FT II – Difusão de Eletrolitos

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Conteúdo

1 Velocidade do ion

$$\boldsymbol{v_i = u_i \left(\nabla \mu_i + z_i \, F \, \nabla \Psi \right)}$$

$$\mu_i = \mu_i^0 + RT \, \ln a_i; \qquad \nabla \mu_i = \frac{RT}{c_i} \, \nabla c_i; \qquad \mathscr{D}_i = u_i \, RT \quad \text{(Relação Einstein)}$$

$$-J_i = c_i \, v_i = \mathscr{D}$$

μ_i: Mobilidade do ion

$\nabla \mu_i$: Potencial químico

z_i: Carga ionica

F: $9.649 \, \mathrm{E}^4$ C/mol (Constante de Faraday)

Ψ: Potencial eletrostático

u_i: Propriedade física do ion: $u_i \sim (6 \, \pi \, \eta \, R_0)^{-1}$ (Stokes-Einstein)

R_0 Raio efetivo (Efeitos solvatação)

2 Equação Nerst-Plank

$$-\boldsymbol{J_i} = \mathscr{D}\left(\boldsymbol{\nabla c_i} + \boldsymbol{c_i}\,\boldsymbol{z_i}\,\frac{\boldsymbol{F}\ \boldsymbol{\nabla \Psi}}{\boldsymbol{RT}}\right)$$

- Soluções Diluidas

Demonstration

$$-J_i = -c_i\,v_i = -c_i\ \left(-u_i\left(\nabla \mu_i + z_i F\ \nabla \Psi\right)\right) = c_i\,u_i\ \left(\left(\frac{RT}{c_i}\ \nabla c_i\right) + z_i F\ \nabla \Psi\right) =$$

$$= \mathscr{D}\ \left(\nabla c_i + z_i\,c_i\,\frac{F\ \nabla \Psi}{RT}\right);$$

$$\mu_i = \mu_i^0 + RT\ \ln a_i \wedge a_i \xrightarrow{\text{Sol diluidas}} c_i \implies \nabla \mu_i = \frac{RT}{c_i}\ \nabla c_i;$$

$\mathscr{D}_i = u_i\,RT$ (Relação Einsntein)

3 Tabela dos coeficientes de difusão de ions em agua a 25°C

Cation	$\mathscr{D}_i$	Anion	$\mathscr{D}_i$
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^-	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 $1\,\mathrm{E}^{-5}\ \mathrm{cm}^2/\mathrm{s}$. Calculated from data of Robinson and Stokes (1960)

3.1 Eletrolitos Fortes (1:1)

$$\boldsymbol{J_+ - J_- = i/|z|}$$

i Densidade de corrente

z Carga ionica

$+$ Cation

$-$ Anion

3.2 Fluxo dos ioes

$$\boldsymbol{J_1 = -\frac{2\,\mathscr{D}_2\ \nabla c_1 + i/|z|}{1 + \mathscr{D}_2/\mathscr{D}_1}}$$

$$J_+ = J_- \impliedby i = 0 \quad \text{(Sem corrente)}$$

$$J_1 = \frac{i/|z|}{1 + \mathscr{D}_2/\mathscr{D}_1} \impliedby \nabla c = 0 \quad \text{(muito agitado)}$$

$$\mathscr{D} = \frac{n}{\sum_{i=1}^{n} \mathscr{D}_i^{-1}} = H(\mathscr{D}_i); \qquad t_i = \frac{\mathscr{D}_i}{\sum \mathscr{D}_j}$$

t_i Numero de transferencia (fração da corrente transportada pelo ion i)

H Média harmonica

Exemplo 1

Difusão Qual o valor do coeficiente de difusão a $25\,^{\circ}\mathrm{C}$ de HCl em água? Calcule o nº de transferência para o protão nestas condições.

Resposta

$$\mathrm{HCl} + \mathrm{H_2O} \longrightarrow \mathrm{H_3O^+} + \mathrm{Cl^-}$$

Coeficiente de difusão

$$\mathscr{D} = \frac{2}{\mathscr{D}_{\mathrm{H_3O^+}}^{-1} + \mathscr{D}_{\mathrm{Cl^-}}^{-1}} \cong \frac{2}{9.31^{-1} + 2.03^{-1}} \cong 3.333\,\mathrm{cm^2/s};$$

Numero de transferencia para $\mathrm{H_3O^+}$

$$t_{\mathrm{H_3O^+}} = \frac{\mathscr{D}_{\mathrm{H_3O^+}}}{\mathscr{D}_{\mathrm{H_3O^+}} + \mathscr{D}_{\mathrm{Cl^-}}} = \left(1 + \mathscr{D}_{\mathrm{Cl^-}}/\mathscr{D}_{\mathrm{H_3O^+}}\right)^{-1} = (1 + 2.03/9.31)^{-1} \cong$$

$$\cong 82.099\,\%$$

4 Ionic conductivity and diffusion at infinite dilution

Inorganic Cations	$\Lambda_{\pm}$ / $\mathrm{E^{-4}\,m^2\,S/mol}$	$\mathscr{D}$ / $\mathrm{E^{-5}\,cm^2/s}$
Ag^{+}	61.90	1.648
$\frac{1}{3}\,Al^{3+}$	19.00	0.541
$\frac{1}{2}\,Ba^{2+}$	63.60	0.847
$\frac{1}{2}\,Be^{2+}$	45.00	0.599
$\frac{1}{2}\,Ca^{2+}$	59.47	0.792
$\frac{1}{2}\,Cd^{2+}$	54.00	0.719
$\frac{1}{3}\,Ce^{3+}$	69.80	0.620
$\frac{1}{2}\,Co^{2+}$	55.00	0.732
$\frac{1}{3}\,[Co(NH_3)_6]^{3+}$	101.90	0.904
$\frac{1}{3}\,[Co(en)_3]^{6+}$	74.70	0.663
$\frac{1}{6}\,[Co_2(trien)_3]^{6+}$	69.00	0.306
$\frac{1}{3}\,Cr^{3+}$	67.00	0.595
Cs^{+}	77.20	2.056

Inorganic Anions	$\Lambda_{\pm}$ / $\mathrm{E^{-4}\,m^2\,S/mol}$	$\mathscr{D}$ / $\mathrm{E^{-5}\,cm^2/s}$
$Au(CN)_2^{-}$	50.00	1.331
$Au(CN)_4^{-}$	36.00	0.959
$B(C_6H_5)_4^{-}$	21.00	0.559
Br^{-}	78.10	2.080
Br_3^{-}	43.00	1.145
BrO_3^{-}	55.70	1.483
CN^{-}	78.00	2.077
CNO^{-}	64.60	1.720
$\frac{1}{2}\,CO_3^{2-}$	69.30	0.923
Cl^{-}	76.31	2.032
ClO_2^{-}	52.00	1.385
ClO_3^{-}	64.60	1.720
ClO_4^{-}	67.30	1.792
$\frac{1}{3}\,[Co(CN)_6]^{3-}$	98.90	0.878
$\frac{1}{2}\,CrO_4^{2-}$	85.00	1.132