the uncertainty as to the concentration of the M_2A solution, which penetrates

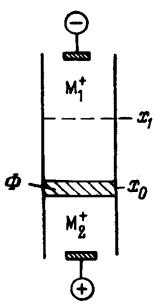


Fig. 7. Analytical form of the moving boundary method: Φ — porous diaphragm; x_0 and x_1 — initial and final positions of the ionic boundary.

into the volume above the filter if the initial concentrations of the leading solutions are not chosen in accordance with the Kohlrausch regulating function. In general, this should lead to a dependence of the results upon the concentration of the leading electrolyte.

The differential method[117] makes use of concentration boundaries[92,94,137,138], i.e. the boundaries formed by solutions of different concentrations c' and c'' of the same salt. The volume swept by the boundary is proportional to the difference in transport number of the ions at concentration c' and c''. Generally, the method is used to measure the concentration dependence of transport numbers, and is useful also when the direct method cannot be used[139]. The formula in this case is:

$$T'_{M+} - T''_{M+} = \frac{V_0(c' - c'')F}{It}. \qquad (33)$$

The main limitation of this method is associated with the stability of concentration boundaries[96].

The precision of measurements by the moving boundary method depends essentially on the accuracy with which the ionic boundaries can be located. According to Spiro's review[2], the maximum attainable precision of the method is 0.03%.

3. Simultaneous Observation of the Motion of the Ions and of the Solution

Kaimakov and Fiks[102] have developed a method of measuring transport numbers which is free from the limitations and shortcomings inherent in the moving boundary method. Whereas in the moving boundary method the system of coordinates is based on the measuring tube, and allowance for the transport of solution has to be made by applying the Miller correction, in the method of simultaneous observation one measures the flow of solvent passing through the ionic boundary by observing the motion of the ions and of the solution at the same time. In general, transport of the solution can be caused by: (a) a difference in levels of the liquids in the cathodic and the anodic limb of the measuring tube (countercurrent); (b) a difference in density between the leading and the indicator solution; (c) electrode processes, and displacement of the boundaries; (d) electro-osmotic flow of the solution.

If the solution undergoes transport under the influence of external forces, the velocity of the boundary v_b is the sum of the velocities v_i of the ions and v_s of the solution:

$$v_b = v_i + v_s, \qquad (34)$$

or

$$v_i = v_b - v_s = \frac{fT_i}{Fc}.$$

This is the basic formula of the method of simultaneous observation of the motion of the ions and of the solution.

The essential features of the measurement of transport numbers are illustrated in Fig. 8. The measurements are made in a U-tube in which a porous plug *3* separates the cathodic limb *1* from the anodic limb *2*. The plug acts as a hydrodynamic resistance, and also as the region where the boundary is formed. The measurement of transport numbers consists, essentially, in measuring the velocity of the boundary and that of the solution over a range of current densities, and plotting $v_b = f(I)$ and $v_s = f(I)$. Clearly, the difference between the two curves

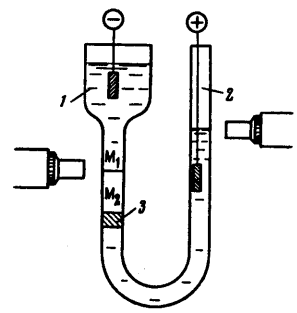


Fig. 8. Measurements by the method of simultaneous observation:
1) cathodic limb of the measuring tube;
2) anodic limb of the measuring tube;
3) porous diaphragm.

must be a straight line whose slope is related to the transport number by the expression

$$\tan\alpha = \frac{T_i}{Fc_i}, \qquad (35)$$

where c_i is the concentration of the ions in equiv. litre^{-1}.

The form of the experimental plots is shown in Fig. 9.

In the method of simultaneous observation there is no need to make a correct choice of the concentration of the indicator electrolyte. The perturbation of the hydrodynamic equilibrium associated with the establishment of the Kohlrausch concentration is automatically allowed for. The use of a countercurrent to control the motion of the boundary, in conjunction with a porous septum, makes a much wider range of temperatures and electrolyte concentrations experimentally accessible.

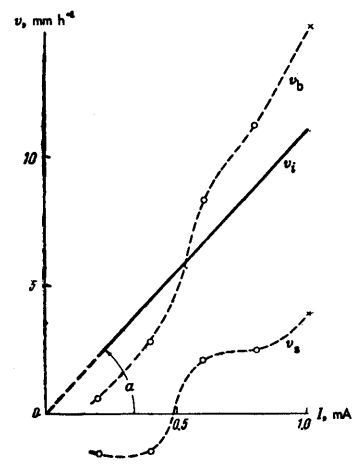


Fig. 9. Experimental curves obtained by the method of simultaneous observation[102] for 3 N solutions of NH_4Cl at 20°:
v_b — velocity of the ionic boundary; v_s — velocity of the solution; v_i — velocity of the ions.

