

Judgment Expressions for a Moving Chemical Reaction Boundary and Isoelectric Focusing

Cheng-Xi Cao,^{1,*} Jian-Hua Zhu,² Hua Liu,² Wei-Hua Fang,² Wen-Zhang Tang,² Lian-Huan Song² and Wen-Kui Chen³

¹Department of Chemistry, University of Science and Technology of China, Anhui Hefei 230026, China, ²Department of Forensic Medicine, Wannan Medical College, Anhui Wuhu 241001, China and ³Institute of Allergy Reaction, Wannan Medical College, Anhui Wuhu 241001, China

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Judgment expressions for a moving or stationary chemical reaction boundary (MCRB, SCRb) and isoelectric focusing (IEF) are defined from the moving chemical reaction boundary equation (MCRBE). The judgment expressions are tested with experiments cited in the literature and with those of a moving precipitate boundary formed by the reaction electrolytes CoCl₂ and NaOH, coupled with the background electrolyte KCl. The judgment expressions are also used in comparisons between the transference numbers of the hydrogen ion in HBr, or HCl or HI solution with concentrations varying from infinite to 0.05 mol l⁻¹ and of the hydroxide ion in NaOH solution ranging from infinite concentration to 0.01 mol l⁻¹. The results show that predictions made with the judgment expressions are in agreement with experiment, that the judgment expressions are useful and convenient for judging the movement of an MCRB and for comparisons of transference numbers of positive and negative reaction ions such as hydrogen and hydroxide ions in IEF. In addition, the results also display the existence of the equal (or quasi-equal) transference numbers of hydrogen and hydroxide ions in Svensson's IEF.

1. Introduction

In 1970 Deman and Rigole first advanced the idea of a chemical reaction boundary, which they termed a 'precipitate reaction front' together with positive and negative reaction ions like cobaltic and hydroxide ions, and they also performed some experiments on the precipitate reaction front formed with cobaltic and hydroxide ions in 1% (w/v) agar gel.^{1,2}

Separately, Bocek and co-workers evolved the concept of a stationary neutralization boundary, and used the concept to study the dynamical mechanism of isoelectric focusing (IEF).^{3,4} With the aid of electrically controlled electrofocusing apparatus, they observed the movement of a neutralization boundary marked with ampholyte dyes and successfully created two stationary neutralization boundaries.^{3,5}

Recently, various authors have developed the concept of a moving or stationary chemical reaction boundary (MCRB, SCRb), advanced the theory of MCRB, and deduced a series of moving chemical reaction equations (MCRBEs).^{6–8} Here, we list some of the MCRBEs:

$$T_+^\alpha - T_-^\beta = V^{\alpha\beta}(c_+^\alpha - c_-^\beta) \quad (1)$$

* To whom correspondence should be addressed.

$$\frac{m_+^\alpha c_+^\alpha}{\kappa^\alpha} - \frac{m_-^\beta c_+^\beta}{\kappa^\beta} = v^{\alpha\beta}(c_+^\alpha - c_-^\beta) \quad (2)$$

$$\frac{\bar{m}_+^\alpha \bar{c}_+^\alpha}{\kappa^\alpha} - \frac{\bar{m}_-^\beta \bar{c}_+^\beta}{\kappa^\beta} = v^{\alpha\beta}(\bar{c}_+^\alpha - \bar{c}_-^\beta) \quad (3)$$

Equations (1) and (2) are used for strong reaction electrolytes, such as CoCl₂ and NaOH, while eqn. (3) is only valid for weak reaction electrolytes like CH₃COOH and CH₃CH₂NH₂. The MCRB is a counterpart of the moving boundary system (MBS) studied by Longworth,⁹ Dole,¹⁰ Svensson,¹¹ Alberty¹² and Nichol¹³ over 50 years ago. The theory of MCRB may be used (1) to design new techniques of analysis and separation, (2) to determine the ionic transference number and mobility, (3) to study a precipitate reaction front boundary and a neutralization reaction boundary, as has been used by Deman and Rigole,^{1,2} Bocek and coworkers,^{3–5} and the present authors,^{14–16} and (4) to study stationary electrolysis and isoelectric focusing (IEF),^{17,18} as has been shown by the present authors.^{19–21}

We found it very inconvenient to use eqns. (1)–(3) for the judgment of movement of a MCRB and for comparisons between the fluxes or transference numbers of

positive and negative reaction ions, such as cobaltic and hydroxide ions in the precipitate reaction boundary^{1,2} and hydrogen and hydroxide ions in the neutralization reaction boundary and IEF.³⁻⁵ Thus, it is necessary to define judgment expressions from eqns. (1)–(3), as will be formulated in Section 3.

Therefore, the purposes of this paper are to define judgment expressions, and to show the validity and convenience of the expressions for judging the motion of a MCRB, and for comparing the transference numbers of positive and negative reaction ions in stationary electrolysis and Svensson's IEF.

