Problem 12-07 Membrane equilibria, Donnan potential

To 0.1 dm^3 of the solution of pepsin $(Cu^{2+})_{10}\,P^{20-}$ of concentration $4{\cdot}10^{-5}$ mol dm^{-3}, such amount of solid $CuSO_4$ was added, that the resulting concentration of the sulphate ions was $5{\cdot}10^{-3}$ mol dm^{-3}. This solution was then dialyzed at 32°C against 0.4 dm^3 of pure water. Calculate the equilibrium concentrations of Cu^{2+} and SO_4^{2-} ions in the pepsin solution and the Donnan potential. All electrolytes are completely dissociated.

[$c_{Cu^{2+}} = 1.25{\cdot}10^{-3}$ mol dm^{-3}; $c_{SO_4^{2-}} = 8.55{\cdot}10^{-4}$ mol dm^{-3}; $E = -2.522$ mV]

Solution:

$(Cu^{2+})_{10}\,P^{20-} = 10\,Cu^{2+} + P^{20-}$ $\qquad c_P = 4{\cdot}10^{-5}$ mol dm^{-3} $\qquad$ (we denote $(Cu^{2+})_{10}\,P^{20-} \equiv P$)

$CuSO_4 = Cu^{2+} + SO_4^{2-}$ $\qquad c_1 = 5{\cdot}10^{-3}$ mol dm^{-3}

Balance:	at the beginning		in equilibrium	
	Left	Right	Left	Right
P^{20-}	c_P	0	c_P	0
Cu^{2+}	$10\,c_P + c_1$	0	$10\,c_P + c_1 - n/V_{Left}$	n/V_{Right}
SO_4^{2-}	c_1	0	$c_1 - n/V_{Left}$	n/V_{Right}

$V_{Left} = 0.1\ dm^3$, $V_{Right} = 0.4\ dm^3$

n = amount of passing ions Cu^{2+} a SO_4^{2-}

Donnan equilibrium: $\qquad (c_{Cu^{2+}} \cdot c_{SO_4^{2-}})_{Left} = (c_{Cu^{2+}} \cdot c_{SO_4^{2-}})_{Right}$

$$(c_1 - n/V_{Left}){\cdot}(10\,c_P + c_1 - n/V_{Left}) = (n/V_{Right}) \cdot (n/V_{Right})$$

$n/V_{Left} = n/0.1 = 10\,n$

$n/V_{Right} = n/0.4 = 2.5\,n$

$$c_1{\cdot}(10\,c_P + c_1) - 10\,n \cdot (10\,c_P + c_1) - 10\,n \cdot c_1 + (10\,n)^2 = (2.5\,n)^2$$

$$(100 - 6.25)\,n^2 - 10\,n \cdot (10\,c_P + 2\,c_1) + c_1{\cdot}(10\,c_P + c_1) = 0$$

$$93.75\,n^2 - 10\,n \cdot (10{\cdot}4{\cdot}10^{-5} + 2{\cdot}5{\cdot}10^{-3}) + 5{\cdot}10^{-3}{\cdot}(10{\cdot}4{\cdot}10^{-5} + 5{\cdot}10^{-3}) = 0$$

$$93.75\,n^2 - 0.104\,n + 2.7{\cdot}10^{-5} = 0$$

$$n = \frac{-0.104 \pm (0.104^2 - 4\cdot 93.75\cdot 2.7\cdot 10^{-5})^{1/2}}{2\cdot 93.75}$$

1. $n = 6.95{\cdot}10^{-4}$ ..... $(c_{Cu^{2+}})_{Left} = c_1 - n/V_{Left} = 5{\cdot}10^{-3} - 6.95{\cdot}10^{-4}/0.1 = -1.95{\cdot}10^{-3}$ mol dm^{-3}

   this value has no physical meaning

2. $n = 4.1447{\cdot}10^{-4}$ mol

$(c_{Cu^{2+}})_{Left} = c_1 - n/V_{Left} = 5{\cdot}10^{-3} - 4.1447{\cdot}10^{-4}/0.1 = 8.553{\cdot}10^{-4}$ mol dm^{-3}

$(c_{SO_4^{2-}})_{Left} = 10\,c_P + c_1 - n/V_{Left} = 10{\cdot}4{\cdot}10^{-5} + 5{\cdot}10^{-3} - 4.1447{\cdot}10^{-4}/0.1 = 1.2553{\cdot}10^{-3}$ mol dm^{-3}