The most important measurements, in practice, are made by keeping the boundary immobile with a suitable countercurrent, and measuring the accumulation of solvent in the anodic limb[101]. The transport number of the cations is calculated by means of the formula

$$T_{M+} = \frac{F}{I} v_s \cdot c_i' S_A, \qquad (36)$$

where v_s is the rate of accumulation of solvent in the anodic limb, c_i' the concentration of the ions in equiv. per kg of solvent, I the total current through the cell, and S_A the internal cross-sectional area of the anodic limb.

Thus, the cross-section of the tube which contains the boundary does not appear in the formula. When calculating transport numbers allowance should be made for possible changes in the volume of the solvent being accumulated[101,140].

The method of simultaneous observation has provided many data relating to concentrated solutions of electrolytes. In principle, this method should give results no less accurate than those of the moving boundary method.

4. Methods Based on Kohlrausch's Regulating Function

In the direct methods transport numbers can be deduced immediately from the results of a single experiment. The methods relying on the regulating function enable transport numbers to be calculated from a knowledge of the steady-state concentrations of the electrolytes moving in constant relative positions, and of the transport number of one of them. The problem of measuring transport numbers consists essentially in making the correct choice of electrolytes and experimentally determining their steady-state concentrations. Cady and Longsworth[106] were the first to measure steady-state concentrations. Hartley[93] proposed a method of measuring steady-state concentrations which he later used in a number of investigations[141-145]. Conductimetric analysis has also been used to measure concentrations[109,146]. Fig. 10 shows part of the measuring tube of Samis and Hartley's apparatus[147]. The leading electrolyte solution, in tube *1* and vessel *2*, was brought into contact with the indicator electrolyte in tube *4* by the air-lock method, using the side-arm *3*. When current was passed the boundary moved along tube *1*. By partial compensation of the motion of the boundary, using a countercurrent, some solution having the Kohlrausch concentration was forced into vessel *5*, provided with measuring electrodes.

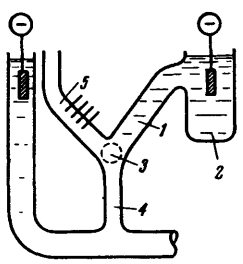


Fig. 10. Part of Samis and Hartley's apparatus[147] for measuring Kohlrausch concentrations:
1) leading electrolyte solution; 2) cathode vessel; 3) capillary connection; 4) indicator electrolyte; 5) auxiliary vessel with leads for measuring the electrical conductance of the electrolytes under study.

The upper limit of experimentally accessible concentrations, 0.1 N, was set by the fact that no precautions were taken to minimise the effect of convective transport.

Refractive analysis has also been used[44,95,148,149] to measure steady-state concentrations.

Some new procedures were developed when the problems associated with readjustment in concentrated solutions were overcome. Work with concentrated solutions is characterised by the need to avoid convective transport effects. This is achieved either by working with small-diameter tubes, or by using porous packing. Konstantinov and Oshurkova[98] made their measurements in capillaries of ~0.1 mm diameter, using large electric fields. Steady-state concentrations were determined by measuring the length of a thread of the experimental solution, "trapped" between the leading and the indicator solution.

Kaimakov and coworkers[150-152] used wide measuring tubes packed with ground quartz. Steady-state concentrations were measured either with platinum electrodes fitted to the tubes or with a miniature thermistor. By this procedure, steady-state concentrations could be measured in a single experiment for a number of electrolytes following each other.

V. MEASUREMENT OF TRANSPORT NUMBERS AND MOBILITIES IN MIXTURES OF ELECTROLYTES

Both the Hittorf method[151-161] and the moving boundary method[117,162-166] have been used to study mixtures of electrolyte solutions. To measure transport numbers by Hittorf's method, the concentration changes of all the components of the solution in the electrode compartments are measured simultaneously by chemical analysis. The lower limit of additive concentration is set only by the precision of the method of chemical analysis of the particular component. The upper limit of the total concentration of the mixture is set by convective mixing[167]. The early investigations of mixtures by Hittorf's method[154,155,292] relied on inadequate methods of analysis, and led the authors to erroneous conclusions as to the structure of mixtures of binary electrolytes. The most accurate results are obtained by the moving boundary method. A boundary is formed between the mixture and the indicator electrolyte, and an electric field is applied which causes the mixture to separate and form a second boundary between ions of different mobility. The velocity of this boundary is proportional to the transport number of the ion of the additive[117]. The use of the moving boundary method is confined to relatively low total concentrations of the mixture under study ($c_{tot} < 0.1$ N). A procedure for measuring the mobilities and transport numbers of ions added at low concentrations (a few per cent, or fractions of one per cent) to concentrated solutions of electrolytes has been described[168-170]. The method depends on separating the mixture in an electric field, the impurity ions accumulating between the mixture and the indicator electrolyte. The boundaries are located within the porous packing. The column of additive is held in a fixed position relative to the measuring tube by a counterflow. The transport number of the additive is found

TABLE 1. Transport numbers of cations in aqueous electrolyte solutions.

