

MEMBRANE PHENOMENON

Donnan and Harris (1911) while measuring the osmotic pressure of solutions of the dyestuff Congo red (Congo red is a sodium salt of a complex sulphonic acid) observed that if sodium chloride dissolved in an aqueous solution of Congo red is brought in contact with water through a membrane, then it was seen that Congo red was impermeable through the membrane, while sodium chloride readily passed through it. It was also found that sodium chloride was present in greater amount in the solution free from the dyestuff than in the other. In other words, if two solutions are separated by a membrane (impermeable to one of the components), then an unequal distribution occurs for the other species, for which the membrane is permeable. At equilibrium, the osmotic pressures of the two solutions are different, and if two reference electrodes (say calomel electrodes) are connected to the two solutions by means of a salt bridge, then a difference of potential between the two electrodes is noticed. This type of equilibrium as first seen by Donnan, is known as *Donnan membrane equilibrium*. The potential developed between the two solutions is thus known as *Donnan potential*.

The two components of Donnan membrane equilibrium are :

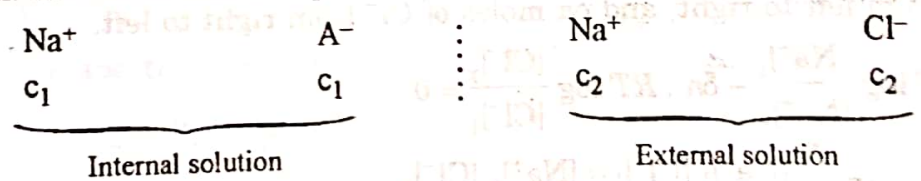
(i) **Internal solution.** This solution may be of any protein, Congo red etc. One of the ions is generally non-diffusible and approaches the colloidal dimensions. The other ion is small enough and is diffusible across the membrane. This solution is taken as the *left* solution.

(ii) **External solution.** This solution is generally a solution of an electrolyte, both ions of which are diffusible across the membrane, e.g., NaCl, CaCl₂ etc. This solution is taken as the *right* solution.

We shall now consider four different types of cases to which Donnan membrane equilibrium is applicable.

CASE I. The electrolytes in the two solutions have an ion in common.

Suppose the initial condition is represented as :



Ion A⁻ represents the non-diffusible ion, c₁ and c₂ are the respective concentrations of the ions, the dotted line represents the semipermeable membrane.

As the left hand solution does not contain chloride ions, therefore, some will diffuse into it from

the right hand solution. Suppose x moles per litre of chloride ions move from right to left solution. Since the two solutions must be electrically neutral, x moles per litre of sodium ions must also diffuse from the right to left solution. The equilibrium concentrations will thus be as follows :



Since the system is in equilibrium, a small change made reversibly at constant temperature and volume, will not bring any change in the free energy, *i.e.*, no work will be done. The change here is the transfer of a small amount, say δn moles of Na^+ and δn moles of Cl^- from right to left. The work done will thus be equal to zero. So,

$$\delta n \cdot RT \log \frac{[\text{Na}^+]_{\text{right}}}{[\text{Na}^+]_{\text{left}}} + \delta n \cdot RT \log \frac{[\text{Cl}^-]_{\text{right}}}{[\text{Cl}^-]_{\text{left}}} = 0$$

$$\frac{[\text{Na}^+]_l}{[\text{Na}^+]_r} = \frac{[\text{Cl}^-]_r}{[\text{Cl}^-]_l}$$

or $[\text{Na}^+]_l [\text{Cl}^-]_l = [\text{Na}^+]_r [\text{Cl}^-]_r$

Substituting the respective concentrations, we get,

$$(c_1 + x)x = (c_2 - x)^2$$

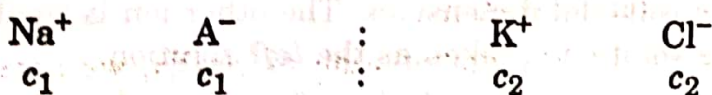
$$x = \frac{c_2^2}{c_1 + 2c_2}$$

$$\frac{c_2 - x}{x} = \frac{c_1 + c_2}{c_2}$$

The quantity $\frac{c_2 - x}{x}$ represents the distribution ratio of NaCl between right and left solutions.

