

Fig. 9.—The effect of increasing column load and column length proportionately: (A) 1.65 g. equimolar Sm_2O_3 - Nd_2O_3 mixture on a 22 mm. \times 30 cm. Amberlite IR-100 bed, (B) 3.30 g. on a 22 mm. \times 60 cm. bed and (C) 4.95 g. on a 22 mm. \times 90 cm. bed; O, total R_2O_3 ; ●, Sm_2O_3 ; ○, Nd_2O_3 ; broken vertical lines indicate amount of overlap between bands.

yields of pure rare earths for a given operating time were obtained at a higher $p\text{H}$.

The slower the flow rate the less was the observed band overlap and the better the separation. Channeling was another effect which was greatly reduced when flow rates were reduced.

With smaller size resin particles less band overlap was observed showing that reduction of particle size affected the separation in a manner similar to reduced flow rate, but with less increase in operating time.

For a fixed charge of rare earth, separation was independent of column length beyond a certain minimum length and in fact became poorer at the longer lengths due to greater opportunity for channeling.

Increasing column length and column load in the same ratio increased the separation. An upper limit on these increases was met in the separations due to a slow-forming rare earth-citrate precipitate.

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Moving Boundary Systems Formed by Weak Electrolytes. Theory of Simple Systems Formed by Weak Acids and Bases

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Introduction.—When an electric current is passed across an initially sharp junction between two different electrolyte solutions, new concentration gradients form and move away from the initial boundary position. In the case of strong electrolytes such moving boundaries have afforded the most precise method for the determination of transference numbers.¹ In the case of solutions of proteins and other colloidal electrolytes the moving boundary method has made possible an important method for the analysis of complex mixtures such as plasma and for the separation of small amounts of material difficult to isolate by other methods.²

The theory of moving boundary systems formed by strong electrolytes has been developed extensively,³ and Dole⁴ has obtained the general solution of the system of moving boundary equations for the case that the relative ion mobilities are constant throughout the system. The theory of moving boundary systems formed by weak electrolytes has not been studied in such detail⁵

(3) Kohlrausch, *Ann. Physik*, **62**, 209 (1897); H. Weber, "Die partiellen Differential-Gleichungen der mathematischen Physik," Braunschweig, 1910, 5th edition, chapter 24; *Sitzungsber. Akad. Wiss. Berlin*, 936 (1897); Henry and Brittain, *Trans. Faraday Soc.*, **29**, 798 (1933); Svensson, *Arkiv Kemi, Mineral, Geol.*, **17A**, No. 14, 1 (1943); **22A**, No. 10, 1 (1946).

(4) Dole, *THIS JOURNAL*, **67**, 1119 (1945).

(5) Miller, *Z. physik. Chem.*, **69**, 436 (1909); Laue, *Z. anorg. Chem.*, **93**, 329 (1915); Hartley and Moilliet, *Proc. Roy. Soc. (London)*, **A140**, 141 (1933).

(1) MacInnes and Longworth, *Chem. Revs.*, **11**, 171 (1932).

(2) Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

and, until recently, few experiments with weak electrolytes other than those of high molecular weight such as proteins had been reported. In moving boundary systems formed by weak electrolytes, new phenomena are observed because of chemical reactions which take place in the moving boundaries.^{6,7} In contrast to strong electrolyte systems, steady-state moving boundaries may be obtained in weak electrolyte systems when the constituent having the faster ion is allowed to follow the constituent having the slower ion.

Experiments by Nichol reported in the following paper⁸ illustrate the effects of chemical reactions taking place in moving boundary systems formed by weak acids and bases, and it is the purpose of this paper to discuss the conditions under which such reactions take place.

The Moving Boundary Equation.—The relationship between the displacement of a single moving boundary (as, for example, the $\alpha\beta$ boundary of Fig. 1) and the transference numbers

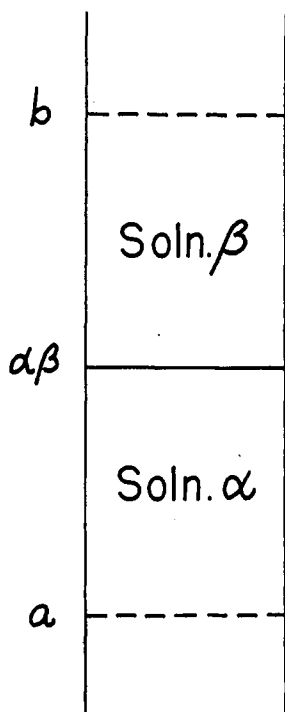


Fig. 1.—Moving boundary system. Planes a and b are fixed with respect to average solvent molecules.

