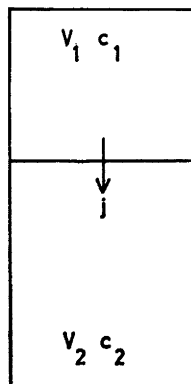# Model Treatment of Diffusion Processes

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A model treatment of diffusion processes is presented. It consists of a division of space into compartments, separated by membranes. All the resistance to diffusion is concentrated in the membranes, which constitute the resistance elements of the model, whereas the compartments constitute the capacity elements. The diffusion coefficient for a solute in the medium may be reproduced by taking the proper value for the permeation coefficient of the membrane. The use of the model for numerical calculations in connection with complicated diffusion problems is indicated.

The general treatment of diffusion processes leads to the diffusion equation, which in the one-dimensional case takes the form

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D(c,x,t)\,\frac{\partial c}{\partial x}\right) \tag{1}$$

Solutions of this equation for special cases of functional dependence of D on concentration c, position x and time t, and for special boundary conditions have been obtained, and may be found in the literature.[1-4] In general, however, an analytical treatment runs into insurmountable difficulties and only a nume-

Fig. 1. The element of the model.

rical treatment of the problem is possible. Here a simple model treatment of diffusion processes is presented, which may be of help in obtaining numerical solutions of practical diffusion problems. The model may be visualized as a division of space into compartments separated by membranes. The membranes have infinitesimal thickness and constitute all of the frictional resistance to diffusion and may thus be looked upon as elements of resistance. The compartments constitute the elements of capacity and contain solutions undergoing instantaneous mixing. The solution in a compartment is thus considered to have a uniform concentration.

We will first apply the model to one-dimensional diffusion and begin by deriving an expression for diffusion in an element of the model, *i.e.* between two compartments separated by a membrane, Fig. 1. We use the following variables

V_1, V_2 volume per unit membrane area of respective compartment
c_1, c_2 concentration of solute in respective compartment
j flux density of solute
a permeation constant for solute

We have the following relations [5-6]

$$j = -a(c_2 - c_1) \tag{2}$$

$$j = -V_1 \frac{dc_1}{dt} = V_2 \frac{dc_2}{dt} \tag{3}$$

Hence

$$\left. \begin{array}{l} \dfrac{dc_1}{dt} = \dfrac{a}{V_1} (c_2 - c_1) \\[2ex] \dfrac{dc_2}{dt} = -\dfrac{a}{V_2} (c_2 - c_1) \end{array} \right\} \tag{4}$$

Subtracting the upper equation from the lower, we get

$$\frac{d(c_2 - c_1)}{dt} = -a \left(\frac{1}{V_1} + \frac{1}{V_2} \right) (c_2 - c_1) \tag{5}$$

and integration gives

$$c_2 - c_1 = (c_2^\circ - c_1^\circ) \exp \left[-a \left(\frac{1}{V_1} + \frac{1}{V_2} \right) t \right] \tag{6}$$

We will now apply this formula to the diffusion model, represented schematically in Fig. 2. We consider a cylindrical region of unit cross section, divided into compartments of equal volume V and separated by the membranes (which are perpendicular to the axial direction of the cylinder). The operation of the model is thought to take place in discontinuous steps. We assume the steps to have an equal length of time τ and let the diffusion across the membranes occur according to eqn. (6) with the initial concentrations being fixed at the values existing at the beginning of the step. At the end of the step the concentration changes due to the two diffusion fluxes are super-
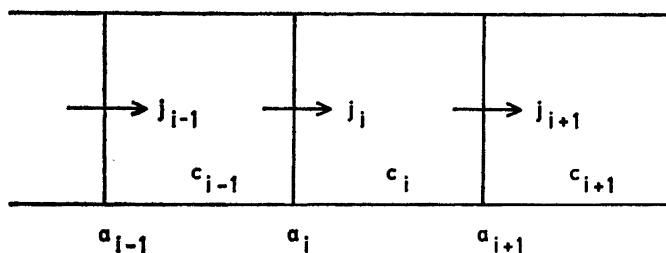
Fig. 2. Schematic representation of the diffusion model.

posed on the initial concentration and the value thus obtained is taken as the initial concentration of the next step. In formulae this takes the form

$$c_{i\,t+\tau} = c_{it} + \frac{1}{V} \int_t^{t+\tau} (j_i - j_{i+1})\ dt \tag{7}$$

where c_{it} and $c_{i\,t+\tau}$ are the concentrations in compartment i at time t and $t + \tau$, and j_i and j_{i+1} are fluxes during the time interval t, $t + \tau$.

