

Moving Chemical Reaction Boundary Formed by Weak Reaction Electrolytes: Theory

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The systemic theory of a moving chemical reaction boundary (MCRB) has not yet been established completely. In this paper, the theory of a moving boundary system (MBS) developed about 50 years ago is reviewed, the concept of an MCRB formed by weak reaction electrolytes is advanced, and a series of moving chemical reaction boundary equations (MCRBEs) are derived from the concept. The theoretic results show that: (1) there is a nice symmetry between the MCRBEs and the moving boundary equations (MBEs) formulated about 50 years ago, and MCRB theory is the counterpart of MBS theory; (2) both the Deman–Rigole equation and the Pospichal–Deml–Bocek equation can be deduced from the MCRBEs in special cases. The validity of MCRB theory has been proved by facts and experiments reported in the literature. Theoretically, MCRB theory may have some potential applications in: (1) the design of new techniques of analysis and separation; (2) determinations of ionic transference number and mobility; (3) studies of the mechanism of ionic electromigration reaction in stationary electrolysis; (4) studies of the mechanism of isoelectric focusing (IEF) and the completion of IEF theory.

1. Introduction

The moving boundary system (MBS) developed about 50 years ago is an important boundary; it is of key importance and is used in physical chemistry, especially in isotachopheresis (ITP), as will be reviewed in Section 3. Another important boundary is the moving chemical reaction boundary (MCRB).

The idea of an MCRB, viz. 'precipitate reaction front', was first advanced by Deman and Rigole.^{1,2} At the same time, some experiments concerning the precipitate reaction front formed with reaction electrolytes like KOH and CoCl₂, together with a background electrolyte KCl, were performed by them.

The concept of a stationary neutralization reaction boundary (SNRB) formed by an acid and a base, coupled with a background electrolyte KCl, was developed by Pospichal *et al.*,³ and some experiments on SNRBs were performed by using electrically controlled electrofocusing in capillary electrophoresis. In their experiments, the movement of the boundary was observed, and two SNRBs were created.

Recently⁴ the concept of a stationary chemical reaction boundary was advanced, and some very useful stationary chemical reaction boundary equations [SCRBEs, see eqns. (27)–(35)] were deduced. The results show that the predictions with eqn. (35) are quantitatively in agreement with computer simulations based on Kohlrausch's

beharrliche function and with the two SNRBs created by Pospichal *et al.*³

At the same time,⁵ the concept of an MCRB formed by strong reaction electrolytes was proposed, and the moving chemical reaction boundary equations [MCRBEs, see eqns. (21) and (22) here] were derived. As stated by the author, the MCRBEs, viz. eqns. (21) and (22), are only valid for strong reaction electrolytes, such as CoCl₂ and KOH used by Deman and Rigole,^{1,2} but not valid for weak reaction electrolytes, for instance acetic acid and ethyl amine discussed here.

Obviously, the model of an MCRB formed by weak reaction electrolytes has not been discussed and the relation theory for the model has not been advanced, and the relationships between the MCRB and MBS theories has not been revealed, up to now.

Therefore, the main purposes of this paper, are to propose the concept of an MCRB formed by weak reaction electrolytes, to develop the theory of an MCRB formed with weak reaction electrolytes, and to show the relations between the MCRB and MBS theories. In addition, the potential applications of MCRB theory are discussed briefly.

2. Notation

+ and – subscripts, in *m* and *c*, indicate the positive and negative reacting ions, respectively.

α and β superscripts denote phases α and β , respectively.

c the equivalent concentration (equiv. m^{-3}). It is positive if the ion carries net positive charge(s), and negative if net negative charge(s), as has been defined by Longworth,⁶ Dole,⁷ Alberty⁸ and Nichol.⁹

m the mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$). It is positive if the ion carries net positive charge(s), and negative if net negative charge(s), as has been defined by Longworth,⁶ Dole,⁷ Alberty⁸ and Nichol.⁹

\bar{c} the constituent concentration (equiv. m^{-3}). It does not apply to an ion but to the equilibrium mixture of all subspecies of a constituent, for more details see eqn. (9).