Compound	t°C	Electrolyte concentration, N																	Method	Literature references
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	1.5	2.0	3.0	5.0	6.0	7.0	9.0	10.0	12.0	15.0	
$AgClO_3$	25			0.499																m.b.	176
$AgClO_4$	25	0.4783	0.4781	0.4774	0.4774															m.b.	177,176
$AgNO_3$	18		0.471	0.471	0.472	0.472	0.473	0.481	0.499	0.513	0.524									Hitt.	176, 19—25,40,120, 162,172,178—186, 188,190,191,282
	25	0.4647	0.4648	0.4652	0.4664															m.b.	177,136
	40			0.4729	0.4737															m.b.	191
$AgNO_3$	25	0.481	0.461																	Hitt.	192
Ag_2SO_4	17				0.446															Hitt.	19—25
Ag_2SiF_6	22			0.475																Hitt.	176
$BaCl_2$	18		0.450	0.450	0.440	0.420	0.408	0.389	0.360	0.350	0.343									Hitt.	172,36,178,180,181,
	25			0.439	0.426	0.418	0.406	0.386	0.377	0.374	0.372									e.m.f.	193—197,49, 52—54
$BaBr_2$	18	0.436	0.441		0.420	0.410														Hitt.	198
BaI_2	18			0.426		0.415														m.b.	197
$Ba(NO_3)_2$	25				0.456	0.456	0.455	0.446												Hitt.	198
$CaBr_2$	18			0.409		0.396														m.b.	172,197,199
$CaCl_2$	15	0.4261	0.4231	0.4188	0.4105	0.4024	0.3964	(0.15)												m.b.	200
	25			0.420	0.413	0.404	0.387	0.339	0.289	0.268	0.259	0.253	0.252	0.251						e.m.f.	49,120,200,201
	35	0.4354	0.4424	0.4281	0.4198	0.4117	0.4057	(0,15)												m.b.	200
CaI_2	18			0.416	0.400															m.b.	202
$Ca(NO_3)_2$	20	0.450																		Hitt.	202,203
$Ca(OH)_2$	25	0.214																		Hitt.	178,180,181
$CaSO_4$	18	0.441																		m.b.	202,203
$CdBr_2$	25			0.434	0.431	0.426	0.408	0.358	0.222	0.152	0.078	0.028	—0.166							e.m.f.	204,178,180,181,194, 196,205
$CdCl_2$	25			0.486	0.463	0.460	0.471	0.499	0.471	0.424	0.381	0.307	0.161	0.095	0.037	—0.105	—0.192			e.m.f.	204,178,180,181,194, 196,205
$CdCl_3$	20					0.4338														m.b.	206
CdI_2	18	0.445	0.442	0.440	0.440	0.317	0.160	0	—0.12	0.18	0.22									Hitt.	172
$CdSO_4$	18		0.388	0.384	0.378	0.369	0.349	0.323	0.294		0.254									Hitt.	194,196,202,203
	25	0.384	0.384	0.384	0.384	0.384	0.369	0.328	0.295	0.279	0.265	0.240	0.195							e.m.f.	204,207,208
$CeCl_3$	25		0.4636	0.4582	0.4494	0.4390														Hitt.	45,87
$CoBr_2$	18		0.397	0.397	0.390															Hitt.	172,209
$CoCl_2$	20					0.346	0.339	0.321	0.299	0.281	0.266	0.247	0.224	0.215	0.209					s.o.	151,178,180,181,210
$Co(NH_3)_6Cl_3$	25		0.5673		0.5647															m.b.	210
CsBr	18			0.497		0.493														m.b.	197
CsCl	25			0.390	0,377	0.365	0.346	0.336												Hitt.	211,178,180,181,197
CsI	18			0,497		0.497														m.b.	197,86,212
$CuBr_2$	25						0.445	0.440	0.420	0.325	0.285	0.138	0.037	0.09	—0.146					Hitt.	209
	35							0.365	0.275	0.165	0.133	0.042	—0.145	—0.238	—0,335					Hitt.	213
$CuCl_2$	20							0.351	0.331	0,315	0.301	0.278	0.251	0.245	0.240	0.233				s.o.	39,178,180,181,198, 209,213
$CuSO_4$	18			0.375	0.375	0.375	0.357	0.328	0.304	0.286	0.280									Hitt.	172, 19—25,178,180, 181,193,194,196, 198,214,215
	25					0.359	0.339	0.304												m.b.	216
$ErBr_3$	25			0.4366	0.4248	0.4121														m.b.	217
$ErCl_3$	25		0.4489	0.4429	0.4338	0.4230														m.b.	45
$EuCl_3$	25		0.4595	0.4564	0.4472	0.4357														m.b.	45,206
$GdBr_3$	25		0.4552	0.4501	0.4380	0.4271														m.b.	217
$GdCl_3$	25		0.4603	0.4548	0.4409	0.4314														m.b.	217,206
HBr	25					0.729														Hitt.	218
HCl	5	0.844	0.845	0.846	0.848	0.850	0.851	0.854	0.855	0.857	0.857	0.858								e.m.f.	219,26,135,162,178, 180,181
	10	0.840	0.841	0.842	0.844	0.846	0.847	0.850	0.852	0.853	0.853	0.854									190,191,193,194,196, 220—229
	15	0.834	0.835	0.836	0.838	0.840	0.843	0.846	0.848	0.849	0.849	0.850								e.m.f.	219
	15								0.848	0.850	0.852	0.850	0.829	0.795	0.726	0.658	0.649	0.629		e.m.f.	290
	20	0.829	0.830	0.832	0.834	0.837	0.839	0.842	0.844	0.845	0.846	0.846								e.m.f.	219, 52—54
	20								0.845	0.846	0.851	0.853	0.822	0.795	0.759	0.661	0.599	0.466		s.o.	101
	25								0.841	0.843	0.844	0.843	0.824	0.791	0.717	0.665	0.647	0.633		e.m.f.	290,289
	30	0.819	0.821	0.822	0.825	0.828	0.830	0.834	0,837	0.839	0.839	0.840								e.m.f.	219
	35	0.814	0.816	0.818	0.821	0.823	0.827	0.831	0.833	0.835	0.835	0.836								e.m.f.	219
	35								0.834	0.835	0.836	0.835	0.816	0.786	0.710	0,654	0,645	0.632		e.m.f.	290
	40	0.809	0.811	0.813	0.816	0.819	0.823	0.827	0.829	0.830	0.831	0.832								e.m.f.	219
	45	0.804	0.806	0.808	0.811	0.814	0.818	0.822	0.824	0.825	0.826	0.827								e.m.f.	219
	50	0.799	0.801	0.803	0.806	0.810	0.814	0.819	0.821	0.822	0.822	0.823								e.m.f.	219