2. Notation

- c : the equivalent concentration (equiv. m^{-3}) The subscripts '+' and '-' indicate the positive and negative reaction ions, respectively, the superscripts α and β imply phase α and β , respectively. The bar '-' over c indicates the constituent concentration, which does not apply to an ion but to the equilibrium mixture of all subspecies of the constituent. It is a signed quantity, positive if the ion carries net positive charge(s), and negative if it carries net negative charge(s), as has been set by Longworth,⁹ Dole,¹⁰ Svensson,¹¹ Alberty¹² and Nichol.¹³
- m : the mobility ($\text{m}^2 \text{s}^{-1} \text{V}^{-1}$). The bar '-' over m indicates the constituent mobility, and the subscripts, '0' and 'act', indicate the absolute and actual mobility, respectively. It is a signed quantity like c .
- F : the Faraday constant ($=9.648\,5309 \times 10^4 \text{ C mol}^{-1}$).
- $V^{\alpha\beta}$: the boundary displacement ($\text{m}^3 \text{C}^{-1}$) swept by the boundary on the passage of 1 C; a signed quantity, positive if the boundary moves towards the cathode, negative if towards the anode; double superscripts indicate the two phases on either side of a boundary (Fig. 1).
- $v^{\alpha\beta}$: the boundary displacement ($\text{m}^3 \text{F}^{-1}$); a signed quantity like $V^{\alpha\beta}$.
- z : the electric charge of an ion.
- I : the ionic strength (mol l^{-1})
- $$= 0.5 \sum c_i z_i^2 \quad (4)$$
- η : the empirical coefficient [see eqn. (21)]. If $z=1$, $\eta=0.5$; if $z \geq 2$, $z=0.77$.
- κ : the conductivity of a solution in a phase (S m^{-1}).
- λ : the equivalent conductivity of an ion ($\text{m}^2 \text{S mol}^{-1}$). The subscript '0' indicates the ionic conductivity in an infinite dilute solution.
- Λ : the equivalent conductivity of an electrolyte solution ($\text{m}^2 \text{S mol}^{-1}$). For a pure solution, such as NaOH, we have
- $$\Lambda_{\text{NaOH}} = \lambda_{\text{Na}^+} + \lambda_{\text{OH}^-} \quad (5)$$
- κ_{ω} : the ion product of water.

- q : the cross-sectional area of the electrophoretic tube (m^2).
- E : the electric field strength (V m^{-1}).
- T : the transference number (dimensionless)
- $$= cmF/\kappa \quad (6)$$

- J : the flux of an ion in its solution (mol s^{-1})
- $$= qcmE \quad (7)$$

R_{abs} : the symbol for the absolute judgment expression ($\text{mol S s}^{-1} \text{V}^{-1} \text{m}^{-2}$). The subscript 'abs' denotes absolute. The physical meaning of R_{abs} is given in eqns. (10a)–(10c).

R_r : the symbol for the relative judgment expression (dimensionless). The subscript 'r' denotes relative. The physical meaning of R_r is the relative comparison between fluxes or transference numbers of positive and negative reaction ions; the significance of $R_r=0$ is that the transference number of the positive reaction ion is equal to that of the negative reaction ion.

3. Judgment expressions

3.1. *Absolute judgment expressions.* Clearly, eqn. (3) may be expressed as

$$\bar{m}_+^{\alpha} \bar{c}_+^{\alpha} \kappa^{\beta} - \bar{m}_-^{\beta} \bar{c}_-^{\beta} \kappa^{\alpha} = v^{\alpha\beta} (\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}) \kappa^{\alpha} \kappa^{\beta} \quad (8)$$

We define the left- and right-hand side of eqn. (8) as R_{abs} , namely, the following equations are given:

$$R_{\text{abs}} = \bar{m}_+^{\alpha} \bar{c}_+^{\alpha} \kappa^{\beta} - \bar{m}_-^{\beta} \bar{c}_-^{\beta} \kappa^{\alpha} \quad (9a)$$

$$R_{\text{abs}} = v^{\alpha\beta} (\bar{c}_+^{\alpha} - \bar{c}_-^{\beta}) \kappa^{\alpha} \kappa^{\beta} \quad (9b)$$

Because $\bar{c}_+^{\alpha} - \bar{c}_-^{\beta} = |\bar{c}_+^{\alpha}| + |\bar{c}_-^{\beta}| > 0$, $\kappa^{\alpha} > 0$ and $\kappa^{\beta} > 0$ always hold, we conclude from eqn. (9b) that

$$\text{if } R_{\text{abs}} > 0, \text{ then } v^{\alpha\beta} > 0; \quad (10a)$$

consequently, the boundary moves toward the cathode

$$\text{if } R_{\text{abs}} = 0, \text{ then } v^{\alpha\beta} = 0; \quad (10b)$$

as a result, the boundary is stationary

$$\text{if } R_{\text{abs}} < 0, \text{ then } v^{\alpha\beta} < 0; \quad (10c)$$

in due course, the boundary moves toward the anode

Thus, eqn. (9b), viz., eqn. (9a), together with eqn. (12) and the relative judgment expression (given in Section 3.2) derived from eqn. (12), can be used to judge the directions of an MCRB. This will be tested by some experiments on the MCRB formed by CoCl_2 and NaOH and of the stationary neutralization boundary created by Bocek's group^{3,5} in Section 4.1.

The following equations always exist:^{12,13}

$$\bar{m}_+^{\alpha} \bar{c}_+^{\alpha} = m_+^{\alpha} c_+^{\alpha}; \quad \bar{m}_-^{\beta} \bar{c}_-^{\beta} = m_-^{\beta} c_-^{\beta} \quad (11a,b)$$

Hence, the combination of eqns. (11a) and (11b) with eqn. (9a) yields

$$R_{\text{abs}} = m_+^{\alpha} c_+^{\alpha} \kappa^{\beta} - m_-^{\beta} c_-^{\beta} \kappa^{\alpha} \quad (12)$$

We term eqns. (9) and (12) absolute judgment expressions.

