2. Metals may be determined in the same solution from which the halogen has been removed.

3. A more compact apparatus can be used and the whole process is simpler and more rapid than in the macro method previously described.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

AN APPLICATION OF MOVING BOUNDARIES TO A STUDY OF AQUEOUS MIXTURES OF HYDROGEN CHLORIDE AND POTASSIUM CHLORIDE

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RECEIVED FEBRUARY 18, 1930 PUBLISHED MAY 8, 1930

Introduction

The purpose of this research was the measurement of the mobilities of the various ion constituents in aqueous mixtures of hydrogen and potassium chlorides. Since the conductances of such solutions do not follow the law of mixtures, it appeared of interest to determine which ion constituents were responsible for these deviations. The moving boundary method was employed in these determinations, boundaries of the rising type being used exclusively. The results, as will be shown below, are also of interest in connection with the recent work on the separation of the rare earth elements by the ionic migration method.[2]

Theoretical

The electrolysis of a mixture of hydrogen and potassium chlorides, using, for instance, a cadmium anode as the source of indicating cations, may be represented diagrammatically as follows. The use of the metallic anode in this manner is the method of Cady and Longsworth,[3] though the source of indicating ions may also be a solution of an appropriate electrolyte. Both methods were employed in these experiments. The tube is initially filled throughout with the mixture of uniform composition as shown in Fig. 1. After current has passed for a time, the hydrogen-ion constituent originally in the lower part of the tube will, due to its high mobility, have forged ahead of a portion of the potassium-ion constituent, and there should be the two boundaries, A and B, as shown in Fig. 2. These two boundaries have been observed and their separate progress has been followed quantitatively.

Fig. 1.

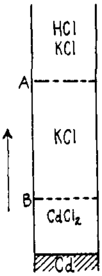

Fig. 2.

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[2] Kendall and Clarke, *Proc. Nat. Acad. Sci.*, **11**, 393 (1925); Kendall and Crittenden, *ibid.*, **9**, 75 (1923); Kendall and White, *ibid.*, **10**, 458 (1924).

[3] Cady and Longsworth, THIS JOURNAL, **51**, 1656 (1929).

The boundary A divides the mixture originally placed in the tube from a region of pure potassium chloride. This boundary travels with a velocity determined by the mobility of the hydrogen-ion constituent and the potential gradient in the mixture.

The slower boundary B is the usual boundary between the indicating electrolyte formed by the electrochemical oxidation of the cadmium anode and a pure potassium chloride solution. The boundary B travels with a velocity determined by the mobility of the potassium-ion constituent and the potential gradient prevailing at the "adjusted" concentration C'_K of the region between the two boundaries. This adjusted concentration can be computed from the expression

$$\frac{C'_K}{T'_K} = \frac{C_H}{R_H} + \frac{C_K}{R_K}$$

in which C denotes concentration, T the transference number and R is a function of the ion mobilities. A derivation of this expression follows.

Throughout this treatment the velocity of an ion constituent will be used. This velocity is a measurable quantity. The velocity of an individual ion cannot, at present, be determined experimentally. If the electrolyte is completely dissociated, the velocity of an ion constituent is identical with the individual ion velocity. If incompletely dissociated, the two velocities differ by a factor equal to the degree of dissociation

Let V_H represent the observed velocity of the hydrogen-ion constituent and U_H the mobility of this ion constituent, then

$$V_H = U_H \frac{dE}{dx}, \text{ and } \Lambda_H = FU_H$$

where Λ_H is the conductance of 1 g. equivalent of hydrogen ion. F is the faraday in coulombs if U_H is expressed in practical units. The total hydrogen-ion concentration in gram equivalents per milliliter of solution is denoted by C_H and the same symbols with appropriate subscripts refer to corresponding quantities for the potassium- and chloride-ion constituents. If A is the (uniform) cross-sectional area in square centimeters of the tube in which electrolysis is taking place, the current flowing in the tube is

$$I = FA(C_H V_H + C_K V_K + C_{Cl} V_{Cl}) \tag{1}$$

The electro-neutrality of the solution is expressed by

$$C_H + C_K = C_{Cl} \tag{2}$$

If x denotes distance along the tube, the quantity of hydrogen ion, Q_H, passing through a given cross section at x in Δt seconds is

$$Q_H = (AC_H V_H)\Delta t \tag{3}$$

and at $x + \Delta x$

$$Q_H + \Delta Q_H = \left[(AC_H V_H) + \frac{\partial}{\partial x}(AC_H V_H)\Delta x\right]\Delta t \tag{4}$$

The change in hydrogen-ion content within the region between x and $x + \Delta x$ is given by the difference between (3) and (4)

$$\Delta Q_{\mathrm{H}} = -\frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}})\,\Delta x\,\Delta t$$

