REACTION ENHANCED DIFFUSION IN SPHERICAL MEMBRANES

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Abstract

The reversible reactions like $A + B \rightleftharpoons C$ in the many-component diffusive system affect the diffusive properties of the constituents. The effective conjugation of irreversible processes of different dimensionality takes place due to the stationarity in the system and can lead to essential increase of the resulting diffusive fluxes. The exact equations for the spatial concentration profiles of the components are difficult to treat analytically. We solve approximately the equations for the concentration profiles of the reaction-diffusion components in the spherical geometry in the application to the problem of the enhanced oxygen transfer through a biological membrane and to the mathematically similar problem of surface diffusion in a solid body. In the latter case the spherical geometry can be an adequate tool for describing the surface of a real solid body which can be modeled as a fractal object formed of sequences of spherical surfaces with different radii.

Keywords: Enhanced diffusion; Transport phenomena; Thermodynamics; Membranes; Reversible chemical reactions

1 Introduction

The phenomenon of “facilitated through chemical reaction diffusion” is familiar to various domains of science. Its essence consists in the diffusion enhancement through the intermittance of some chemical reaction involving the diffusive components. A straightforward example is the so called “vacancy enhanced diffusion” of doped impurity into a solid body. Since long ago it was widely known that the presence of crystal imperfections is able to facilitate the impurity penetrating thus considerably enlarging the effective diffusion coefficient. From the thermodynamical point of view the facilitation comes from the presence of several fluxes of the diffusant (as if it were propagating through several different channels, or rather consist of several species having different diffusivity) and intermence of the reversible chemical reaction between them. Thus, in a solid body the impurity atoms are known to reside either in the nodes of the crystalline lattice, (substitutional impurity) or in the space between nodes (interstitial impurity), the latter being fast diffusants and the former - slow ones. The reversible interchange of these two species takes place and is facilitated by the presence of vacancies and eigen interstitial atoms of the matrix. An another example is taken from the biology domain and it concerns the phenomenon of the facilitated oxygen transfer through cellular membranes \[1\]. The principal reaction scheme consists in reversible “tying” the ligande molecules by some slow macromolecular carrier. The facilitated transport of oxygen is possible via some fermentative kinetics (which should not however affect the chemical properties of $O_2$) and especially through reversible reaction with haemoglobin or myoglobin. In what follows we refer for concreteness to this example though our consideration can be applied to the vast variety of situations falling into the same reaction scheme. The reaction process with $Hb$ and oxygen can be (although very schematically) represented by the following expression

\[ O_2 + Hb \rightleftharpoons HbO_2 \] (1)

which means the formation of an (unstable) complex $HbO_2$; the rates of forward and reverse reactions are $k_1$ and $k_-$. The system of balance equations for three constituents can be written as follows:

\[ D\Delta c = \rho + q \]
\[ D_p\Delta c_p = \rho \]
\[ D_p\Delta c_c = -\rho \] (2)

where $c$, $c_p$ and $c_c$ stand for concentrations of $O_2$, $Hb$, and $HbO_2$ respectively.


2 Reaction-Diffusion System in Spherical Geometry

We start with considering the problem (2)-(3) within the spheroidal shell of internal and external radii \(a\) and \(b\). The consideration of this problem within plain and cylindric geometry was performed not long ago \(^{11}\) and was intended to describe the problem of oxygen saturation in the muscular tissue. Our choice of the spherical form of the membranes, besides purely mathematical interest, is motivated by several reasons. Besides the interest in elucidating the biological problem of facilitated oxygen transport in the (spherically shaped) alveols we refer also to the above mentioned diffusion problem in crystalline bodies. Usually the mathematical models of impurity diffusion use the plane geometry as a tool to represent the boundary of a solid body as the platform for the diffusion in a bulk. But the surface of a crystal is by no means plain, and its inhomogeneities can affect the diffusion effects (intuitively it is clear from the fact that merely the effective diffusive surface is bigger than the mathematical surface of the body). So, plain model for the boundary is an approximation which can be improved. Namely, it is possible to model the surface as a highly irregular sequence of spheres of different radii, perhaps, forming fractal structure. Therefore the consideration of the spherical geometry (on a single sphere) is believed to yield some improved approximation than just considering the straight plane.