3.2. Relative judgment expressions. Equations (9a) and (12) can be used to judge the direction of an MCRB, but it is impossible to use them to compare the flux (or transference number) of a positive reaction ion like the proton with that of a negative reaction ion, such as the hydroxide ion. Thus, it is necessary to formulate relative judgment expressions that can compare the transference numbers (or fluxes) of positive and negative reaction ions conveniently.

If $R_{\text{abs}} \geq 0$, divide the two sides of eqn. (12) by $m_{-}^{\beta} c_{-}^{\beta} \kappa^{\alpha}$, we have

$$\frac{R_{\text{abs}}}{m_{-}^{\beta} c_{-}^{\beta} \kappa^{\alpha}} = \frac{m_{+}^{\alpha} c_{+}^{\alpha} \kappa^{\beta}}{m_{-}^{\beta} c_{-}^{\beta} \kappa^{\alpha}} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (13)$$

Now, using R_r to stand for the left-hand side of eqn. (13), we obtain

$$R_r = \frac{m_{+}^{\alpha} c_{+}^{\alpha} \kappa^{\beta}}{m_{-}^{\beta} c_{-}^{\beta} \kappa^{\alpha}} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (14a)$$

Similarly, if $R_{\text{abs}} < 0$, we get

$$R_r = 1 - \frac{m_{-}^{\beta} c_{-}^{\beta} \kappa^{\alpha}}{m_{+}^{\alpha} c_{+}^{\alpha} \kappa^{\beta}} \quad (\text{used for } R_{\text{abs}} < 0) \quad (14b)$$

Inserting eqn. (6) into eqns. (14a) and (14b), one gets

$$R_r = T_{+}^{\alpha} / T_{-}^{\beta} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (15a)$$

$$R_r = 1 - T_{-}^{\beta} / T_{+}^{\alpha} \quad (\text{used for } R_{\text{abs}} < 0) \quad (15b)$$

Similarly, the insertion of eqn. (7) into eqns. (14a) and (14b) yields

$$R_r = J_{+}^{\alpha} / J_{-}^{\beta} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (16a)$$

$$R_r = 1 - J_{-}^{\beta} / J_{+}^{\alpha} \quad (\text{used for } R_{\text{abs}} < 0) \quad (16b)$$

If phase α and β are pure reaction electrolytes, for instance HCl and NaOH, respectively, i.e. no background electrolyte KCl exists in an MCRB system, then the conductivities of phase α and β can be, respectively, written as^{20,21}

$$\kappa^{\alpha} = \Lambda^{\alpha} c^{\alpha} = \Lambda^{\alpha} c_{+}^{\alpha}; \quad \kappa^{\beta} = \Lambda^{\beta} c^{\beta} = \Lambda^{\beta} c_{-}^{\beta} \quad (17a,b)$$

Note here that c^{α} and c^{β} are the equivalent concentrations of pure positive and negative reaction electrolytes, such as HCl and NaOH, respectively, and c_{+}^{α} and c_{-}^{β} are equivalent concentrations of positive and negative reaction ions, for instance hydrogen and hydroxide ions, respectively. Thus, inserting eqns. (17a) and (17b) into eqns. (14a) and (14b), respectively, we have

$$R_r = \frac{m_{+}^{\alpha} \Lambda^{\beta}}{m_{-}^{\beta} \Lambda^{\alpha}} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (18a)$$

Similarly, if $R_{\text{abs}} < 0$, we get

$$R_r = 1 - \frac{m_{-}^{\beta} \Lambda^{\alpha}}{m_{+}^{\alpha} \Lambda^{\beta}} \quad (\text{used for } R_{\text{abs}} < 0) \quad (18b)$$

If the positive and negative reaction electrolytes are

diluted synchronously and infinitely, we have the limiting value of R_r

$$\lim_{c_{+}^{\alpha}, c_{-}^{\beta} \rightarrow 0} R_r = R_{0,r} = T_{0,+}^{\alpha} / T_{0,-}^{\beta} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (19a)$$

$$\lim_{c_{+}^{\alpha}, c_{-}^{\beta} \rightarrow 0} R_r = R_{0,r} = 1 - T_{0,-}^{\beta} / T_{0,+}^{\alpha} \quad (\text{used for } R_{\text{abs}} < 0) \quad (19b)$$

Apparently, eqns. (9a) and (12) should be called absolute judgment expressions, whereas eqns. (14)–(16), (18) and (19) ought to be called relative judgment expressions. Equation (18) is only used for pure positive and negative reaction electrolytes like HCl and NaOH, and eqn. (19) is only used to compare the transference numbers between positive and negative reaction electrolytes, diluted infinitely.

The significance of relative judgment expressions, viz., eqns. (14)–(16), (18) and (19), is clearly as a comparison between fluxes (or transference numbers) of positive and negative reaction ions. Therefore, if the value of relative judgment expressions is equal or near to zero, this means that the flux or transference number of the positive reaction ion is equal or near to that of the negative reaction ion.