Since the corresponding concentration change, ΔC_{H}, is equal to ΔQ_{H} divided by the volume, $A\,\Delta x$, in which the change occurs

$$\Delta Q_{\mathrm{H}} = A\,\Delta x\,\Delta C_{\mathrm{H}} = -\frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}})\,\Delta x\,\Delta t \tag{5}$$

In the limit, Equation 5 becomes

$$A\frac{\partial C_{\mathrm{H}}}{\partial t} + \frac{\partial}{\partial x}(AC_{\mathrm{H}}V_{\mathrm{H}}) = 0 \tag{6}$$

and similarly for the potassium-ion constituent

$$A\frac{\partial C_{\mathrm{K}}}{\partial t} + \frac{\partial}{\partial t}(AC_{\mathrm{K}}V_{\mathrm{K}}) = 0 \tag{7}$$

Multiply (6) by $F(V_{\mathrm{H}} + V_{\mathrm{Cl}})/V_{\mathrm{H}}$ and (7) by $F(V_{\mathrm{K}} + V_{\mathrm{Cl}})/V_{\mathrm{K}}$, assuming the ratios $(V_{\mathrm{H}} + V_{\mathrm{Cl}})/V_{\mathrm{H}}$ and $(V_{\mathrm{K}} + V_{\mathrm{Cl}})/V_{\mathrm{K}}$ to be independent of the concentration, and add the resulting equations

$$AF\frac{V_{\mathrm{H}} + V_{\mathrm{Cl}}}{V_{\mathrm{H}}}\frac{\partial C_{\mathrm{H}}}{\partial t} + AF\frac{V_{\mathrm{K}} + V_{\mathrm{Cl}}}{V_{\mathrm{K}}}\frac{\partial C_{\mathrm{K}}}{\partial t} + \frac{\partial}{\partial x}[FAC_{\mathrm{H}}(V_{\mathrm{H}} + V_{\mathrm{Cl}})] + \frac{\partial}{\partial x}[FAC_{\mathrm{K}}(V_{\mathrm{K}} + V_{\mathrm{Cl}})] = 0$$

Collecting terms and setting $1/R_{\mathrm{H}} = (V_{\mathrm{H}} + V_{\mathrm{Cl}})/V_{\mathrm{H}}$ and $1/R_{\mathrm{K}} = (V_{\mathrm{K}} + V_{\mathrm{Cl}})/V_{\mathrm{K}}$,[4]

$$\frac{AF}{R_{\mathrm{H}}}\frac{\partial C_{\mathrm{H}}}{\partial t} + \frac{AF}{R_{\mathrm{K}}}\frac{\partial C_{\mathrm{K}}}{\partial t} + \frac{\partial}{\partial x}[FA(C_{\mathrm{H}}V_{\mathrm{H}} + C_{\mathrm{K}}V_{\mathrm{K}} + C_{\mathrm{H}}V_{\mathrm{Cl}} + C_{\mathrm{K}}V_{\mathrm{Cl}})] = 0 \tag{8}$$

From (1) and (2) it is seen that the bracketed expression in (8) is the current I, and since this is uniform throughout the tube

$$\frac{\partial I}{\partial x} = 0$$

The resulting differential equation can then be integrated to give

$$\frac{C_{\mathrm{H}}}{R_{\mathrm{H}}} + \frac{C_{\mathrm{K}}}{R_{\mathrm{K}}} = \text{constant} + f(x) \tag{9}$$

This corresponds to, but is not identical with, the "beharrlichen" function of Kohlrausch.[5] For any given value of x it retains its initial value (neglecting diffusion and convection) throughout electrolysis. If the composition of the solution originally present in the tube is uniform, $f(x)$ also becomes constant. Application of this function, which will henceforth be termed the "regulating" function, to the experiments described here yields the relation

$$\frac{C_{\mathrm{H}}}{R_{\mathrm{H}}} + \frac{C_{\mathrm{K}}}{R_{\mathrm{K}}} = \frac{C'_{\mathrm{K}}}{T'_{\mathrm{K}}} = \text{constant} \tag{10}$$

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[4] The symbol R is identical with the transference number for a simple binary electrolyte but is not the transference number of an ion constituent in a mixture. In the latter case the transference number is given by a more complicated expression; see D. A. MacInnes, This Journal, **47**, 1922 (1925).

[5] Kohlrausch, *Ann. Physik*, **62**, 209 (1897).

The primed quantities in (10) refer to the region of pure potassium chloride solution between the two boundaries, A and B, Fig. 2.