\bar{m} the constituent mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$). For more details see eqn. (8).

κ the conductivity (S m^{-1}).

F Faraday's constant
($=9.648\,5309 \times 10^4 \text{ C mol}^{-1}$).

T the transference number of an ion (dimensionless).

$$T = mcF/\kappa \quad (1)$$

J the ionic flux through a conductor (equiv. $\text{s}^{-1} \text{m}^{-2}$)

I the electric current (A).

q the cross-sectional area (m^2).

E the electric field strength (V m^{-1}).

$$E = I/q\kappa \quad (2)$$

$dx^{\alpha\beta}$ the displacement (m) of a boundary in the delta-time dt . It is positive if the boundary moves towards the cathode, negative if towards the anode, and double superscripts indicate the two phases on either side of a boundary.

$\mu^{\alpha\beta}$ the velocity of boundary displacement (m s^{-1}). It is positive if the boundary moves towards the cathode, negative towards the anode, and double superscripts indicate the two phases on either side of a boundary.

$$\mu^{\alpha\beta} = dx^{\alpha\beta}/dt \quad (3)$$

$v^{\alpha\beta}$ the boundary displacement ($\text{m}^3 \text{C}^{-1}$) swept by a boundary during the passage of one unit of charge.

$V^{\alpha\beta}$ the boundary displacement ($\text{m}^3 \text{F}^{-1}$) swept by a moving boundary during the passage of one unit of capacitance.

\bar{r}_R the relative constituent mobility of constituent R (dimensionless).⁸

$$\bar{r}_R = m_R/m_{\text{Na}^+} \quad (4)$$

σ the relative conductance (C m^{-3}).⁸

$$\sigma = \kappa/m_{\text{Na}^+} \quad (5)$$

3. Short reviews of the moving boundary system (MBS)

In order to show the excellent symmetry between MCRBEs and moving boundary equations (MBEs) it is necessary to review the MBS theory briefly.

The relationship between the displacement of a moving boundary and the transference numbers of the homogeneous solutions on either side is fundamental to the theory of moving boundaries and is well known as the moving boundary equations (MBEs). The MBEs, as given by Longworth,⁶ Dole,⁷ and Alberty⁸ for strong electrolytes, are

$$T_j^\alpha - T_j^\beta = V^{\alpha\beta}(c_j^\alpha - c_j^\beta) \quad (6)$$

$$\frac{m_j^\alpha c_j^\alpha}{\kappa^\alpha} - \frac{m_j^\beta c_j^\beta}{\kappa^\beta} = v^{\alpha\beta}(c_j^\alpha - c_j^\beta) \quad (7)$$

Equations (6) and (7) are valid for an MBS formed by strong electrolytes, but not for that formed by weak electrolytes. Since in the case of weak electrolytes, there are various subspecies of a constituent, which are in equilibrium with each other in its phase (or solution). Tiselius and Alberty⁸ have 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

$$\bar{m} = \sum a_i m_i \quad (8)$$

Equation (8) is the expression of 'constituent mobility', and the 'constituent concentration' is defined as

$$\bar{c} = \sum c_i \quad (9)$$

where m_i and c_i are, respectively, the mobility and concentration of subspecies i , a_i is the fraction of subspecies i with mobility m_i , viz.

$$a_i = \frac{a_i}{\bar{c}} = a_i / \sum c_i \quad (10)$$

Thus, in the case of weak electrolyte R , the MBE can also be expressed, with constituent mobility [i.e. eqn. (8)] and constituent concentration [eqn. (9)], as given in Ref. 8

$$\frac{\bar{m}_R^\alpha \bar{c}_R^\alpha}{\kappa^\alpha} - \frac{\bar{m}_R^\beta \bar{c}_R^\beta}{\kappa^\beta} = v^{\alpha\beta}(\bar{c}_R^\alpha - \bar{c}_R^\beta) \quad (11)$$

