

DONNAN DIALYSIS

T.A. Davis

Independent Consultant, 5 Davis Farm Road, Annandale, NJ 08801 USA

Keywords: Donnan dialysis, Neutralization, Economic Relevance, Supplier Industry

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Summary

Donnan dialysis utilizes counter diffusion of two or more ions through an ion exchange membrane to achieve a separation. For example, if a cation exchange membrane separates two solution, one containing CuSO_4 and the other containing H_2SO_4 , the H^+ and Cu^{2+} ions will diffuse in opposite directions across the membrane until an equilibrium is reached. Since the cation exchange membrane is impermeable to SO_4^{2-} ions, equivalent amounts of H^+ and Cu^{2+} ions must be transferred through the membrane to maintain electroneutrality. The process can be described as a continuous ion exchange process where the regenerating solution is constantly supplying H^+ ions to exchange for the Cu^{2+} ions so that they can be removed continuously from their original solution. Differences in the volumes and concentrations of the two solutions can be exploited to achieve some interesting and useful separations. Donnan dialysis can be used for water softening, pollution control, and even deionization of a process stream. The deionization process, called neutralization dialysis, combines Donnan dialysis through both cation exchange and anion exchange membranes with H^+ and OH^- ions exchanging for the cation and anion of a salt.

1. Introduction

Donnan dialysis is a mass transfer process that utilizes ion exchange membranes to achieve separation or concentration of ionic species. The process is named in honor of F. G. Donnan (1924) who described the equilibrium that resulted when a semipermeable membrane separated two solutions of electrolytes, NaA on one side and KA on the other. Modern polymeric ion exchange membranes were not available then, but he synthesized a membrane by filling the pores of parchment paper with a gel of copper ferrocyanide and used ferrocyanide for the common anion A of the two salts. When the

initial volumes and concentrations of the two salt solutions were the same, counter diffusion of equal amounts of Na and K through the membrane led to an equilibrium condition where the two solutions had equal concentrations of NaA and KA. But when initial concentrations were different, counter diffusion of equal amounts of Na and K through the membrane produced solutions with equal ratios of Na/K on both sides of the membrane at equilibrium.

Subsequent development of polymeric ion exchange membranes allowed Donnan dialysis to be performed in a continuous, counter current process so that a substantial portion of a cation from a dilute solution could be concentrated into a small volume. Moreover, Donnan dialysis is also effective in anion exchange membranes.

When the processes of anion and cation transport are combined into one apparatus, the technique can be used to remove salts from solutions. When an acid and a base are used to supply the diffusing ions that drive the process, the process is called "neutralization dialysis".

In the discussions that follow, the principles of Donnan dialysis and some of its applications and capabilities will be described. The type of equipment and membrane arrangements appropriate for both Donnan dialysis and neutralization dialysis will be presented.

2. Principles and Fundamentals

Modern Donnan dialysis utilizes ion exchange membranes to separate the two solutions that are involved in the transport process. Since most experiments and separation processes have utilized cation exchange membranes, that will be the membrane for these discussions.

As Donnan pointed out in his seminal description of the theory, a precise treatment of the equilibria would require the use of activities rather than concentrations of ions in the solutions. But the use of molar concentrations greatly simplifies the presentation of the theory, so that is the approach taken here.

Figure 1 shows the system to be examined. Two dilute salt solutions NaA and KA are separated by a membrane labeled C because it is permeable to the cations Na^+ and K^+ but impermeable to the common anion A^- .

The concentration difference of Na^+ ions across the membrane provides a driving force for their diffusion through the membrane. There is no net flow of electric current through the membrane, so any net transfer of Na^+ to the right must be balanced by transfer of an equivalent amount of K^+ to the left. Those diffusive processes will occur until an equilibrium is established.

In the simplest situation, one can imagine, the initial volumes and concentrations of the two solutions are equal. When equilibrium is reached, both solutions have the same composition, which makes this a trivial case. Indeed that outcome would have occurred without the semipermeable membrane. For all other cases, the membrane has a

substantial effect on the equilibrium.

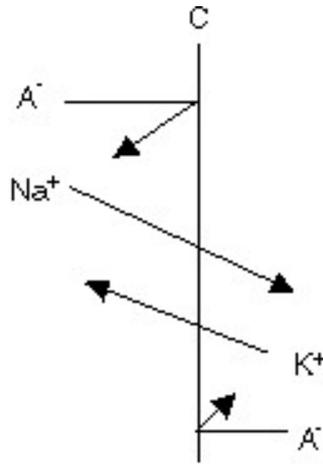


Figure 1. Donnan dialysis through a cation exchange membrane.

A nontrivial situation arises when the volumes of the two solutions are equal and unchanging, but the two solutions have different concentrations. As indicated in Figure 1, that situation results in downhill transport of Na^+ ions to the right and uphill transport of K^+ ions to the left. Figure 2 illustrates the concentration changes from the initial concentrations shown by the dotted lines to the final concentrations shown by the solid lines. Because the initial concentration of NaA on the left is higher than the initial concentration of KA on the right, the large driving force for diffusion of Na^+ ions to the right causes the K^+ ions to move to the left well past the point of equal concentrations. Indeed, at equilibrium the ratios of the concentrations of the two cations will be the same in both solutions in Case 1. In the equations developed below, the solution on the left is designated by the subscript 1, and that on the right by subscript 2.

$$[\text{Na}^+]_1/[\text{K}^+]_1 = [\text{Na}^+]_2/[\text{K}^+]_2 \text{ or } [\text{Na}^+]_1/[\text{Na}^+]_2 = [\text{K}^+]_1/[\text{K}^+]_2 \quad (1)$$