4. Experiments and applications

4.1. Validity of judgment expressions. In order to test the validity and convenience of the judgment expressions, some experiments on an MCRB formed with CoCl_2 and NaOH, together with 0.1 N KCl as background electrolyte, were performed.

The reagents used here were $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, NaOH, KCl and agarose. The former three were AR grade (Shanghai Chemical Reagent Co., Shanghai, China), the latter, used to prepare the 1% (w/v = weight/volume) agarose gel, was a biochemical reagent (Shanghai Huang-Hua Pharmaceutical Factor, Shanghai). A power supply (model DYY III8A, Beijing Luyi Instrument Factor, Beijing, China), with constant voltage 0–150 or 0–600 V, constant current 0–25 or 0–100 mA and timer equipment, was used to yield a direct current.

The procedure was mainly according to those used by Deman and Rigole^{1,2} and the present authors,¹⁴ but with some modifications (see Fig. 1). (1) The anti-convection medium was the 1% (w/v) agarose gel, which has nearly complete absence of electro-osmotic flow (EOF);²²

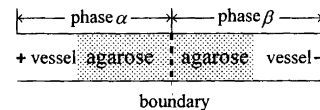


Fig. 1. The procedure for the MCRB experiments formed with CoCl_2 and NaOH, coupled with 0.1 N KCl. The '+' and '-' indicate the anode and cathode, respectively. The electrophoretic tubes are fixed in a disk electrophoretic vessel (model DYYIII27, Beijing Luyi Instrument Factor, Beijing, China).

Table 1. Comparisons between the experiments and the predictions with eqns. (9a) and (22).^a

No. ^b	Phase $\alpha(+)^c$	Phase $\beta(-)^c$	R_{abs}	R_r	Prediction ^c	Experiment ^c
1	0.014 N CoCl ₂	0.001 N NaOH	> 0	2.576	Toward -	Toward -
2	0.014 N CoCl ₂	0.002 N NaOH	> 0	0.788	Toward -	Toward -
3	0.014 N CoCl ₂	0.004 N NaOH	< 0	-0.119	Toward +	Toward +
4	0.014 N CoCl ₂	0.006 N NaOH	< 0	-0.678	Toward +	Toward +
5	0.014 N CoCl ₂	0.008 N NaOH	< 0	-1.237	Toward +	Toward +
6	0.014 N CoCl ₂	0.010 N NaOH	< 0	-1.769	Toward +	Toward +
7	0.014 N CoCl ₂	0.014 N NaOH	< 0	-2.915	Toward +	Toward +
8	0.014 N CoCl ₂	0.020 N NaOH	< 0	-4.573	Toward +	Toward +
9	5.5×10^{-5} N H ⁺ (pH 4.26)	1.0×10^{-4} N OH ⁻ (pH 10)	< 0	-0.028	No motion	No motion
10	1.8×10^{-6} N H ⁺ (pH 5.75)	3.2×10^{-6} N OH ⁻ (pH 8.5)	< 0	-0.005	No motion	No motion

^aThe absolute mobilities of H⁺, OH⁻ and Co²⁺ are, respectively, 36.3, 20.5 and 5.7×10^{-8} m² V⁻¹ s⁻¹ (calculated from their equivalent conductivities in infinitely dilute solution²⁴ with $m_{0,i} = \lambda_{0,i}/F$). ^bExperiments 1–8 were performed by us, those of 9 and 10 are quoted from Ref. 3. ^cThe symbols '+' and '-' imply the anode and cathode, respectively (Fig. 1).

(2) phase α , connected with the anode, contained 0.014 N CoCl₂ and 0.1 N KCl (Table 1); (3) phase β , attached to the cathode, held 0.001–0.020 N NaOH and 0.1 N KCl (Table 1); (4) the conditions were: ID of tube 4.6 mm, length 90 mm, constant voltage 50 V, and run time 10 min.

In the experiments by the present authors and those cited from Ref. 3, there was high background electrolyte KCl. Thus, the conductivities in two phases may, approximately, be uniform, namely,

$$\kappa^\alpha = \kappa^\beta \quad (20)$$

holds, as has been treated by others;^{1–3} the absolute mobilities (see the footnote in Table 1), which will be used in eqns. (22a) and (22b), ought to be corrected with

$$m_{\text{act}} = m_0 \exp[-\eta(zI)^{1/2}] \quad (21)$$

(if $z = 1$, $\eta = 0.5$; if $z \geq 2$, $z = 0.77$)

which is valid for both large ions with low electric charge intensity^{24,25} and small ions, such as proton and cobaltic ions, with high electric charge intensity,^{26,27} if the ionic strength is not over 0.1 mol l⁻¹.

Therefore, by using eqns. (20) and (21), eqns. (14a) and (14b) are simply written as

$$R_r = \frac{m_{\text{act},+}^\alpha + c_+^\alpha}{m_{\text{act},-}^\beta - c_-^\beta} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (22a)$$

$$R_r = 1 - \frac{m_{\text{act},-}^\beta - c_-^\beta}{m_{\text{act},+}^\alpha + c_+^\alpha} \quad (\text{used for } R_{\text{abs}} < 0) \quad (22b)$$

The comparisons between the MCRB experiments, together with those of stationary neutralization boundaries,^{3,5} and the predictions with eqns. (9a) and (22) are collected in Table 1.

