

(4)

(2) Determination of transport number.

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

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

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

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

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

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

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

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

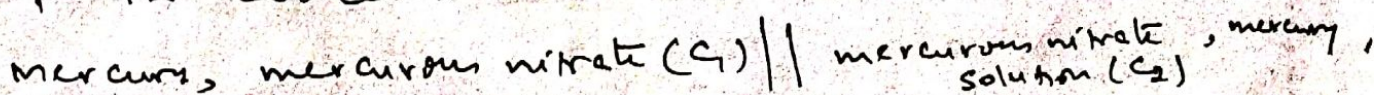
$$\therefore t_+ + t_- = 1$$

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

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



(5)

$$\text{EMF of the cell} = \frac{RT}{nF} \ln \frac{C_2}{C_1}$$

where $n =$ valency of mercuron ion

and $C_2 > C_1$

$$E = \frac{0.059}{n} \log \frac{C_2}{C_1} \quad \text{at } 25^\circ\text{C}$$

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

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

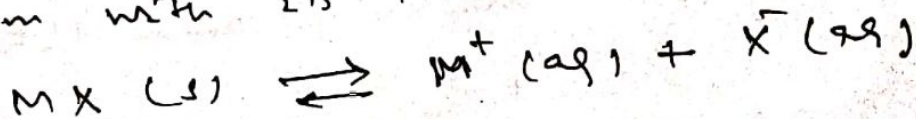
$$0.0295 = \frac{0.059}{n} \times 1$$

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

Therefore, valency of mercuron ion is 2.

(4) Determination of Solubility product constants (K_{sp}).

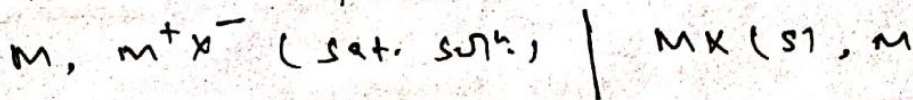
We consider a sparingly soluble salt MX in equilibrium with its ions in saturated solutions



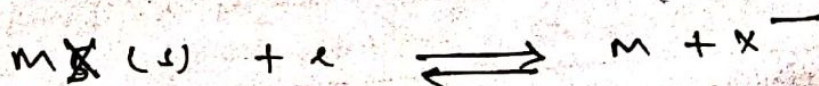
So, solubility product of the salt is given by

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

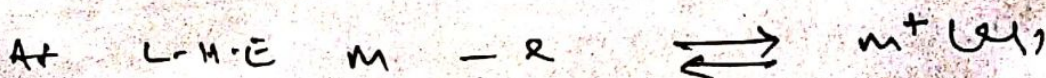
The cell reaction for above reaction is



At R.H.E



At L.H.E



$$E^0 = E_R^0 - E_L^0$$

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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,

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

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

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

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

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

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