The integral in (7) is obtained from (2) and (6) with $V_1 = V_2 = V$. Thus

$$\int_t^{t+\tau} j_i\ dt = \tfrac{1}{2}\ V(c_{i-1t} - c_{it})(1 - \exp\ [-2a_{it}\tau/V]) \tag{8}$$

Putting $1 - \exp[-2a_{it}\tau/V] = \alpha_{it}$ we get finally

$$c_{i\,t+\tau} = c_{it} + \tfrac{1}{2}[\alpha_{it}(c_{i-1t} - c_{it}) - \alpha_{i+1t}(c_{it} - c_{i+1t})] \tag{9}$$

The next step is to obtain a relationship between the parameters α_{it}, τ and V, and the conventional diffusion coefficient D. This may be effected by taking the limit $\tau \to 0$, $V \to 0$ in (9). Introducing the spacial variable x and observing that $\Delta t = \tau$ and $\Delta x = V$ we get from (9)

$$c(x,t + \tau) - c(x,t) = \tfrac{1}{2}\ [a(x + V,t)\ \Delta_x c(x + V,t) - a(x,t)\ \Delta_x c(x,t)] \tag{10}$$

where $\Delta_x c(x,t) = c(x,t) - c(x - V,t)$
and $\Delta_x c(x + V,t) = c(x + V,t) - c(x,t)$

Hence

$$\frac{c(x,t + \tau) - c(x,t)}{\tau} = \frac{\Delta_x}{V} \left(\tfrac{1}{2}\ \frac{V^2}{\tau}\ a(x,t)\ \frac{\Delta_x c(x,t)}{V} \right) \tag{11}$$

In the limit $\tau \to 0$, $V \to 0$ we get

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D\ \frac{\partial c}{\partial x} \right) \tag{12}$$

with $D = \lim_{\substack{\tau=0 \\ V=0}} \tfrac{1}{2}\ \dfrac{V^2}{\tau}\ \alpha$ $\tag{13}$

Obviously, in order to get a finite limit other than zero, restrictions have to be imposed on the ways τ and V may tend to zero. As the upper limit of α is 1, we must always have $V^2/\tau > 0$. The definition of α therefore imposes lim $\alpha = 0$, and it may thus be approximated by the first term of its series expansion, i.e. $\alpha = 2a\tau/V$. From (13) we then get the following expression for a

$$a = D/V \tag{14}$$

In approximate calculations we may use the relation

$$D_{it} = \tfrac{1}{2}\,\frac{V^2}{\tau}\,\alpha_{it} \tag{15}$$

where D_{it} is the diffusion coefficient in the i-th cell at time t. It is convenient to keep the values of τ and V fixed. Then α_{it} is a function of D_{it} given by (15). If D_{it} is a function of concentration, position and time, this may readily be taken into account in (15) and a numerical solution of the diffusion problem is possible with the help of (9). We will here illustrate the procedure for the simplest case of a constant diffusion coefficient.

We put arbitrarily $\alpha = \tfrac{1}{2}$, and use only a small number of compartments (twenty) and let at $t = 0$ a sharp boundary (concentration $= 1$ in arbitrary units) be situated between the 10th and 11th compartment. Using eqn. (9) we then calculate the elements of the matrix in Table 1, the columns of which represent the concentration distribution at different times.

According to the method of moments the diffusion coefficient is given by

$$D = \frac{m_2}{2\,t} \tag{16}$$

where m_2 is the second moment of the normalized concentration distribution, i.e.

Table 1.

