actual contact or not. Depending on this we have two types of electrolyte concentration cells.

Concentration Cells without Transport

The concentration cells, in which the two electrolyte solutions are not in direct contact and the transfer of ions from one electrolyte solution to the other does not take place directly, is called concentration cell without transport or transference & liquid junction. The emf arises from difference in concentrations of electrolyte solutions.

Let us consider one cell having the electrodes reversible with respect to H^+ and Cl^- as:

$$H_2\ (1\ atm.)\ \ HCl\ (a_1)\ AgCl\ (s) \mid Ag$$

When the cell starts functioning, the hydrogen at the left hand electrode dissolves to form hydrogen ions, whereas from silver chloride, silver is deposited at the right hand electrode as represented by

$$\frac{1}{2}H_2\,(1\,atm.) \rightleftharpoons H^+ + e^-$$

$$AgCl(s) + 1e^- \rightleftharpoons Ag + Cl^-$$

The net cell reaction may be obtained by adding the above two half-cell reactions.

$$\frac{1}{2}H_2\,(1\ atm.) + AgCl(s) \rightleftharpoons HCl(a_1) + Ag(s)$$

As H^+ ions are formed in hydrochloric acid solution activity, then emf of the cell may be taken as

$$E_1 = -E^o \frac{RT}{F}\ \ln a_1 \tag{10.28}$$

Let us consider the cell with different activities of HCl. This is represented by

$$H_2\ (1\ atm.) \mid HCl\ (a_2)\ AgCl(s) \mid Ag$$

As proved earlier, the net reaction occurring in the cell is

$$\frac{1}{2}H_2\ (1\ atm.) + AgCl(s) \rightleftharpoons HCl(a_2) + Ag(s)$$

The emf for this cell is

$$E_2 = E^o - \frac{RT}{F}\ \ln a_2 \tag{10.29}$$

Now connect the two cells containing HCl of activities a_1 and a_2 with emf's E_1 and E_2 in opposition. The resulting cell will be

$$H_2\ (1\ atm.) \mid HCl\ (a_1),\ AgCl(s) \mid Ag \mid AgCl(s),\ HCl\ (a_2) \mid H_2\ (1\ atm.)$$

Since both the simple cells are combined oppositely, the overall cell reaction of this concentration cell without transport will be the difference of above cell reaction. That is

$$\frac{1}{2}H_2(1\text{ atm.}) + AgCl(s) \rightleftharpoons Ag(s) + HCl\,(a_1)$$

$$\frac{1}{2}H_2(1\text{ atm.}) + AgCl(s) \rightleftharpoons Ag(s) + HCl\,(a_2)$$

Substracting $0 + 0 \rightleftharpoons HCl(a_1) - HCl(a_2)$

or $HCl(a_2) \rightleftharpoons HCl(a_1)$

Now the emf of the cell is

$$E = E_1 - E_2$$

$$E = \left(E^{\circ} - \frac{RT}{F}\ln a_1\right) - \left(E^{\circ} - \frac{RT}{F}\ln a_2\right)$$

$$E = \frac{RT}{F}\ln\frac{a_2}{a_1} \qquad (10.30)$$

As $a_2 > a_1$, there occurs a transfer of electrolyte from concentrated to dilute solution which follows from equation (10.30)

Concentration Cells with Transport

The cells in which two solutions containing the same electrolyte but at different concentrations are in direct contact and the identical electrode reversible to either ions of the electrolyte are placed in these solutions are called *concentration cells with transport or with liquid junction*. In these cells the liquid junction potential at the interface of two solutions is taken into account.

The typical concentration cell with transport is

$$Pt, H_2(1\text{ atm.}) | HCl(a_1) \vdots\vdots HCl(a_2) | H_2(1\text{ atm.}), Pt$$

In the above cell the two solutions of HCl are in contact with each other and thus there is a direct transfer of HCl from the more concentrated solution (a_2) to the less concentrated solution (a_1). In general, whenever two solutions of the electrolyte of two concentrations are placed together and the electrode reversible with respect to one of the ions of the electrolyte is kept is each solution, then a concentration cell with transport is obtained. In the above cell, the double dotted lines represent the liquid junction potential the electrode reactions for each faraday of electricity drawn from the cell are:

Left electrode (oxidation): $\frac{1}{2}H_2 \rightleftharpoons H^+(a_1) + e^-$

Right electrode (reduction): $H^+(a_2) + e^- \rightleftharpoons \frac{1}{2}H_2$

Overall cell reaction is given by adding the above two equation.

$$H^+(a_2) \rightleftharpoons H^+(a_1) \qquad (10.31)$$

Hence, when current flows, the H^+ ions generated at the left electrode are consumed at the right electrode. Since the solutions ore in direct contact with each other, the ions (H^+ and Cl^-) are free to move from one solution to the other with the flow of current in the cell. This current in the cell is composed, of course, not of free electrons but of negative chloride ions (Cl^-). Moving from right to left and positive ions (H^+) moving across the liquid junction from left to right.

Suppose t_c and t_a are the transport numbers of H^+ and Cl^- ions respectively. for the passage of one faraday of electricity through the cell, the tc faraday is carried by tc gram ion of hydrogen from left to right, i.e., from the solution of activity a_1 to a_2. Thus we can write

$$t_c.\ H^+(a_1) = t_c.\ H^+(a_2) \qquad (10.32)$$

As $\quad t_c + t_a = 1 \text{ or } t_c = 1 - t_a$

$$\therefore (1 - t_a)\ H^+(a_1) = (1 - t_a)\ H^+(a_2) \qquad (10.33)$$

Also t_a faraday of electricity will be carried by t_a g of chloride ion from right to left, i.e., from the solution of activity a_2 to a_1, thus we can write

$$t_a\ Cl^-(a_2) = t_a\ Cl^-(a_1) \qquad (10.34)$$

Therefore in order to obtain the net transfer of material, we must add equations (10.31) (10.33) and (10.34)

$$H^+(a_2) + (1-t_a)H^+(a_1) + t_a.Cl^-(a_2) = H^+(a_1) + (1-t_a).H^+(a_2) + t_a.Cl^-(a_1)$$

but $\quad t_a + t_c = 1, \qquad \therefore t_c = 1 - t_a$

$$H^+(a_2) + H^+(a_1) - t_a.\ H^+(a_1) + t_a.Cl^-(a_2) = H^+(a_1) + H^+(a_2) - t_a.\ H^+(a_2) + t_a.Cl^-(a_1)$$

$$-t_a.\ H^+(a_1) + t_a.Cl^-(a_2) = -t_a.\ H^+(a_2) + t_a.\ Cl^-(a_1).$$

$$t_a.H^+(a_2) + t_a.Cl^-(a_2) = t_a.\ H^+(a_1) + t_a.\ Cl^-(a_1)$$

$$t_a\ [H^+(a_2) + Cl^-(a_2)] = t_a[H^+(a_1) + Cl^-(a_1)]$$

$$t_a.\ HCl\ (a_2) = t_a.\ HCl\ (a_1) \qquad (10.35)$$

Equation (10.35) shows that t_a equivalents of HCl are transferred from solution of activity a_2 to solution of activity a_1 for the passage of any faraday of electricity.

The emf of the complete cell is given by

$$E = E_1 - E_2$$

$$E = \left(E^\circ - \frac{RT}{F}\ln a_1^{t_a}\right) - \left(E^\circ - \frac{RT}{F}\ln a_2^{t_a}\right)$$

$$E = -\frac{RT}{F}\ln a_1^{t_a} + \frac{RT}{F}\ln a_2^{t_a}$$

$$E = -\frac{RT}{F}\ln\left(\frac{a_1}{a_2}\right)^{t_a}$$

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

$$E = t_a\frac{RT}{F}\ln\frac{a_2}{a_1} \qquad (10.36)$$

Thus is such cell the emf of the cell depends upon the transference number of the ions other than to which the electrode is reversible. Such cells therefore, provide very convenient means of determining the transference number of the ions other than the one to which the electrodes are reversible, through the emf measurements.

10.13. LIQUID JUNCTION POTENTIAL

When two electrolytic solutions of different concentrations are brought in contact with one another, a potential difference develops at the junction of two solutions. This potential difference is called *liquid junction potential* or *diffusion potential*.

When two salt solutions of different concentrations are placed in contact with one another, the ions from the concentrated solution will tend to diffuse into the dilute one. The rate of diffusion of each ion is approximately proportional to the speed of the ions in the electric field. The liquid junction potential arises mainly due to