TABLE 1 (contd.)

Compound	T, °C	Electrolyte concentration, N																	Method	Literature references
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	1.5	2.0	3.0	5.0	6.0	7.0	9.0	10.0	12.0	15.0	
$HClO_4$	25			0.8462	0.8471	0.8453														m.b.	187
HI	25				0.825	0.828	0.825													Hitt.	189,55,56
HIO_3	25		0.9013	0.9034	0.9065	0.908														m.b.	128
HF	25			0.860	0.845	0.821	0.787	0.732	0.694	0.677	0.664									Hitt.	230
HNO_3	18	0.8336	0.8348	0.8360	0.8400	0.8437	0.8492													m.b.	231,194,196,222
H_3PO_4	25	0.959	0.958	0.956	0.953	0.946	0.938	0.927	0.919	0.914	0.909	0.904	0.898	0.896	0.891	0.891	0.889		(19.4)	e.m.f.	89,232
H_2SO_4	0					0.839	0.838	0.836	0.834	0.832	0.827	0.821	0.806	0.797	0.786	0.763	0.750	0.720	0.512	e.m.f.	
	10					0.834	0.834	0.831	0.828	0.826	0.821	0.819	0.797	0.787	0.776	0.754	0.741	0.708	0.508	e.m.f.	
	15					0.830	0.829	0.827	0.824	0.821	0.817	0.809	0.792	0.782	0.771	0.747	0.733	0.702	0.506	e.m.f.	210,178,180,181,
	25					0.819	0.819	0.818	0.817	0.815	0.807	0.799	0.781	0.770	0.759	0.736	0.722	0.691	0.502	e.m.f.	196, 233—236
	35					0.807	0.807	0.805	0.801	0.798	0.793	0.785	0.767	0.756	0.744	0.721	0.707	0.676	0.498	e.m.f.	
	45					0.793	1.793	0.791	0.787	0.784		0.769	0.751	0.741	0.729	0.707	0.693	0.663	0.494	e.m.f.	
	60					0.770	0.770	0.768	0.764			0.744	0.724	0.713	0.704	0.652	0.640	0.641	0.488	e.m.f.	
$HoBr_3$	25		0.4456	0.4385	0.4286	0.4169														m.b.	45
KBr	18		0.494	0.493	0.493	0.492	0.491	0.487	0.486	0.485	0.485	0.484								Hitt.	237,120,197,238
$KBrO_3$	18			0.567		0.570														m.b.	197
KCl	0	0.493	0.493	0.493	0.493	0.492	0.491													Hitt.	176,19—25,38,178, 180,181,
	10		0.495	0.495	0.495	0.495														Hitt.	135,190,196,197, 202,203,239
	15	0.4926	0.4925	0.4924	0.4923	0.4921														m.b.	240,26,36,104,111, 167,191, 240—248
	25		0.494	0.493	0.493	0.492	0.491	0.487	0.486	0.485	0.485	0.484								Hitt.	172,52—54
	25	0.4903	0.4902	0.4901	0.4900	0.4898		0.4887	0.4883											Hitt.	38,117,201, 249—251
	35	0.4887	0.4886	0.4885	0.4885	0.4888														m.b.	240
	45	0.4869	0.4868	0.4868	0.4869	0.4873														m.b.	240
$KClO_3$	18			0.534		0.536														m.b.	202, 19—25,197
$KClO_4$	25					0.570														m.b.	202,197
K_2CO_3	18				0.61	0.60	0.59	0.565	0.566	0.579	0.587	0.596	0.62							Hitt.	178,180,181
$K_3Fe(CN)_6$	25	0.485	0.515	0.555	0.604	0.647														m.b.	252,104
$K_4Fe(CN)_6$	25		0.4315		0.4384	0.4406														m.b.	252,104
KI	18		0.494	0.495	0.493	0.492	0.491	0.487	0.486	0.485	0.485	0.484								Hitt.	237, 19—25,54—58. 120,178,180,181, 197,212,253
$KMnO_4$	20	0.548	0.547	0.540	0.538	0.540	0.555	0.678	(0.4)											m.b.	254,178,180,181,
KNO_3	18					0.503	0.504	0.508	0.513	0.518	0.521									m.b.	172,19—25,162,197, 245
	25		0.5084	0.5087	0.5093	0.5103	0.5120													Hitt.	19—25,136,245
KOH	25			0.263	0.263	0.263	0.263	0.263	0.263											Hitt.	255
K_2SO_4	25	0.4818	0.4829	0.4848	0.4870	0.4890	0.4949													Hitt.	104,19—25, 194— —196,245,104,159,252
	35	0.494	0.488	0.489	0.483															Hitt.	197
$LaBr_3$	25					0.4574	0.4516	0.4426	0.4325											Hitt.	185
$LaCl_3$	25										0.4216	0.3935	0.3669	0.3459	0.3282	0.3012				Hitt.	257,36,45,256,258
LiCl	20																			s.o.	259,135,140,178,180, 181
	25			0.3296	0.3240	0.3192	0.3126	0.2994	0.2863	0.2765	0.265 0.2688	0.244 0.2571	0.224	0.218	0.217	0.216	0.214	0.210		Hitt.	110,48,52—55,167, 198,260,283,284
	40											0.264	0.242	0.240	0.238	0.236	0.235	0.234	(11.0)	s.o.	259,47,253,261
	60											0.277	0.260	0.257	0.255	0.255	0.256	0.257		s.o.	259
	90											0.300	0.276	0.278	0.279	0.283	0.286	0.289		s.o.	259
LiI	20		0.318																	Hitt.	262
	25						0.317		0.267											centr.	55,56,86,87,212
$LiNO_3$	20												0.312	0.323	0.334	0.358	0.376	0.412	0.420 (13.0)	s.o.	263
	30												0.307	0.318	0.330	0.359	0.375	0.408	0.425	s.o.	263
	40												0.313	0.322	0.334	0.360	0.378	0.411	0.422	s.o.	263
LiOH	18					0.150	0.150	0.140	0.13	0.11										Hitt.	198,172,262,97
Li_2SO_4	25			0.385	0.386	0.350			0.283	0.259	0.236	0.226	0.211							s.o.	264,262,97
$MgBr_2$	18																			m.b.	202
$MgCl_2$	18																			Hitt.	202,172,178,180,181, 265
							0.320	0.308	0.291	0.280	0.271	0.250	0.224								
										0.292	0.277	0.253	0.226	0.217	0.212	0.209				s.o.	175,64,159,198
MgI_2	20			0.388		0.350														m.b.	202
$MgSO_4$	18		0.385	0.382	0.372	0.360	0.350	0.310	0.250	0.249	0.247	0.240								Hitt.	172,159,178,180,181

TABLE 1 (contd.)