In the experiments on MCRB formed with CoCl₂ and NaOH coupled with 0.1 N KCl, the concentration of CoCl₂ is fixed at 0.014 N. We observed that, if the concentration of NaOH is less than 0.004 N, for example 0.001 and 0.002 N, the boundary moves towards the cathode; if the concentration of NaOH is equal to or

over 0.004 N, such as 0.006 and 0.020 N, the boundary drifts towards the anode. These observations are all in coincidence with the predictions made by the judgment expressions as shown by Nos. 1–8 in Table 1. We find it is convenient to use judgment expressions for comparing the transference numbers between positive and negative reaction ions and for judging the direction of movement of an MCRB.

We also use judgment expressions to analyze the stationary neutralization boundary created by Bocek's group with electrically controlled electrofocusing apparatus.^{3,5} As shown by Nos. 9 and 10, the values of R_r for two stationary neutralization boundaries, one being pH 4.26–10 and another being pH 5.75–8.5, are -0.028 and -0.005, respectively, values which are very near to zero. Those values mean that the two boundaries should be stationary. The predictions are quantitatively in agreement with the experimental results by Bocek's group. Those results also show that judgment expressions are useful for studying the stationary neutralization boundary and IEF.

4.2. Applications to stationary electrolysis and IEF.

Svensson pointed out in his famous papers:^{17,18} 'In the case of electrolysis of sodium sulfate, one gets evolution of hydrogen at the cathode and of oxygen at the anode, while sodium hydroxide collects in the catholyte and sulfuric acid in the anolyte. ... The IEF is based on the stationary electrolysis of salt'. The last consequence of stationary electrolysis can be simply achieved by using acid and base as the catholyte and anolyte, respectively.

Here, the authors use judgment expressions for comparisons between the transference numbers of hydrogen and hydroxide ions in stationary electrolysis and IEF.

As shown by Table 2 here, the molar conductivities of HBr, HI and NaOH at 25 °C are originated from Ref. 28. The mobilities of hydrogen and hydroxide ions should also be corrected with eqn. (21). Equations (18a) and (18b) are used to calculate the values of R_r , since pure acid and base are considered here. In the calculations of R_r , we used a computer (486DX/80, 16Mbyte RAM,

Table 2. The molar conductivities ($\times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$) of HBr, HI and NaOH at various concentrations at 25 °C.^a

Conc./mol l ⁻¹	HBr	HI	NaOH
Infinite ^b	4.2775	4.2645	2.477
0.0001	4.259 ^c	4.246 ^d	—
0.0005	4.243	4.230	2.455
0.001	4.229	4.217	2.446
0.005	4.176	4.164	2.407
0.01	4.137	4.128	2.379
0.05	4.004	4.008	—

^aThe molar conductivities of HCl also originates from Ref. 28 (not shown here). ^bThe limited molar conductivities are obtained from the limited molar conductivities of ion in infinitely dilute solutions (cited in Ref. 11) with the equation $\Lambda_{0,\text{NaOH}} = \lambda_{0,\text{Na}^+} + \lambda_{0,\text{OH}^-}$ (using NaOH as an example). ^cThe value is obtained from the curve of the molar conductivities of HBr under the concentrations of 0.0002 (4.255), 0.0003 (4.250), 0.0004 (4.246), ... and 0.0009 M ($4.232 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$) at 25 °C (cited in Ref. 28). ^dThe value is also from the curve of the molar conductivities of HI under the concentration of the infinite, 0.00050 (4.230), 0.00055 (4.229), 0.00060 (4.227), 0.00065 (4.226), ... and 0.001 M ($4.217 \times 10^{-2} \text{ S m}^2 \text{ mol}^{-1}$) at 25 °C (cited in Ref. 28).

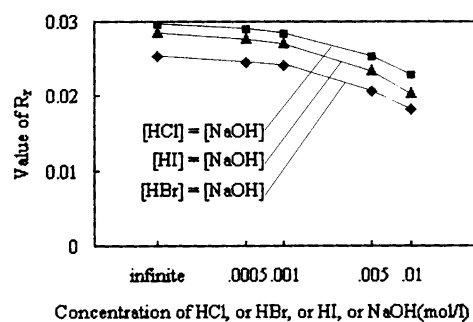


Fig. 2. The values of R_r for the reaction electrolytes of HCl–NaOH, HBr–NaOH and HI–NaOH with equal concentrations, as a function of the concentration of HCl, HBr, HI or NaOH (expressed on a logarithmic scale on the abscissa).

540Mbyte hard disk, Copam Electric Co., Taiwan, China) and EXCEL 5.0 software (Microsoft, Redmond, WA, USA) to treat the experimental data cited in Refs. 23 and 28.

Values of R_r for the acid and base with equal concentrations. By using eqn. (18), we can conveniently calculate the values of R_r for the positive and negative reaction electrolytes such as HCl–NaOH, HBr–NaOH and HI–NaOH, with equal concentrations. The computed data are given in Fig. 2, which shows the values of R_r for HCl–NaOH, HBr–NaOH and HI–NaOH are less than 3%, values that are very small and almost equal to zero. Figure 2 also demonstrates the values are almost constant with the synchronous enormous increases of concentration varying from infinite to 0.01 mol l⁻¹. Those data prove that the transference number of the hydrogen ion in the acids HCl, HBr and HI are almost equal to that of the hydroxide ion in the alkaline NaOH, regardless of whether the concentrations of the acids and

base are high (0.01 mol l⁻¹) or very low (towards 0 mol l⁻¹). The result will be further documented in the following data from Figs. 3–7.