In connection with this regulating function it should be pointed out that the derivations given by Kohlrausch[5] and von Laue[6] are based on the Arrhenius theory of solutions of electrolytes with the attendant assumption of constant ion mobility. Experimentally, the mobility of an ion constituent varies more rapidly with the concentration than does a ratio of these mobilities. Consequently the assumption of R independent of concentration is a more limited assumption than the constancy of the individual mobilities. Otherwise the treatment given here is similar to that of von Laue and the generalized Equation 5, page 332, in his development is identical in form with Equation 9.

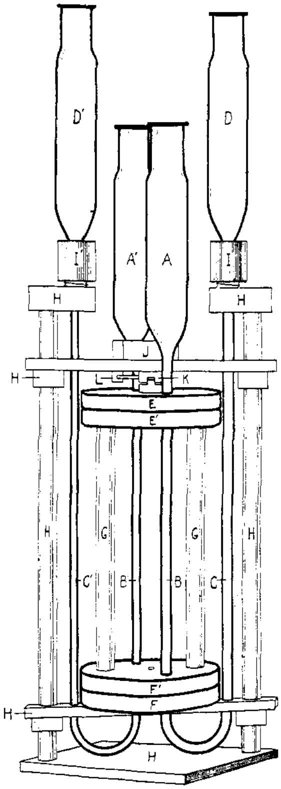

Fig. 3.

The Moving Boundary Apparatus

The cell used for these measurements in which the source of indicator ion is a solution is shown in Fig. 3. The shearing mechanism of MacInnes and Brighton[7] was utilized for forming the boundary. The plate glass disks EE' and FF' are etched in the manner described by these authors and the electrode chambers AA'D and D' are designed according to their recommendations. Tubes B and B' are graduated[8] and calibrated tubes in which the motion of the boundary is observed. The system ABCD is quite independent of the system A'B'C'D', the tube B having an average cross-sectional area about twice that of B'. Only one of these tube systems is used in a determination. The glass disks E' and F', together with the brass supporting rods GG and the tubes BB', constitute an independent unit of the cell and may be removed for cleaning. By clamping this central unit to the lower disk F and turning E over E', boundaries may be formed which can reach the graduations by descending. On the other hand, clamping the central unit to the upper disk E and turning F' over F gives rise to boundaries that can be observed if they ascend the tube. The cell may thus be adapted for the study of either rising or falling boundaries, though all observations made in this paper were on the first mentioned type.

The parts H are of brass and constitute the supporting framework for the glass parts of the cell which are traced in heavier lines. I and I' are threaded bakelite couplings to permit removal of the electrode chambers D and D' for cleaning.

The manipulation using the tube system ABCD and observing a rising boundary is as follows. The plates E and E' are lubricated and clamped together with the tube B

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[6] M. von Laue, *Z. anorg. Chem.*, **93**, 329 (1915).

[7] MacInnes and Brighton, This Journal, **47**, 994 (1925).

[8] MacInnes, Cowperthwaite and Huang, *ibid.*, **49**, 1710 (1927).

and chamber A in alignment. This unit is then filled with the solution whose transference number is to be determined. The tube C and chamber D are filled with solution of indicator electrolyte. Silver–silver chloride electrodes are introduced into the electrode chambers and, if necessary, a few milliliters of a more concentrated solution introduced around these electrodes. The disks F and F′ are then lubricated and pressed together with the protruding drops of solution from B and C in their respective recesses in the opposite disk, as described by MacInnes and Brighton.[7] The cell is then placed in a vibration-free thermostat and allowed to come to thermal equilibrium. Potential is then applied and the circuit tested to see that no current is flowing. The boundary is next formed in the following manner.

A coil spring J of phosphor bronze furnishes power for shearing the plate glass disks in initially forming the boundary. The brass coupling K transmits this power to the disk, also permitting the removal of the disk, E, together with the electrode chambers AA′ which are sealed into it, for cleaning. A release mechanism L is operated by a flexible camera shutter cable (not shown in the diagram). This arrangement permits the turning of the plates and the formation of the boundary without starting vibration. The desirability of such an arrangement has been discussed by MacInnes, Cowperthwaite and Shedlovsky.[9] Upon the release of the spring tension, due to the viscosity of the lubricant between the plates, the plate F′, together with the cell units rigidly connected to it, smoothly turns about its center until tube B is exactly over tube C. The boundary is thus formed and starts to rise immediately, since the electrical circuit is now complete.

For rising boundaries where, according to the method described by Cady and Longsworth,[3] a metallic anode is used as the source of indicator ions, a similar cell was employed. It differs from the one just described in that a cylindrical recess was ground in the lower plate glass disk in which a small disk of anode metal was placed, and also in that no shearing mechanism is necessary.

The current through the cell was maintained constant throughout a determination by means of an improved constant current regulator.[10] This regulator is a modification of the apparatus used by MacInnes, Cowperthwaite and Blanchard,[11] modified so as to give a constant current in a circuit in which both increases and decreases of resistance may occur.