during the passage of one faraday. The boundary

of the homogeneous solutions on either side is fundamental to the theory of moving boundaries and is known as the moving boundary equation. This equation, in the form derived by Longworth,⁹ is

$$T_j^\alpha - T_j^\beta = V^{\alpha\beta} (C_j^\alpha - C_j^\beta) \quad (1)$$

where T_j^α is the number of equivalents of an ion constituent¹⁰ j which pass through plane a in the α solution per faraday and C_j^α is the concentration of this constituent in the α solution in equivalents per liter. In Fig. 1 planes a and b are fixed with respect to the average solvent molecules in the corresponding phases and are located at a sufficient distance from the moving boundary so that the boundary does not reach them

displacement $V^{\alpha\beta}$ is expressed in liters per faraday and is given a positive sign if the boundary moves with the current and a negative sign if it moves against the current. The concentrations are taken with a sign corresponding to the charge on the ion so that $\sum C_j = 0$.

It is useful to discuss the application of equation (1) to strong electrolyte systems and weak electrolyte systems separately in order to bring out the differences in the behaviors of these systems. In the case of strong electrolytes complete ionization is assumed, and so T_j^α is equal to the number of equivalents of electrical charge transported per faraday by the j ion through plane a in the α solution. Thus in the case of strong electrolytes the transference number is always positive and is equal to the fraction of the current carried by the j ion.

$$T_j = \frac{u_j C_j}{u_1 C_1 + u_2 C_2 + \dots + u_n C_n} = \frac{u_j C_j F}{\kappa 1000} \quad (2)$$

where u_j is the mobility of the j ion in $\text{cm.}^2 \text{ volt}^{-1} \text{ sec.}^{-1}$, κ is the specific conductance of the solution in $\text{ohm}^{-1} \text{ cm.}^{-1}$ and F is the faraday. The moving boundary equation (1) may be written in terms of ion mobilities by introducing equation (2)

$$\frac{u_j^\alpha C_j^\alpha}{\kappa^\alpha} - \frac{u_j^\beta C_j^\beta}{\kappa^\beta} = v^{\alpha\beta} (C_j^\alpha - C_j^\beta) \quad (3)$$

where $v^{\alpha\beta}$ is the boundary displacement in ml./coulomb ($V^{\alpha\beta} 1000/F$). If ion j is present only in the α solution, its mobility may be determined directly since equation 3 becomes $u_j^\alpha = v^{\alpha\beta} \kappa^\alpha$.

In the case of weak electrolytes chemical reactions may occur in the moving boundaries, and so the number of equivalents of electrical charge associated with a given mass of constituent is not constant. Svensson⁶ has discussed the application of the moving boundary equation to systems formed by weak electrolytes¹¹ and has pointed out the difficulties in defining the equivalent concentration and transference number in this case. The moving boundary equation for the R weak electrolyte constituent may be written in terms of the constituent mobility \bar{u}_R and constituent concentration \bar{c}_R as follows,

$$\frac{\bar{u}_R^\alpha \bar{c}_R^\alpha}{\kappa^\alpha} - \frac{\bar{u}_R^\beta \bar{c}_R^\beta}{\kappa^\beta} = v^{\alpha\beta} (\bar{c}_R^\alpha - \bar{c}_R^\beta) \quad (4)$$

The quantities applying to the constituent have been written with bars to indicate that they do not apply to ions but to the equilibrium mixture of all forms of the constituent. The constituent concentration \bar{c}_R is the total concentration of the R constituent including all forms and will be used in gram formula weights per liter in this paper. The constituent mobility \bar{u}_R is the average velocity of R in a unit electric field measured over a

(11) The application of the moving boundary equation to univalent weak electrolyte systems had been made independently in this Laboratory.⁷

(6) Svensson, *Acta Chem. Scand.*, **2**, 855 (1948).

(7) Alberty and Nichol, *THIS JOURNAL*, **70**, 2297 (1948).

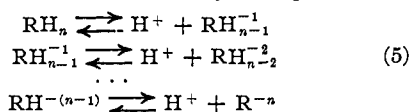
(8) Nichol, *ibid.*, **73**, 2367 (1950).

(9) Longworth, *ibid.*, **67**, 1109 (1945).

