

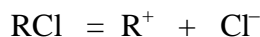
Problem 12-05 Membrane equilibria, Donnan potential

A membrane permeable for ions Ca^{2+} and Cl^- , but not for high-molecular ions R^+ , separates the inner compartment of the dialysis cell at the beginning containing the polyelectrolyte RCl in concentration c_1 and CaCl_2 in concentration $(c_2)_0 = 200 \text{ mmol dm}^{-3}$, from the outer compartment containing only calcium chloride solution in concentration $(c_3)_0 = 300 \text{ mmol dm}^{-3}$. In equilibrium, established at the temperature of 27°C , the concentration of Ca^{2+} in the inner compartment was found to be 230 mmol dm^{-3} . (a) What is the concentration of RCl in the inner compartment? (b) Calculate the equilibrium Donnan potential.

[(a) $c_1 = 125 \text{ mmol dm}^{-3}$; (b) $E = 2.07 \text{ mV}$]

Solution:

$$c(\text{RCl})_{\text{in}, 0} = c_1$$



$$c(\text{CaCl}_2)_{\text{in}, 0} = c_2 = 200 \text{ mmol dm}^{-3}$$



$$c(\text{CaCl}_2)_{\text{out}, 0} = c_3 = 300 \text{ mmol dm}^{-3}$$

$$c(\text{CaCl}_2)_{\text{in, equil}} = c_4 = 230 \text{ mmol dm}^{-3}$$

$$c(\text{CaCl}_2) = c(\text{Ca}^{2+})$$

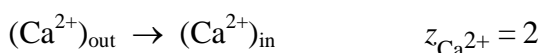
Balance:	at the beginning		in equilibrium	
	in	out	in	out
R^+	c_1	0	c_1	0
Ca^{2+}	c_2	c_3	$c_2 + x$	$c_3 - x$
Cl^-	$2 c_2 + c_1$	$2 c_3$	$2 c_2 + c_1 + 2 x$	$2 c_3 - 2 x$

$$c_4 = 230 \text{ mmol dm}^{-3} = c_2 + x \Rightarrow x = c_4 - c_2 = 230 - 200 = 30 \text{ mmol dm}^{-3}$$

Donnan equilibrium condition for CaCl_2 :

$$\begin{aligned} (c_{\text{Ca}^{2+}})_{\text{in}} \cdot (c_{\text{Cl}^-})_{\text{in}}^2 &= (c_{\text{Ca}^{2+}})_{\text{out}} \cdot (c_{\text{Cl}^-})_{\text{out}}^2 \\ (c_2 + x) \cdot (2 c_2 + c_1 + 2 x)^2 &= (c_3 - x) \cdot (2 c_3 - 2 x)^2 \\ (200 + 30) \cdot (400 + c_1 + 60)^2 &= (300 - 30) \cdot (600 - 60)^2 \\ c_1 &= 125 \text{ mmol dm}^{-3} \end{aligned}$$

(b) Ions Ca^{2+} and Cl^- pass through the membrane from the outer to the inner compartment ($T = 300.15 \text{ K}$)



$$\mu_{\text{Ca}^{2+}}^{\ominus}(p_{\text{out}}) + RT \ln(a_{\text{Ca}^{2+}})_{\text{out}} + z_{\text{Ca}^{2+}} \cdot F \cdot \varphi_{\text{out}} = \mu_{\text{Ca}^{2+}}^{\ominus}(p_{\text{in}}) + RT \ln(a_{\text{Ca}^{2+}})_{\text{in}} + z_{\text{Ca}^{2+}} \cdot F \cdot \varphi_{\text{in}}$$

$$\mu_{\text{Ca}^{2+}}^{\ominus}(p_{\text{out}}) \doteq \mu_{\text{Ca}^{2+}}^{\ominus}(p_{\text{in}})$$

$$E = \varphi_{\text{in}} - \varphi_{\text{out}} = \frac{RT}{2F} \ln \frac{(a_{\text{Ca}^{2+}})_{\text{out}}}{(a_{\text{Ca}^{2+}})_{\text{in}}} = \frac{RT}{2F} \ln \frac{c_3 - x}{c_2 + x}$$

$$E = \frac{8.314 \cdot 300.15}{2 \cdot 96485.3} \cdot \ln \frac{300 - 30}{200 + 30} = 0.00207 \text{ V}$$

or



$$\mu_{\text{Cl}^-}^{\ominus}(p_{\text{out}}) + RT \ln(a_{\text{Cl}^-})_{\text{out}} - z_{\text{Cl}^-} \cdot F \cdot \varphi_{\text{out}} = \mu_{\text{Cl}^-}^{\ominus}(p_{\text{in}}) + RT \ln(a_{\text{Cl}^-})_{\text{in}} - z_{\text{Cl}^-} \cdot F \cdot \varphi_{\text{in}}$$

$$\mu_{\text{Cl}^-}^{\ominus}(p_{\text{out}}) \doteq \mu_{\text{Cl}^-}^{\ominus}(p_{\text{in}})$$

$$E = \varphi_{\text{in}} - \varphi_{\text{out}} = -\frac{RT}{F} \ln \frac{(a_{\text{Cl}^-})_{\text{out}}}{(a_{\text{Cl}^-})_{\text{in}}} = -\frac{RT}{F} \ln \frac{2c_3 - 2x}{2c_2 + c_1 + 2x}$$

$$E = -\frac{8.314 \cdot 300.15}{96485.3} \cdot \ln \frac{600 - 60}{400 + 125 + 60} = 0.00207 \text{ V}$$