Compound	T, °C	Electrolyte concentration, N																	Method	Literature references
		0.005	0.01	0.02	0.05	0.1	0.2	0.5	1.0	1.5	2.0	3.0	5.0	6.0	7.0	9.0	10.0	12.0	15.0	
$MnBr_2$	18		0.490	0.490	0.486	0.470														Hitt.	172
$MnCl_2$	18		0.497	0.497	0.485	0.471														Hitt.	172
NaBr	18	0.395	0.395	0.395																Hitt.	178,180,181,172,198,202,19—26,48,52—54,120,135,176,
NaCl	18		0.396	0.395	0.392	0.389	0.380	0.377	0.363	0.360	0.358	0.354	0,350							Hitt.	172
	25	0.3930	0.3918	0.3903	0.3878	0.3853															
	35	0.3970	0.3958	0.3944	0.3919	0.3822														m.b.	267 } 178,180
	45	0.4008	0.3996	0.3982	0.3957	0.3932														m.b.	267 } 181,198,202,237
Na_2CO_3	18				0.48	0.47	0.47	0.46	0.452	0.454	0.458									m.b.	267 } 244,266,97
NaI	18				0.381	0.376														Hitt.	198,172,178,180,181
	25						0.3827		0.384											m.b.	202,212
$NaHPO_3$	25		0.42		0.48	0.46														centr.	55,56,60
$NaNO_2$	19				0.371															Hitt.	269,268
NaOH	25		0.203	0.197	0.189	0.183	0.177	0.169	0.163											Hitt.	198,136,172,178,180,181,285
																				e.m.f.	270,172,178,180,181,198,202,271
$Na_3P_3O_{10}$	25		0.42		0.46	0.47														Hitt.	238
$Na_4P_2O_7$	25		0.42		0.48	0.54														Hitt.	258
$(NaPO_3)_n$	0				0.56	(0.041)														Hitt.	237
	25			0.56	(0.04)	0.54	(0.09)													Hitt.	253
Na_2SO_4	9						0.367	0.363	0.360	0.359										Hitt.	19—25
	25		0.3848	0.3836	0.3829	0.3828	0.3828													m.b.	120,178,180,181
NH_4Br	18			0.483		0.481														m.b.	19—25
NH_4Cl	25		0.4907	0.4906	0.4905	0.4907	0.4915													m.b.	172,19—25,120,178,180,181,202,97
NH_4I	18			0.489		0.484														m.b.	202
NH_4NO_3	25					0.513														m.b.	162
$NdBr_3$	25		0.4602	0.4533	0.4442	0.4328														m.b.	45
$NdCl_3$	25		0.4629	0.4574	0.4500	0.4392														m.b.	217,206
$NiBr_2$	18		0.394	0.391	0.388						(2.5)									Hitt.	172
$NiCl_2$	20										0.320	0.264	0.200	0.191	0.189					s.o.	152,172
$Pb(NO_3)_2$	25				0.487	0.487														Hitt.	183
$PrBr_3$	25		0.4574	0.4531	0.4426															m.b.	217
$PrCl_3$	25	0.4664	0.4636	0.4587	0.4502	0.4396														m.b.	45
RbBr	18			0.495		0.492														m.b.	197
RbCl	18			0.497		0.494														m.b.	197,178,180,181,202
RbI	18			0.498		0.497														m.b.	197,86,212
$SmCl_3$	25		0.4634	0.4571	0.4425	0.4398														m.b.	45,176,178,180,181,198,202,206
$SrBr_2$	18			0.410		0.392														m.b.	203
$SrCl_2$	25			0.424	0.415	0.405	0.393	0.370	0.343	0.322	0.306	0.287	0.274	0.276						e.m.f.	49,171
SrI_2	18			0.416		0.393														m.b.	203
$ThCl_4$	20			0.10	0.24	0.24	0.24	0.24	0.24											Hitt.	36
TlCl	25					0.481														m.b.	178,180,181,207
$TlClO_4$	25				0.531	0.533	0.534													e.m.f.	207
TlF	25					0.481														e.m.f.	207
$TlNO_3$	17					0.512														Hitt.	272,273
	25					0.516														e.m.f.	207
TlOAc	25					0.656														e.m.f.	207
$Tl_2(SO_4)_3$	18			0.475	0.475	0.475														Hitt.	172,178,180,181,183,198,274
	25					0.468														e.m.f.	207
UO_2Cl_2	20								0.268	0.237	0.217	0.191								s.o.	275
	40								0.281	0.241	0.223	0.218								s.o.	275
	60								0.285	0.247	0.233	0.234								s.o.	275
$UO_2(NO_3)_2$	25	0.19	0.23	0.33	0.18	0.16	0.02	(0.15)												Hitt.	276
$YbCl_3$	25		0.4496	0.4461	0.4345	0.4235														m.b.	45
$ZnBr_2$	25				0.383	0.366	0.349	0.324	0.305	0.294	0.284	0.216	0.032	—0.108	—0.168	—0.284	—0.336		—0.563	e.m.f.	277,198,205,211
	40		0.4076	0.4073	0.4044	0.3894														m.b.	191
$ZnCl_2$	20						0.365	0.345	0.306	0.258	0.207	—0.09	—0.128	—0.220	—0.296	—0.417	—0.444			s.o.	12,172,198,211,278,279
	40							0.320	0.195	0.105	0.025	—0.108	—0.306	—0.377	—0.425	—0.512	—0.550			s.o.	12
	60							0.348	0.248	0.188	0.136	0.05	—0.108	—0.183	—0.253	—0.400	—0.470			s.o.	12
	80							0.360	0.270	0.210	0.156	0.066	—0.092	—0.163	—0.212					s.o.	12
$Zn(ClO_4)_2$	25						0.409		0.361		0.325	0.317	0.291	0.281	0.275	0.271	(8.0)			e.m.f.	88
ZnI_2	25					0.382	0.363	0.336	0.320	0.308	0.291	0.236	0.115	0.056	0.040	—0.116	—0.19	—0.291	—0.55(20)	e.m.f.	88,205,211
$ZnSO_4$	20				0.364	0.361	0.356	0.347	0.334	0.321	0.309	0.240	0.222							Hitt.	202, 19—25, 203, 205,280
»	25					0.392	0.392	0.350	0.301	0.276	0.267	0.230	0.165							e.m.f.	204,208,281

by measuring the quantity of matter in the column. The accuracy of the results obtained by this method is 2–3%.