Values of R_r for acid and base with different concentrations. With eqn. (18) one can also easily compute the values of R_r for the reaction electrolytes of HBr–NaOH and HI–NaOH with different concentrations and compare the transference numbers of hydrogen and hydroxide ions in the reaction electrolytes.

Figure 3a displays the values of R_r for the reaction electrolytes of HBr–NaOH as a function of the concentration of NaOH, and Fig. 3b shows the dependence of the values on the concentration of HBr. Similarly, Fig. 4a indicates the values of R_r for HI–NaOH as a function of the concentration of NaOH, and Fig. 4b the dependence of the values on the concentration of HI.

As shown by Figs. 3a and 4a, if the concentration of positive reaction electrolyte HBr or HI is fixed at a certain value, for instance 0.0005 or 0.05 mol l⁻¹, the value of R_r increases with an increase in the concentration of negative reaction electrolyte NaOH. Figures 3b and 4b show that if the concentration of NaOH keeps constant, the value of R_r decreases with an increase in the concentration of HBr and HI. Both Figs. 3 and 4 prove that the values of R_r are all less than 4% and in some cases are equal to zero, values that are much smaller and more close to zero as compared with values for the reaction electrolytes of HCl–NaOH (the highest value of R_r can reach 7%).²⁰ These data imply the transference numbers (or fluxes) of hydrogen and hydroxide ions in the reaction electrolytes of HBr–NaOH and HI–NaOH, in conjunction with HCl–NaOH,²⁰ are almost equal to each other, no matter how high or low the concentrations of the acids and the alkali of NaOH. These findings have been observed in the strong reaction electrolytes of HCl–NaOH.²⁰

Limited value of R_r for pure acid and base diluted infinitely. In the calculation above, with judgment expressions, we have conveniently and effortlessly compared transference numbers of hydrogen and hydroxide ions in the reaction electrolytes with both equal and different concentrations. In the following computation, we will also display the convenience of the expressions for the attainment of a limiting value of R_r for the reaction electrolytes discussed just above.

Obviously, in eqn. (18), if the pure positive and negative reaction electrolytes, for example HBr and NaOH, are infinitely dilute, in other words the concentrations of hydrogen in an acid and hydroxide ion in an alkali, coupled with the ionic strength of acid and base, are close to zero, we can get the following limited equations from the relative judgment expressions:

$$\lim_{c_{\text{H}^+} \text{ and } c_{\text{OH}^-} \rightarrow 0} (R_r) = R_{0,r} = \frac{m_{0,\text{H}^+}^\alpha \Lambda_{0,\text{base}}^\beta}{m_{0,\text{OH}^-}^\beta \Lambda_{0,\text{acid}}^\alpha} - 1 \quad (\text{used for } R_{\text{abs}} \geq 0) \quad (23a)$$

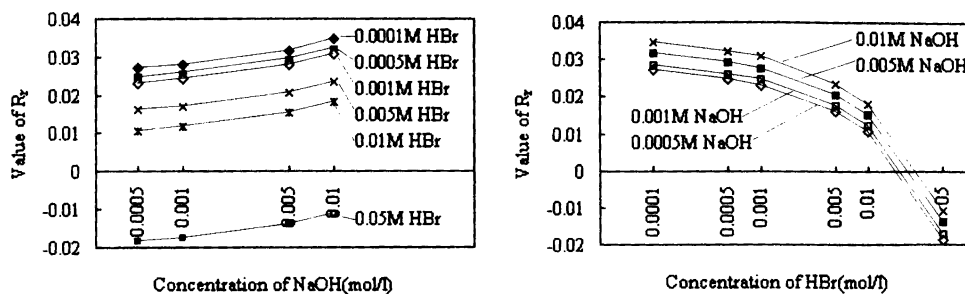


Fig. 3. The values of R_r for the reaction electrolytes of HBr–NaOH with different concentrations: (a) the values of R_r as a function of NaOH concentration; (b) the dependence of the values on the concentration of HBr. The concentrations on the abscissa are given on a logarithmic scale.

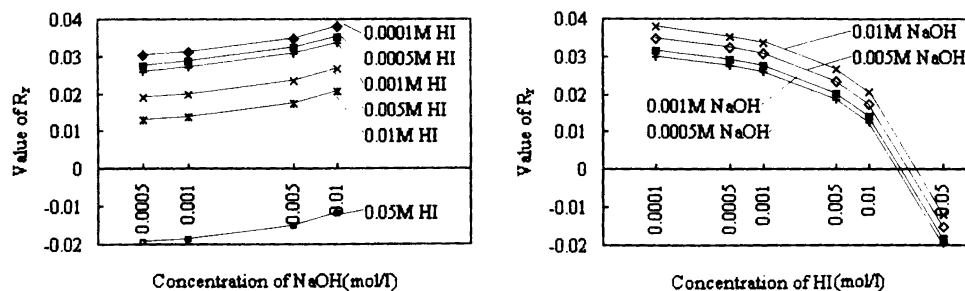


Fig. 4. Values of R_r for the reaction electrolytes of HI–NaOH with different concentrations: (a) the values of R_r as a function of NaOH concentration; (b) the dependence of the values on the concentration of HI. The concentrations on the abscissa are expressed on a logarithmic scale.

