ChE-402: Diffusion and Mass Transfer

Lecture 13

Intended Learning Outcome

- To analyze diffusion of ions under applied electric field using the Nernst-Plank equation.
- To analyze the effect of ion charge on diffusion.

Exercise problem

Can the flux of an ion decrease if one increases the electric field ?

A. No, flux will always increase.
B. Flux is not a function of electric field.
C. Can decrease in some cases.
D. Flux will always decrease when electric field is increased.

Exercise problem

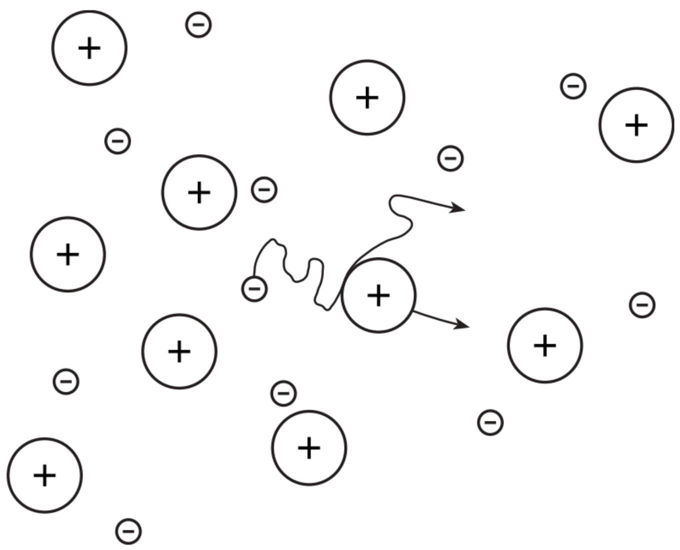
An ion is moving in a liquid under applied chemical potential gradient (concentration difference) and electric field. What would NOT determine its velocity?

A. Viscosity of the liquid.
B. Ion size
C. Diffusivity of a neutral molecule that is also dissolved in the liquid.
D. Ion charge

Coupled diffusion of ions in dilute solution

$$\begin{pmatrix}\text{ion}\\\text{velocity}\end{pmatrix} = \begin{pmatrix}\text{ion}\\\text{mobility}\end{pmatrix}\begin{pmatrix}\text{chemical}\\\text{forces}\end{pmatrix} + \begin{pmatrix}\text{electrical}\\\text{forces}\end{pmatrix}$$

$$v_i = -u_i(\nabla\mu_i + z_i F \nabla\psi)$$



u_i = representation of ion mobility $= \frac{1}{6\pi\eta r} = \frac{1}{f}$

z_i = charge on ion

F = Faraday constant = eN_A

$\nabla\psi$ = electrostatic potential gradient

Coupled diffusion of ions in dilute solution

$$v_i = -u_i(\nabla \mu_i + z_i F \nabla \psi)$$

$$\Rightarrow v_i = -u_i\left(\frac{RT}{c_i}\nabla c_i + z_i F \nabla \psi\right)$$

$$\Rightarrow c_i v_i = -u_i RT\left(\nabla c_i + z_i c_i \frac{F \nabla \psi}{RT}\right)$$

$$\Rightarrow J_i = -u_i RT\left(\nabla c_i + z_i c_i \frac{F \nabla \psi}{RT}\right)$$

$$\mu_i = \mu_{i,0} + RT \ln \frac{P_i}{P}$$

$$\mu_i = \mu_{i,0} + RT \ln \frac{c_i}{c}$$

$$\nabla \mu_i = RT \nabla \ln c_i = \frac{RT}{c_i} \nabla c_i$$

$$N_i = c_i v_i$$

In the absence of convective flux (dilute solution)

$$J_i = N_i = c_i v_i$$

Coupled diffusion of ions in dilute solution

$$\Rightarrow J_i = -u_i RT\left(\nabla c_i + z_i c_i \frac{F\nabla\psi}{RT}\right)$$

$$u_i = \text{ion mobility} = \frac{1}{6\pi\eta r} = \frac{1}{f}$$

$$u_i RT = \frac{RT}{6\pi\eta r} = \frac{RT}{f} = D_i$$

$$\Rightarrow J_i = -D_i\left(\nabla c_i + z_i c_i \frac{F\nabla\psi}{RT}\right)$$

Nernst-Plank Equation

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Exercise problem

NaCl (ionized form Na+, Cl-) is diffusing in a liquid under applied chemical potential gradient (concentration difference) and electric field. You decided to remove electric field (voltage). Will the measured current become zero ?

