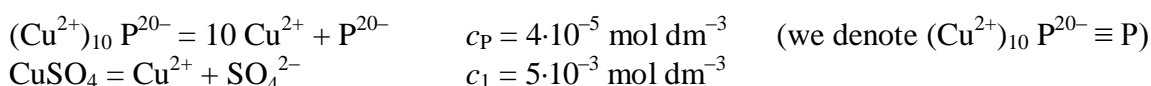


### Problem 12-07 Membrane equilibria, Donnan potential

To 0.1 dm<sup>3</sup> of the solution of pepsin (Cu<sup>2+</sup>)<sub>10</sub> P<sup>20-</sup> of concentration 4·10<sup>-5</sup> mol dm<sup>-3</sup>, such amount of solid CuSO<sub>4</sub> was added, that the resulting concentration of the sulphate ions was 5·10<sup>-3</sup> mol dm<sup>-3</sup>. This solution was then dialyzed at 32°C against 0.4 dm<sup>3</sup> of pure water. Calculate the equilibrium concentrations of Cu<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> ions in the pepsin solution and the Donnan potential. All electrolytes are completely dissociated.

$$[c_{\text{Cu}^{2+}} = 1.25 \cdot 10^{-3} \text{ mol dm}^{-3}; c_{\text{SO}_4^{2-}} = 8.55 \cdot 10^{-4} \text{ mol dm}^{-3}; E = -2.522 \text{ mV}]$$

**Solution:**



<i>Balance:</i>	at the beginning		in equilibrium	
	Left	Right	Left	Right
P <sup>20-</sup>	c <sub>P</sub>	0	c <sub>P</sub>	0
Cu <sup>2+</sup>	10 c <sub>P</sub> + c <sub>1</sub>	0	10 c <sub>P</sub> + c <sub>1</sub> - n/V <sub>Left</sub>	n/V <sub>Right</sub>
SO <sub>4</sub> <sup>2-</sup>	c <sub>1</sub>	0	c <sub>1</sub> - n/V <sub>Left</sub>	n/V <sub>Right</sub>

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

$n$  = amount of passing ions Cu<sup>2+</sup> a SO<sub>4</sub><sup>2-</sup>

**Donnan equilibrium:**

$$(c_{\text{Cu}^{2+}} \cdot c_{\text{SO}_4^{2-}})_{\text{Left}} = (c_{\text{Cu}^{2+}} \cdot c_{\text{SO}_4^{2-}})_{\text{Right}}$$

$$(c_1 - n/V_{\text{Left}}) \cdot (10 c_{\text{P}} + c_1 - n/V_{\text{Left}}) = (n/V_{\text{Right}}) \cdot (n/V_{\text{Right}})$$

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

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

$$c_1 \cdot (10 c_{\text{P}} + c_1) - 10 n \cdot (10 c_{\text{P}} + c_1) - 10 n \cdot c_1 + (10 n)^2 = (2.5 n)^2$$

$$(100 - 6.25) n^2 - 10 n \cdot (10 c_{\text{P}} + 2 c_1) + c_1 \cdot (10 c_{\text{P}} + c_1) = 0$$

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

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

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

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

this value has no physical meaning

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

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

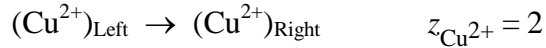
$$(c_{\text{SO}_4^{2-}})_{\text{Left}} = 10 c_{\text{P}} + c_1 - n/V_{\text{Left}} = 10 \cdot 4 \cdot 10^{-5} + 5 \cdot 10^{-3} - 4.1447 \cdot 10^{-4}/0.1 = 1.2553 \cdot 10^{-3} \text{ mol dm}^{-3}$$

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

$$(c_{\text{SO}_4^{2-}})_{\text{Right}} = n/V_{\text{Right}} = 4.1447 \cdot 10^{-4}/0.4 = 1.036 \cdot 10^{-3} \text{ mol dm}^{-3}$$

### Donnan potential

Ions  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$  pass from the Left compartment into the Right one,  $T = 305.15 \text{ K}$



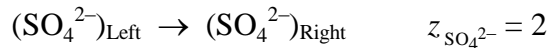
$$\mu_{\text{Cu}^{2+}}^{\ominus}(p_{\text{Left}}) + RT \ln (a_{\text{Cu}^{2+}})_{\text{Left}} + z_{\text{Cu}^{2+}} \cdot F \cdot \phi_{\text{Left}} = \mu_{\text{Cu}^{2+}}^{\ominus}(p_{\text{Right}}) + RT \ln (a_{\text{Cu}^{2+}})_{\text{Right}} + z_{\text{Cu}^{2+}} \cdot F \cdot \phi_{\text{Right}}$$

$$\mu_{\text{Cu}^{2+}}^{\ominus}(p_{\text{Left}}) \doteq \mu_{\text{Cu}^{2+}}^{\ominus}(p_{\text{Right}})$$

$$E = \phi_{\text{Right}} - \phi_{\text{Left}} = \frac{RT}{2F} \ln \frac{(a_{\text{Cu}^{2+}})_{\text{Left}}}{(a_{\text{Cu}^{2+}})_{\text{Right}}} = \frac{RT}{2F} \ln \left( \frac{c_1 - n/V_{\text{Left}}}{n/V_{\text{Right}}} \right)$$

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

or



$$\mu_{\text{SO}_4^{2-}}^{\ominus}(p_{\text{Left}}) + RT \ln (a_{\text{SO}_4^{2-}})_{\text{Left}} - z_{\text{SO}_4^{2-}} \cdot F \cdot \phi_{\text{Left}} = \mu_{\text{SO}_4^{2-}}^{\ominus}(p_{\text{Right}}) + RT \ln (a_{\text{SO}_4^{2-}})_{\text{Right}} - z_{\text{SO}_4^{2-}} \cdot F \cdot \phi_{\text{Right}}$$

$$\mu_{\text{SO}_4^{2-}}^{\ominus}(p_{\text{Left}}) \doteq \mu_{\text{SO}_4^{2-}}^{\ominus}(p_{\text{Right}})$$

$$E = \phi_{\text{Right}} - \phi_{\text{Left}} = \frac{RT}{2F} \ln \frac{(a_{\text{SO}_4^{2-}})_{\text{Right}}}{(a_{\text{SO}_4^{2-}})_{\text{Left}}} = \frac{RT}{F} \ln \left( \frac{n/V_{\text{Right}}}{10 c_{\text{P}} + c_1 - n/V_{\text{Left}}} \right)$$

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