Re-expressing eqn. (11) with the relative constituent mobility and conductance [eqns. (4) and (5)], one has⁸

$$\frac{\bar{r}_R^\alpha \bar{c}_R^\alpha}{\sigma^\alpha} - \frac{\bar{r}_R^\beta \bar{c}_R^\beta}{\sigma^\beta} = v^{\alpha\beta}(\bar{c}_R^\alpha - \bar{c}_R^\beta) \quad (12)$$

The MBEs, viz. eqns. (6) and (7) and eqns. (11) and (12), have been quantitatively proved by the experiments performed by Longworth⁶ and Nichol.⁹ The MBEs are of key importance, since (1) they may be used to determine ionic transference number and mobility;^{10,11} (2) they lay the theoretic base for isotachopheresis (ITP), which has important uses in analytic chemistry, biochemistry and biomedicine;¹²⁻¹⁷ (3) they may be used to form a pH gradient for the separation of proteins.¹⁸

4. Chemical reaction boundary

4.1. Model. We assume that an MCRB is formed with an acid and a base, for instance, the weak acid CH_3COOH and the weak base $\text{CH}_3\text{CH}_2\text{NH}_2$, with or without a background electrolyte like KCl , as shown in Fig. 1. The system formed by acetic acid and ethyl amine may be expressed as $\text{CH}_3\text{COOH}(+, \alpha) \parallel \text{CH}_3\text{CH}_2\text{-NH}_2(-, \beta)$.

The following assumptions are explicitly given:¹⁸ (1) constant mobility of the ion, (2) zero mobilities for uncharged species, (3) additivity of ion mobilities, (4) constancy of ionization constants, (5) idealized steady state of the boundary, (6) absence of bulk flow of solvent caused by Joule heating and diffusion. These assumptions have been used by many researchers.^{6-11,18}

4.2. Moving chemical reaction boundary equations (MCRBEs). Let us consider Fig. 1 and eqn. (8) here. As pointed out by Alberty,⁸ a substance that consists of several forms with different mobilities in equilibrium with each other will generally migrate as a uniform substance with a mobility defined by eqn. (8). Hence, the weak acid in phase α and the weak base in phase β , on the passage of electric current, will move with the velocities of eqns. (13) and (14), respectively:

$$\bar{\mu}_+^\alpha = \bar{m}_+^\alpha E^\alpha \quad (13)$$

$$\mu_-^\beta = \bar{m}_-^\beta E^\beta \quad (14)$$

In addition, during the electromigration of positive and negative reacting ions migrating in opposite directions, some chemical reactions always occur in a chemical reaction boundary. The chemical reactions, for example those in the system of $\text{CH}_3\text{COOH}(+, \alpha) \parallel \text{CH}_3\text{CH}_2\text{-NH}_2(-, \beta)$ in Fig. 1, may include: (1) the reaction

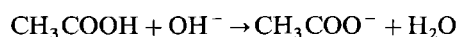
between the free positive and negative reacting ions, H^+ and OH^-



(2) that between the free positive reacting ion H^+ and the bonded negative reacting subspecies $\text{CH}_3\text{CH}_2\text{NH}_2$,



(3) that between the reacting species CH_3COOH and free negative reacting ion OH^- ,



Apparently, all the positive and negative reacting subspecies, including free H^+ and OH^- , take part in the chemical reaction of electromigration in the MCRB. Hence, like the formulation of eqns. (11) and (12), we should use the constituent concentrations \bar{c} , which is the total concentration of a constituent including all forms [eqn. (9)], but not only the concentration of free positive or negative reacting ions like H^+ or OH^- , to formulate the MCRBEs for the boundary formed by weak reaction electrolytes.

Thus, with the aid of constituent mobility [eqn. (8)] and constituent concentration [eqn. (9)], coupled with eqns. (13) and (14), we may, at first, formulate the MCRBEs for an MCRB formed by a weak acid and base, such as acetic acid and ethyl amine.