$$\lim_{c_{H^+} \text{ and } c_{OH^-} \rightarrow 0} (R_r) = R_{0,r} = 1 - \frac{m_{0,OH}^\beta \Lambda_{0,acid}^\alpha}{m_{0,H}^\alpha \Lambda_{0,base}^\beta} \quad (\text{used for } R_{abs} < 0) \quad (23b)$$

With the limiting expressions, we may obtain the limiting values of R_r for such reaction electrolytes as HCl–NaOH, HBr–NaOH, HI–NaOH and H_2SO_4 –NaOH diluted infinitely. These data are collected in Fig. 5. It is clearly shown in Fig. 5 that the limited values for HCl–NaOH, HBr–NaOH, HI–NaOH and H_2SO_4 –NaOH are 0.0296, 0.0253, 0.0277 and 0.0200, respectively, values very near to zero.

Semi-limited value of R_r for pure acid or base diluted infinitely. If only the positive reaction electrolyte of acid

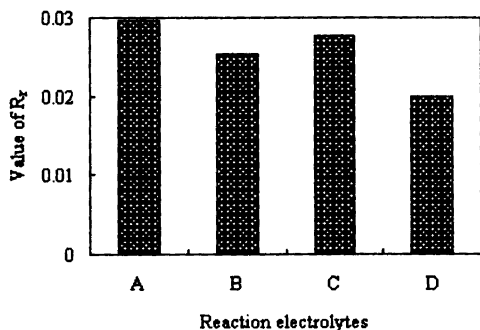


Fig. 5. The limited value of R_r for the pure positive and negative reaction electrolytes of A=HCl–NaOH, B=HBr–NaOH, C=HI–NaOH and D= H_2SO_4 –NaOH diluted infinitely.

is diluted infinitely, while the concentration of negative reaction electrolyte NaOH keeps changing, we can have the semi-limited expressions from eqn. (18) shown below:

$$\lim_{c_{H^+} \rightarrow 0} (R_r) = R_{semi,r} = \frac{m_{0,H}^\alpha + \Lambda_{NaOH}^\beta}{m_{OH}^\beta - \Lambda_{0,acid}^\alpha} - 1 \quad (\text{used for } R_{abs} \geq 0) \quad (24a)$$

$$\lim_{c_{H^+} \rightarrow 0} (R_r) = R_{semi,r} = 1 - \frac{m_{OH}^\beta - \Lambda_{0,acid}^\alpha}{m_{0,H}^\alpha + \Lambda_{NaOH}^\beta} \quad (\text{used for } R_{abs} < 0) \quad (24b)$$

Similarly, if only the negative reaction electrolyte NaOH is diluted infinitely, one may also get the following semi-limited expressions

$$\lim_{c_{OH^-} \rightarrow 0} (R_r) = R_{semi,r} = \frac{m_{H^+}^\alpha + \Lambda_{0,NaOH}^\beta}{m_{0,OH}^\beta - \Lambda_{acid}^\alpha} - 1 \quad (\text{used for } R_{abs} \geq 0) \quad (25a)$$

$$\lim_{c_{OH^-} \rightarrow 0} (R_r) = R_{semi,r} = 1 - \frac{m_{0,OH}^\beta - \Lambda_{acid}^\alpha}{m_{H^+}^\alpha + \Lambda_{0,NaOH}^\beta} \quad (\text{used for } R_{abs} < 0) \quad (25b)$$

where the subscript ‘semi’ in eqns. (24) and (25) denotes the semi-limited value of R_r .

The results of calculation with eqns. (24a) and (24b) are depicted in Fig. 6, and those with eqns. (25a) and (25b) are given in Fig. 7. The values of R_r in Fig. 6 are all less than 3%, a value very near to zero. The changes in R_r are very similar to those in Figs. 3b and 4b above

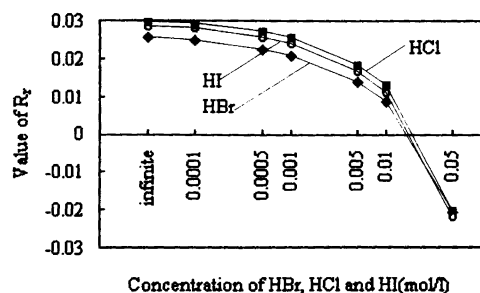


Fig. 6. The semi-limited values of R_r for the reaction electrolytes of HCl-NaOH, HBr-NaOH and HI-NaOH (under the conditions of infinitely dilute NaOH), as a function of the concentration of positive reaction electrolyte of HCl, or HBr or HI (logarithmic scale).

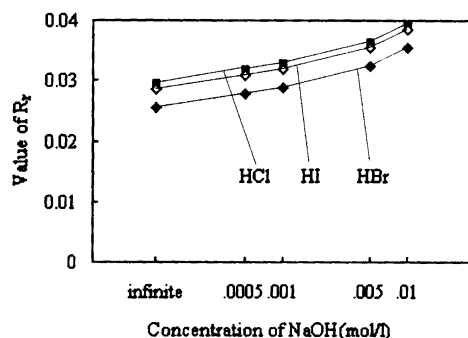


Fig. 7. The semi-limited values of R_r for the reaction electrolytes of HCl-NaOH, HBr-NaOH and HI-NaOH (under the conditions of infinitely dilute HCl, HBr and HI), as a function of the concentration of negative reaction electrolyte of NaOH (logarithmic scale).

and those of Fig. 2a in Ref. 20. The values of R_r in Fig. 7 are all not over 4%. The shapes of R_r are like those of Figs. 3a and 4a, and of Fig. 2b in Ref. 20.