Materials and Purification.—The potassium chloride was recrystallized twice from conductivity water and fused in a platinum crucible. The hydrochloric acid was a pure product, diluted to constant boiling strength and distilled, the end fractions being rejected as recommended by Foulk and Hollingsworth.[12] The concentration of this constant boiling acid was interpolated from the data of these authors.

The materials used as indicators were treated as follows. The potassium iodate was recrystallized from water and dried over phosphorus pentoxide *in vacuo*. The sodium salt of iodeosin (tetra-iodofluorescein) was especially prepared by the makers and was further purified by four recrystallizations from water in this Laboratory. The cadmium metal and iodic acid were of a good grade and were not further purified.

Conductivity Measurements.—The conductances of the solutions were measured on the shielded bridge developed by Dr. Theodore Shedlovsky of these Laboratories. Since this bridge has been described in a separate communication,[13] the following brief notes will suffice here. Pipet cells of the Washburn type were calibrated with 0.1 demal potassium chloride solution according to the recommendations of Parker and

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[9] MacInnes, Cowperthwaite and Shedlovsky, THIS JOURNAL, **51**, 2671 (1929).

[10] Longsworth and MacInnes, *J. Opt. Soc. Am.*, **19**, 50 (1929).

[11] MacInnes, Cowperthwaite and Blanchard, THIS JOURNAL, **48**, 1909 (1926).

[12] Foulk and Hollingsworth, *ibid.*, **45**, 1220 (1923).

[13] Shedlovsky, *ibid.*, **52**, 1793 (1930).

Parker.[14] An audion oscillator operating at a frequency of 2000 cycles supplied the bridge current, which was amplified by two stages of audio frequency amplification before passing to the telephones. The bridge was of the direct reading type with equal ratio arms. The thermostat in which the conductivity cells were immersed was filled with oil. The temperature was maintained constant at 25 ± 0.002°. The temperature was determined by means of a carefully calibrated platinum resistance thermometer.

Rising Boundaries.—Since MacInnes, Cowperthwaite and Huang,[8] working with rising boundaries, observed convection currents due to heating, it seemed necessary to investigate this effect in detail. Their experiment with a rising boundary between potassium chloride and potassium permanganate, used as indicator electrolyte, was repeated and the same phenomena were observed. These were a diffuse color margin, and a "chimney" tinged with the purple color of the permanganate ion in the potassium chloride solution above the boundary. However, I have found that when the much heavier and less mobile iodeosin ion is substituted for the permanganate ion, an extremely sharp margin results with no trace of the intense red color of this ion in the colorless solution in advance of the boundary. The iodeosin ion has been used as an indicator by Franklin and Cady.[15]

If the mobilities of the chloride- and permanganate-ion constituents, and also the densities of the two solutions under the conditions of the experiment, are compared, it appears quite likely that the differences in these properties are not great enough to permit the development of an effective margin. An effective moving boundary results when the restoring effect due to the potential gradient change at the boundary is strong enough to overcome the disturbing effects of convection, diffusion and, possibly, electro-osmosis. The restoring effect has been described in a paper by MacInnes and Cowperthwaite.[16]

[14] Parker and Parker, THIS JOURNAL, **46,** 312 (1924).

[15] Franklin and Cady, *ibid.*, **26,** 499 (1904).

[16] MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.*, **15,** 18 (1929). These authors find experimentally that upon interruption of the current the two solutions forming the boundary begin to diffuse into each other. However, though the current may be interrupted for as much as thirty minutes, upon closing the circuit again the boundary reforms and soon recovers its original sharpness. After reformation and during the period between the reclosing of the circuit and the return to its original sharpness, the boundary moves at the correct velocity. The authors explain this restoring effect of the current as due to the change of potential gradient occurring at the boundary. The lower specific conductance of the indicator solution means a steeper potential gradient in this region. If a more mobile ion in front of the boundary diffuses into the indicator region, it will be subject to a steeper potential slope and will forge ahead of the surrounding less mobile indicator ions until it has regained the boundary. Conversely, if an indicator ion diffuses across the boundary into the region of lower potential slope prevailing in the solution under observation, it will, of necessity, lag behind until it has fallen back into the indicator region. This restoring mechanism of the potential gradient change at the boundary tends to keep the two ion constituents separated and the boundary sharp.

With rising boundaries mixing due to convection will be greater than with falling boundaries because with the former the hotter solution is underneath, an arrangement which tends to produce circulation in the cooler solution. Due to this greater tendency to mix, the restoring effect must, therefore, be greater in rising boundaries. However, mixing of the two solutions at the boundary will be decreased if there is a large difference in the density of those solutions. The choice of the proper indicator will, therefore, be a matter of experiment. For the determination of the anion mobilities in the solutions studied in this investigation, iodic acid and potassium iodate were used as the indicating electrolytes. The low mobility of the iodate-ion constituent and the high density of the solutions of its salts apparently eliminated the troubles, mentioned above, due to heating and convection.

