Transference & Transference number of Transport number

Current is transported through solution by migration of positive & negative ions. Fraction of the total current carried by each ion is not necessarily same. Ions which move faster carry greater fraction of the total current.

$$I_+ = \frac{N_+ v_+ z_+ e}{d}, \quad I_- = \frac{N_- v_- z_- e}{d} \quad \text{(done earlier)}$$

$$I = I_+ + I_- = \frac{e}{d}(N_+ z_+ v_+ + N_- z_- v_-) = \frac{N_+ z_+ e}{d}(v_+ + v_-)$$

$(N_+ z_+ = N_- z_-)$

Condition of electroneutrality

$$t_+ = \frac{I_+}{I} = \frac{N_+ v_+ z_+ e\, d}{d\, N_+ z_+ e\,(v_+ + v_-)}$$

$$\boxed{t_+ = \frac{I_+}{I_-} = \frac{v_+}{v_+ + v_-}} \quad \text{Similarly,} \quad \boxed{t_- = \frac{v_-}{v_+ + v_-}}$$

$$\frac{t_+}{t_-} = \frac{v_+}{v_-}$$

Transport no. of ions $\propto$ absolute velocity

t_+ = Fraction of total current carried by positive ions.

t_- = Fraction of total current carried by negative ions.

If $t_+ = t_-$, both ions contribute equally to the transport of current.

$$t_+ + t_- = 1$$

$$t_+ + t_- = \frac{v_+}{v_+ + v_-} + \frac{v_-}{v_+ + v_-}$$

$$= \frac{v_+ + v_-}{v_+ + v_-} = 1$$

If $v_+ \neq v_-$, then $t_+ \neq t_-$, if velocity of ions is different, they would carry different amounts of current & hence, their transport number will be different.

Experimental determination of Transport number of Ions

(1) Hittorf's method:

On passing the current through a solution, concentration changes occur in the vicinity of electrodes due to:

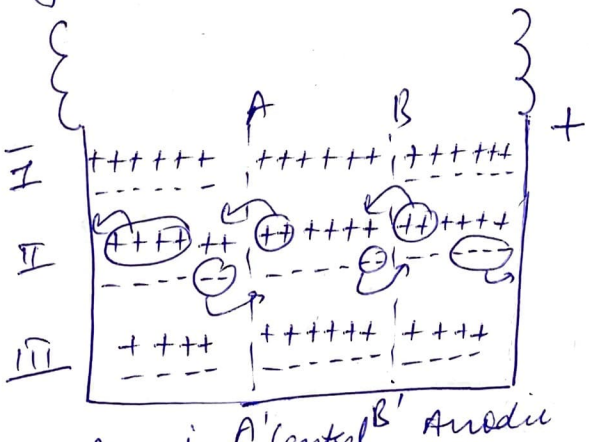
(i) Electrode reaction

At cathode, cations are reduced & at anode, anions are oxidized. Amount of ions reduced or oxidized on either of the electrodes = no. of electrons passed through electricity / charge or no. 6

(ii) Migration effect:

Charge is carried due to movement of ions.

This was explained by taking an electrolytic cell & dividing it into (hypothetically) 3 compartments i.e. cathodic, central & anodic compartments by imaginary planes AA' & BB'.



I: let each compartment contain equal amounts of uni-univalent electrolyte (say AB ~~is~~ having A^+ & B^- ion) Let us say 6 mol each of positive & negative ions are there.

II: let 4 mol of electrons be passed through the solution.

Assumption: $V_+ = V_-$ i.e. velocities of both ions is assumed to be the same. So each ion will carry half the total charge i.e. 2F mol by cations & 2F mol by anions.

Cathodic compartment:
4 mol of cations are deposited at the cathode due to electrode reaction

$$A^+ + e^- \rightleftharpoons A \text{ (Reduction)}$$

To maintain electroneutrality or to make for loss of positive ion, 2 positive ions migrate from anodic to central compartment & 2 from central to cathodic compartment.
2 anions move out from cathodic to central compartment.
In central compartment, no electrode reaction takes place. Only 2 mol of cations move in from anodic compartment & move out to cathodic compartment.
Similarly, two mol of anions move in from cathodic compartment & 2 mol move out to anodic compartment.

In anodic compartment,
4 mol of anions are deposited

$$B^- \rightleftharpoons B + e^- \text{ (Oxidation)}$$

2 mol of cation move out & 2 mol of anions move in from central compartment.

Since 4 mol of current was given, there is migration of 4 mol each of cations & anions & also electrode reaction of 4 mol each of cation & anion.

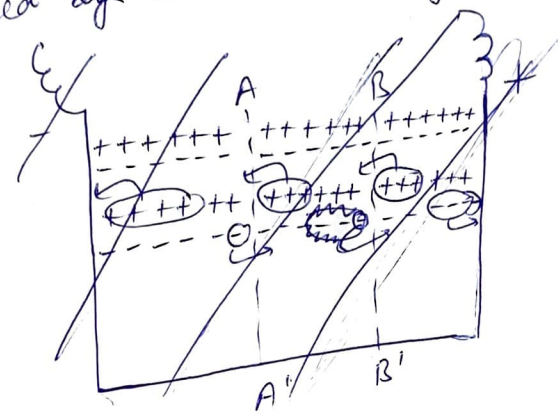
Loss of 2 pairs of cation & anion ~~from~~ each from cathodic & anodic compartment.

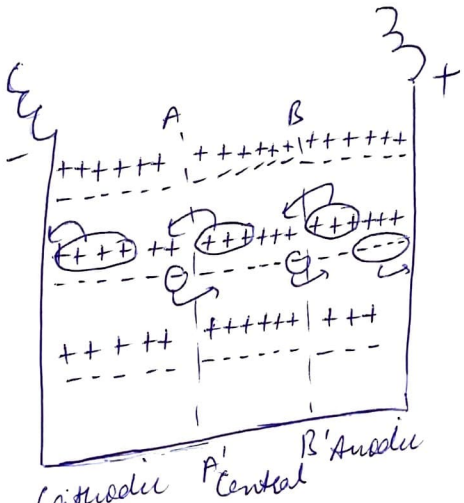
Now, consider a case where cation & anion have different velocities.

Let $v_+ = 3v_-$

Since speed of cation is 3 times that of anion, cations will carry 3 times as much as electric charge as the anion.

Out of 4F mol of electric charge passed, 3F mol will be carried by cations & 1F by anions.





So electrode reactions are the same, 4 mol of cations are reduced & 4 mol of anions are oxidized. since there is difference in speed of ion, for movement of every 3 cations, there is movement of only one anion. Because of this, overall loss of 4 pairs of cations & anions but 3 pairs from anodic compartment & 1 from cathodic compartment.