Let us consider Fig. 1. During the chemical reaction of electromigration, obviously, the equivalent numbers of weak acid and base that move from their phases into the MCRB are always equal to each other, i.e.

$$(\bar{m}_+^\alpha E^\alpha - \mu_{\text{weak}}^{\alpha\beta}) \bar{c}_+^\alpha = (-\bar{m}_-^\beta E^\beta + \mu_{\text{weak}}^{\alpha\beta}) (-\bar{c}_-^\beta) \quad (15)$$

Note that here \bar{m}_-^β and \bar{c}_-^β are negative, as has been suggested by Longworth,⁶ Dole⁷ and Alberty.⁸ Evidently, the combination of eqns. (2), (3) and (15) yields

$$\frac{\bar{m}_+^\alpha \bar{c}_+^\alpha}{\kappa^\alpha} - \frac{\bar{m}_-^\beta \bar{c}_-^\beta}{\kappa^\beta} = \frac{q}{I} \frac{dx^{\alpha\beta}}{dt} (\bar{c}_+^\alpha - \bar{c}_-^\beta) \quad (16)$$

Since we can define

$$v_{\text{weak}}^{\alpha\beta} = q \frac{dx^{\alpha\beta}}{I dt} \quad (17)$$

after inserting eqn. (17) into (16) we have

$$\frac{\bar{m}_+^\alpha \bar{c}_+^\alpha}{\kappa^\alpha} - \frac{\bar{m}_-^\beta \bar{c}_-^\beta}{\kappa^\beta} = v^{\alpha\beta} (\bar{c}_+^\alpha - \bar{c}_-^\beta) \quad (18)$$

Re-expressing eqn. (18) with the relative constituent mobility and conductance [eqns. (4) and (5)], we have

$$\frac{\bar{r}_+^\alpha \bar{c}_+^\alpha}{\sigma^\alpha} - \frac{\bar{r}_-^\beta \bar{c}_-^\beta}{\sigma^\beta} = v^{\alpha\beta} (\bar{c}_+^\alpha - \bar{c}_-^\beta) \quad (19)$$

If strong reaction electrolytes are used to form an MCRB, apparently, the following equalities always hold due to the complete ionization of reaction electrolytes⁸

$$\bar{m}_+^\alpha = m_+^\alpha; \quad \bar{m}_-^\beta = m_-^\beta; \quad \bar{c}_+^\alpha = c_+^\alpha; \quad \bar{c}_-^\beta = c_-^\beta \quad (20a-d)$$

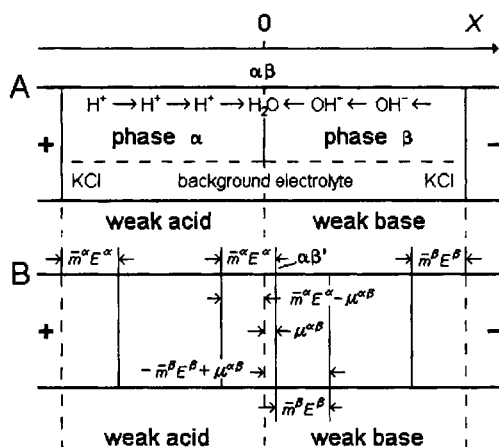


Fig. 1. The model of a moving chemical reaction boundary formed by a weak acid and base. (A) shows the initial boundary, (B) shows the movements of the boundary and phase α and β , on the passage of electric current. The '+' and '-' indicate the anodic and cathodic sides, respectively, the ' α ' and ' β ' phase α and β , respectively, the double '|' indicate a chemical reaction boundary that may be stationary or moving. For other symbols see the text.