One important advantage of rising boundaries over the descending type is the wider concentration range throughout which there is automatic concentration adjustment of the indicator solution. It is, therefore, not so necessary to make determinations at a series of indicator electrolyte concentrations as when working with falling boundaries. The data of Table I show the effect of indicator-ion concentration upon the observed anion transference number of potassium chloride at 0.1 normal or 0.1 g. equivalent per liter of solution. This unit of concentration differs from the one defined in the theoretical part by a constant factor of 10^{-3}, that is, for 0.1 normal potassium chloride, $C_{\text{KCl}} = 10^{-4}$. From Table I the transference number is seen to be independent of the concentration of the indicator solution of potassium iodate if the latter is between about 0.06 and 0.15 normal. A normality of about 0.06 is the value required by the "regulating" function applied to this simple boundary. To understand why concentration adjustment over such a wide range is not attained in the case of falling boundaries, let us consider the following comparison of the two methods.

TABLE I

THE EFFECT OF THE INDICATOR CONCENTRATION ON THE OBSERVED TRANSFERENCE NUMBER OF POTASSIUM CHLORIDE

Normality KCl	Normality KIO_3	dE/dx volts/cm.	T_a
0.1	0.05	3.086	[a]
.1	.066	3.692	0.5100
.1	.075	3.995	.5103
.1	.1	3.086	.5100
.1	.1	4.298	.5101
.1	.15	4.298	.5106
.1	.2	4.298	.5120

[a] Margin quite distorted and computed value of T_a changed from 0.532 at beginning of run to 0.513 at the close.

If a margin is formed between 0.1 normal potassium iodate and 0.1 normal potassium chloride, Fig. 4 represents the initial condition. On passage of a current the boundary will rise and after some time Fig. 5 will represent the new conditions in the tube. That is, a concentration gradient between 0.1 normal and 0.06 normal potassium iodate will remain at C. Since the relation of the densities d are $d_{0.1\,N\ \mathrm{KCl}} < d_{0.06\,N\ \mathrm{KIO_3}} < d_{0.1\,N\ \mathrm{KIO_3}}$, the lighter solution is on top and this distribution will not be disturbed by gravity. On the other hand, consider an analogous case for falling boundaries where the boundary is initially formed between 0.1 normal potassium chloride and 0.1 normal lithium chloride, Fig. 6. After the boundary has fallen some distance, Fig. 7 would represent conditions were it not for the fact that a denser solution of lithium chloride would thus be left on top. These two solutions of lithium chloride would consequently tend to mix and destroy the concentration adjustment as fast as it was made. Both rising and falling boundaries are found, however, to give erroneous results when the indicator-ion concentration is initially too low.

Fig. 4.

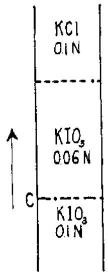

Fig. 5.

Fig. 6.

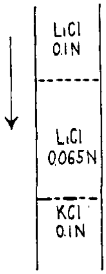

Fig. 7.

Experimental Results

Table II contains the results of transference measurements on the anion constituents. The chloride-ion concentration in all mixtures was maintained at 0.1 normal. The composition of the mixtures will be indicated by the ratio y of hydrogen-ion content to the chloride-ion content, that is, $y = C_{\mathrm{H}}/C_{\mathrm{Cl}}$ and $(1 - y) = C_{\mathrm{K}}/C_{\mathrm{Cl}}$. The indicator solutions for the anion constituents of the mixtures were made up to a total iodate-ion concentration of 0.1 normal, the ratio of hydrogen to potassium-ion content in these solutions being the same as that of the solution for which they were to serve as indicators.

TABLE II

CHLORIDE-ION CONDUCTANCE IN MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE AT A TOTAL CONCENTRATION OF 0.1 N AND 25°

Solution $C_{\mathrm{H}}/C_{\mathrm{Cl}}$	T_{Cl}	Λ	Λ_{Cl}	Λ_{Cl} (calcd.)
1.00	0.1693	391.28	66.32*	...
0.75	.2041	324.31	66.19	66.18
.50	.2560	258.07	66.07	66.03
.25	.3414	192.83	65.83	65.89
.00	.5101	128.89	65.75	...

The value of Λ_{Cl} marked with an asterisk is computed from the value of $T_{\mathrm{H}} = 0.8305$ recorded in Table III. This value is given preference since it is the mean of a larger number of determinations. Comparison of the results for the solutions of pure hydrogen chloride and pure potassium chloride as given in Tables II, III and V shows that $T_c + T_a = 0.9998$ for the former and 0.9999 for the latter. The deviation from the theoretical value of unity is within the experimental error.