(10) MacInnes, ("The Principles of Electrochemistry," Reinhold Publishing Corp., New York, N. Y., 1939) has defined an ion constituent as the ion-forming portion of an electrolyte without reference to the extent to which it may actually exist in the dissociated state.

long period so that random fluctuations average out. Equation (4) may be derived by noting that $\bar{u}_R^\alpha c_R^\alpha / (1000 \kappa^\alpha)$ is the number of gram formula weights of the R constituent which pass through plane *a* (Fig. 1) in the α solution per coulomb,¹² so that the right and left hand sides of equation (4) are simply different expressions for the loss, in gram formula weights, of the R constituent from the volume between planes *a* and *b* during the passage of one coulomb. The constituent mobility of a weak electrolyte may be determined directly by means of a moving boundary experiment in which the constituent exists in only the α solution since equation (4) becomes $\bar{u}_R^\alpha = v^{\alpha\beta} \kappa^\alpha$.

The relationship between the constituent mobility of a weak acid or base and the ionic mobilities of the various forms which are in equilibrium may be derived by assuming that the constituent is present only in the homogeneous α solution of the moving boundary system illustrated in Fig. 1 and that the $\alpha\beta$ boundary is descending. The equilibria in a solution containing an uncharged weak acid RH_n and its salts may be represented as



The following derivation has been based upon equivalent concentrations (molar concentration times valence) in order to emphasize the importance of the chemical reaction which must take place in the $\alpha\beta$ boundary if the R constituent is to disappear in this boundary. This derivation assumes that (1) we know the mobilities and concentrations of the various ions in equilibrium, (2) the salts present are completely ionized, and (3) the mobility of the uncharged weak acid RH_n is zero.¹³ The concentrations of the various subspecies of the R constituent in gram formula weights per ml. will be represented by c_i where *i* is the number of electronic charges 0, 1, 2 . . . ,

so that the constituent concentration is $\sum_{i=0}^n c_i$ gram formula weights per ml. Concentrations will be taken as signed quantities in agreement with the convention for strong electrolytes, and the concentration of the uncharged form will be given the sign of the charge of the ionic forms.¹⁴ The number of equivalents of electrical charge carried by the R constituent through plane *a* of Fig. 1 per coulomb is $\frac{1}{\kappa^\alpha} \sum_{i=1}^n i c_i^\alpha u_i^\alpha$. The apparent number

of equivalents of electrical charge carried by the R constituent from the volume $v^{\alpha\beta}$ (ml./coulomb) is $v^{\alpha\beta} \sum_{i=1}^n i c_i^\alpha$. However, since all forms of the R constituent disappear in the $\alpha\beta$ boundary, chemical reactions between the leading and indicator electrolytes forming higher valence forms of R from the lower valence forms must take place in the $\alpha\beta$ boundary. The increase in the number of equivalents of electrical charge carried by the R constituent may be calculated as follows. Since the mobility of the RH_n molecules is assumed to be zero, they may be swept from the volume $v^{\alpha\beta}$ only by being changed into univalent or multivalent ions. As a minimum univalent ions must be formed so that the gain in electrical charge associated with the R constituent is $v^{\alpha\beta} c_0^\alpha$ equivalents. Some of these univalent ions may be transformed into multivalent ions to make up for a deficiency which would occur ahead of the $\alpha\beta$ boundary as a result of the fact that the ions with higher mobility move with a higher velocity than the $\alpha\beta$ boundary. In the absence of a chemical reaction the ions of valence *i* which start at the initial boundary position move through a volume of $u_i^\alpha / \kappa^\alpha$ ml. per coulomb while the $\alpha\beta$ boundary moves through $v^{\alpha\beta}$ ml. per coulomb. Thus $(u_i^\alpha / \kappa^\alpha - v^{\alpha\beta})(i - 1) c_i^\alpha$ equivalents of electrical charge are gained by the R constituent when this deficiency is made up by the reaction between RH_{n-1}^- and the indicator electrolyte. The total gain in equivalents of electrical charge by R must be equal to the difference between the number of equivalents of charge carried by R through plane *a* and the apparent number of equivalents transported calculated from the boundary displacement.

$$\frac{1}{\kappa^\alpha} \sum_{i=1}^n (i c_i^\alpha u_i^\alpha) - v^{\alpha\beta} \sum_{i=1}^n i c_i^\alpha = v^{\alpha\beta} c_0^\alpha + \sum_{i=1}^n \left(\frac{u_i^\alpha}{\kappa^\alpha} - v^{\alpha\beta} \right) (i - 1) c_i^\alpha \quad (6)$$

or

$$\frac{1}{\kappa^\alpha} \sum_{i=1}^n c_i^\alpha u_i^\alpha = v^{\alpha\beta} \sum_{i=0}^n c_i^\alpha$$

