range. In each case the adsorption curve is S-shaped. The component having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. When the component of lower adhesion tension is present in very low concentration it is, however, preferentially adsorbed.

An equation

$$H\Delta x/m = ax^n(1-x) - b(1-x)^d x$$

is used to represent the preferential adsorption over the entire concentration range. The derivation of this equation is made on the assumption that the adsorption of each component follows the Freundlich equation.

It is pointed out that the adsorption at a given interface must depend on the rate of change of that particular interfacial tension with the concentration of the bounding phases. The importance of the measurement of adhesion tension values of solutions is pointed out since the rate of change of adhesion tension is equal and opposite in sign to the rate of change of interfacial tension with concentration.

The Gibbs principle is restated in terms of adhesion tension rather than interfacial tension. "*There will be an excess in the concentration of the solute in the interfacial layer if the rate of change of the adhesion tension of the solution against the adsorbent is positive.*" It is pointed out that the usual formulation of the principle of Gibbs does not take into consideration a number of existing factors. It is felt that a correlation of the data from adsorption and adhesion tension measurements will permit a more complete formulation of this principle.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF KANSAS]

A MODIFICATION OF THE MOVING BOUNDARY METHOD FOR THE DETERMINATION OF TRANSFERENCE NUMBERS

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Introduction

An adaptation of the method of moving boundaries for the determination of transference numbers, involving two differences from recent procedure, has been developed and studied by the authors. The novel features are, first, a single ascending boundary only is observed and, second, a metal anode soluble under the action of the electric current is the source of indicator ions. For example, metallic silver was electrolyzed into a solution of potassium nitrate. Under the conditions of the experiment, this silver furnishes silver nitrate which serves as the indicating electrolyte for the potassium ion constituent of potassium nitrate. The necessity of previous adjustment of the concentration of the indicator electrolyte is thus avoided and no special mechanism is required in the initial formation of the boundary. It was the object of this research to determine the effect of the various factors involved on the stability and velocity of the boundary thus produced.

Apparatus and Method

(a) The Cell.—The apparatus used is shown in Fig. 1. The cylindrical metal anode, J, is machined to fit the graduated and calibrated tube, I, in which the boundary is developed and moves. This anode fits the tube rather snugly and is wedged onto the platinum tip sealed into the glass tube leading the anode connection out of the thermostat. The general design of the cathode chamber is as described by MacInnes and Brighton,[1] and is arranged to have the cathode at some distance from the calibrated tube in which the boundary ascends. The cathode is designed so as to avoid influences which might disturb the progress of the boundary in the graduated tube.[2]

The assembled cell is then mounted in a thermostat furnished with parallel plate glass sides and equipped with the optical system whose profile is shown in Fig. 2. The microscope, F, contains a scale in the eyepiece and is of such depth of focus as to have the tube in which the boundary moves within its focal range.[3] The frosted glass background, H, was illuminated from behind and the narrow black screen, I, on this background, together

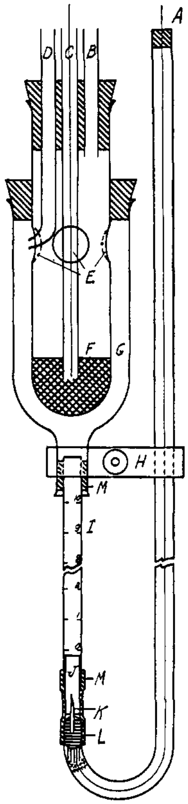

Fig. 1.—Moving boundary cell. *A*, Anode lead; *B*, vent tube; *C*, cathode lead; *D*, tube for filling cell; *E*, holes in cathode tube; *F*, cathode, lead dipping in paste of PbO_2 and H_3BO_3; *G*, cathode chamber; *H*, clamp; *I*, graduated tube in which boundary ascends; *J*, cylindrical metal anode; *K*, platinum tip sealed in tube leading anode connection out of thermostat; *L*, mercury globule making contact with platinum tip and anode held in place by de Khotinsky cement; *M*, rubber connections.

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[1] MacInnes and Brighton, THIS JOURNAL, 47, 994 (1925).

[2] A cylinder of fused silver chloride with a helix of silver wire as core was used with equal success.

