Problem 12-10 Membrane hydrolysis, Donnan potential

The solution of ferrous salt $(Fe^{2+})_6P^{12-}$ of concentration $2\cdot10^{-4}$ mol dm^{-3} is at the temperature of 36 °C in the left compartment of the dialysis cell, separated from the same volume of pure water in the right compartment by a semipermeable membrane. The membrane is not permeable for high-molecular ions P^{12-}.

Calculate

(a) pH in both compartments in equilibrium
(b) Donnan potential

The ionic product of water at given temperature is $K_w = 2.255\cdot10^{-14}$ (standard state $c^{st} = 1$ mol dm^{-3}).

[$pH_{Left} = 5.982$; $pH_{Right} = 7.664$; $E = 103.1$ mV]

Solution:

$T = 309.15$ K

$Fe_6P = 6\ Fe^{2+} + P^{12-}$ $\qquad c_0 = 0.0002$ mol dm^{-3}

$H_2O = H^+ + OH^-$

x – concentration of passing ions

Balance:	at the beginning		in equilibrium	
	Left	Right	Left	Right
P^{12-}	c_0	0	c_0	0
Fe^{2+}	$6\ c_0$	0	$6\ c_0 - x$	x
OH^-			K_w/x	$2\ x$
H^+			$2\ x$	K_w/x

Donnan equilibrium condition (for passing ions Fe^{2+} a OH^-):

$$(c_{Fe^{2+}})_{Left}\cdot(c^2_{OH^-})_{Left} = (c_{Fe^{2+}})_{Right}\cdot(c^2_{OH^-})_{Right}$$

$$(6\,c_0 - x)\cdot\left(\frac{K_w}{2x}\right)^2 = x\cdot(2x)^2 \quad , \quad (c_{OH^-})_{Left} = \frac{K_v}{(c_{H^+})_{Left}} = \frac{K_v}{2x}$$

$$x_1 = \sqrt[5]{\frac{(6\,c_0 - x)\cdot K_w^2}{16}} \doteq \sqrt[5]{\frac{(6\cdot2\cdot10^{-4})\cdot(2.255\cdot10^{-14})^2}{16}} = 5.2032\cdot10^{-7} \text{ mol dm}^{-3}$$

$$x_2 = \sqrt[5]{\frac{(6\,c_0 - x_1)\cdot K_w^2}{16}} \doteq \sqrt[5]{\frac{(6\cdot2\cdot10^{-4} - 5.2032\cdot10^{-7})\cdot(2.255\cdot10^{-14})^2}{16}} = 5.2027\cdot10^{-7} \text{ mol dm}^{-3}$$

$$x_3 = \sqrt[5]{\frac{(6\,c_0 - x_2)\cdot K_w^2}{16}} \doteq \sqrt[5]{\frac{(6\cdot2\cdot10^{-4} - 5.2027\cdot10^{-7})\cdot(2.255\cdot10^{-14})^2}{16}} = 5.2027\cdot10^{-7} \text{ mol dm}^{-3}$$

(the approximative calculation – x_1 – would be sufficient)

(a) $(c_{H^+})_{Right} = \dfrac{K_w}{(c_{OH^-})_{Right}} = \dfrac{K_w}{2x} = \dfrac{2.255\cdot10^{-14}}{2\cdot5.2027\cdot10^{-7}} = 2.167\cdot10^{-8}$ mol dm^{-3}

$pH_{Right} = 7.664$

$pH_{Left} = -\log 2\ x = (2\cdot5.2027\cdot10^{-7}) = 5.982$

(c) Ions Fe^{2+} and OH^- pass from the Left into the Right compartment,
$z_{Cation} = 2$, $z_{Anion} = 1$, $T = 309.15$ K

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

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

$$E = \varphi_{Right} - \varphi_{Left} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \frac{(a_{Fe^{2+}})_{Left}}{(a_{Fe^{2+}})_{Right}} = \frac{\boldsymbol{R}T}{2\boldsymbol{F}} \ln \frac{6\,c_0 - x}{x}$$

$$E = \frac{8.314 \cdot 309.15}{2 \cdot 96485.3} \cdot \ln \frac{6 \cdot 0.0002 - 5.2027 \cdot 10^{-7}}{5.2027 \cdot 10^{-7}} = 0.1031 \text{ V}$$

or

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

$$\mu^{\ominus}_{OH^-}(p_{Left}) \doteq \mu^{\ominus}_{OH^-}(p_{Right})$$

$$E = \varphi_{Right} - \varphi_{Left} = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{(a_{OH^-})_{Right}}{(a_{OH^-})_{Left}} = \frac{\boldsymbol{R}T}{\boldsymbol{F}} \ln \frac{2x}{\frac{K_w}{2x}}$$

$$E = \frac{8.314 \cdot 309.15}{96485.3} \cdot \ln \frac{2 \cdot 5.2027 \cdot 10^{-7}}{\frac{2.255 \cdot 10^{-14}}{2 \cdot 5.2027 \cdot 10^{-7}}} = 0.1031 \text{ V}$$