A. Yes, current will be zero as there is no electric field.
B. Current may not be zero
C. Current does not depend on electric field.
D. None of the above.

Case of strong 1:1 electrolyte (for example NaCl)

Although the concentrations of ions may vary through the solutions, the concentrations and the concentration gradients of anions and cations are equal everywhere because of electroneutrality.

Species 1: cation   Species 2: anion

$$c_1 = c_2$$

$$\nabla c_1 = \nabla c_2$$

$$J_1 \neq J_2$$

When a current density *i* is maintained, $J_1 - J_2 = \frac{i}{|z|}$

$$J_i = -D_i\left(\nabla c_i + z_i c_i \frac{F\nabla\psi}{RT}\right)$$

z =1 for Na^+, and -1 for Cl^-

i is positive when it flows from positive to negative electrode

Applying Nernst-Plank equation for cations and anions

$$J_1 = -D_1\left(\nabla c_1 + |z|c_1 \frac{F\nabla\psi}{RT}\right) \qquad J_2 = -D_2\left(\nabla c_2 - |z|c_2 \frac{F\nabla\psi}{RT}\right)$$

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Case of strong 1:1 electrolyte (for example NaCl)

$$J_1 - J_2 = \frac{i}{|z|} \qquad J_1 = -D_1\left(\nabla c_1 + |z|c_1\frac{F\nabla\psi}{RT}\right) \qquad J_2 = -D_2\left(\nabla c_2 - |z|c_2\frac{F\nabla\psi}{RT}\right)$$

$$\Rightarrow \frac{i}{|z|} = (D_2\nabla c_2 - D_1\nabla c_1) - (D_1c_1 + D_2c_2)|z|\frac{F\nabla\psi}{RT}$$

Current is not zero when the electrostatic potential is zero

We can now try to remove the electrostatic potential in the flux equation

$$|z|\frac{F\nabla\psi}{RT} = -\frac{\frac{i}{|z|} - (D_2\nabla c_2 - D_1\nabla c_1)}{(D_1c_1 + D_2c_2)}$$

Electrostatic potential is not zero when i=0

$$\Rightarrow J_1 = -D_1\left(\nabla c_1 - c_1\frac{\frac{i}{|z|} - (D_2\nabla c_2 - D_1\nabla c_1)}{(D_1c_1 + D_2c_2)}\right)$$

Case of strong 1:1 electrolyte (for example NaCl)

$$J_1 = -D_1\left(\nabla c_1 - c_1 \frac{\frac{i}{|z|} - (D_2 \nabla c_2 - D_1 \nabla c_1)}{(D_1 c_1 + D_2 c_2)}\right)$$

$$\Rightarrow J_1 = -D_1\left(\frac{\nabla c_1(\cancel{D_1 c_1} + D_2 c_2) - c_1 \frac{i}{|z|} + c_1(D_2 \nabla c_2 - \cancel{D_1 \nabla c_1})}{(D_1 c_1 + D_2 c_2)}\right)$$

$$c_1 = c_2$$

$$\nabla c_1 = \nabla c_2$$

$$\Rightarrow J_1 = -D_1\left(\frac{D_2 \nabla c_1 - \frac{i}{|z|} + D_2 \nabla c_1}{D_1 + D_2}\right)$$

$$\Rightarrow J_1 = -\left[\frac{2D_1 D_2}{D_1 + D_2}\right] \nabla c_1 + \left[\frac{D_1}{D_1 + D_2}\right] \frac{i}{|z|}$$

Case of strong 1:1 electrolyte (for example NaCl)

$$J_1 = -\left[\frac{2D_1D_2}{D_1+D_2}\right]\nabla c_1 + \left[\frac{D_1}{D_1+D_2}\right]\frac{i}{|z|} \qquad J_2 = -\left[\frac{2D_1D_2}{D_1+D_2}\right]\nabla c_2 + \left[\frac{D_2}{D_1+D_2}\right]\frac{-i}{|z|}$$

