

# Chapter I.3 A Thermodynamic Consideration of Permeability Coefficients of Membranes

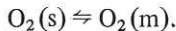
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## 1 Introduction

The permeability coefficient of the membrane appears in various places in this volume either as  $P_m$  with units of  $[\text{m}^2 \text{s}^{-1}]$  or as  $P_m$  with units of  $[\text{mol m}^{-1} \text{s}^{-1} \text{kPa}^{-1}]$ . Here we show how these permeability coefficients arise and how they are related.

## 2 Oxygen Distribution Between a Solution and a Membrane

If we consider the distribution of oxygen between a test solution (s) and a membrane (m) then we can write an equilibrium



From basic thermodynamics we can write for the test solution

$$\mu_s = \mu_s^\circ + RT \ln a_s \quad (1)$$

and for the membrane

$$\mu_m = \mu_m^\circ + RT \ln a_m, \quad (2)$$

where  $\mu_s$  and  $\mu_m$  are the chemical potentials of the oxygen in the two phases,  $\mu_s^\circ$  and  $\mu_m^\circ$  are the corresponding chemical potentials in the standard state, and  $a_s$  and  $a_m$  are relative activities [4]. The standard state for defining  $\mu_s^\circ$  and  $\mu_m^\circ$  is taken as the hypothetical state at unit molarity of dissolved oxygen, but in which the environment of each molecule is the same as at infinite dilution of oxygen. Since these environments will clearly not be the same in the case of the membrane and the test solution then the chemical potentials in each phase under standard-state conditions will be different. The dimensionless relative activities are defined by:

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$$a_s = y_s \frac{c_s}{c_s^\circ} \quad (3)$$

and

$$a_m = y_m \frac{c_m}{c_m^\circ}, \quad (4)$$

where  $y_s$  and  $y_m$  are the activity coefficients for the two phases,  $c_s$  and  $c_m$  are the concentrations in terms of molarities, and  $c_s^\circ$  and  $c_m^\circ$  are standard concentrations, which are usually chosen to be  $1 \text{ mol dm}^{-3}$ . Since for most practical situations that one is concerned with in using a POS the interaction between oxygen molecules is negligible [1], then, on the basis of the standard state that has been chosen for defining the  $\mu^\circ$  values, the activity coefficients in Eqs. (3) and (4) will only deviate from unity if there are any other solutes which change the environment of the dissolved oxygen; e.g., ionized salts (App. A).

For equilibrium at the test solution/membrane interface

$$\mu_s = \mu_m \quad (5)$$

and hence

$$\ln \frac{a_m}{a_s} = \frac{\mu_s^\circ - \mu_m^\circ}{RT} = - \frac{\Delta G^\circ}{RT}, \quad (6)$$

where  $\Delta G^\circ$  is the difference in molar standard free energy between oxygen in the membrane and the test solution. However, since  $\Delta G^\circ$  is simply related to the thermodynamic equilibrium constant  $K$  then we can write

$$K = \frac{a_m}{a_s}. \quad (7)$$

This equation shows that  $K$  is the dimensionless distribution or partition coefficient in terms of activities [3].

### 3 The Current at a POS and the Permeability Coefficient $P_m$

The signal normally obtained with a POS is a function of the flux of oxygen to the cathode. Figure 1 shows schematically the situation at the electrode under steady-state conditions. It is assumed that there is an equilibrium distribution of oxygen between the test solution and the membrane, that there is no limitation on transport of oxygen to the cathode through the electrolyte layer between the membrane and the cathode (cf. Chap. I.1), and that the transport is completely one-dimensional (cf. Chap. I.2). The flux,  $J_{O_2}$  [ $\text{mol m}^{-2} \text{ s}^{-1}$ ], of oxygen to the cathode is given by Fick's Law:

$$J_{O_2} = D_m \left( \frac{dc_{m,z}}{dz} \right)_{z=0}, \quad (8)$$

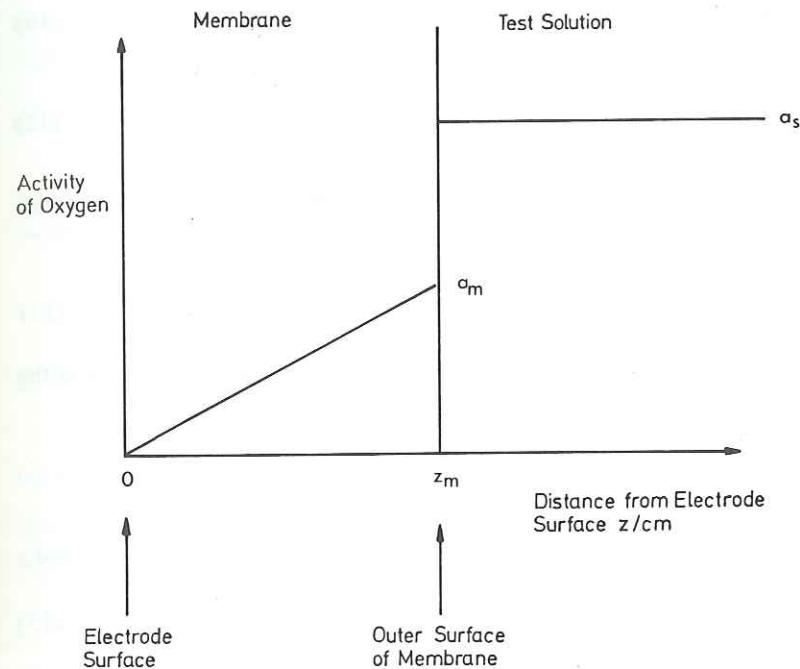


Fig. 1. Scheme of the situation at the electrode under steady-state conditions

where  $(dc_{m,z}/dz)_{z=0}$  is the concentration gradient [ $\text{mol m}^{-3} \text{ m}^{-1}$ ] in the membrane at the electrode surface and  $D_m$  [ $\text{m}^2 \text{ s}^{-1}$ ] is the diffusion coefficient for the oxygen in the membrane. Assuming that the concentration gradient is linear over the total membrane thickness ( $z_m$ ), then with  $c_{m,0} = 0$  Eq. (8) becomes

$$J_{O_2} = D_m \frac{c_m}{z_m}, \quad (9)$$

where  $c_m$  is simply written for the dissolved oxygen at the outer edge of the membrane. Using Eqs. (4) and (7), this equation becomes

$$J_{O_2} = \frac{c_m^\circ}{y_m} \frac{KD_m}{z_m} a_s. \quad (10)$$

The term  $c_m^\circ/y_m$  will be unity provided that there is, for example, no salting out of oxygen in the membrane; i.e.,  $y_m = 1$ . This is likely to be the case since membranes used in practice for POS are impermeable to electrolytes. The product of  $K$  and  $D_m$  we can write as

$$P_m = KD_m, \quad (11)$$

where  $P_m$  is the permeability coefficient with the same units as  $D_m$  i.e. [ $\text{m}^2 \text{ s}^{-1}$ ], since  $K$  is dimensionless. It is a constant at a given temperature and, since  $K$  is defined in

terms of activities, it is independent of any salt effects in the test solution. Eq. (10) can now be written as

$$J_{O_2} = \frac{P_m}{z_m} a_s. \quad (12)$$

Although  $a_s$  is dimensionless [Eq. (3)], the units of  $J_{O_2}$  are  $[\text{mol m}^{-2} \text{s}^{-1}]$ , as is required for a flux, since the equation contains the "hidden" concentration  $c_m^\circ$ .

The transport limited current,  $I_1$ , at a POS will be given by

$$I_1 = nFAJ_{O_2}, \quad (13)$$

where  $n$  is the number of electrons associated with the oxygen reduction,  $F$  is the Faraday, and  $A$  is the cathode area. Hence

$$I_1 = nFA \frac{P_m}{z_m} a_s. \quad (14)$$

In the case where there is no salting-out in the test solution,  $y_s$  is unity in Eq. (3) and

$$a_s = \frac{c_s}{c_s^\circ}. \quad (15)$$

Equation (14) can thus be written as

$$I_1 = nFA \frac{P_m}{z_m} \frac{c_m^\circ}{c_s^\circ} c_s, \quad (16)$$

where we have reintroduced  $c_m^\circ$  to show that the right hand side of the equation is still dimensionally correct. Since  $c_m^\circ = c_s^\circ = 1 \text{ mol dm}^{-3}$  then the equation becomes

$$I_1 = nFA \frac{P_m}{z_m} c_s. \quad (17)$$

This is the equation as originally obtained by Mancy et al. [5] and as given by Eq. (1) in Chap. I.2. For some applications this equation can be used to describe the current obtained with a POS, but in many cases the activity coefficient  $y_s$  has to be considered and then Eq. (14) must be used.