It is demonstrated by Fig. 6 that even when the concentration of NaOH is fixed at infinite, the changes in R_r are very small, with tremendous increases in the concentrations of HCl, HBr and HI from infinite to 0.05 mol l^{-1} . Similar findings are also observed in Fig. 7, in Figs. 3 and 4 as has been analyzed above, and in Ref. 20. As will be proved in a subsequent paper, it is the 'self-correction effect' existing in stationary electrolysis and Svensson's IEF that leads to the quite constant value of R_r regardless of whether the concentration of positive reaction electrolyte is high or low, or the concentration of negative reaction electrolyte is high or low, and regardless of whether the temperatures of the reaction electrolytes are high or low.

5. Discussion and conclusions

The transference number is an important physico-chemical quantity, having important use in the moving boundary system (MBS). The transference number may be determined with Hittorf's method or with the moving boundary method (MBM).^{9-13,23,29,30} Before 1940, a great number of data on the transference numbers of

small ions in different electrolytes were monitored,³⁰ with which one can, in conjunction with the equivalent conductivity of the electrolyte, calculate the ionic mobilities under different ionic strengths.^{26,27} Later, Longworth⁹ and Dole¹⁰ developed the theory of MBS formed with strong electrolytes and formulated the moving boundary equations (MBEs) which describe the relationships between the transference numbers of ions in two phases and the boundary movement. Almost at the same time, the technique of ITP was developed from the MBM and Tiselius' moving boundary electrophoresis.^{29,31} With the utility of the systemic theory of MBS,⁹⁻¹³ together with the advancement of relative techniques, ITP has gradually become a ripe technique of analysis and separation.

Before the 1990s it seemed that the ionic transference number was of no important use in Svensson's IEF, because the transference number was used for strong electrolytes only, but could not be used for weak electrolytes, including the carrier ampholyte described by Svensson^{17,18} and synthesized by Vesterberg.³² However, work by Bocek's group³⁻⁵ has shown the importance of the transference number in Svensson's IEF. In their experiments with electrically controlled electrofocusing, they manifested that, if the transference number, viz. flux, of the hydrogen ion in the anolyte is greater than that of hydroxide ion in the catholyte, the neutralization boundary marked with ampholyte dyes moves toward the cathode; conversely, the boundary drifts towards the anode, and if the transference numbers of hydrogen and hydroxide ions are equal, the boundary is stationary. Recently, the present authors advanced the theory of the moving chemical reaction boundary (MCRB), formulated the MCRBEs, some of which directly manifest relations between the transference numbers of reaction ions such as cobaltic and hydroxide ions and the movement of the MCRB,⁶⁻⁸ and revealed the relationships between the MCRB and Svensson's IEF.¹⁹⁻²¹ These researches show that the transference number is of key importance for Svensson's IEF.

Clearly, from the MCRBEs the authors deduced a series of judgment expressions. These expressions, especially the relative ones, have a significance that implies, in essence, the relative comparison of transference numbers (or fluxes) of positive and negative reaction ions in an MCRB or an IEF. With the simple expressions, the performance of the comparisons can be achieved very easily.

The judgment expressions are of validity for judging the movement of an MCRB, including both precipitate and neutralization reaction boundaries. As shown in Table 1, the predictions with the expressions are qualitatively in coincidence with the experiments from Nos. 1-8, and quantitatively in agreement with those of the stationary neutralization reaction boundary by Bocek's group.⁵

Judgment expressions are of usefulness and convenience for comparisons between the transference numbers of reaction ions in the precipitate reaction boundary, stationary electrolysis and in Svensson's IEF. With those

expressions, one can, conveniently and effortlessly, study the transference numbers of hydrogen and hydroxide ions in stationary electrolysis and Svensson's IEF and reveal the dynamical mechanism of the IEF, as has been shown by Ref. 20 and the calculations in Section 4.2.

In our previous work¹⁹ we inferred that the equal (or quasi-equal) fluxes (or transference numbers) of hydrogen ion and hydroxide ions must be present in stationary electrolysis and Svensson's IEF. This inference has been partly demonstrated with the analyses of transference numbers of hydrogen and hydroxide ions in the reaction electrolytes of HCl-NaOH.²⁰ The results in this report prove that values of R_t from Figs. 2 to 7 are all less than 4%, a value very near to zero and a better value in comparison with the results (the highest values reach 7%) in Ref. 20. We will also verify the existence of the equal (or quasi-equal) fluxes of hydrogen and hydroxide ions in some systems of weak reaction electrolytes. We will demonstrate that it is the self-correction effect that causes the quite constant value of R_t regardless of whether the concentration of the positive reaction electrolyte (e.g HCl) is high or low, or the concentration of negative reaction electrolyte such as NaOH is high or low, and regardless of whether the temperatures of the reaction electrolytes are high or low.

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