From Table II it is seen that Λ_{Cl} from 0.1 normal hydrogen chloride is slightly higher than from 0.1 normal potassium chloride. This is at variance with the constant value of Λ_{Cl} from these two salts found by MacInnes and Smith.[17] The author, however, has determined the chloride-ion conductance from a series of uni-univalent chlorides over the concentration range from 0.1 to 0.02 normal. The results deviate by a few tenths of one per cent. from the constancy found by MacInnes and coworkers at the higher concentration. These deviations from constancy tend to disappear, however, as the concentration is reduced. The chloride-ion conductance from these uni-univalent chlorides seems to be a function of the conductance of the co-ion.

The values of Λ_{Cl} quoted in the last column of Table II were computed on the basis of linear variation between the chloride-ion conductances in pure hydrogen chloride and pure potassium chloride solutions. The conductance of the chloride-ion constituent in the mixtures is thus seen to vary linearly between its values in the pure solutions. This is in complete agreement with the findings of MacInnes, Cowperthwaite and Shedlovsky[9] on mixtures of sodium chloride and potassium chloride. These authors find that though the conductances of the mixtures deviate from additivity, the conductance of the chloride ion remains constant. In other words, the mobility of the common ion constituent is not the cause for the deviation from additivity of the conductances of mixtures of this valence type.

Table III contains the results of observations on the leading boundary A of Fig. 2. As explained in a preceding section, this boundary is that which arises between the mixture of acid and salt and the region of pure potassium chloride. This boundary was visible as a refraction margin in only one of the mixtures ($y = 0.75$), where it was faint but sharp. In the other two mixtures the progress of this boundary was ascertained by

TABLE III

HYDROGEN-ION CONDUCTANCE IN MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE AT A TOTAL CONCENTRATION OF 0.1 N AND 25°

Solution C_H/C_{Cl}	Λ_H	$y\Lambda_H$	$T_H = y\,\Lambda_H/\Lambda$
1.00	324.96	324.96	0.8305
0.75	322.4	241.8	.7456
.50	319.9	159.9_5	.6198
.25	316.9	79.2_3	.4109
.00	...	0.00	.0000

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[17] MacInnes and Smith, THIS JOURNAL, **47**, 1009 (1925).

the color change induced in a trace of methyl violet introduced into the solution. In Table IV are given data showing that the presence of the trace of dye did not materially affect the progress of the boundary in the one mixture where direct comparison could be made. V'_A and V'_B of Table IV are quantities proportional to the velocities of the boundaries A and B, respectively, Fig. 2.

TABLE IV

EFFECT OF PRESENCE OF METHYL VIOLET ON THE BOUNDARY VELOCITIES IN THE MIXTURE 0.075 N HCL–0.025 N KCL

Experiment	Dye present		← Dye absent →		
No.	1	2	3	4	5
V'_A	9954	9952	9952	..	..
V'_B	7055	7055	7063	7058	7057

The equivalent conductance Λ_K of the potassium-ion constituent in the mixtures may be computed by the relation

$$(1 - y)\,\Lambda_K' = \Lambda - \Lambda_{Cl} - y\Lambda_H$$

These values, together with those of the other ion constituents, are collected in Table V.

TABLE V

CONDUCTANCE OF THE ION CONSTITUENTS OF MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE AT A TOTAL CONCENTRATION OF 0.1 N AND 25°

Solution C_H/C_{Cl}	$(1 - y)\,\Lambda_K$	T_K	Λ_H	Λ_K	Λ_{Cl}
1.00	0.00	0.0000	324.96	65.5*	66.32
0.75	16.3	.0503	322.4	65.2	66.19
.50	32.0_5	.1242	319.9	64.1	66.07
.25	47.8	.2477	316.9	63.7	65.83
.00	63.14	.4898	314.0*	63.14	65.75

The values marked with an asterisk are extrapolated, assuming linear variation with the concentration of that constituent. They represent, respectively, the equivalent conductance of vanishingly small quantities of hydrogen ion in 0.1 normal potassium chloride and of potassium ion in 0.1 normal hydrochloric acid.

As the experimental work here presented was being completed, Bennewitz, Wagner and Kuchler[18] reported an extension of the Onsager[19] equations for the conductance of strong binary electrolytes to the case of a ternary ion mixture in which one ion constituent is present in very small quantities. The theory, as developed, is valid only at high dilutions where the equivalent conductance varies as the square root of the concentration. To extrapolate from this region of validity to 0.1 normal solutions can yield predictions of only a qualitative nature. In any event, their theory predicts that the equivalent conductance of vanishingly small quantities of hydrogen ion in 0.1 normal potassium chloride will be

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[18] Bennewitz, Wagner and Kuchler, *Physik. Z.*, **30**, 623 (1929).