[3] In order to locate the boundary with respect to the graduations on the tube, the virtual image, K, of the dark–light margin, I, must be near enough to the graduated tube so that it also comes within the focal depth of the microscope. This may be accomplished by moving the screen and background, H, I, in closer to the moving boundary cell or by working with higher concentrations in the moving boundary cell. The first expedient, however, reduces the sensitivity of this means of detecting the boundary, and the second necessitates the use of solutions of such concentrations as are almost outside the range of the method as developed thus far. With certain solutions of the alkali acetates in anhydrous acetic acid as solvent, it has been found possible to use a microscope in this manner and to a very marked advantage, but for most of the work in water where the concentrations varied from 0.2 to 0.02 *N* it was found necessary to dispense with the microscope and this was replaced by a tube with rectangular openings at either end—merely to insure uniform line of sight in locating the boundary.

with the microscope carriage, E, were arranged on threaded rods, D, provided with bevel pinions, B, so that the two could be raised or lowered together.

The source of potential for these experiments has been four hundred volts of storage "B" batteries. The current in the circuit was maintained constant throughout any given experiment by hand regulation of a rheostat in series with the moving boundary cell and the source of potential. The value and constancy of this current was ascertained by means of a potentiometric determination of the potential drop across a standard resistance inserted in the circuit.

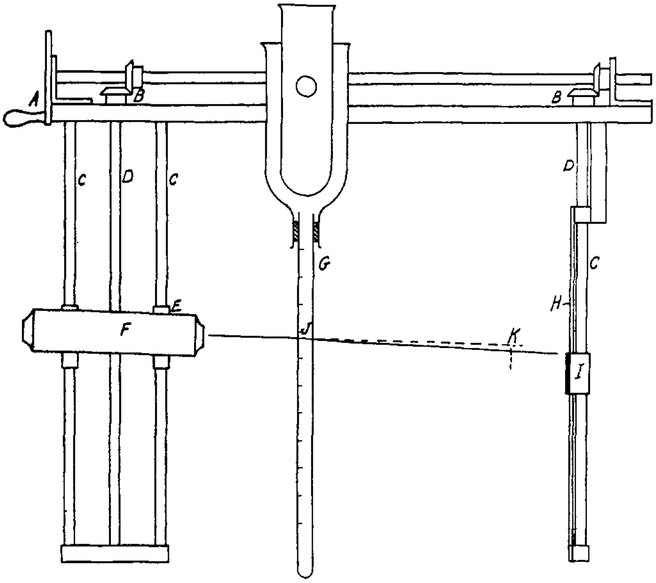

Fig. 2.—Profile of optical system. *A*, Crank; *B*, bevel pinions; *C*, guide rods; *D*, threaded rods; *E*, microscopic carriage; *F*, microscope; *G*, moving boundary cell and tube; *H*, ground glass background—illuminated from behind; *I*, movable opaque screen; *J*, position of margin; *K*, refraction (?) image of upper edge of I.

The tube was graduated as described by MacInnes, Cowperthwaite and Huang,[4] and is calibrated for total volume between the first and last marks only[5] by means of mercury and a dividing engine. The boundary is caused to sweep through the entire volume between these marks and the intermediate marks were used to ascertain the constancy of the boundary velocity under a constant potential gradient. Such constancy is one criterion of a properly functioning boundary.

(b) Location and Visibility of the Boundary.—The boundary we are dealing with in this research is the liquid junction between the solution of electrolyte originally placed in the cell and the ever-increasing column of heavier electrolyte having a common anion and an unlike cation formed from the metal anode. The characteristics which this in-

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[4] MacInnes, Cowperthwaite and Huang, This Journal, 49, 1710 (1927).

[5] The uniformity of bore was not determined directly but the boundary velocities indicated that all of the tubes employed, save one, were sufficiently uniform.

dicator cation must have are described in detail by Franklin and Cady[6] in their article on ion velocities in liquid ammonia.

A necessary condition for a visible boundary is a difference in refractive indices of the two solutions of electrolytes meeting at the boundary. Due to this difference of refractive index the upper edge of the movable opaque screen on the illuminated background (see Fig. 2) will appear distorted when in line with the boundary; this distortion serves as a means of locating the boundary. However, the visibility of a boundary seems to depend also on a sharpening[7] produced by the sudden change of the potential gradient at the boundary as well as on the difference in the refractive indices. Thus cadmium nitrate as indicator electrolyte formed by electrolysis of metallic cadmium into 0.1 N potassium nitrate gave more distinct boundaries than did either lead or silver nitrate—due to its relatively high specific resistance, though the difference in refractive index at the boundary would favor the other indicator electrolytes.