Limit 1: i = 0

$$J_1 = -\left[\frac{2D_1D_2}{D_1+D_2}\right]\nabla c_1$$

$$J_1 = -\left[\frac{2}{1/D_1+1/D_2}\right]\nabla c_1$$

$$J_1 = -D_{eff}\nabla c_1$$

Slow moving species will dominate transport

Also, $J_1 = J_2$

Limit 2: solution is well mixed

$$J_1 = \left[\frac{D_1}{D_1+D_2}\right]\frac{i}{|z|} = t_1\frac{i}{|z|}$$

$$J_2 = \left[\frac{D_2}{D_1+D_2}\right]\frac{-i}{|z|} = t_2\frac{-i}{|z|}$$

t_i is called transference number

Fast moving ion will mainly carry current

$$J_1 \neq J_2$$

Case of strong non 1:1 electrolyte (for example $CaCl_2$)

c_T = 1M, $CaCl_2$ | c_1 = 1M Ca^{+2} | c_2 = 2M Cl^{-1}

$z_1 = 2$ | $z_2 = -1$

$$z_1 c_1 = -z_2 c_2 \qquad z_1 \nabla c_1 = -z_2 \nabla c_2$$

We can apply the Nernst-Planck equation, and equate flux to current to find new equation

$$J_i = -D_i\left(\nabla c_i + z_i c_i \frac{F \nabla \psi}{RT}\right) \qquad z_1 J_1 + z_2 J_2 = i$$

$$\Rightarrow J_1 = -\left[\frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] \nabla c_1 + \left[\frac{D_1 z_1 c_1}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] i$$

Reduces to our previous result when $|z_1| = |z_2|$

$$J_1 = -\left[\frac{2 D_1 D_2}{D_1 + D_2}\right] \nabla c_1 + \left[\frac{D_1}{D_1 + D_2}\right] \frac{i}{|z|}$$

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Proof:

$$z_1 J_1 + z_2 J_2 = i$$

$$J_1 = -D_1\left(\nabla c_1 + z_1 c_1 \frac{F\nabla\psi}{RT}\right) \qquad J_2 = -D_2\left(\nabla c_2 + z_2 c_2 \frac{F\nabla\psi}{RT}\right)$$

$$\Rightarrow i = -(z_2 D_2 \nabla c_2 + z_1 D_1 \nabla c_1) - (z_1^2 D_1 c_1 + z_2^2 D_2 c_2)\frac{F\nabla\psi}{RT}$$

We can now try to remove the electrostatic potential in the flux equation

$$\frac{F\nabla\psi}{RT} = -\frac{i + (z_2 D_2 \nabla c_2 + z_1 D_1 \nabla c_1)}{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)}$$

$$\Rightarrow J_1 = -D_1\left(\nabla c_1 - z_1 c_1 \frac{i + (z_2 D_2 \nabla c_2 + z_1 D_1 \nabla c_1)}{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)}\right)$$

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Proof:

$$J_1 = -D_1\left(\nabla c_1 - z_1 c_1 \frac{i + (z_2 D_2 \nabla c_2 + z_1 D_1 \nabla c_1)}{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)}\right)$$

$$\Rightarrow J_1 = -D_1\left(\frac{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)\nabla c_1 - z_1 c_1\, i - z_1 c_1 (z_2 D_2 \nabla c_2 + z_1 D_1 \nabla c_1)}{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)}\right)$$

$$\Rightarrow J_1 = -D_1\left(\frac{z_2^2 D_2 c_2 \nabla c_1 - z_1 c_1\, i - z_1 z_2 D_2 c_1 \nabla c_2}{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)}\right)$$

$$z_1 c_1 = -z_2 c_2$$

$$z_1 \nabla c_1 = -z_2 \nabla c_2$$

$$\Rightarrow J_1 = -D_1\left(\frac{z_2^2 D_2 c_2 \nabla c_1 - z_1 c_1\, i + z_1^2 D_2 c_1 \nabla c_1}{(z_1^2 D_1 c_1 + z_2^2 D_2 c_2)}\right)$$

$$\Rightarrow J_1 = -\left[\frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right]\nabla c_1 + \left[\frac{D_1 z_1 c_1}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2))}\right] i$$

Case of strong non 1:1 electrolyte (for example $CaCl_2$)

$$J_1 = -\left[\frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] \nabla c_1 + \left[\frac{D_1 z_1 c_1}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] i$$

When $i = 0$

$$J_1 = -\left[\frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] \nabla c_1 \qquad \Rightarrow J_1 = -\left[\frac{(z_1^2 c_1 + z_2^2 c_2)}{\left(\frac{z_1^2 c_1}{D_2} + \frac{z_2^2 c_2}{D_1}\right)}\right] \nabla c_1$$

