Problem 12-06 Membrane equilibria, Donnan potential

At pH = 7.3 a protein carries charge −5. You have an aqueous solution containing 3 mmol dm^{-3} of potassium salt of this protein and at the same time potassium chloride in concentration 0.12 mol dm^{-3}. Both salts are completely dissociated at these conditions. At the temperature of 27 °C you need to reduce the amount of potassium ions in this solution. Calculate

(a) What should be the volume of pure water which you must take to dialysis of 0.1 dm^3 of your protein solution in order that the concentration of K^+ ions in equilibrium dropped to 0.02 mol dm^{-3}.

(b) The Donnan potential in equilibrium.

[(a) $V = 1.15$ dm^3; (b) $E = 17.9$ mV]

Solution:

$(K^+)_5\,P^{5-} = 5\,K^+ + P^{5-}$ $\qquad c_P = 3$ mmol dm^{-3} = 0.003 mol dm^{-3} (we denote $(K^+)_5\,P^{5-} \equiv P$)

$KCl = K^+ + Cl^-$ $\qquad c_1 = 0.12$ mol dm^{-3}

Balance:

	at the beginning		in equilibrium	
	Left	Right	Left	Right
P^{5-}	c_P	0	c_B	0
K^+	$5\,c_P + c_1$	0	$5\,c_B + c_1 - n/V_{Left}$	n/V_{Right}
Cl^-	c_1	0	$c_1 - n/V_{Left}$	n/V_{Right}

n = amount of K^+ and Cl^- ions passing through the membrane

$V_{Left} = 0.1$ dm^3 , $V_{Right} = ?$ dm^3

(a) Equilibrium: $\qquad (c_{K^+}\cdot c_{Cl^-})_{\mathbf{Left}} = (c_{K^+}\cdot c_{Cl^-})_{\mathbf{Right}}$

$$(c_1 - n/V_{Left})\cdot(5\,c_B + c_1 - n/V_{Left}) = (n/V_{Right})\cdot(n/V_{Right})$$

$c_{K^+} = 5\,c_B + c_1 - n/V_{Left} = 0.02$ mol dm^{-3}

$$5\cdot 0.003 + 0.12 - \frac{n}{0{,}1} = 0.02 \quad\Rightarrow\quad n = 0.0115\ ,\quad n/V_{Left} = 0.115$$

$$(0.12 - 0.115)\cdot(5\cdot 0.003 + 0.12 - 0.115) = \left(\frac{0.0115}{V_{Right}}\right)^2$$

$$V_{Right} = \frac{0.0115}{\sqrt{0.005\cdot 0.02}} = 1.15\ \text{dm}^3$$

(b) Ions K^+ and Cl^- pass from the **L**eft to the **R**ight compartment, $z_{K^+} = 1$, $z_{Cl^-} = 1$, $T = 300.15$ K

$$\mu^{\ominus}_{K^+}(p_L) + \boldsymbol{RT}\ln(a_{K^+})_L + z_{K^+}\cdot\boldsymbol{F}\cdot\varphi_L = \mu^{\ominus}_{K^+}(p_R) + \boldsymbol{RT}\ln(a_{K^+})_R + z_{K^+}\cdot\boldsymbol{F}\cdot\varphi_R$$

$$\mu^{\ominus}_{K^+}(p_L) \doteq \mu^{\ominus}_{K^+}(p_R)$$

$$E = \varphi_R - \varphi_L = \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{(a_{K^+})_L}{(a_{K^+})_R} = \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{5\,c_P + c_1 - n/V_{Left}}{n/V_{Right}}$$

$$E = \frac{8.314\cdot 300.15}{96485.3}\cdot\ln\frac{5\cdot 0.003 + 0.12 - 0.0115/0.1}{0.0115/1.15} = 0.01793\ \text{V}$$

or

$$\mu^{\ominus}_{Cl^-}(p_L) + \boldsymbol{RT}\ln(a_{Cl^-})_L - z_{Cl^-}\cdot\boldsymbol{F}\cdot\varphi_L = \mu^{\ominus}_{Cl^-}(p_R) + \boldsymbol{RT}\ln(a_{Cl^-})_R - z_{Cl^-}\cdot\boldsymbol{F}\cdot\varphi_R$$

$$\mu^{\ominus}_{Cl^-}(p_L) \doteq \mu^{\ominus}_{Cl^-}(p_R)$$

$$E = \varphi_R - \varphi_L = \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{(a_{Cl^-})_R}{(a_{Cl^-})_L} = \frac{\boldsymbol{RT}}{\boldsymbol{F}}\ln\frac{n/V_{Right}}{c_1 - n/V_{Right}}$$

$$E = \frac{8.314\cdot 300.15}{96485.3}\cdot\ln\frac{0.0115/1.15}{0.12 - 0.0115/0.1} = 0.01793\ \text{V}$$