Consideration of Factors Affecting the Results

The expression, $T_c = (LCFA)/(1000IT)$, correlating the quantities determined in a single boundary experiment with the transference number of the given ion constituent has been derived by a number of investigators. In this expression the symbols have the following significance. The boundary travels L centimeters in T seconds in a tube whose (uniform) average cross-sectional area is A square centimeters. I is the current in amperes flowing in the tube. C is the number of equivalents per liter of solution of electrolyte originally placed in the tube and F is the Faraday in coulombs. The ratio L/T thus corresponds to the boundary velocity when the current, and hence the potential gradient, is maintained constant. The various quantities measured and the factors influencing the motion of the boundary are discussed in the following.

(a) **The Concentration Range Studied.**—Sharp and easily visible boundaries were obtained with potassium nitrate at 0.02, 0.1, 0.2 and 1.0 N with either lead or silver as indicator ion at the three lower concentrations and silver only at the higher concentration. In the 1.0 N solution the formation of ions at the silver anode could not be made to proceed smoothly for any great period of time and oxygen evolution would usually destroy the boundary after it had risen two or three centimeters from the face of the electrode. Also, convection currents in the indicator solution at this concentration are marked and their disturbing effect on the boundary velocity probably renders concentrations of this magnitude outside the range of the method in its present state of development—at least, in tubes of the size employed.

(b) **Tube Area.**—Boundaries with 0.1 N potassium nitrate were run in four sizes of tubes, their average cross-sectional areas being 0.1934, 0.1102, 0.06702 and 0.03909 sq. cm., respectively. Both silver and lead anodes were used as sources of indicator ions and a variety of potential gradients employed. In the two larger tubes the measured values of the transference numbers were found to be independent of the tube area whereas in the two smaller tubes these values decreased with the size of the tube—the measured transference number in the smallest tube being about 0.8% lower than the values obtained in the two largest tubes.

These results are recorded in Table I.

[6] Franklin and Cady, This Journal, **26,** 499 (1904).

[7] MacInnes and Cowperthwaite, *Proc. Nat. Acad. Sci.,* **15,** 18 (1929).

TABLE I

EFFECT OF TUBE AREA

Measured transference number of the potassium-ion constituent of 0.1 *N* potassium nitrate at 25°.

Anode	Ag	Pb	Pb	Ag	Pb	Ag
Tube area	0.1934	0.1934	0.1102	0.06702	0.03909	0.03909
Poten. grad., v./cm.	8.615	12.92	Table II	12.34	12.69	10.57
T_c	0.5122	0.5123	0.5121	0.5096	0.5089	0.5076

The possibility of electro-endosmotic forces affecting the boundaries in small-bore tubes has been suggested by Dr. D. A. MacInnes.

(c) **Potential Gradient.**—The simple theory requires the measured transference number to be independent of the potential gradient. This was tested by making several series of runs over a considerable range of potential gradients. The results of one such set of determinations are recorded in Table II.

TABLE II

EFFECT OF POTENTIAL GRADIENT

Measured transference number of the potassium-ion constituent of 0.1 *N* potassium nitrate at 25° with a lead anode as the source of indicator ions.

Tube area, sq. cm.	0.1102	0.1102	0.1102	0.1104	0.1102	0.1102	0.1102
Poten. grad., v./cm.	3.781	7.562	11.34	11.34	15.12	18.91	22.69
T_c	0.5119	0.5121	0.5120	0.5122	0.5151	0.5165	0.5228

All values for the transference numbers have been corrected for the volume changes at the electrodes as described by Lewis.[8] The constant value obtained at low potential gradients ($T_c = 0.5120$) is in good agreement with that of MacInnes, Cowperthwaite and Blanchard[9] ($T_c = 0.5122$) obtained from observations on descending boundaries.

Table II serves to illustrate a rather significant feature of the method, namely, the range of potential gradient over which the transference number is independent of that gradient. The range over which the measured transference number is independent of the potential gradient is greater the smaller the cross-sectional area of the tube.

(d) **Metals Used as Indicators.**—Cadmium, used as a source of indicator ions for the potassium ion constituent of potassium nitrate, did not electrolyze smoothly and values obtained by its use are somewhat inconsistent and persistently low, due probably to secondary electrode reactions producing faster ions that forged ahead of the ions under observation, thus slowing up the boundary. Cadmium, however, electrolyzed very smoothly in halide solutions and gave consistent values for the transference number of the potassium ion constituent of potassium chloride and bromide, respectively. The values obtained, while differing but slightly from the accepted values, will not be quoted here. They probably do not

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[8] G. N. Lewis, THIS JOURNAL, **32**, 862 (1910).

[9] MacInnes, Cowperthwaite and Blanchard, *ibid.*, **48**, 1909 (1926).

represent the accuracy of which the method is capable since two refinements, automatic current control and elimination of vibration, were not made in the prosecution of this research.

