Exercise Problem 1

Calculate the effective diffusion coefficient for HCl in water at 25 °C, 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).

Solution

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

$$D_{eff} = \left[\frac{2}{1/D_1 + 1/D_2}\right] = \left[\frac{2 * 10^{-5}}{1/9.31 + 1/2.03}\right] = 3.33 * 10^{-5} \ \mathrm{cm^2/s}$$

In absence of current, diffusion is restricted by slower moving ion (Cl^-)

Calculate the transference number for proton and Cl^- ion

$$t_1 = \left[\frac{D_1}{D_1 + D_2}\right] = \left[\frac{9.31}{9.31 + 2.03}\right] = 0.82$$

$$t_2 = \left[\frac{D_2}{D_1 + D_2}\right] = \left[\frac{2.03}{9.31 + 2.03}\right] = 0.18$$

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

The current is mainly carried by H^+ (82%)

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).

$$J_T = -\left[\frac{(|z_1| + |z_2|)}{\left(\frac{|z_1|}{D_2} + \frac{|z_2|}{D_1}\right)}\right]\nabla c_T \qquad D_{eff} = \left[\frac{(|z_1| + |z_2|)}{\left(\frac{|z_1|}{D_2} + \frac{|z_2|}{D_1}\right)}\right] = 1.29 * 10^{-5}\ \text{cm}^2/\text{s}$$

Faster Cl^- but +3 charge on La^{+3}

EPFL

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
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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).

La^{3+} $\qquad$ Cl^-

$c_1 = 0.001$ M $\qquad$ $c_2 = 1 + 3 * 0.001 = 1.003$ M

When $i = 0$

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

$$\Rightarrow D_{eff,\,La^{3+}} = \left[\frac{D_1 D_2 (z_1^2 c_1 + z_2^2 c_2)}{(D_1 z_1^2 c_1 + D_2 z_2^2 c_2)}\right] = \left[\frac{0.62 * 2.03(9 * 0.001 + 1 * 1.003)}{(0.62 * 9 * 0.001 + 2.03 * 1 * 1.003)}\right] = 0.62 * 10^{-5}\ cm^2/s$$

The diffusion of the lanthanum chloride in this solution is the same as the solitary lanthanum ion.