(2) Determination of transport number.

The EMF of the concentration cell with transference $(E_{w.t})$ is given by

$$E_{w.t} = t_- \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (1)$$

The EMF of the same cell with same solution but without transference is given by

$$E_{w.o.t} = \frac{RT}{F} \ln \frac{a_2}{a_1} \qquad (2)$$

Dividing equation (1) by equation (2) we get,

$$\frac{E_{w.t}}{E_{w.o.t}} = \frac{t_- \frac{RT}{F} \ln \frac{a_2}{a_1}}{\frac{RT}{F} \ln \frac{a_2}{a_1}}$$

$$\boxed{t_- = \frac{E_{w.t}}{E_{w.o.t}}} \qquad (3)$$

The the ratio of the EMFs of two cells one with transference and other without transference gives the transport number of anion (t_-)

$$\because \quad t_+ + t_- = 1$$

$$\therefore \quad t_+ = 1 - t_-$$

Thus, by knowing transport number of anion, the transport number of cation can be determined.

(3) Determination of valency of ions of Doubtful Cases

The valency of mercurous ion was in doubt for a considerable time. It was determined by EMF of the concentration cell

Mercury, mercurous nitrate (C_1) || mercurous nitrate solution (C_2), mercury, Emf of the cell $= \frac{RT}{nF} \ln \frac{C_2}{C_1}$

where $n =$ valency of mercurous ion

and $C_2 > C_1$ at $25^\circ C$

$E = \frac{0.059}{n} \log \frac{C_2}{C_1}$

It has been found that when $\frac{C_2}{C_1} = 10$, $E = 0.0295$ volt,

$0.0295 = \frac{0.059}{n} \log 10$

$0.0295 = \frac{0.059}{n} \times 1$

$n = \frac{0.059}{0.0295} = 2$

Therefore, valency of mercurous ion is 2.

(4) **Determination of Solubility product constants (Ksp).**

we consider a sparingly soluble salt MX in equilibrium with its ions in saturated solutions

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

So, solubility product of the salt is given by

$$K_{sp} = [M^+][X^-]$$

The cell reaction for above reaction is

$$M, M^+X^- \text{(sat. soln.)} \,|\, MX(s), M$$

At R.H.E

$$MX(s) + e \rightleftharpoons M + X^-$$

At L.H.E $\quad M - e \rightleftharpoons M^+(aq)$

Overall rxn $\quad MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$

$$E^\circ = E^\circ_R - E^\circ_L$$

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The values of E°_{R} and E°_{L} are determined from table.

Knowing the value of E° for the cell, the value of K_{sp} can be determined as,

$$\Delta G^{\circ} = -nFE^{\circ}$$

and $$\Delta G^{\circ} = -2.303\,RT \log K_{sp}$$

$$-nFE^{\circ} = -2.303\,RT \log K_{sp}.$$

$$E^{\circ} = \frac{2.303\,RT}{nF} \log K_{sp}$$

$$E^{\circ} = \frac{0.059}{n} \log K_{sp}$$

Thus, by knowing the value of E°, we can determined the value of K_{sp}.