12.7: Membrane Equilibria

A semipermeable membrane used to separate two liquid phases can, in principle, be permeable to certain species and impermeable to others. A membrane, however, may not be perfect in this respect over a long time period. We will assume that during the period of observation, those species to which the membrane is supposed to be permeable quickly achieve transfer equilibrium, and only negligible amounts of the other species are transferred across the membrane.

Section 12.2.2 sketched a derivation of the conditions needed for equilibrium in a two-phase system in which a membrane permeable only to solvent separates a solution from pure solvent. We can generalize the results for any system with two liquid phases separated by a semipermeable membrane: in an equilibrium state, both phases must have the same temperature, and any species to which the membrane is permeable must have the same chemical potential in both phases. The two phases, however, need not and usually do not have the same pressure.

12.7.1 Osmotic membrane equilibrium

An equilibrium state in a system with two solutions of the same solvent and different solute compositions, separated by a membrane permeable only to the solvent, is called an **osmotic membrane equilibrium**. We have already seen this kind of equilibrium in an apparatus that measures osmotic pressure (Fig. 12.2).

Consider a system with transfer equilibrium of the solvent across a membrane separating phases α and β. The phases have equal solvent chemical potentials but different pressures:

$$\mu_A^\beta(p^\beta) = \mu_A^\alpha(p^\alpha) \tag{12.7.1}$$

The dependence of μ_A on pressure in a phase of fixed temperature and composition is given by $(\partial \mu_A/\partial p)_{T,\{n_i\}} = V_A$ (from Eq. 9.2.49), where V_A is the partial molar volume of A in the phase. If we apply this relation to the solution of phase β, treat the partial molar volume V_A as independent of pressure, and integrate at constant temperature and composition from the pressure of phase α to that of phase β, we obtain

$$\mu_A^\beta(p^\beta) = \mu_A^\beta(p^\alpha) + V_A^\beta(p^\beta - p^\alpha) \tag{12.7.2}$$

By equating the two expressions for $\mu_A^\beta(p^\beta)$ and rearranging, we obtain the following expression for the pressure difference needed to achieve transfer equilibrium:

$$p^\beta - p^\alpha = \frac{\mu_A^\alpha(p^\alpha) - \mu_A^\beta(p^\alpha)}{V_A^\beta} \tag{12.7.3}$$

The pressure difference can be related to the osmotic pressures of the two phases. From Eq. 12.2.11, the solvent chemical potential in a solution phase can be written $\mu_A(p) = \mu_A^*(p) - V_A \Pi(p)$. Using this to substitute for $\mu_A^\alpha(p^\alpha)$ and $\mu_A^\beta(p^\alpha)$ in Eq. 12.7.3, we obtain

$$p^\beta - p^\alpha = \Pi^\beta(p^\alpha) - \left(\frac{V_A^\alpha}{V_A^\beta}\right)\Pi^\alpha(p^\alpha) \tag{12.7.4}$$

12.7.2 Equilibrium dialysis

Equilibrium dialysis is a useful technique for studying the binding of a small uncharged solute species (a ligand) to a macromolecule. The macromolecule solution is placed on one side of a membrane through which it cannot pass, with a solution without the macromolecule on the other side, and the ligand is allowed to come to transfer equilibrium across the membrane. If the same solute standard state is used for the ligand in both solutions, at equilibrium the unbound ligand must have the same activity in both solutions. Measurements of the total ligand molality in the macromolecule solution and the ligand molality in the other solution, combined with estimated values of the unbound ligand activity coefficients, allow the amount of ligand bound per macromolecule to be calculated.

12.7.3 Donnan membrane equilibrium

If one of the solutions in a two-phase membrane equilibrium contains certain *charged* solute species that are unable to pass through the membrane, whereas other ions can pass through, the situation is more complicated than the osmotic membrane equilibrium

described in Sec. 12.7.1. Usually if the membrane is impermeable to one kind of ion, an ion species to which it is permeable achieves transfer equilibrium across the membrane only when the phases have different pressures and different electric potentials. The equilibrium state in this case is a **Donnan membrane equilibrium**, and the resulting electric potential difference across the membrane is called the **Donnan potential**. This phenomenon is related to the membrane potentials that are important in the functioning of nerve and muscle cells (although the cells of a living organism are not, of course, in equilibrium states).

