On Calculating Residence and Transfer Times

BRIAN MARTIN

School of Physics, Sydney University, Sydney, New South Wales, Australia

The method presented by Hewitt and Martin (1973) for calculating residence times is elaborated and extended. A simple modification of the procedure allows the calculation of transfer times (a transfer time is the average time it takes a particle at a given place to move to a certain other place). Exact results relevant to the use of the method are discussed. The method is used to calculate times for transfer from the northern to the southern stratosphere.

Consider a system of particles in motion in a region of space, such as part of the atmosphere or ocean. Often it is useful to know the average time it takes for a particle at a given place to move to a certain other place. This average time will be called a transfer time. If the certain other place is anywhere exterior to the region, then the transfer time is called a residence time.

Hewitt and Martin [1973] presented a straightforward method for calculating residence times from properties of a medium such as winds and diffusion rates. In this paper new results concerning that technique are presented. First, it is shown how to determine where, on the average, particles spend their time before exiting from the system and how residence times may be calculated when the transport parameters vary with time. Second, it is shown how to simply extend the method so as to calculate transfer times. Third, an exact solution for residence times is obtained for a one-dimensional problem and used to gain insight into the method for calculating residence and transfer times. The technique for calculating transfer times is used to determine times for movement from the northern to the southern stratosphere. Finally, we offer some cautionary remarks on the calculation of residence and transfer times.

Residence Times

A residence time is the average time required for a particle at a given place to exit from a particular region of space. Let us consider briefly how residence times may be calculated from properties of the medium. Divide the region of space into N boxes and time into intervals of duration τ, and let A_{ij} be the probability that a particle in box i moves to box j during any time interval. For example, in a calculation of stratospheric residence times the N boxes will partition the volume of the stratosphere, and the probabilities A_{ij} will depend on movements of particles due to processes such as winds and turbulence. The residence time T_i is defined to be the average time for a particle in box i to escape from the system of boxes. We may write (see *Hewitt and Martin* [1973], equation (2), where T_i is written $n_i\tau$)

$$T_i = \sum_{j=1}^{N} A_{ij}T_j + \tau \qquad i = 1, \cdots, N \tag{1}$$

In the stratospheric case, T_i is the average time taken for a particle to physically move out of the stratosphere, for example, by movement to the troposphere or through rainout, or to be chemically transformed.

The solution to (1) is

$$\mathsf{T} = (\mathsf{I} - \mathsf{A})^{-1}\mathsf{U} \tag{2}$$

Here we have written the transition probabilities A_{ij} as a matrix A and the times T_i as a column vector T; I is the unit matrix and U is a column vector each of whose elements equals τ. Thus if we know the transition probabilities A, the same for each time interval of duration τ, then the average time T_i for removal from the region of a particle beginning in box i may be calculated using (2).

By conservation of particles during a time interval, used in deriving (2) above,

$$B_i + \sum_{j=1}^{N} A_{ij} = 1 \qquad i = 1, \cdots, N$$

where B_i is the probability that a particle in box i moves out of the set of boxes during a time interval. In most physical problems any particle will eventually escape from the system, so that the residence times are finite. For our model to reflect this fact there must exist for each box i at least one sequence of nonzero transition probabilities A_{ij}, A_{jk}, $\cdots$, A_{pq}, in which q labels a box for which $B_q > 0$. This condition is necessary and sufficient for the existence of the matrix $(\mathsf{I} - \mathsf{A})^{-1}$.

Sometimes one would like to know not only the residence times but also where the particles spend their time before they escape from the system. In our picture this is equivalent to knowing the average time a particle starting in a particular box spends in any given box before escaping. For example, a thermonuclear explosion may inject certain amounts of nitrogen oxides into the stratosphere at various locations. One may wish to know not only the average length of time spent by the nitrogen oxide molecules in the stratosphere but also how long they spend on average in any stated region, say, as a means for calculating the expected catalytic destruction of ozone in that region. We now show how the average time a particle starting in a particular box spends in any given box before escaping may be simply obtained from the matrix $(\mathsf{I} - \mathsf{A})^{-1}$.