So in the following we speak on the biological problem of oxygen transport and consider the spherical membrane. We assume the spherical symmetry so only one coordinate, namely \(r\) resides. As boundary conditions for the problem it is natural to take \(c = c_a\) at \(r = a\) and \(c = c_b\) at \(r = b\) and the zero flux of other components \(dc_p/dr = dc_p/dr = 0\). But strictly speaking, the boundary conditions for all three constituents in real membranes can not be specified basing on a set of biological measurements \(^{11}\). As it can be demonstrated, the specification of one or other type of boundaries does not affect cardinally the shape of the solution across the whole width of the membrane except thin layers at the edges. In any case at chosen way of handling the problem (see the next chapter) the set of boundary conditions should be included in the solution by some kind of self-matching procedure.

Integrating the sum of two last equations in (2) yields

\[
c_p + c_c = \text{const} \equiv K
\]

(the conservation of the protein content). If we introduce the new function

\[
Y \equiv c_c/K
\]

which has a meaning of the ferment saturation function the system of equations is cast as:

\[
D \cdot \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c}{\partial r}) = \rho
\]

\[
K \cdot D_p \cdot \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial Y}{\partial r}) = -\rho
\]

with

\[
\rho = k_1 K c - Y \cdot K (k_1 c + k_-)
\]

Keeping in mind everything said about the boundary conditions specifications we now try to handle the problem setting

\[
c_{a|a} = c_a \quad c_{b|b} = c_b \\
Y_{a|a} = Y_a \quad Y_{b|b} = Y_b
\]

where \(c_b\) and both \(Y_a, Y_b\) should be further determined basing upon restrictions imposed by the biological sense of the problem.

Using the boundary conditions add eqs (6-7) and integrate twice thus obtaining an expression relating \(c(r)\) and \(Y(r)\):

\[
D \left( c_b - c(r) \right) + D_p K (Y_b - Y(r)) = \frac{b - r}{br} \cdot \frac{ab}{b - a} \cdot \left[ D(c_b - c_a) + D_p K (Y_b - Y_a) \right]
\]
3 External Solutions and Facilitated Transport

Expressing $Y$ from (10) and inserting it into (6) and (8) following equation results:

\[
\frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c}{\partial r}) = -\frac{k_0}{D_p} \left[D c_b + Y b K D_p + c \left\{k_0 \frac{D}{D_p} - k_1 K [Y b - 1 + \frac{D}{D_p} c_b]\right\}\right] - (11)
\]

The values $Y_b$, $Y_a$ and $c_b$, $c_a$ as said above should be determined from self-matching conditions. The equation (11) is extremely difficult (if not impossible) to solve analytically. Instead of looking for its exact solution we notice that (11) can be cast (after scaling variables) as the equation in the form:

\[
\varepsilon \Delta c = f(c, r),
\]

and $\varepsilon$ appears to be a small parameter ($\sim D/k_1$). This parameter is smaller if the reaction is more intensive; for biological issues its value varies within $10^{-4} - 10^{-6}$ [1], which allows approximate perturbative treatment of the problem. Since this parameter enters the equation near the term of the highest derivative, the problem appears to be that of the singular perturbation theory. Dropping out the $\varepsilon$ term one gets so-called “external solution” to the problem. In general this equation of smaller order can’t satisfy the boundary conditions and need "suturing" with the internal (exact) solution around the boundaries. The external solutions may suit for practical purposes within the bulk of the body, and would yield the desired solution of (11) provided that the constants (like $Y_b$, $Y_a$, $c_b$, $c_a$ etc) are chosen properly, namely by means of the self-matching procedure. In this case (11) turns out to be an ordinary algebraic equation, whose coefficients depend on the values of $Y_b$, $Y_a$, $c_b$, $c_a$. But in fact these latter themselves are solutions to the equation at the boundaries. To ensure that this is the case one must set following self-matching conditions:

\[
Y_b = \frac{k_1 c_b}{k_1 c_b + k_-}, \quad Y_a = \frac{k_1 c_a}{k_1 c_a + k_-} \quad (12)
\]

(These expressions could be easily obtained from (8) setting $\rho = 0$ at the boundaries).

The variation of the saturation function and the total oxygen flux are:

\[
Y_a - Y_b \equiv s = \frac{k_1 k_- (c_a - c_b)}{(k_1 c_a + k_-)(k_1 c_b + k_-)} \quad (13)
\]

and

\[
F(r) \equiv -D \frac{\partial c}{\partial r} - K \cdot D_p \frac{\partial Y}{\partial r} = \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 \frac{\partial c}{\partial r}) + \frac{k_1 c_s}{D_p} \left[D(c_a - c_b) + D_p K (Y_a - Y_b)\right] + \frac{k_1 D}{D_p} c^2
\]

which is the sum of two terms, first of which, $F_d$ is the ordinary diffusive flux, and the second one, $F_f$ is the additional flux caused by the reaction.