Hence, inserting eqns. (20a–d) into eqn. (19), we obtain

$$\frac{m_+^\alpha c_+^\alpha}{\kappa^\alpha} - \frac{m_-^\beta c_-^\beta}{\kappa^\beta} = v^{\alpha\beta}(c_+^\alpha - c_-^\beta) \quad (21)$$

$$T_+^\alpha - T_-^\beta = V^{\alpha\beta}(c_+^\alpha - c_-^\beta) \quad (22)$$

4.3. *Velocity equations.* Clearly, the re-arrangement of eqn. (15), for a boundary formed by weak reaction electrolytes, yields

$$\mu_{\text{weak}}^{\alpha\beta} = (\bar{m}_+^\alpha \bar{c}_+^\alpha E^\alpha - \bar{m}_-^\beta \bar{c}_-^\beta E^\beta) / (\bar{c}_+^\alpha - \bar{c}_-^\beta) \quad (23)$$

If strong reaction electrolytes are used to form an MCRB, then one inserts eqns. (20a–d) into (23) and gets

$$\mu_{\text{strong}}^{\alpha\beta} = (m_+^\alpha c_+^\alpha E^\alpha - m_-^\beta c_-^\beta E^\beta) / (c_+^\alpha - c_-^\beta) \quad (24)$$

and if a uniform electric field strength exists over a whole conductor,^{1–3} viz.

$$E^\alpha = E^\beta \quad (25)$$

then combining eqn. (25) with (24), one gets

$$\mu_{\text{strong}}^{\alpha\beta} = \frac{m_+^\alpha c_+^\alpha - m_-^\beta c_-^\beta}{c_+^\alpha - c_-^\beta} E \quad (26)$$

Since, m_-^β and c_-^β are negative, as defined by Longworth,⁶ Dole⁷ and Alberty,⁸ thus, eqn. (26) is the same as eqn. (2) in Ref. 2 or eqn. (5') in Ref. 1, viz. the Deman–Rigole equation. This shows theoretically that the Deman–Rigole equation can be derived from the MCRBEs in a special case, namely, the ideal of a 'precipitate reaction front' advanced by Deman and Rigole^{1,2} is a special case of MCRB, in which uniform electric field strength exists over a whole conductor.

4.4. Stationary chemical reaction equations (SCRBEs).

If the boundary displacement is set to be stationary for a chemical reaction boundary, viz.

$$v^{\alpha\beta} = 0; \quad \text{or} \quad V^{\alpha\beta} = 0 \quad (27a-b)$$

then eqns. (18), (21) and (22) become eqns. (28), (29) and (30), respectively

$$\bar{m}_+^\alpha \bar{c}_+^\alpha \kappa^\beta = \bar{m}_-^\beta \bar{c}_-^\beta \kappa^\alpha \quad (28)$$

$$m_+^\alpha c_+^\alpha \kappa^\beta = m_-^\beta c_-^\beta \kappa^\alpha \quad (29)$$

$$T_+^\alpha = T_-^\beta \quad (30)$$

Considering Fig. 1, if the boundary is formed by a weak acid and base/or a strong acid and base, then eqns. (28)–(30) can be expressed as eqns. (31)–(33), respectively

$$\bar{m}_{\text{H}^+}^\alpha \bar{c}_{\text{H}^+}^\alpha \kappa^\beta = \bar{m}_{\text{OH}^-}^\beta \bar{c}_{\text{OH}^-}^\beta \kappa^\alpha \quad (31)$$

$$m_{\text{H}^+}^\alpha c_{\text{H}^+}^\alpha \kappa^\beta = m_{\text{OH}^-}^\beta c_{\text{OH}^-}^\beta \kappa^\alpha \quad (32)$$

$$T_{\text{H}^+}^\alpha = T_{\text{OH}^-}^\beta \quad (33)$$

Equation (33) can be re-expressed as

$$J_{\text{H}^+}^\alpha = J_{\text{OH}^-}^\beta \quad (34)$$

$$\text{pH}^\alpha = \lg\left(\frac{m_{\text{H}^+}^\alpha}{m_{\text{OH}^-}^\beta}\right) - \lg\left(\frac{\kappa^\alpha}{\kappa^\beta}\right) - \text{p}\kappa_w - \text{pH}^\beta \quad (35)$$

where pH^α and pH^β are, respectively, the pH values of phase α (viz. acid) and β (viz. base), and κ_w is the ion product of water.

