

Exercise problem 1

Helium/Argon mixture is diffusing through a 100 nm pore at 1 bar and 25 °C. Report $D_{\text{molecular}}$, D_K and D_{vis} for helium at 1 bar and 10 bar. Calculate D_{total} at 1 and 10 bar pressures.

$$D_{\text{He,Ar}} = 0.7 \text{ cm}^2\text{s}^{-1} \text{ at 1 bar}$$

At 1 bar,

$$D_K = \sqrt{\frac{8k_B T d^2}{9\pi m}}$$

$$D_{\text{vis}} = \frac{d^2}{32\eta_1} P_1$$

$$\eta_{\text{He}} = 2 * 10^{-5} \text{ Pa s}$$

$$D_{\text{molecular}} = 0.7 \text{ cm}^2/\text{s}$$

$$D_K = \sqrt{\frac{8 * 1.38 * 10^{-23} * 298 * (100 * 10^{-9})^2}{9 * 3.14 * 0.004 / (6.022 * 10^{23})}} = 0.419 \text{ cm}^2/\text{s}$$

$$D_{\text{vis}} = \frac{(100 * 10^{-9})^2}{32 * 2 * 10^{-5}} * 10^5 = 0.016 \text{ cm}^2/\text{s}$$

$$1/D = 1/D_K + 1/D_{\text{molecular}} \Rightarrow D = 0.262 \text{ cm}^2/\text{s}$$

$$D_{\text{Total}} = D + D_{\text{vis}} = 0.278 \text{ cm}^2/\text{s}$$

At 10 bar,

$$D_{\text{molecular}} = 0.7/10 = 0.07 \text{ cm}^2/\text{s}$$

$$D_K = 0.419 \text{ cm}^2/\text{s}$$

$$D_{\text{vis}} = 0.016 * 10 = 0.16 \text{ cm}^2/\text{s}$$

$$1/D = 1/D_K + 1/D_{\text{molecular}} \Rightarrow D = 0.06 \text{ cm}^2/\text{s}$$

$$D_{\text{Total}} = D + D_{\text{vis}} = 0.22 \text{ cm}^2/\text{s}$$

Exercise Problem 2

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 ₃ COO ⁻	1.09
NH ₄ ⁺	1.96	CH ₃ CH ₂ COO ⁻	0.95
N(C ₄ H ₉) ₄ ⁺	0.52	B(C ₆ H 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 cm²/sec. Calculated from data of Robinson and Stokes (1960).

Solution

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

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

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 cm²/sec. Calculated from data of Robinson and Stokes (1960).

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

Exercise problem 3

Calculate the diffusion coefficient for 0.001 M LaCl₃ in water at 25 °C 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
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Note: Values at infinite dilution in 10⁻⁵ cm²/sec. Calculated from data of Robinson and Stokes (1960).

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

Faster Cl⁻ but +3 charge on La⁺³