Thus the constituent mobility \bar{u}_R^α calculated from the boundary displacement in the usual way is

$$\bar{u}_R^\alpha = v^{\alpha\beta} \kappa^\alpha = \frac{\sum_{i=1}^n c_i^\alpha u_i^\alpha}{\sum_{i=0}^n c_i^\alpha} \quad (7)$$

Although c_i was introduced as the concentration in gram formula weights per ml., concentrations in gram formula weights per liter will generally be used since the volume units cancel in equation (7). The use of this equation for the calculation of constituent mobilities of weak electrolytes is limited by our ignorance of the mobilities of the

(12) The distance moved by R in an electric field of strength *E* in time *t* is $\bar{u}_R E t$, and so the number of gram formula weights of R transported through a cm^2 normal to the field in time *t* is $\bar{u}_R c_R E t / 1000$ or $\bar{u}_R c_R / 1000 \kappa$ gram formula weights per coulomb.

(13) This is an approximation since Longworth (THIS JOURNAL, 69, 1288 (1947)) has shown that non-electrolytes such as raffinose and urea move with respect to the solvent in an electric field.

(14) This convention would not apply in case the constituent consists of positive and negative ions in equilibrium with each other.

individual ions in the equilibrium mixture and of their concentrations. In the case of simple weak electrolytes, however, these quantities may be estimated quite well as indicated in the following paper.⁸

Tiselius¹⁵ pointed out that a substance consisting of several forms with different mobilities in equilibrium with each other will generally migrate as a uniform substance with a mobility

$\bar{u} = \sum_{i=0}^n a_i u_i$ where a_i is the fraction of the substance with mobility u_i , provided that the time of existence of each subspecies is small in comparison with the duration of the experiment. This is in agreement with the conclusion from equation (7) since $a_i = c_i^\alpha / \sum_{i=0}^n c_i^\alpha$.

Most textbooks of physical chemistry define the transference number as the fraction of the current carried by a given ion species. This is not an operational definition but if it is assumed that the electrolyte is completely dissociated, as in the case of strong electrolytes, the transference number determined by a moving boundary or Hittorf experiment may be considered to be the fractional conductance.^{9,4} In the case of weak electrolytes the transference number calculated in the usual way from a moving boundary or Hittorf experiment is not equal to the partial conductance. In the case of a simple weak electrolyte (RH_n) for which the mobilities of the various ions in equilibrium can be obtained in separate experiments, the fraction of the current carried by the R constituent is $F \sum_{i=1}^n i c_i^\alpha u_i^\alpha / (1000 \kappa^\alpha)$. Since this calculation cannot be made

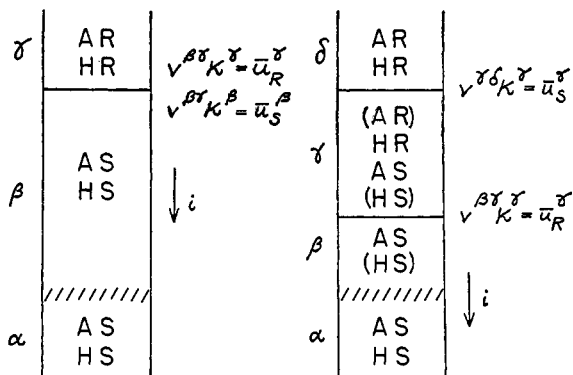


Fig. 2.—Moving boundary systems in which the leading weak electrolyte consists of an uncharged weak acid HR in equilibrium with its salt AR. (a) The chemical reaction $AS + HR \rightarrow AR + HS$ goes to completion in the $\beta\gamma$ boundary. (b) The chemical reaction does not go to completion. The arrow indicates the direction of the current. The concentration boundary near the initial boundary position is indicated by //, and the moving boundaries are indicated by —.

(15) Tiselius, *Nova Acta Reg. Soc. Sci. Upsal.*, **IV**, 7, no. 4 (1930).

with accuracy, the definition of the transference number as the partial conductance is not satisfactory for weak electrolytes, and the definition in terms of equation (1) is to be preferred.