#### 4 The Current at a POS and the Permeability Coefficient $P_m$

In order to obtain an expression for the flux of oxygen to the cathode of a POS in terms of the permeability coefficient  $P_m$  with units of  $[\text{mol m}^{-1} \text{s}^{-1} \text{kPa}^{-1}]$ , we define a solubility,  $S_s$

$$S_s = \frac{c_s}{p_s} \quad [\text{mol dm}^{-3} \text{kPa}^{-1}], \quad (18)$$

where  $c_s$  is concentration in terms of molarity and  $p_s$  is the partial pressure (kPa) of oxygen in the test environment. With the definition of  $a_s$  [Eq. (3)] we obtain

$$S_s = \frac{a_s c_s^\circ}{y_s p_s}. \quad (19)$$

Substituting from this equation for  $a_s$  into Eq. (10) for the oxygen flux to the cathode we then have

$$J_{O_2} = \frac{y_s c_m^\circ}{y_m c_s^\circ} \frac{KD_m}{z_m} S_s p_s. \quad (20)$$

If we now write the flux in the general form [cf. Eq. (12)]

$$J_{O_2} = \frac{1}{z_m} \times (\text{Permeability Coefficient}) \times (\text{Measure of Oxygen "Concentration"}) \quad (21)$$

then with the partial pressure being a measure of the oxygen concentration, we can write

$$J_{O_2} = \frac{P_m}{z_m} p_s, \quad (22)$$

where the permeability coefficient is now defined by

$$P_m = KD_m S_s \frac{y_s c_m^\circ}{y_m c_s^\circ} \quad [\text{mol m}^{-1} \text{s}^{-1} \text{kPa}^{-1}]. \quad (23)$$

This permeability coefficient, like  $P_m$ , is a constant at a given temperature. Since  $S_s$  is in terms of concentration [Eq. (18)], and thus inversely proportional to  $y_s$ , then the presence of the product  $S_s y_s$  means that  $P_m$  is also independent of salt effects in the test solution.

#### 5 The Relationship Between $P_m$ and $P_m$

From Eqs. (11) and (23) it is obvious that

$$P_m = P_m S_s \frac{y_s c_m^\circ}{y_m c_s^\circ}. \quad (24)$$

It is also interesting to note that from the two equations for the oxygen flux [Eqs. (10) and (20)], which of necessity must be equal, we get the relationship

$$P_s = \frac{c_s^\circ}{S_s y_s} a_s. \quad (25)$$



This equation is simply a form of Henry's Law in which the proportionality constant  $k_s$  between partial pressure (or more strictly fugacity) and activity is given by

$$k_s = \frac{c_s^\circ}{S_s y_s} \text{ [kPa]} . \quad (26)$$

Now since the oxygen flux at the cathode can be expressed in terms of partial pressure as well as in terms of activity, then the chemical potentials of oxygen in the test solution and membrane can also be expressed in terms of partial pressures. In other words, instead of Eqs. (1) and (2) we can write

$$\mu_s = \mu_s^* + RT \ln \frac{p_s}{p_s^\circ} \quad (27)$$

and

$$\mu_m = \mu_m^* + RT \ln \frac{p_m}{p_m^\circ} , \quad (28)$$

where the  $\mu^*$  can be regarded as the chemical potential of the gas in each phase when the partial pressure is unity. From Eqs. (1) and (2) we know that the  $\mu^\circ$  are the chemical potentials at unit activity and that the state of unit activity is the standard state. If this standard state is chosen as that in which the partial pressure of the gas is also unity, then this choice makes the  $\mu^\circ$  in Eqs. (1) and (2) numerically equal to the corresponding  $\mu^*$  in Eqs. (27) and (28). Or, looking at it another way, the Henry's Law constant  $k_s$  [Eq. (26)] has a value of unity. We can then write instead of Eq. (25)

$$\frac{p_s}{p_s^\circ} = a_s , \quad (29)$$

where  $p_s^\circ = p_m^\circ$  represents unit partial pressure ( $k_s = k_m = 1 \text{ atm} = 101.325 \text{ kPa}$ ).

For a gaseous system it is often advantageous to choose the standard state of unit activity as that in which the partial pressure of the gas is unity at a given temperature [2]. With this choice of standard state, from the equation relating the two permeability coefficients [Eq. (24)], it can be seen that  $P_m$  and  $P_m$  become numerically identical.

## References

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