1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	1
1	1	1	1	1	1	1	1	1	0.9999
1	1	1	1	1	1	1	0.9999	0.9997	0.9993
1	1	1	1	1	1	0.9998	0.9991	0.9979	0.9962
1	1	1	1	1	0.9990	0.9968	0.9936	0.9894	0.9846
1	1	1	1	0.9961	0.9893	0.9808	0.9714	0.9617	0.9520
1	1	1	0.9844	0.9649	0.9454	0.9271	0.9103	0.8950	0.8811
1	1	0.9375	0.8906	0.8555	0.8282	0.8062	0.7881	0.7728	0.7597
1	0.7500	0.6875	0.6563	0.6367	0.6231	0.6128	0.6048	0.5982	0.5928
0	0.2500	0.3125	0.3437	0.3633	0.3769	0.3872	0.3952	0.4018	0.4072
0	0	0.0625	0.1094	0.1445	0.1718	0.1938	0.2119	0.2272	0.2403
0	0	0	0.0156	0.0351	0.0546	0.0729	0.0897	0.1050	0.1189
0	0	0	0	0.0039	0.0107	0.0192	0.0286	0.0383	0.0480
0	0	0	0	0	0.0010	0.0032	0.0064	0.0106	0.0154
0	0	0	0	0	0	0.0002	0.0009	0.0021	0.0038
0	0	0	0	0	0	0	0.0001	0.0003	0.0007
0	0	0	0	0	0	0	0	0	0.0001
0	0	0	0	0	0	0	0	0	0
0	0	0	0	0	0	0	0	0	0

$$m_2 = \frac{1}{\Delta c} \int_{-\infty}^{\infty} x^2 \, dc(x) \tag{17}$$

For the discreet distribution represented by the matrix it takes the form

$$m_{2j} = \sum_i x_i^2 \, \Delta c_{ij} \tag{18}$$

Denoting the elements of the matrix by c_{ij} we find that the j:th column represents the situation at time $(j-1)\, \tau$ and that for the i:th row $x_i = (i-10)\, V$ and further $\Delta c_{ij} = c_{ij} - c_{i+1j}$. Calculating the diffusion coefficient according to this procedure we get

$$D = \tfrac{1}{4} \frac{V^2}{\tau} \tag{19}$$

which is in agreement with (15) for $\alpha = \tfrac{1}{2}$. Calculations of this type may conveniently be carried out with digital computers.

The model treatment may also be applied to problems concerning diffusion into bodies of different kinds, *e.g.* gel particles. To a first order approximation we specify the process as diffusion into a cell of the form of the body, its surface acting as the membrane. We consider diffusion in the body to be the rate determining step. Eqn. (6) may then be applied directly and we get

$$\Delta c = \Delta c^\circ \exp\left[-a\left(\frac{1}{V} + \frac{1}{V_e}\right)t\right] \tag{20}$$

where V and V_e are the per area volumes of the body and the external solution, respectively.

We now have to relate the parameter a to the diffusion coefficient in the body. This may be done by generalizing the result in (13). We observe that the equations that led to (13) represent an analogy to (20), with $V = V_e$ and with rate determining diffusion occurring in both volumes. As in (20) rate determining diffusion was assumed to occur only in the internal volume of the body, the parameter a there must have twice the value of that in (13). Hence $a = 2\,D/V$ and (20) takes the form

$$\Delta c = \Delta c^\circ \exp\left[-\frac{2D}{V}\left(\frac{1}{V} + \frac{1}{V_e}\right)t\right] \tag{21}$$

From (21) we may also obtain the following formula for the half-time for attainment of equilibrium

$$\tau_{1/2} = \frac{V \ln 2}{2D\left(\dfrac{1}{V} + \dfrac{1}{V_e}\right)} \tag{22}$$

We observe that in the model the solutions in the volumes V and V_e were assumed to have uniform concentrations. Therefore (21) is valid for bodies with all kinds of geometrical form. The only parameters are the diffusion coefficient in the body, D, and the per area internal and external volumes V and V_e.

As an example we calculate the half-time for diffusion into a sphere in an infinite external solution of uniform concentration. For a sphere with radius r the volume to area ratio is $\frac{1}{3} r$. Hence with $V = \frac{1}{3} r$ and $V_e = \infty$ in (22) we get

$$\tau_{1/2} = 0.039 \ r^2/D \tag{23}$$

This may be compared with the approximate formula of Vermeulen,[7-8] which gives

$$\tau_{1/2} = 0.030 \ r^2/D \tag{24}$$

We see that the two formulae are in good agreement. Eqn. (22) can of course be used for an approximate treatment of diffusion into bodies of different kinds such as cylindrical rods, ellipsoids etc. We have only to determine the volume to area ratio V of the body and insert it into (22).

We thus find that the model treatment of diffusion processes provides a convenient method for the approximate solution of various diffusion problems. Especially, it provides an excellent means for numerical calculations with digital computers of complicated diffusion problems.

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