Simple Moving Boundary Systems Formed by Two Weak Acids of the Uncharged-acid Type.—

Two types of systems involving uncharged weak acids HR and HS and their salts, AR and AS, are illustrated in Fig. 2a and b. It is convenient to represent moving boundary systems in the text by the notation of Longworth⁹ according to which a moving boundary is represented by an arrow and a concentration boundary is represented by a double colon. The current is taken as flowing from left to right, and the phases are designated $\alpha, \beta, \gamma, \dots$ in order of decreasing density. In the hypothetical systems discussed here no significance is to be attached to the fact that a given boundary ascends or descends since in actual cases this depends on the relative densities of the solutions involved.

AR, HR(γ) \leftarrow AS, HS(β)::AS, HS(α).—This moving boundary system which is illustrated in Fig. 2a is analogous to those used for the determination of anion transference numbers of strong electrolytes since two anion constituents disappear in the $\beta\gamma$ boundary. An example of such a system is NaOAc, HOAc(γ) \leftarrow NaCac, HCac(β)::NaCac(α) which is discussed in the following paper.⁸ The moving boundary equation (equation 4) for the R constituent at the $\beta\gamma$ boundary becomes $\bar{u}_R^\gamma = v^{\beta\gamma} \kappa^\gamma$. Therefore, this type of moving boundary system yields directly the constituent mobility of the leading constituent which, according to equation (7) may be written

$$\bar{u}_R^\gamma = v^{\beta\gamma} \kappa^\gamma = u_R^\gamma c_R^\gamma / (c_R^\gamma + c_{HR}^\gamma) \quad (8)$$

where u_R^γ and c_R^γ are the ionic mobility and molar concentration of the R⁻ ion in the γ solution. The constituent mobility of S in the β solution may similarly be determined by using the specific conductance of the β solution.

$$\bar{u}_S^\beta = v^{\beta\gamma} \kappa^\beta = u_S^\beta c_S^\beta / (c_S^\beta + c_{HS}^\beta) \quad (9)$$

In the case of strong electrolytes steady state moving boundaries of the two salt type are obtained if the mobility of the indicator ion constituent is less than the mobility of the leading ion constituent.¹⁶ In order to obtain a steady state moving boundary in a weak electrolyte system of the type illustrated in Fig. 2a, it is necessary for the reaction



to go to completion to the right in the $\beta\gamma$ boundary. If HS is a weaker acid than HR, reaction 10 will be favored, but this condition is not sufficient to cause the reaction to go to completion. However, if the R⁻ ion is removed at a sufficient rate as a reaction product by the separating effect of the electric current, no HR or

(16) Longworth, *THIS JOURNAL*, **66**, 449 (1944).

R⁻ will remain behind the moving boundary. The necessary condition for a steady state boundary of this type in which two weak electrolyte constituents disappear is that the R constituent have a higher velocity in the β solution than in the γ solution. This may be expressed by

$$|\bar{u}_R^\beta E^\beta| > |\bar{u}_R^\gamma E^\gamma| \quad (11)$$

where E is the electric field strength and \bar{u}_R^β is the constituent mobility of a trace of R placed in the homogeneous β solution. The calculation of the composition of the β solution which is required for further consideration of this inequality is described in the following paragraph.

The composition of the β solution may be calculated from the composition of the γ solution and the mobilities of the various ions involved by eliminating $v^{\beta\gamma}$ between equations (8) and (9) and assuming that $c_{HS}^\beta = c_{HR}^\gamma$. This assumption is expected to be quite satisfactory for weak acids because of the stoichiometry of reaction 10. The specific conductances are eliminated by means of the relations $\kappa^\gamma = (F/1000)(u_R^\gamma - u_A^\gamma)c_S^\gamma$ and $\kappa^\beta = (F/1000)(u_S^\beta - u_A^\beta)c_S^\beta$. Equation (12) which expresses the concentration of S⁻ in the β solution in terms of the concentration of the γ solution and the various ion mobilities, is obtained by rearrangement.

$$c_S^\beta = \frac{c_R^\gamma(u_R^\gamma - u_A^\gamma)u_S^\beta + c_{HR}^\gamma(u_A^\beta u_R^\gamma - u_S^\beta u_A^\gamma)}{(u_S^\beta - u_A^\beta)u_R^\gamma} \quad (12)$$

Equation (12) may be rewritten in terms of relative mobilities (r) provided these are constant. If the relative ion mobility of cation A is taken as unity, equation (12) becomes

$$c_S^\beta = \frac{c_R^\gamma(r_R - 1)r_S + c_{HR}^\gamma(r_R - r_S)}{(r_S - 1)r_R} \quad (13)$$

Since c_S^β is the concentration of an anion, it may have only negative values. If $|r_S| < |r_R|$ and c_R^γ/c_{HR}^γ is sufficiently small, this condition will not be satisfied. The maximum values for the ratio r_R/r_S satisfying equation (13) for various values of r_R and c_R^γ/c_{HR}^γ are given in Table I. For values of the ratio r_R/r_S greater than the maximum values given in Table I, AS would be expected to be absent from the β solution, assuming reaction 10 occurs and ignoring the ionization of HS.