Obviously, eqns. (27)–(35) should be called SCRBEs, and eqns. (31)–(35) SNRBEs. Equation (34) is the mathematical expression of stationary neutralization reaction boundary (SNRB) given by Pospichal *et al.* [eqn. (1) in Ref. 3], this shows that Pospichal's equation is also a special case of an MCRBEs.

5. Discussions and conclusions

The concept of an MCRB formed by weak reaction electrolytes is advanced, and the MCRBEs are derived from the concept for both weak and strong reaction electrolytes. Comparing eqns. (18), (19), (21) and (22) with eqns. (11), (12), (6) and (7), respectively, one finds, clearly, that there is an elegant symmetry between the MCRBEs and MBEs; this indicates that the MCRB theory is the counterpart of the MBS theory advanced about 50 years ago.^{6–11}

However, the MCRBEs are, in nature, different from the MBEs. Since the former describe the movement of a boundary, in which there is (are) always a chemical reaction(s), for example the precipitate reaction of electromigration between Co^{2+} and OH^- (Refs. 1 and 2) and the neutralization reaction of electro-migration,³ but the latter outlines the motion of a boundary in which there is not such a chemical reaction of electromigration.

This paper also shows that both the Deman–Rigole equation [eqn. (26)] and Pospichal's equation [eqn. (34)] can be deduced from the MCRBEs. This implies that the Deman–Rigole and Pospichal equations are special cases of MCRBEs.

The validity of the MCRB theory has been proved by the following facts and experiments: (1) this paper shows there is an elegant symmetry between the MCRBEs and MBEs, and the MCRB theory is the counterpart of the MBS theory; this shows good self-evidence; (2) the Deman–Rigole equation [eqn. (26)] can be deduced from the MCRBEs in a special case, the former has been proved by the Deman–Rigole experiments;^{1,2} (3) Pospichal's equation [eqn. (34)] can also be derived from the MCRBEs in a special case; this equation has been proved by Pospichal's experiments;³ (4) the predications with eqn. (35) are exactly in coincidence with the computer simulations rested on Kohlrausch's *beharrliche* function and the experiments of two SNRBs created by Pospichal;⁴ (5) in a further paper²¹ we will show the predications with eqn. (24) are in agreement with the experiments of electromigration reaction between Co^{2+} and OH^- quantitatively.

Theoretically, MCRB theory may have the following potential applications.

Firstly, it may be used to design new techniques of analysis and separation, for instance, the ionic separations during electromigration reactions advanced and performed by Deman and Rigole.^{1,2}

Secondly, it may be used to determine the ionic transference number and mobility; this application is very similar to that of MBS theory as performed by others 40–60 years ago.^{10,11} It may also be used to determine the pK -value for a weak acid or base.

Thirdly, as shown by eqns. (26) and (34), it may be used to study a precipitate reaction front as performed by Deman and Rigole^{1,2} and a neutralization reaction boundary.³

Lastly, it may also be used to study stationary electrolysis and isoelectric focusing (IEF). As has been pointed out by Svensson in his famous papers^{19,20} that laid the theoretical base for IEF: 'In the case of electrolysis of sodium sulfate, one gets evolution of hydrogen at the cathode and of oxygen at the anode (which should be of platinum or carbon), while sodium hydroxide collects in the catholyte and sulfuric acid in the anolyte. ... the IEF is based on the stationary electrolysis of salt'. Obviously, there is a neutralization reaction of electromigration between the proton and hydroxyl ion and a chemical reaction boundary is created in the stationary electrolysis.³ Thus, the theory of MCRB is useful for the study of stationary electrolysis and IEF;^{3,19,20} this has been shown in Refs. 22 and 23 and will be illustrated further.

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