The value of the measured transference number quoted in Table II is that obtained from the time required for the boundary to travel the full ten centimeters. At high potential gradients, however, time readings per centimeter showed that the boundary was being accelerated, even when acted upon by a constant potential gradient. The initial velocity obtained by graphical methods gave a value of T_c much nearer the constant value obtained at low potential gradients. The lower limit of potential gradient seems to be determined by the sensitivity of the optical system employed and by the sharpening effect of the potential gradient change at the boundary. On the other hand, the upper limit is controlled almost entirely by the convection currents in the indicator solution due to the larger quantity of heat developed in this portion of the tube. It should be noted that long before convection currents become sufficiently vigorous to destroy the boundary entirely, it has become quite convex and its velocity is no longer an indication of the true velocity of the preceding ion constituent.

Automatic Concentration Adjustment

According to Kohlrausch[10] the concentration of the indicator ion will be automatically adjusted to the relation, $C/C' = T_c/T'_c$, where C and T_c are the concentration and cation transference numbers of the solution under observation and the primed symbols the corresponding quantities for the indicator solution.

Two methods of attack have been employed in ascertaining to what extent this concentration adjustment was automatically made. The first depends on the fact that the total resistance of the cell increases as the boundary ascends the tube, since the indicator ions have lower mobilities than the ions they are replacing. The rheostat resistance in the circuit must, therefore, be continually decreased in order to maintain the current constant. The rate of this decrease is a direct indication—except for the effect of the diffusion layer at the electrode—of the velocity of the indicator ion constituent and hence, indirectly, its transference number. If we take the anode as the origin, the length of the tube as L, and the position of the boundary as x, the total resistance of the tube is

$$R = \frac{L - x}{KA} + \frac{x}{K'A}$$

The dimensions of the cathode chamber permit the resistance of this portion to be neglected. The variation of the total resistance with the position of the boundary is

$$\frac{\mathrm{d}R}{\mathrm{d}x} = \frac{1}{K'A} - \frac{1}{KA}$$

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

from which

$$K' = \frac{K}{1 + KA\,\dfrac{\mathrm{d}R}{\mathrm{d}x}}$$

where K is the specific conductance of the solution under observation and K' the corresponding quantity for the indicator solution. A is the cross-sectional area of the tube. Hence if we know K' as a function of C', we can determine C'. The values of C' were read directly from a plot of K' against C' and the error involved in this procedure may be rather large since conductance data on some of the electrolytes under consideration at 25° are not very concordant. The effects of the formation of a diffusion layer, to be discussed, and of convection, are both to reduce the measured value of $\mathrm{d}R/\mathrm{d}x$. We therefore use the highest value obtained in any given series of runs, this maximum occurring at fairly low potential gradients. According to the equation, C/C' should equal T_c/T'_c. By means of the values of C' obtained as just described, we can determine with the aid of the transference numbers in the literature whether adjustment to the conditions predicted by Kohlrausch has been made. These computations are made in Table III.

TABLE III

CONCENTRATION ADJUSTMENT

Solution	Indicator	C	C'	T_c	T_c	C/C'	T_c/T'_c
KNO_3	Pb	0.0997	0.0961	0.512	0.487	1.04	1.05
KNO_3	Ag	.0997	.0932	.512	.468	1.07	1.09
KCl	Cd	.1000	.0891	.492	.431	1.12	1.14
KBr	Cd	.1008	.0925	.485	.432	1.09	1.12

The ratios, C/C' and T_c/T'_c, given in the last two columns should be the same for each salt measured. The fact that they are nearly so indicates that automatic "adjustment" is attained by the method described in this article. The ratio C/C' is, however, consistently slightly lower than T_c/T'_c. This may arise from the fact that there is a diffusion layer next to the electrode which has the effect of making the concentration appear too high.

The second method consisted in directly measuring the conductance between two platinized platinum tips sealed in the side of the tube. Such measurements were made before and after the boundary had moved by them. The concentration, C', was then interpolated from existing con-

TABLE IV

CONCENTRATION ADJUSTMENT

Solution	Indicator	C	C'	T_c	T'_c	C/C'	T_c/T'_c
KNO_3	Pb	0.1004	0.0932	0.512	0.487	1.07	1.05
KNO_3	Ag	.1004	.0909	.512	.468	1.10	1.09
KCl	Cd	.1000	.0873	.492	.431	1.14	1.14
KBr	Cd	.1008	.0912	.485	.432	1.10	1.12

ductance data as has been described in the previous paragraph, and used to test whether "adjustment" had been attained. The results of our measurements by this method are recorded in Table IV.