A Donnan potential can be measured electrically, with some uncertainty due to unknown liquid junction potentials, by connecting silver-silver chloride electrodes (described in Sec. 14.1) to both phases through salt bridges.

General expressions

Consider solution phases α and β separated by a semipermeable membrane. Both phases contain a dissolved salt, designated solute B, that has ν_+ cations and ν_- anions in each formula unit. The membrane is permeable to these ions. Phase β also contains a protein or other polyelectrolyte with a net positive or negative charge, together with counterions of the opposite charge that are the same species as the cation or anion of the salt. The presence of the counterions in phase β prevents the cation and anion of the salt from being present in stoichiometric amounts in this phase. The membrane is impermeable to the polyelectrolyte, perhaps because the membrane pores are too small to allow the polyelectrolyte to pass through.

The condition for transfer equilibrium of solute B is $\mu_B^\alpha = \mu_B^\beta$, or

$$(\mu_{m,B}^\circ)^\alpha + RT \ln a_{m,B}^\alpha = (\mu_{m,B}^\circ)^\beta + RT \ln a_{m,B}^\beta \tag{12.7.5}$$

Solute B has the same standard state in the two phases, so that $(\mu_{m,B}^\circ)^\alpha$ and $(\mu_{m,B}^\circ)^\beta$ are equal. The activities $a_{m,B}^\alpha$ and $a_{m,B}^\beta$ are therefore equal at equilibrium. Using the expression for solute activity from Eq. 10.3.16, which is valid for a multisolute solution, we find that at transfer equilibrium the following relation must exist between the molalities of the salt ions in the two phases:

$$\Gamma_{m,B}^\alpha (\gamma_\pm^\alpha)^\nu (m_+^\alpha)^{\nu_+} (m_-^\alpha)^{\nu_-} = \Gamma_{m,B}^\beta \left(\gamma_\pm^\beta\right)^\nu \left(m_+^\beta\right)^{\nu_+} \left(m_-^\beta\right)^{\nu_-} \tag{12.7.6}$$

To find an expression for the Donnan potential, we can equate the single-ion chemical potentials of the salt cation: $\mu_+^\alpha(\phi^\alpha) = \mu_+^\beta(\phi^\beta)$. When we use the expression of Eq. 10.1.15 for $\mu_+(\phi)$, we obtain

$$\phi^\alpha - \phi^\beta = \frac{RT}{z_+ F} \ln \frac{\Gamma_+^\beta \gamma_+^\beta m_+^\beta}{\Gamma_+^\alpha \gamma_+^\alpha m_+^\alpha} \tag{12.7.7}$$
$$\text{(Donnan potential)}$$

The condition needed for an osmotic membrane equilibrium related to the solvent can be written

$$\mu_A^\beta(p^\beta) - \mu_A^\alpha(p^\alpha) = 0 \tag{12.7.8}$$

The chemical potential of the solvent is $\mu_A = \mu_A^\circ + RT \ln a_A = \mu_A^\circ + RT \ln(\Gamma_A \gamma_A x_A)$. From Table 9.6, we have to a good approximation the expression $RT \ln \Gamma_A = V_A^*(p - p^\circ)$. With these substitutions, Eq. 12.7.8 becomes

$$RT \ln \frac{\gamma_A^\beta x_A^\beta}{\gamma_A^\alpha x_A^\alpha} + V_A^* \left(p^\beta - p^\alpha\right) = 0 \tag{12.7.9}$$

We can use this equation to estimate the pressure difference needed to maintain an equilibrium state. For dilute solutions, with γ_A^α and γ_A^β set equal to 1, the equation becomes

$$p^\beta - p^\alpha \approx \frac{RT}{V_A^*} \ln \frac{x_A^\alpha}{x_A^\beta} \tag{12.7.10}$$

In the limit of infinite dilution, $\ln x_A$ can be replaced by $-M_A \sum_{i \neq A} m_i$ (Eq. 9.6.12), giving the relation

$$p^\beta - p^\alpha \approx \frac{M_A RT}{V_A^*} \sum_{i \neq A} \left(m_i^\beta - m_i^\alpha\right) = \rho_A^* RT \sum_{i \neq A} \left(m_i^\beta - m_i^\alpha\right) \tag{12.7.11}$$

Example

As a specific example of a Donnan membrane equilibrium, consider a system in which an aqueous solution of a polyelectrolyte with a net negative charge, together with a counterion M^+ and a salt MX of the counterion, is equilibrated with an aqueous solution

of the salt across a semipermeable membrane. The membrane is permeable to the H_2O solvent and to the ions M^+ and X^-, but is impermeable to the polyelectrolyte. The species in phase α are H_2O, M^+, and X^-; those in phase β are H_2O, M^+, X^-, and the polyelectrolyte. In an equilibrium state, the two phases have the same temperature but different compositions, electric potentials, and pressures.