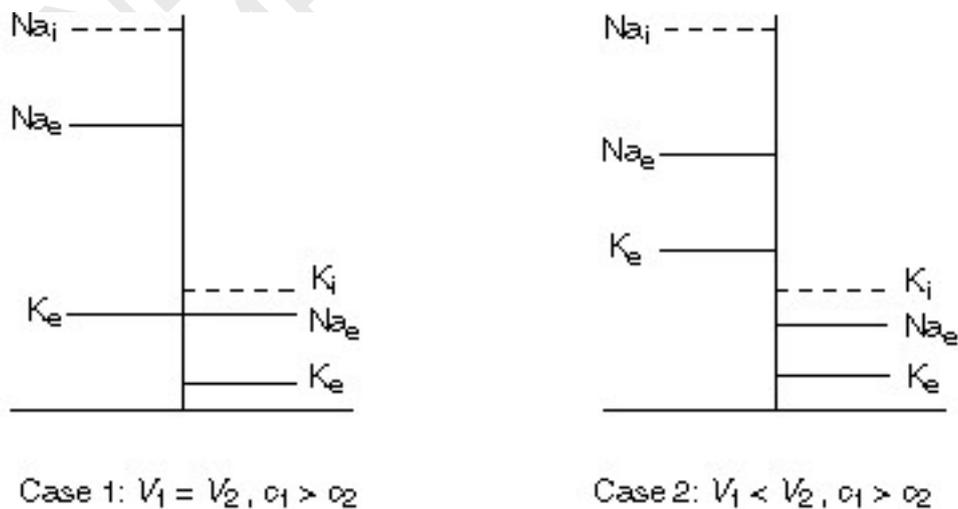


Figure 2. Concentrations in Donnan dialysis initially and at equilibrium.

Subscript i and ---- indicate initial conditions. Subscript e and ——— indicate the equilibrium states.

These equilibrium concentrations can be expressed in terms of the initial molar concentrations c_1 of NaA on the left and c_2 of KA on the right, x moles transported through the membrane (still the same for both cations) and the volumes V_1 and V_2 of the solutions, expressed in liters.

$$(c_1 - x/V_1)/(x/V_1) = (x/V_2)/(c_2 x/V_2) \quad (2)$$

Solving this equation for x yields

$$x = c_1 c_2 / (c_1/V_2 + c_2/V_1) \quad (3)$$

Case 2 in Figure 2 shows the situation where $V_1 < V_2$, but $c_1 > c_2$. Under this condition the salt KA can be recovered at a higher concentration than in its original solution. It should be pointed out that these concentrations represent what would occur in a batch or parallel-flow experiment. Greater removals would be expected with the counter current flows that would be used in an industrial dialyzer.

Donnan dialysis is particularly effective for recovery or removal of multivalent ions. The Donnan equilibrium for a divalent CaA_2 and a univalent salt KA is described by the equation

$$([\text{Ca}^{2+}]_1/[\text{Ca}^{2+}]_2)^{1/2} = [\text{K}^+]_1/[\text{K}^+]_2 \quad (4)$$

To maintain electroneutrality in the system the transport of x moles of Ca^{2+} ions through the membrane requires the transport of $2x$ moles of K^+ ions in the opposite direction. Thus Eq. 2 becomes

$$((c_1 - x/V_1)/(x/V_1))^{1/2} = (2x/V_2)/(c_2 - 2x/V_2) \quad (5)$$

For $V_1 = V_2 = 1$ and initial concentrations of $c_1 = 0.1$ and $c_2 = 1$, the value of $x = 0.0948$, which means that almost 95 per cent of the calcium would be driven through the membrane. The effect of valence is even more dramatic when c_1/c_2 ratio is much lower than the value used in this example.

Now that the equations that describe Donnan equilibrium have been presented, it is beneficial to examine the thermodynamic equations from which they were derived. Under conditions of equilibrium the chemical potential m of any dissolved species i is the same in every phase present.

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (6)$$

Here R is the gas constant, T is the absolute temperature, and a_i is the activity of species i . However, when the species are ionic, the electrochemical potential η_i must be used to

describe the equilibrium,

$$\eta_i = \mu_i^0 + RT \ln a_i + z_i F \theta \quad (7)$$

where z_i is the ionic charge, F is Faraday's constant, and θ is the electrical potential. Since there is equilibrium between the two liquid phases, the electrochemical potential of any mobile species i in the two phases can be equated.

$$\eta_{i1} = \eta_{i2}, \text{ or } RT \ln a_{i1} + z_i F \theta_1 = RT \ln a_{i2} + z_i F \theta_2 \quad (8)$$

It should be noted that the

$$\mu_i^0$$

terms cancel because the same standard state exists in both liquid phases. But the anions are not free to move through the cation exchange membrane that separates the two liquid phases, so there is no opportunity for their concentrations to change. Thus, except in the trivial case mentioned above where the initial salt concentrations are the same on both sides of the membrane, there will be a potential difference across the membrane caused by the concentration difference. This potential difference, called the Donnan potential, E_{Don} , is described by rearrangement of the above equation.

$$E_{Don} = \theta_2 - \theta_1 = RT / z_i F (\ln a_{i1} - \ln a_{i2}) = RT / F \ln (a_{i1} / a_{i2})^{1/z_i} \quad (9)$$

which acts on all mobile ionic species. Thus, the value of $(a_{i1}/a_{i2})^{1/z_i}$ is the same for all of the cations in the system, and this is the thermodynamic basis for Eqs (1) and (4) shown above.

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