TABLE I

MAXIMUM VALUES FOR r_R/r_S SATISFYING EQUATION 13

c_R^γ/c_{HR}^γ	$r_R = -0.70$	$r_R = -1.00$	$r = -1.30$
0.1	1.17	1.20	1.23
0.2	1.34	1.40	1.46
1.0	2.70	3.00	3.30
2.0	4.40	5.00	5.60
10.0	18.00	19.00	24.00

If a small amount of the R constituent diffuses back into the β solution, its relative constituent mobility in that phase, \bar{r}_R^β , will depend upon the

concentration of HS and AS in the β solution and may be expressed as

$$\bar{r}_R^\beta = r_R \frac{c_R^\beta}{c_R^\beta + c_{HR}^\beta} = r_R \left(1 + \frac{c_{HS}^\beta}{c_S^\beta} \times \frac{K'_{HS}}{K'_{HR}} \right)^{-1} \quad (14)$$

where K'_{HR}/K'_{HS} is the equilibrium constant (in terms of concentrations) of reaction 10. The concentration terms in this equation, c_{HS}^β and c_{AS}^β , may be replaced by c_{HR}^γ and by equation (13) respectively.

The conditions under which inequality 11 will be satisfied may now be examined. Since this inequality cannot be written in terms of relative ion mobilities, it is necessary to make the assumption of constant ion mobilities throughout the system. The relations which follow will be written in terms of relative mobilities, however, because the expressions are simplified. The ratio of the field strengths E^β/E^γ is inversely proportional to the ratio of the corresponding specific conductances. If ion mobilities are constant throughout the system

$$\frac{E^\beta}{E^\gamma} = \frac{c_R^\gamma(r_R - 1)}{c_S^\beta(r_S - 1)} \quad (15)$$

Inequality 11 may be rearranged after the introduction of equations (12), (14) and (15) to yield

$$\frac{K'_{HS}}{K'_{HR}} < \frac{(r_R - r_S)[(c_R^\gamma/c_{HR}^\gamma)(r_R - 1) - 1]/r_R + (r_R - 1)}{(r_S - 1)} \quad (16)$$

This inequality gives maximum values of K'_{HS}/K'_{HR} for which the R constituent will have a higher velocity in the β solution than in the γ solution. These maximum values may be represented by a graph such as Fig. 3. In this graph the difference between the pK 's for the following and leading weak electrolytes is plotted *versus* log (r_R/r_S) for $c_R^\gamma/c_{HR}^\gamma = 1/2, 1, 5$ and 10 . For the

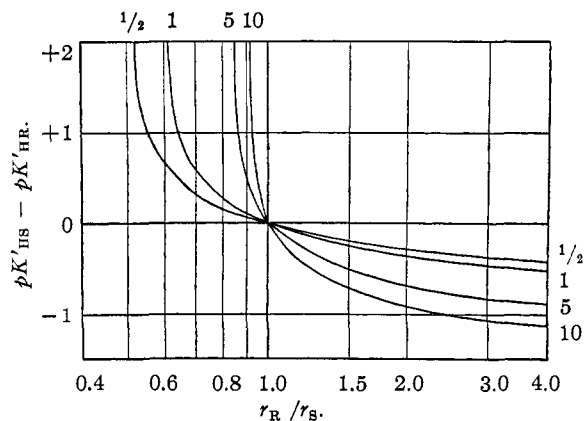


Fig. 3.—Requirements for a steady state boundary yielding the constituent mobility of the leading weak electrolyte in the system AR, HR ← AS, HS::AS. Steady state boundaries are to be expected in the region above the curves which are given for $c_R^\gamma/c_{HR}^\gamma = 1/2, 1, 5$ and 10 for $r_R = -0.77$.