Data on transport numbers and mobilities in mixed solutions are few, and mostly of a tentative nature.

VI. EXPERIMENTAL DATA ON TRANSPORT NUMBERS IN AQUEOUS SOLUTIONS OF ELECTROLYTES

Many papers on the measurement of transport numbers, by different methods, have been published. Collected tables of transport numbers have appeared in many works of reference [171-174]. The fullest information, relating both to aqueous and to non-aqueous solutions of electrolytes, is to be found in Landolt and Börnstein's Tabellen [171]. However, these data are difficult to use, because the experimental results are reported uncritically. Furthermore, a significant volume of recent work, dealing mainly with concentrated aqueous solutions of electrolytes, has not yet found its way into standard tabulations. In the Russian literature tables of transport numbers can be found in "Spravochnik Khimika" (The Chemist's Handbook) [174] and in "Spravochnyi Tom Tekhnicheskoi Entsiklopedii" (Reference Volume of the Technical Encyclopaedia) [173]. However, the results given in those tabulations are based on early measurements of transport numbers in aqueous solutions of electrolytes, and do not provide a balanced account of recently developed new methods, or of the results obtained thereby.

Experimental values of the transport number for a given electrolyte are usually in marked disagreement. For dilute solutions, the discrepancies are relatively small: their causes have been discussed in the literature many times [2,3,36,117,172]. In the region of high solution concentrations the scatter of results is often very large [12,39,75]. For this reason, we adopted the following precedure to construct a general table of the transport numbers of cations in aqueous electrolyte solutions (Table 1) and a table of transport numbers for aqueous solutions of mixtures of electrolytes (Table 2):

(a) For each compound, the results covering the widest range of concentrations and temperatures were tabulated.

(b) When the results obtained by different methods in the same range of concentrations and temperatures showed serious disagreement, measurements by the moving boundary method were selected for the low-concentration region and measurements by the simultaneous observation method for the high-concentration region.

(c) In the few cases where the results obtained by different methods for a given compound were in good agreement, the values were combined.

The first column in Table 1 lists the chemical compounds. The second column gives the temperature at which the measurements were made. The concentration range from 0.005 N to 15 N is divided into 15 intervals; concentrations are expressed in equiv. litre^{-1} (N). Values of the transport number at intermediate concentrations, not given in the original paper, were found by graphical interpolation. Anion transport numbers were recalculated as cation transport numbers, assuming that $T_c + T_a = 1$. Figures in brackets denote the concentration corresponding to the transport numbers tabulated underneath. The column headed "method" indicates the method of measurement used, with the following abbreviations: Hitt. for Hittorf's method, e.m.f. for the e.m.f. method, m.b. for the

TABLE 2. Cation transport numbers in aqueous electrolyte solutions.

