Chapter 4

(2.) 0.1M $Fe(ClO_4)_3$ (+3)   0.1M $Fe(ClO_4)_2$ (+2)

λ (conductance) $\Rightarrow \lambda_{Fe^{+3}} = \lambda_{Fe^{+2}} = \lambda_{ClO_4^-} = \lambda$ assume.

$10e^-$ passed in the process per unit time so this means $10e^-$ are removed at the anode and $10e^-$ are produced at the cathode.

Balance sheet

This problem is really addressing the fraction of current carried by the different ions with migration and diffusion contributing to the transport.

Net ovrs:

$$10\,Fe(ClO_4)_3 + 10e^- \rightleftharpoons 10\,Fe(ClO_4)_2$$

Fraction of total current carried by an ion is given by the transference number.

$$t_j = \frac{i_j}{i_{TOTAL}} = \frac{|z_j|C_j\lambda_j}{\sum_k |z_k|C_k\lambda_k}$$

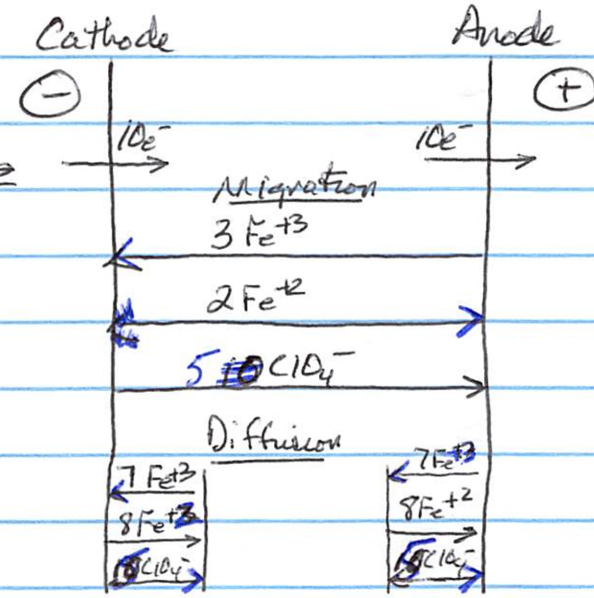
$$\sum_k = |z_k|C_k\lambda_k$$

$$= (+3)(0.1)(1) + (+2)(0.1)(1) + (+1)(0.1)(5)(1)$$

$$= 0.3 + 0.2 + 0.5 = \underline{\underline{0.10}}$$

		fraction of current	
$t_{Fe^{+3}} = \frac{(+3)(0.1)(1)}{0.10} = 3$		0.3	e.g. 3/10
$t_{Fe^{+2}} = \frac{(+2)(0.1)(1)}{0.10} = 2$		0.2	
$t_{ClO_4^-} = \frac{(+1)(0.1)(5)(1)}{0.10} = 5$		0.5	

$10\,Fe(ClO_4)_3 + 10e^- \rightleftharpoons 10\,Fe(ClO_4)_2$



$10\,Fe(ClO_4)_2 \rightleftharpoons 10\,Fe(ClO_4)_3 + 10e^-$

~~10 equivalents of~~ ClO_4^-

According to the stoichiometry, 10 equivalents of

~~ClO4⁻ are consumed, 5 ClO4⁻ leave cathode by migration so 5 ClO4⁻ must diffuse back to equate the~~

ClO_4^- is not involved in the reaction so it is not consumed or generated.

3. For semi-infinite linear diffusion conditions, cell wall must be at least 5 diffusion layer thickness from electrode

$D = 1\times10^{-5}\ cm^2/s \qquad t = 100\,s$

$\ell\,(cm) = \sqrt{Dt}$

$\ell = 5d = 5\sqrt{(1\times10^{-5}\ cm^2/s)(100\,s)}$

$\ell = 0.16\ cm$

in 1 sec, a normal size molecule will move 0.0032 cm or ~30 μm