Because the polyelectrolyte in this example has a negative charge, the system has more M^+ ions than X^- ions. Figure 12.9(a) is a schematic representation of an initial state of this kind of system. Phase β is shown as a solution confined to a closed dialysis bag immersed in phase α. The number of cations and anions shown in each phase indicate the relative amounts of these ions.

For simplicity, let us assume the two phases have equal masses of water, so that the molality of an ion is proportional to its amount by the same ratio in both phases. It is clear that in the initial state shown in the figure, the chemical potentials of both M^+ and X^- are greater in phase β (greater amounts) than in phase α, and this is a nonequilibrium state. A certain quantity of salt MX will therefore pass spontaneously through the membrane from phase β to phase α until equilibrium is attained.

The equilibrium ion molalities must agree with Eq. 12.7.6. We make the approximation that the pressure factors and mean ionic activity coefficients are unity. Then for the present example, with $\nu_+ = \nu_- = 1$, the equation becomes

$$m_+^\alpha m_-^\alpha \approx m_+^\beta m_-^\beta \tag{12.7.12}$$

There is furthermore an electroneutrality condition for each phase:

$$m_+^\alpha = m_-^\alpha \qquad m_+^\beta = m_-^\beta + |z_P| m_P \tag{12.7.13}$$

Here z_P is the negative charge of the polyelectrolyte, and m_P is its molality. Substitution of these expressions into Eq. 12.7.12 gives the relation

$$(m_-^\alpha)^2 \approx \left(m_-^\beta + |z_P| m_P \right) m_-^\beta \tag{12.7.14}$$

This shows that in the equilibrium state, m_-^α is greater than m_-^β. Then Eq. 12.7.12 shows that m_+^α is less than m_+^β. These equilibrium molalities are depicted in Fig. 12.9(b).

The chemical potential of a cation, its activity, and the electric potential of the phase are related by Eq. 10.1.9: $\mu_+ = \mu_+^\circ + RT \ln a_+ + z_+ F\phi$. In order for M^+ to have the same chemical potential in both phases, despite its lower activity in phase α, the electric potential of phase α must be greater than that of phase β. Thus the Donnan potential $\phi^\alpha - \phi^\beta$ in the present example is positive. Its value can be estimated from Eq. 12.7.7 with the values of the single-ion pressure factors and activity coefficients approximated by 1 and with z_+ for this example set equal to 1:

$$\phi^\alpha - \phi^\beta \approx \frac{RT}{F} \ln \frac{m_+^\beta}{m_+^\alpha} \tag{12.7.15}$$

> The existence of a Donnan potential in the equilibrium state is the result of a very small departure of the phases on both sides of the membrane from exact electroneutrality. In the example, phase α has a minute net positive charge and phase β has a net negative charge of equal magnitude. The amount of M^+ ion transferred across the membrane to achieve equilibrium is slightly greater than the amount of X^- ion transferred; the difference between these two amounts is far too small to be measured chemically. At equilibrium, the excess charge on each side of the membrane is distributed over the boundary surface of the solution phase on that side, and is not part of the bulk phase composition.

The pressure difference $p^\beta - p^\alpha$ at equilibrium can be estimated with Eq. 12.7.11, and for the present example is found to be positive. Without this pressure difference, the solution in phase α would move spontaneously through the membrane into phase β until phase α completely disappears. With phase α open to the atmosphere, as in Fig. 12.9, the volume of phase β must be constrained in order to allow its pressure to differ from atmospheric pressure. If the volume of phase β remains practically constant, the transfer of a minute quantity of solvent across the membrane is sufficient to cause the pressure difference.

It should be clear that the existence of a Donnan membrane equilibrium introduces complications that would make it difficult to use a measured pressure difference to estimate the molar mass of the polyelectrolyte by the method of Sec. 12.4, or to study the binding of a charged ligand by equilibrium dialysis.