Substance: component I	Substance: component II	T, °C	Concentration, N: c_1	Concentration, N: c_2	$T_{M^+(1)}$	$T_{M^+(2)}$	Method	Literature references
$BaCl_2$	HCl	18	0.05	0.05	0.0955	0.648	Hitt.	160
$BaCl_2$	KCl	18	0.05	0.05	0.191	0.271	Hitt.	160
$CaCl_2$	HCl	25	0.000	0.100		0.8314	m.b.	120
			0.025	0.075		0.7619		
			0.05	0.05		0.6518		
			0.075	0.025		0.4537		
$CaCl_2$	LiCl	20	0.1	5.0	0.0028		m.c.	169
			0.12	6.0	0.0014			
			0.16	8.0	—0.0048			
			0.20	10.0	—0.011			
			0.24	12.0	—0.0093			
CsCl	NaCl	25	0.1	1.9	0.026		Hitt.	161
			0.05	1.95	0.014			
			0.2	3.8	0.026			
			0.1	3.9	0.013			
		20	0.05	5.0	0.0038		m.c.	169
			0.06	6.0	0.0020			
			0.07	7.0	0.0009			
			0.08	8.0	0.0002			
			0.09	9.0	—0.0007			
			0.1	10.0	—0.0012			
$CuCl_2$	LiCl	20	0.04	4.0	0.00007		m.c.	169
			0.06	6.0	—0.0014			
			0.08	8.0	—0.0032			
			0.1	10.0	—0.0050			
			0.12	12.0	—0.0042			
			0.04	2.0	0.0055			
			0.07	3.5	0.0019			
			0.1	5.0	—0.0001			
			0.13	6.25	—0.0035			
			0.17	8.5	—0.0061			
			0.215	10.75	—0.0102			
			0.25	12.50	—0.0083			
		20	0.20	5.0	0.0025		m.c.	168
			0.24	6.0	0.0074			
			0.32	8.0	—0.0027			
			0.40	10.0	—0.0077			
			0.48	12.0	—0.011			
		40	0.11	5.5	—0.0032			
			0.17	8.5	—0.012			
		60	0.10	5.0	0.0015			
$CuCl_2$	LiCl	60	0.14	7.0	0.0000		m.c.	168
			0.16	8.0	—0.0030			
			0.20	10.0	—0.0061			
			0.24	12.0	—0.0062			
HCl	KCl	17	0.1123	1.978	0.116	0.400	Hitt.	167
		18	0.0999	0.1005	0.637	0.123		
			0.1060	0.2509	0.475	0.220		
			0.1042	0.509	0.337	0.307		
			0.1020	1.008	0.191	0.380		
			0.1105	2.685	0.074	0.464		
		20	0.1129	3.100	0.074	0.457		
		25	0.075	0.025	0.7456	0.0503	m.b.	117,160
			0.05	0.05	0.6198	0.1242		
			0.025	0.075	0.4109	0.2477		
HCl	LiCl	17	0.0998	0.3074	0.476	0.148	Hitt.	167
		20	0.1165	0.0888	0.705	0.055		
			8.0	0.16		0.0020	m.c.	170
			9.0	0.18		0.0002		
			10.0	0.20		0.0008		
			11.0	0.22		0.0022		
HCl	NaCl	14	0.1055	1.905	0.232	0.266	Hitt.	167,157
			0.15	0.05	0.770	0.0333		
		20	0.1005	0.0967	0.662	0.086		
			0.1081	2.272	0.111	0.347		
HCl	NaCl	21	0.0977	1.019	0.392	0.208	Hitt.	167,157
			0.0944	1.900	0.119	0.310		
			0.1041	4.332	0.049	0.330		
KCl	LiCl	25	0,050	0,050	0.2774	0.1435	m.b.	166
			0.1	1.9		0.036	Hitt.	161
			0.05	1.95		0.019		
			0.2	3.80		0.036		
			0.1	3.90		0.022		
KCl	NaCl	25	0.798	0.202	0.368	0.063	Hitt.	158
			0.745	0.254	0.372	0.084		
			0.664	0.336	0.338	0.109		
			0.517	0.493	0.262	0.169		
			0.491	0.509	0.256	0.157		
			0.322	0.678	0.159	0.246		
			0.224	0.776	0.129	0.239		
			0.198	0.802	0.108	0.288		
			0.2	1.8	0.057		Hitt.	161,291
			0.08	1.92	0.019			
			0.04	1.96	0.010			
			0.10	3.9	0.017			
			0.20	3.8	0.038			
			0.2	4.8	0.025			
			0.50	4.5	0.052			
NaCl	RbCl	25	1.9	0.10		0.034	Hitt.	161