Total electrolyte flux = $J_T = J_1/|z_2| = J_2/|z_1|$

Total electrolyte concentration = $c_T = c_1/|z_2| = c_2/|z_1|$

c_T = 1M, $CaCl_2$

c_1 = 1M Ca^{+2} $\quad$ c_2 = 2M Cl^{-1}

$|z_1| = 2$ $\quad$ $|z_2| = 1$

$$\Rightarrow J_T = -\left[\frac{(|z_1| + |z_2|)}{\left(\frac{|z_1|}{D_2} + \frac{|z_2|}{D_1}\right)}\right] \nabla c_T$$

- Slow moving species is likely to dominate transport
- If fast species has lower charge, it can reduce the domination of slow species.

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Case of strong non 1:1 electrolyte (for example $CaCl_2$)

$$J_1 = -\left[\frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] \nabla c_1 + \left[\frac{D_1 z_1 c_1}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] i$$

Well-mixed case

$$J_1 = \left[\frac{D_1 z_1 c_1}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] i$$

- Fast moving species is likely to carry current

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Exercise Problem 1

Calculate the effective diffusion coefficient for HCl in water at 25 ºC, neglecting i

Calculate the transference number for proton and Cl^- ion

Table 6.1-1 *Diffusion coefficients of ions in water at 25 °C*

Cation	D	Anion	D
H^+	9.31	OH^-	5.28
Li^+	1.03	F^-	1.47
Na^+	1.33	Cl^-	2.03
K^+	1.96	Br^-	2.08
Rb^+	2.07	I^-	2.05
Cs^+	2.06	NO_3^-	1.90
Ag^+	1.65	CH_3COO^-	1.09
NH_4^+	1.96	$CH_3CH_2COO^-$	0.95
$N(C_4H_9)_4^+$	0.52	$B(C_6H_5)_4^-$	0.53
Ca^{2+}	0.79	SO_4^{2-}	1.06
Mg^{2+}	0.71	CO_3^{2-}	0.92
La^{3+}	0.62	$Fe(CN)_6^{3-}$	0.98

Note: Values at infinite dilution in 10^{-5} cm^2/sec. Calculated from data of Robinson and Stokes (1960).

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Exercise problem 2

Calculate the diffusion coefficient for 0.001 M $LaCl_3$ in water at 25 ºC in the absence of a current flow.

Table 6.1-1 *Diffusion coefficients of ions in water at 25 °C*

Cation	*D*	Anion	*D*
H^+	9.31	OH^-	5.28
Li^+	1.03	F^-	1.47
Na^+	1.33	Cl^-	2.03
K^+	1.96	Br^-	2.08
Rb^+	2.07	I^-	2.05
Cs^+	2.06	NO_3^-	1.90
Ag^+	1.65	CH_3COO^-	1.09
NH_4^+	1.96	$CH_3CH_2COO^-$	0.95
$N(C_4H_9)_4^+$	0.52	$B(C_6H_5)_4^-$	0.53
Ca^{2+}	0.79	SO_4^{2-}	1.06
Mg^{2+}	0.71	CO_3^{2-}	0.92
La^{3+}	0.62	$Fe(CN)_6^{3-}$	0.98

Note: Values at infinite dilution in 10^{-5} cm^2/sec. Calculated from data of Robinson and Stokes (1960).

Exercise problem 3

Calculate the diffusion coefficient for La^{+3} at 25 ºC in absence of current when we also have 1 M NaCl in addition to 0.001 M $LaCl_3$. Assume negligible interaction of Na^+ with La^+.

Table 6.1-1 *Diffusion coefficients of ions in water at 25 °C*

Cation	*D*	Anion	*D*
H^+	9.31	OH^-	5.28
Li^+	1.03	F^-	1.47
Na^+	1.33	Cl^-	2.03
K^+	1.96	Br^-	2.08
Rb^+	2.07	I^-	2.05
Cs^+	2.06	NO_3^-	1.90
Ag^+	1.65	CH_3COO^-	1.09
NH_4^+	1.96	$CH_3CH_2COO^-$	0.95
$N(C_4H_9)_4^+$	0.52	$B(C_6H_5)_4^-$	0.53
Ca^{2+}	0.79	SO_4^{2-}	1.06
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Note: Values at infinite dilution in 10^{-5} cm^2/sec. Calculated from data of Robinson and Stokes (1960).

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