[19] Onsager, *ibid.*, **27**, 388 (1926); **28**, 277 (1927).

less than in 0.1 normal hydrogen chloride, while the conductance of the potassium ion will be slightly increased in going from 0.1 normal potassium chloride to 0.1 normal hydrogen chloride. Reference to Table V shows that the extrapolated ion conductances are in qualitative agreement with their theory.

Concentration Changes and Test of the Regulating Function

Referring once more to Fig. 2, if the theoretical treatment leading to Equation 10

$$\frac{C_\mathrm{H}}{R_\mathrm{H}} + \frac{C_\mathrm{K}}{R_\mathrm{K}} = \frac{C'_\mathrm{K}}{T'_\mathrm{K}}$$

is valid, this equation provides a means for computing the "adjusted" concentration C'_K from the ionic mobility relationships across the boundary A and the known concentrations above this leading boundary. Since the leading solution of boundary B is the indicator solution of boundary A, this adjusted concentration C'_K can also be computed independently from observations on the motion of boundary B. If the results of the two methods agree, this is evidence for the correctness of Equation 10, which is an expression of the "regulating" function.

For a boundary between two simple solutions such as those meeting at the boundary B, there is the relation

$$T = \frac{VCF}{It} \tag{11}$$

In this equation, T is the transference number, V the volume swept through by the boundary in t seconds and the other terms represent, as before, the concentration, the faraday and the current. It is evident, therefore, that if T is known, the concentration C may be found. From the observed velocity of the boundary B and the independently determined transference number of potassium chloride over the range of concentrations involved, C'_K has been computed by means of Equation 11. If the transference number changed very rapidly with the concentration, such a computation would require a series of approximations. For potassium chloride solutions, however, the transference number varies so slightly with concentration that one approximation is sufficient. The concentrations thus obtained are given in Col. 4 of Table VI, which also includes the data necessary for these computations. These data are the

TABLE VI

DETERMINATION OF THE "ADJUSTED" CONCENTRATION OF THE REGION OF PURE POTASSIUM CHLORIDE SOLUTION FORMED ON ELECTROLYSIS OF MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

Solution $C_\mathrm{H}/C_\mathrm{Cl}$	VF/It	T'_K	$C'_\mathrm{K} \times 10^3$
0.75	7065	0.4897	69.31
.50	6154	.4898	79.59
.25	5452	.4899	89.86

values of VF/It determined experimentally from the velocity of B, and the independently determined values of T'_K for pure potassium chloride solutions.

For comparison the values of C'_K (2) calculated by means of Equation 10 are recorded in Col. 7 of Table VII. The values of R_H and R_K used in this calculation and recorded in Cols. 2 and 4 are computed from the data of Table V. Reference to the values of the ion conductances given in Table V indicates, however, that the velocity ratio, $V_K(V_K + V_{Cl}) = \Lambda_K/(\Lambda_K + \Lambda_{Cl})$, is slightly different on the two sides of the boundary A. Thus the assumption as to the constancy of this ratio is only an approximation, but a rather close one in this case. The values of C'_K (3) recorded in the last column of Table VII are computed assuming the ratio R_K to remain constant on the two sides of the boundary A and equal to T'_K, the ratio or cation transference number in pure potassium chloride at the "adjusted" concentration C'_K. The independently computed values (1) are copied from Table VI to facilitate comparison.

TABLE VII

TEST OF THE REGULATING FUNCTION FOR MIXTURES OF HYDROCHLORIC ACID AND POTASSIUM CHLORIDE

$C_H \times 10^6$	R_H	$C_K \times 10^8$	R_K	T_K'	$C'_K \times 10^6$ (1)	$C'_K \times 10^6$ (2)	$C'_K \times 10^6$ (3)
75	0.8296	25	0.4962	0.4897	69.31	68.93	69.27
50	.8288	50	.4923	.4898	79.59	79.29	79.55
25	.8281	75	.4919	.4899	89.86	89.49	89.79

In Table VII the agreement between the independently computed values for the adjusted concentration of the region of pure potassium chloride solution between the two boundaries is quantitative evidence for the validity of the regulating function (Equation 10) under the conditions of the experiments. Furthermore, in this region between the two boundaries a portion of the potassium-ion constituent has been concentrated free from the more mobile hydrogen ion present in the original mixture. Though the differences in the mobilities of the two cation constituents of these mixtures are very large, it is probable that the same regulating mechanism is operating in cases where the ion constituents have more nearly the same mobilities, as in mixtures of the rare earths.

Discussion of Results

All experimental values quoted in this paper are the mean of several closely agreeing determinations. The boundary velocities have been corrected for the volume changes as described by Lewis.[20] The apparent equivalent volume was used in making these corrections, this being assumed additive for the mixtures.