construction of this graph r_R has been taken as -0.77 . However, the graph is not particularly sensitive to variations in r_R , the curve for $r_R = -0.60$ lying within the width of a line to the curve for $r_R = -0.77$. If the properties of the weak electrolytes involved places the system in the region above the curve, a steady state boundary yielding the constituent mobility is to be expected, provided the maximum values for r_R/r_S given in Table I are not exceeded. Figure 3 shows that a steady state moving boundary may be obtained when the following ion S^- has a higher mobility than the leading ion provided the concentration of weak acid in the leading solution is sufficiently high and HS is a weaker acid. It is seen that as the concentration of the leading weak acid HR is decreased the curve approaches the vertical line $r_R/r_S = 1$ which represents the requirement for a strong electrolyte system, namely, the leading ion must have a higher mobility than the indicator ion. The deductions from inequality 16 cannot, in general, be expected to apply to real systems with precision because it has been assumed in the derivation that ionic mobilities are constant throughout the system and that the ionization constants are independent of concentration.

The sharpening effect at a moving boundary resulting from a gradient in pH through the boundary was first described by Longworth.¹⁷ He referred to this effect as the pH effect in analogy to the conductivity effect which refers to the sharpening or spreading caused by the gradient in conductivity through a moving boundary.

AR, HR(δ) \leftarrow (AR), HR, AS, (HS) (γ) \leftarrow AS, (HS), (β)::AS, (HS) (α). If the ionization constants of HR and HS and the mobilities of R^- and S^- do not have values which permit a complete chemical reaction at the moving boundary, the system illustrated in Fig. 2b may be obtained. An example of such a system is NaOAc, HOAc(δ) \leftarrow NaT, HOAc(NaOAc) (γ) \leftarrow NaT(β)::NaT(α) which is discussed in the following paper.⁸ The concentrations of AR and HS in the γ solution and of HS in the α and β solutions are enclosed in parentheses to show their concentrations may be very low. Neither the R constituent nor the R^- ion disappears in the $\gamma\delta$ boundary, and so the velocity of this boundary does not yield directly \bar{u}_R^0 or u_R^0 . The S constituent does, however, disappear in this boundary so that $v^{\gamma\delta}k^{\gamma} = \bar{u}_S^0$, but this information is not of much value since the composition of the solution cannot be chosen before the experiment and would have to be determined analytically.

The HR molecules left behind the $\gamma\delta$ boundary are partially ionized, and so the R constituent will move away from the initial boundary position. This produces the $\beta\gamma$ boundary which yields the constituent mobility of R in the γ

solution. In the experiments reported by Nichol⁸ this boundary spreads rapidly and is not suitable for quantitative measurements.

The moving boundary system illustrated in Fig. 2b may be obtained in the determination of the anion transference number of a salt of a weak acid if the salt is appreciably hydrolyzed and a strong electrolyte is used as indicator. Application of moving boundary equation 2 to the R constituent at the $\gamma\delta$ boundary shows that $v^{\gamma\delta}k^{\delta}$ will be less than the ion mobility u_R^0 but will approach it if the degree of ionization of HR is very low. If the degree of hydrolysis of AR in the leading solution is sufficiently high, the concentration of hydroxyl ions must be taken into account, a fact which is neglected in the present treatment.

Discussion.—The above treatment of systems formed by weak acids also applies to moving boundary systems formed by weak bases of the uncharged-base type. Figure 3 may be used to predict whether a steady state moving boundary yielding the constituent mobility will be obtained for the system B, BHT::B, BHT \rightarrow C, CHT where B and C are uncharged bases and T is the anion of a strong acid. It is convenient to use pK_a for the bases, and, in general, the salt of the base with the lower pK_a and the lower cation mobility is used as the indicator electrolyte although this is not a necessary condition. In order to apply Fig. 3 to this weak base system, the ordinate is changed to $pK_c - pK_b$, the abscissa to r_C/r_B , and the concentration ratios to c_{CH}/c_C .

In order to determine the mobility of a constituent, it is necessary to choose the indicator electrolyte so that the constituent disappears in a moving boundary. It is desirable to have this boundary move into the original solution containing the constituent since the concentration of this solution may be chosen before the experiment rather than being obtained by analysis of a phase produced during the experiment. Brattsten and Svensson¹⁸ have found that a propionate buffer is a satisfactory indicator for the determination of the acetate constituent mobility in an acetate buffer which is in agreement with the prediction of Fig. 3. In experiments in which acetic acid was present on both sides of a moving boundary they found the concentration change of the acetate constituent at the moving boundary to be in agreement with the moving boundary equation.

