Problem 12-08 Membrane hydrolysis

An aqueous solution of a polyelectrolyte $(Na^+)_2R^{2-}$ was dialyzed against pure water. Polyelectrolyte is completely dissociated. Measurement of pH has shown the value of 5.366 for equilibrium solution. Calculate

(a) pH in the compartment initially containing only pure water,

(b) the initial concentration of the polyelectrolyte.

Ionic product of water is for the standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}, is $K_w = 10^{-14}$.

[(a) pH = 8.634 ; (b) 0.004 mol dm^{-3}]

Solution:

$(Na^+)_2R^{2-} = 2\ Na^+ + R^{2-}$ $\qquad c = ?$

$pH_I = 5.366$

$K_w = 10^{-14}$

Balance:	at the beginning		in equilibrium	
	I	II	I	II
R^{2-}	c	0	c	0
Na^+	$2\,c$	0	$2\,c - x$	x
OH^-			K_w/x	x
H^+			x	K_w/x

Donnan equilibrium condition for NaOH:

$$(c_{Na^+})_I \cdot (c_{OH^-})_I = (c_{Na^+})_{II} \cdot (c_{OH^-})_{II}$$

$$(2\,c - x)_I \cdot (c_{OH^-})_I = x^2$$

$$(c_{OH^-})_I \cdot (c_{H^+})_I = K_w = 10^{-14} \quad \Rightarrow \quad (c_{OH^-})_I = \frac{K_w}{(c_{H^+})_I} = \frac{K_w}{x}$$

$$(2\,c - x) \cdot \frac{K_w}{x} = x^2$$

(a) In compartmen I : $\quad pH_I = 5.366 \quad \Rightarrow \quad -\log x = 5.366 \quad \Rightarrow \quad x = 4.30526 \cdot 10^{-6}$

In compartmen II : $\quad (c_{OH^-})_{II} = x$

$$(c_{H^+})_{II} = \frac{K_w}{(c_{OH^-})_{II}} = \frac{K_w}{x}$$

$$pH_{II} = -\log (c_{H^+})_{II} = -\log \frac{K_w}{x} = 14 + \log 4.30526 \cdot 10^{-6} = 8.634$$

(b) $\qquad (2\,c - x) \cdot \frac{K_w}{x} = x^2$

$$c = \frac{1}{2} \cdot \left(\frac{x^3}{K_v} + x \right) = \frac{1}{2} \cdot \left(\frac{(4.30526 \cdot 10^{-6})^3}{1 \cdot 10^{-14}} + 4.30526 \cdot 10^{-6} \right) = 0.004 \text{ mol dm}^{-3}$$