		25	1.95	0.05		0.017		
			3.8	0.20		0.031		
			3.9	0.10		0.015		

moving boundary method, s.o. for the method of simultaneous observation for the motion of the ions and of the solution, centr. for the method based on e.m.f. measurements in a gravity cell.

Column 1 of Table 2 lists the components of the mixture of aqueous electrolyte solutions, column 2 lists the temperatures. Columns 3 and 4 give the concentrations of the components (in equiv. litre^{-1}) in the order in which the components appear in column 1. Columns 5 and 6 give the transport numbers of the cations of the components, in the same order. The abbreviations used to indicate the method are the same as for Table 1. The abbreviation m.c. refers to the method of measuring transport numbers of minor constituents. The last column in both tables lists the literature references: the first number quoted is the paper from which the tabulated values were taken, other numbers refer to independent studies of the same compound.

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AZIRIDINE: SYNTHESIS, STRUCTURE, PROPERTIES

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I. INTRODUCTION

Aziridine and its derivatives have a number of very interesting physical, chemical, and biological properties, and they are attracting increasing attention of workers in different specialities. In addition to their theoretical and scientific interest, aziridine, some of its derivatives, and polyaziridine have found considerable practical uses. The object of the present review is to discuss briefly the main methods of synthesis, features of molecular structure and properties, and the chemical reactivity of aziridine together with its main uses in medicine and technology.

II. METHODS OF SYNTHESIS OF AZIRIDINE

The overwhelming majority of known methods of synthesis of aziridine and its derivatives may be divided according to reaction type into four groups of methods, leading to closure of a three-membered heterocycle: (1) intramolecular condensation reactions with elimination of the elements of an acid; (2) thermolysis of other nitrogen-containing heterocycles; (3) cyclisation reactions of nitrogen-substituted derivatives (oximes, hydrazones, dichloroamines); (4) addition reactions to C=C or C=N bonds.

Intramolecular condensation reactions. Aziridine was first synthesised by Gabriel in 1888 by the action of moist silver oxide on β-bromoethylamine hydrobromide[1]. Gabriel erroneously ascribed the structure of vinylamine to the compound obtained. This error was corrected by Marckwald, who showed that the product obtained by Gabriel was a secondary amine with a cyclic structure[2-4]; at the same time the true mechanism of