Bennewitz, Wagner and Kuchler[18] report measurements by the Hittorf

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[20] Lewis, THIS JOURNAL, **32**, 862 (1910).

method on several mixtures at a total concentration of 0.1 normal and at 18°. The only solution where comparison is possible, however, is that which is 0.05 normal to both hydrogen and potassium chlorides. For this solution at 18°, they obtain $T_H = 0.622$, $T_K = 0.124$ and $T_{Cl} = 0.254$. At 25°, the values recorded by the author are $T_H = 0.6198$, $T_K = 0.1242$ and $T_{Cl} = 0.2560$.

With regard to solutions of the pure electrolytes, reference has already been made to the work of MacInnes and co-workers. Denison and Steele,[21] using lithium chloride and potassium acetate as indicators, obtained 0.492 as the cation transference number of 0.1 normal potassium chloride at 18°. Using potassium chloride and iodic acid as indicators for the ions of hydrogen chloride, they obtained a cation transference number of 0.835 for this electrolyte at 0.1 normal and 18°. A comparison of the published values by the moving boundary method is given in Table VIII. The agreement is only fair. The data of this paper fulfil the following conditions, however. (1) They are independent of the potential gradient within wide limits. (2) They are independent of the nature and concentration of the indicator ion within certain limits. (3) They are very reproducible. (4) The sum of the anion and cation transference numbers is very nearly unity.

TABLE VIII

COMPARISON OF THE TRANSFERENCE NUMBERS OF THE SOLUTIONS OF THE PURE SALTS AS OBTAINED BY DIFFERENT INVESTIGATORS

Solution	Dennison and Steele, 18°	MacInnes, *et al.*, 25°	This paper, 25°
0.1 *N* HCl	0.835	0.8320	0.8305
0.1 *N* KCl	.492	.4920	.4899

The author wishes to express appreciation to Dr. D. A. MacInnes of these laboratories for the inspiring supervision of this work, to Dr. Theodore Shedlovsky for his coöperation in the determination of the conductivities of the solutions, and to Professor H. P. Cady of the University of Kansas for many helpful suggestions.

Summary

Ion mobility relations and concentration changes on electrolysis in mixtures of hydrogen and potassium chlorides at a total chloride-ion concentration of 0.1 normal have been studied by means of the moving boundary method, using rising boundaries.

Two cation boundaries are formed simultaneously and proceed at different rates. The velocity of the leading boundary yields the mobility of the hydrogen-ion constituent in the mixture. A portion of the less mobile potassium-ion constituent lags behind the hydrogen-ion constituent

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[21] Denison and Steele, *Z. physik. Chem.*, **57**, 110 (1907).

and gives rise to a second boundary whose velocity yields information as to the concentration adjustment occurring in the region of the solution which contains pure potassium chloride between the two boundaries. From data on both boundaries it is shown that within this latter region the hydrogen ion has been quantitatively separated from the potassium ion and that the concentration of the potassium chloride residue is accurately determined by the "regulating" function of Kohlrausch,[5] a derivation of which is given.

It is shown experimentally that the mobility of the chloride-ion constituent varies linearly between its slightly different values in 0.1 normal hydrogen chloride and 0.1 normal potassium chloride.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

SURFACE REACTIONS OF ATOMS AND RADICALS. I. A NEW APPROACH TO THE PROBLEM OF SPECIFIC SURFACE ACTION

BY HUGH S. TAYLOR AND GEORGE I. LAVIN

RECEIVED FEBRUARY 24, 1930 PUBLISHED MAY 8, 1930

The problem of specificity in the action of surfaces is still the outstanding problem of chemical reactivity at solid surfaces. The solution of the problem will contribute materially to the explanation of the varied phenomena grouped under the title of contact catalytic action. Hitherto, discussion of this problem has been confined mainly to the reactions which molecules undergo at various surfaces. Little attention has been paid to the influence of surfaces on reactions of atoms and of radicals. Frequently it has been implicitly assumed that, for reactions between atoms and radicals, a surface only was necessary; little regard has been paid to the influence of the nature of the surface. It is the purpose of the present communication to demonstrate that the surface is of importance in atom–radical reactions as in molecular reactions; that great differences in velocity of such reactions at different surfaces occur, though the actual time of reaction is many orders less than with molecules; that the available data, together with other experimental data presented herewith, indicate a connection between the activity of surfaces in atomic reactions and corresponding processes involving molecules. The evidence already in the literature is diffuse and only assumes important proportions when coördinated. It suggests, however, an extended experimental program of which the first results will be here detailed.

The Recombination of Halogen Atoms at Surfaces.—The specific influence of surface in the rate of recombination of halogen atoms is well illustrated by a recent publication of Senftleben and Germer.[1] In this

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[1] Senftleben and Germer, *Ann. Physik*, 2, 847 (1929).