The values of T_c and T_c' employed in Tables III and IV are those of MacInnes and co-workers where available; otherwise they are taken from the compilation of Noyes and Falk. In all cases they are values at the nearest concentration and temperature to those of the experiment which are available.

This method, which is more nearly independent of errors due to the diffusion layer just mentioned, shows even better concordance between the ratios C/C' and T_c/T_c'.

The Diffusion Layer

For each Faraday of electricity passed through the cell, one gram equivalent of metallic ion is formed at the anode by the electrochemical reaction there. However, only T_c' equivalents are carried away from the electrode by electrolytic migration. Thus $(1 - T_c')$ equivalents of indicator electrolyte is left in the neighborhood of the electrode. Hence, there is a diffusion layer of indicator electrolyte, of higher concentration than the adjusted value, C', formed at the anode. Our observations and computations[11] from existing theory both show that under the conditions of the experiment pure diffusion will at no time alter the adjusted concentration of the indicator solution immediately behind the boundary. If, however, the convection currents developed in the column of indicator electrolyte penetrate and disturb this diffusion layer, this excess electrolyte will be partially distributed throughout the region of the indicator column. If we can utilize the experience of Smith and MacInnes,[12] which tends to show that an indicator electrolyte concentration greater than C' causes the boundary to move too rapidly, this would explain the high values shown by T_c in Table II at high potential gradients.

In conclusion a word should be said as to the range of the method. With lead and silver as sources of indicator ions the electrolytes to be observed would be restricted to those whose anions give soluble salts with these two metals—which greatly restricts the field—but with cadmium as a source of indicator ions the halides and several other anions are possible but the cations must not be too heavy. Metallic thallium has been made to serve as indicator ion for one of the faster cations in some work in anhydrous acetic acid as solvent. Amalgam electrodes and electrodes of the second class, that is, reversible with respect to the anion, have been investigated to a certain extent and their use would still further extend the range of the method.

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[11] Sand, *Phil. Mag.*, **6**, 1, 45 (1901).

[12] Smith and MacInnes, THIS JOURNAL, **46**, 1398 (1924).

The authors wish to express their appreciation to Dr. D. A. MacInnes for many helpful suggestions and constructive criticisms in the preparation of this manuscript.

Summary

1. A modification of the moving boundary method for determining transference numbers, in which rising boundaries are used, has been studied. In this new method the boundary starts at the surface of the metal electrode, which furnishes the "indicator" ions by electrochemical solution of the metal.

2. When applicable the new method furnishes a simpler means of obtaining boundaries than has been so far proposed. The method also avoids the necessity of making measurements with indicator solutions of varying concentration, since it has been shown experimentally that there is, with this method, automatic adjustment to the condition, $C/C' = T_c/T'_c$. (C and C', and T_c and T'_c, are, respectively, the normality and cation transference number of the leading and indicator solution.)

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A GRAVIMETRIC AND COLORIMETRIC METHOD FOR THE DIRECT DETERMINATION OF SODIUM

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It is a curious and interesting fact that no satisfactory method for the direct determination of sodium had ever been produced before the recent appearance of the paper by Barber and Kolthoff,[1] and it is also interesting to note that the present independent experimental study of the same subject had just been completed when the above paper was published. Barber and Kolthoff precipitated the sodium with zinc uranyl acetate. The method described here is analogous but uses magnesium uranyl acetate.[2] The sodium is thrown down as magnesium sodium uranyl acetate, $NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_2 \cdot 3UO_2 \cdot (C_2H_3O_2)_2 \cdot 6^1/_2H_2O$, which can then either be dried and weighed or, if small in amount, dissolved in water and measured colorimetrically.

This method, which was first suggested by Streng[3] for the qualitative detection of sodium, was also studied by Miholic[4] and Blanchetière[5] and

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[1] H. H. Barber and I. M. Kolthoff, This Journal, **50**, 1625 (1928).

[2] Weiland, *Mitt. Kali-Forsch. Anst.*, **1927**; *C. A.*, **22**, 3600 (1928), used this reagent but gives a formula of the precipitate containing nine molecules of water. We did not have access to his original paper.

[3] A. Streng, *Z. wiss. Mikroskop.*, **3**, 129–130 (1886).

[4] S. S. Miholic, *Bull. Acad. Sci. Zagrab.*, **1920**, 16–23.

[5] A. Blanchetière, *Bull. soc. chim.*, **33**, 807–818 (1923).