Case II. The electrolytes on both the sides have no common ions.

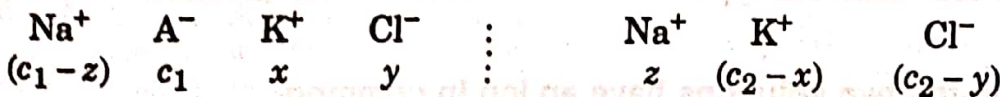
Suppose the initial condition is represented as :



Let x mole per litre of K^+ ions and y mole per litre of Cl^- ions diffuse from right to left solution.

During this change, let z moles per litre of Na^+ ions diffuse from left to right solution.

The condition at equilibrium is then represented as :



For an infinitesimal change, the following amounts are transferred :

δn moles of Na^+ from left to right, and δn moles of Cl^- from right to left.

Therefore, $\delta n \cdot RT \log \frac{[\text{Na}^+]_l}{[\text{Na}^+]_r} - \delta n \cdot RT \log \frac{[\text{Cl}^-]_r}{[\text{Cl}^-]_l} = 0$

or

$$[\text{Na}^+]_l [\text{Cl}^-]_l = [\text{Na}^+]_r [\text{Cl}^-]_r \quad \dots (1)$$

Similarly,

$$[\text{K}^+]_l [\text{Cl}^-]_l = [\text{K}^+]_r [\text{Cl}^-]_r \quad \dots (2)$$

Substituting the respective concentrations in expression (1), we get,

$$(c_1 - z)y = z(c_2 - y)$$

or
$$x = \frac{y(c_1 + c_2)}{c_2} \quad [\text{As } z = x - y] \quad \dots (3)$$

From (2),
$$xy = (c_2 - x)(c_2 - y)$$

or
$$x = c_2 - y \quad \dots (4)$$

From equations (3) and (4), we get

$$\frac{y(c_1 + c_2)}{c_2} = c_2 - y$$

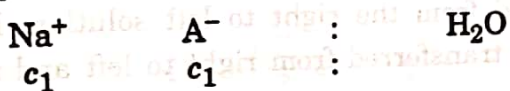
$$\frac{c_2 - y}{y} = \frac{c_1 + c_2}{c_2}$$

$$y = \frac{c_2^2}{c_1 + 2c_2}$$

Once the value of y is thus known, the value of x can be calculated from equation (4), and that of z from the expression $z = x - y$.

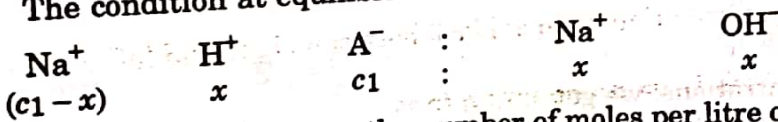
CASE III. One of the solutions is water alone.

Suppose the initial condition is represented as :



The sodium ions will migrate from left to right solution and do so when equivalent amount of OH^- ions, furnished by water in left solution, can migrate through it in order to maintain electrical neutrality.

The condition at equilibrium is then represented as :



The value x represents the number of moles per litre of Na^+ ions which migrate. The solution on left is acidic, whereas on the right the solution is alkaline.

By applying the principle of virtual work, for the distribution of NaOH , we have for the transfer of δn moles of Na^+ from left to right and δn moles of OH^- from left to right,

$$\delta n \cdot RT \log \frac{[\text{Na}^+]_l}{[\text{Na}^+]_r} + \delta n \cdot RT \log \frac{[\text{OH}^-]_l}{[\text{OH}^-]_r} = 0$$

$$\frac{[\text{Na}^+]_l}{[\text{Na}^+]_r} = \frac{[\text{OH}^-]_r}{[\text{OH}^-]_l}$$

$$[\text{Na}^+]_l [\text{OH}^-]_l = [\text{Na}^+]_r [\text{OH}^-]_r$$

or Substituting the respective concentrations, we get,

$$(c_1 - x) \frac{K_w}{x} = x^2$$

[Remembering that $[\text{H}^+][\text{OH}^-] = K_w$, i.e., $[\text{OH}^-] = \frac{K_w}{x}$ on the left side, where K_w is the ionic product of water] So,