The self-matching conditions yield two relations between four values $c_a$, $c_b$, $Y_a$ and $Y_b$ (or equally $s$). From the point of view of experimentalists these values are not treatable in the same fashion. Depending on whether we consider the biological problem of facilitated oxygen flux or mathematically similar problem of impurity diffusion, the set of good-to-operate values changes. For the oxygen transfer we can operate only the value $c_a$ within wide range of magnitudes, and measure $s$, but this latter only for extremely big $c_a$, where it is known to tend to a constant $\bar{s}$ ($\sim 0.6 - 0.8$ [1]). And thus in order to get fluxes and concentrations within moderate $c_a$ values one recourses to an interpolation which is expected to yield semi-quantitative results. Let us express $c_b$ from (13):

\[
c_b = \frac{k_- c_a (1 - s) - k^2}{k_1 c_s + k_- (1 + s)}. \quad (15)
\]

This expression is exact. However the flux $s$ is itself a function of $c_a$ to be determined (only its value $\bar{s}$ at $c_a \to \infty$ is available), so let us go to the semiquantitative interpolation:

\[
c_b \simeq \frac{k_- c_a (1 - \bar{s})}{k_1 c_s + k_- (1 + \bar{s})}. \quad (16)
\]

The expression (16): a) satisfies the limiting condition $c_b \to 0$ at $c_a = 0$; b) at big $c_a$ ($k_1 c_s \gg k_-$) is consistent with (15). For intermediate $c_a$ this is believed to be a plausible interpolation. So from (16) the approximate expression for saturation function is

\[
s \simeq \frac{k_1 c_a \bar{s}}{(k_1 c_a + k_-)} \left[\frac{k_1 c_a + 2k_-}{k_1 c_a + k_-(1 + \bar{s})}\right] \quad (17)
\]
From (16)-(17), substituting it into (14), we get the expression for the complete flux through a membrane. The flux at the external \((r = b)\) layer equals

\[
F = F_d + F_f \simeq 4\pi \frac{a}{b} \left( k_1 c_a + 2k_- \right) \times
\]

\[
\left[ \frac{D}{k_1 c_a + k_- (1 + \bar{s})} + \frac{D_p K k_1}{(k_1 c_a + k_- (1 + \bar{s}))} \right]
\]

and is schematically depicted on Fig. 1 where the ordinary diffusion flux and facilitated one are shown as functions of \(c_a\).

![Image of Figure 1](image-url)

**Figure 1:** Diffusion and reaction facilitated oxygen flux as function of \(c_a\) (arbitrary units).

It is interesting to note different character of two fluxes from the latter formula and from Fig. 1: at big \(c_a\) the diffusion flux grows linearly, but the flux component due to selfconjugation with reaction tends to a constant value. For both biological problem, and for the problem of vacansies diffusion enhancement this is clear intuitively: since the amount of carrier is limited at big values of \(c_a\) the substrate simply gets saturated. As to the moderate or small \(c_a\) the relation of two fluxes is

\[
\frac{F_f}{F_d} = \frac{D_p K k_1}{D k_-}.
\]

The value \(D \gg D_p\) (since \(D\) stands for "fast species"), but under condition \(k_1 \gg k_-\) which is true far from chemical equilibrium, and if it is the case, the facilitated transport dominates over diffusion.

![Image of Figure 2](image-url)

**Figure 2:** Space concentration of the free component \(c(r)\) and total diffusion component \(c(r) + c_c(r)\).

In the solid body physics the role of the reversible reaction is undertaken by the process of reversible transitions of impurity atoms between interstitial and substitutional positions. The process of this interchange can be represented as the chemical reaction with vacansies:

\[
I + V \rightleftharpoons S
\]

(\(I\) and \(S\) standing for interstitial and substitutinal impurities, \(V\) for vacansies). Thus vacansies can be formally understood as "impurity carriers" like \(Hb\) complexes. Another mechanism is so called Watkins mechanism which also involves the interchange of fast and slow species, but by the intermittency of eigen interstitial atoms of the matrix. It is known (e.g., [2]) that such reversible reactions are crucial for understanding the impurity redistribution in the depth of a crystal. In order to handle analytically the impurity profile, the authors of [2] used similar assumptions of rapid chemical equilibrium establishing compared to the ordinary diffusion. In conclusion on Fig. 2 we show the approximate solution for space oxygen concentration in a spherical slab (between inner \(a\) and outer \(b\) boundary). Shown are both diffusion \(c(r)\) component and the value \(c + c_c\), that is total oxygen concentration.

**References**

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