Moving boundary experiments with substances which form complexes or take part in oxidation or reduction reactions in the moving boundary may be treated in the same way as systems formed by weak acids and bases provided the reactions involved are sufficiently fast that equilibrium between the various ionic species may be assumed. The foundations for the interpretation of electrophoresis experiments with interacting systems

(17) Longworth, *J. Phys. Colloid Chem.*, **51**, 171 (1947).

(18) Brattsten and Svensson, *Acta Chem. Scand.*, **3**, 359 (1949).

were laid by Longworth and MacInnes¹⁹ in their study of the interaction of ovalbumin and yeast nucleic acid. Further information concerning such interactions may be obtained by use of the concept of constituent mobility.^{20,21}

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(19) Longworth and MacInnes, *J. Gen. Physiol.*, **25**, 507 (1942).

(20) Alberty and Marvin, *J. Phys. Colloid Chem.*, **54**, 47 (1950).

(21) Smith and Briggs *ibid.*, **54**, 33 (1950).

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Summary

The application of the moving boundary equation to systems formed by weak electrolytes has been discussed. The constituent mobility of a weak electrolyte may be determined with precision if this constituent disappears in a steady state moving boundary which moves into the original solution. The conditions under which such boundaries are obtained in simple systems formed by weak acids of the uncharged-acid type and by weak bases of the uncharged-base type are discussed.

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Moving Boundary Systems Formed by Weak Acids and Bases. An Experimental Study¹

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Introduction.—Moving boundary systems containing strong electrolytes, for which relative ion mobilities are constant, can be described by the general theory of Dole.³ Thus, if the relative ion mobilities of all the species present in the system and the compositions of the two end solutions forming the initial boundary are known, Dole's theory can be applied to calculate the concentrations of the ions in all the newly formed phases, as well as the displacements of the separated boundaries.

If weak electrolytes are present in one or both of the end solutions, the strong electrolyte theory in many cases is inadequate for the description of the system because chemical reactions occur in the moving boundaries.^{4,5} This fact is important because the majority of electrophoresis experiments involve weak polyelectrolytes such as proteins and nucleic acids. Studies of simple weak electrolyte systems are required as a preparation for work with the more complicated polyelectrolytes. For example, an understanding of moving boundary systems in which chemical reactions take place is necessary for the interpretation of electrophoresis experiments with antigen-antibody mixtures or protein-nucleic acid mixtures.

A striking illustration of a chemical reaction is provided when an initial boundary is formed between a solution of sodium caproate and a solution of sodium acetate and acetic acid and a potential is applied so that caproate ions descend into the acetate solution (*i. e.*, the caproate ions follow the

faster acetate ions). At first a new boundary forms and can be seen moving into the acetate solution. However, the reaction of caproate ions with acetic acid molecules which otherwise would be left behind this boundary soon results in a layer of insoluble caproic acid droplets which completely obscures the boundary position.

If all the products of the reaction in a system similar to the above are soluble, then the velocity of the moving boundary can be determined. The mobility calculated in the ordinary way will be found to be lower than that obtained from similar measurements on systems where none of the acid form is present (Fig. 1).

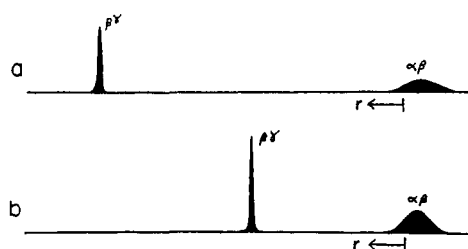


Fig. 1.—Schlieren patterns of the systems (a) NaOAc(0.05)(γ) \leftarrow NaCac(β):NaCac(α), (b) NaOAc(0.05), HOAc(0.05)(γ) \leftarrow NaCac, HCac(β):NaCac(α) 40 coulombs of electricity passed in each experiment.

Another result of the chemical reaction is the formation under certain conditions of a steady state moving boundary even when the faster ion follows the slower. In strong electrolyte experiments the corresponding boundary always spreads with time.

In the preceding paper Alberty⁶ has developed a theory on the basis of the weak electrolyte moving

(6) Alberty, *ibid.*, **72**, 2361 (1950).

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(3) Dole, *THIS JOURNAL*, **67**, 1119 (1945).

(4) Svensson, *Acta Chem. Scand.*, **2**, 841 (1948).

(5) Alberty and Nichol, *THIS JOURNAL*, **70**, 2297 (1948).