$(c_{Cu^{2+}})_{Right} = n/V_{Right} = 4.1447{\cdot}10^{-4}/0.4 = 1.036{\cdot}10^{-3}$ mol dm^{-3}

$(c_{SO_4^{2-}})_{Right} = n/V_{Right} = 4.1447{\cdot}10^{-4}/0.4 = 1.036{\cdot}10^{-3}$ mol dm^{-3}

Donnan potential

Ions Cu^{2+} and SO_4^{2-} pass from the Left compartment into the Right one, T = 305.15 K

$$(\mathrm{Cu}^{2+})_{\mathrm{Left}} \rightarrow (\mathrm{Cu}^{2+})_{\mathrm{Right}} \qquad z_{\mathrm{Cu}^{2+}} = 2$$

$$\mu^{\ominus}_{\mathrm{Cu}^{2+}}(p_{\mathrm{Left}}) + \boldsymbol{R}T\ln(a_{\mathrm{Cu}^{2+}})_{\mathrm{Left}} + z_{\mathrm{Cu}^{2+}}\cdot\boldsymbol{F}\cdot\varphi_{\mathrm{Left}} = \mu^{\ominus}_{\mathrm{Cu}^{2+}}(p_{\mathrm{Right}}) + \boldsymbol{R}T\ln(a_{\mathrm{Cu}^{2+}})_{\mathrm{Right}} + z_{\mathrm{Cu}^{2+}}\cdot\boldsymbol{F}\cdot\varphi_{\mathrm{Right}}$$

$$\mu^{\ominus}_{\mathrm{Cu}^{2+}}(p_{\mathrm{Left}}) \doteq \mu^{\ominus}_{\mathrm{Cu}^{2+}}(p_{\mathrm{Right}})$$

$$E = \varphi_{\mathrm{Right}} - \varphi_{\mathrm{Left}} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ \ln\ \frac{(a_{\mathrm{Cu}^{2+}})_{\mathrm{Left}}}{(a_{\mathrm{Cu}^{2+}})_{\mathrm{Right}}} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ln\left(\frac{c_1 - n/V_{\mathrm{Left}}}{n/V_{\mathrm{Right}}}\right)$$

$$E = \frac{8.314\cdot 305.15}{2\cdot 96485.3}\cdot\ln\frac{8.553\cdot 10^{-4}}{4.1447\cdot 10^{-4}/0.4} = -0.002522\ \mathrm{V}$$

or

$$(\mathrm{SO_4}^{2-})_{\mathrm{Left}} \rightarrow (\mathrm{SO_4}^{2-})_{\mathrm{Right}} \qquad z_{\mathrm{SO_4}^{2-}} = 2$$

$$\mu^{\ominus}_{\mathrm{SO}_4^{2-}}(p_{\mathrm{Left}}) + \boldsymbol{R}T\ln(a_{\mathrm{SO}_4^{2-}})_{\mathrm{Left}} - z_{\mathrm{SO}_4^{2-}}\cdot\boldsymbol{F}\cdot\varphi_{\mathrm{Left}} = \mu^{\ominus}_{\mathrm{SO}_4^{2-}}(p_{\mathrm{Right}}) + \boldsymbol{R}T\ln(a_{\mathrm{SO}_4^{2-}})_{\mathrm{Right}} - z_{\mathrm{SO}_4^{2-}}\cdot\boldsymbol{F}\cdot\varphi_{\mathrm{Right}}$$

$$\mu^{\ominus}_{\mathrm{SO}_4^{2-}}(p_{\mathrm{Left}}) \doteq \mu^{\ominus}_{\mathrm{SO}_4^{2-}}(p_{\mathrm{Right}})$$

$$E = \varphi_{\mathrm{Right}} - \varphi_{\mathrm{Left}} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}}\ \ln\ \frac{(a_{\mathrm{SO}_4^{2-}})_{\mathrm{Right}}}{(a_{\mathrm{SO}_4^{2-}})_{\mathrm{Left}}} = \frac{\boldsymbol{R}T}{\boldsymbol{F}}\ln\left(\frac{n/V_{\mathrm{Right}}}{10\,c_{\mathrm{P}} + c_1 - n/V_{\mathrm{Left}}}\right)$$

$$E = \frac{8.314\cdot 305.15}{2\cdot 96485.3}\cdot\ln\frac{4.1447\cdot 10^{-4}/0.4}{1.2553\cdot 10^{-3}} = -0.002522\ \mathrm{V}$$