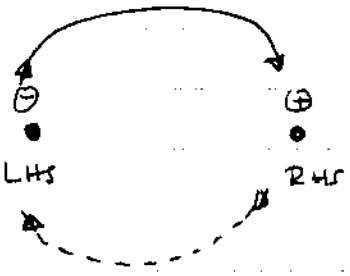
NOTES ON CONCENTRATION CELLS & TRANSPORT

General



external current flow (-ve electrons)

circuit completed by internal flow of negative charge made up of

⊖ ions ⟸ R to L

⊕ ions ⟹ L to R

CONSIDER TWO CASES

CELL REVERSIBLE TO CATION (+)

$\overset{\ominus}{H_2}$ | HCl : HCl | $\overset{\oplus}{H_2}$

Pt | a_1 : a_2 | Pt

REVERSIBLE TO H^+

For 1 Faraday passing externally

L $\xrightarrow[H^+]{+1\text{ mole}}$ $\xrightarrow[H^+]{t_+}$ $\xrightarrow[H^+]{-1\text{ mole}}$ R

$\xleftarrow[a^-]{t_-}$

$\Delta[H^+] = +1 - t_+ = t_-$ $\qquad$ $\Delta[H^+] = -1 + t_+ = -t_-$

$\Delta[Cl^-] = t_-$ $\qquad$ $\Delta[Cl^-] = -t_-$

∴ overall cell reaction for 1 Faraday

$$t_- HCl(a_2) \Longrightarrow t_- HCl(a_1)$$

$$\mathcal{E} = -t_- \frac{RT}{F} \ln \frac{a_1}{a_2}$$

$$= +t_- \frac{RT}{F} \ln \frac{a_2}{a_1}$$

Notes:

① t_- appears for cell reversible to ⊕

② a_1 refers to a_{HCl};

$$a_{HCl} \equiv a_{H^+} a_{Cl^-}$$

So that

$$\mathcal{E} = +t_- 2\frac{RT}{F} \ln \frac{a_{H^+(2)}}{a_{H^+(1)}} \text{ etc}$$

CELL REVERSIBLE TO ANION (−)

$\overset{\ominus}{Ag}$ | HCl : HCl | $\overset{\oplus}{Ag}$

AgCl | a_1 : a_2 | AgCl

REVERSIBLE TO a^-

For 1 Faraday passing externally

L $\xleftarrow[a^-]{-1\text{ mole}}$ $\xleftarrow[a^-]{t_-}$ $\xleftarrow[a^-]{+1\text{ mole}}$

$\xrightarrow[H^+]{t_+}$

$\Delta[a^-] = -1 + t_- = -t_+$ $\qquad$ $\Delta[a^-] = +1 - t_- = t_+$

$\Delta[H^+] = -t_+$ $\qquad$ $\Delta[H^+] = t_+$

∴ overall cell reaction for 1 Faraday

$$t_+ HCl(a_1) \longrightarrow t_+ HCl(a_2)$$

$$\mathcal{E} = -t_+ \frac{RT}{F} \ln \frac{a_2}{a_1}$$

Notes:

① t_+ appears here

② a_2/a_1 for cell reversible to ⊖ replaces a_1/a_2 for cell reversible to ⊕

$$\mathcal{E} = -t_+ 2\frac{RT}{F} \ln \frac{a_{H^+(2)}}{a_{H^+(1)}}$$