First we note that the steady state mass distribution resulting from a continuous point source is of the same functional form as the expected time distribution of a single particle released at the position of the point source. That is, the fraction of the total mass in a particular box in the steady state distribution equals the expected fraction of the residence time spent in the particular box by a single particle released at the point of the continuous source. This may be seen by viewing the single particle as a member of the ensemble of particles released by the continuous source.

Consider the mass transfer equation for the system with continuous source in box i, written in a numerical representation of the form

$$m_k(n + 1) = \sum_{j=1}^{N} m_j(n) A_{jk} + S\delta_{ik} \qquad (3)$$

$$k = 1, \cdots, N$$

Here $m_k(n)$ is the mass in box k at the nth time interval and S is the amount of mass added to box i during this interval. Note that if (3) is written in matrix form, $\mathbf{m}(n)$ is a row vector (as contrasted to the column vector $\mathbf{T}$) which multiplies A on the left. The steady state solution is found by setting $\mathbf{m}(n + 1) = \mathbf{m}(n) \equiv \mathbf{m}$. Then

$$\mathbf{m} = \mathbf{S}(i)\,(\mathsf{I} - \mathsf{A})^{-1} \qquad (4)$$

where $\mathbf{S}(i)$ is a row vector with an S in position i and zeroes elsewhere. The fraction of the total mass in box j is $m_j/\sum_{k=1}^{N} \cdot m_k$. Therefore for a particle starting in box i the average time spent in box j before escape is seen to be given by the jth component of

$$\mathrm{U}(i)(\mathsf{I} - \mathsf{A})^{-1} \qquad (5)$$

where $\mathrm{U}(i)$ is a row vector with a τ in position i and zeroes elsewhere. That is, a particle starting in box i spends an average time equal to τ times the i, jth element of $(\mathsf{I} - \mathsf{A})^{-1}$ in box j before exiting from the system. The sum of all the elements in the ith row of $\tau(\mathsf{I} - \mathsf{A})^{-1}$ is then equal to the residence time T_i, as obviously must be the case.

The motions of different particles are independent. Therefore if a set of particles is released in the same box or in different boxes, the expected total time spent in particular boxes may be determined by adding the appropriate times given by (5).

Let us say we introduce certain masses of particles at various places in the stratosphere and wish to determine the average length of time spent by any of these particles in any given region of the stratosphere. That is, we might wish to know, for example, the expected number of particle days (a particle spending a day), due to the masses introduced, spent north of a certain latitude. Let $\mathbf{M}$ be a row vector of the total masses introduced into each box. Then by using (5) the time spent in box j by any of this mass, measured in units of mass time (a certain mass of particles spending a certain length of time in box j), is simply given by the jth component of $\mathbf{M}\tau(\mathsf{I} - \mathsf{A})^{-1}$. Of course if one wishes to know exactly when the particles on average spend their time in each box, then one must solve the time-dependent mass transfer equation (3).

In summary, a particle released in box i spends on the average a certain amount of time in box j before exiting from the region. This time has been determined to be equal to τ times the i, jth element of $(\mathsf{I} - \mathsf{A})^{-1}$. The residence time is the sum over all the boxes $j = 1, \cdots, N$ of the average times spent in box j and thus equals $(\mathsf{I} - \mathsf{A})^{-1}\mathbf{U}$.

The solution (2) holds only if A is independent of time. If A varies in time, the solution (2) will be accurate to the extent that the time for change in A is large in comparison to the times $\mathbf{T}$. However, it is also possible to calculate residence times more exactly when A is a function of time. This may be useful, for example, in calculating more accurate stratospheric residence times, since the stratospheric transport coefficients show a fairly pronounced seasonal variation. Denote the residence time for particles in box i at the nth time interval by $T_i(n)$: this is the average time for a particle located in box i at the nth time interval to move out of the region. Analogous to (1), we may write

$$T_i(n) = \sum_{j=1}^{N} A_{ij}(n) T_j(n + 1) + \tau(n) \qquad (6)$$

$$i = 1, \cdots, N$$

where the $A_{ij}(n)$ are the transition probabilities for the nth time interval which has duration $\tau(n)$. The residence times must be calculated independently for each time interval. For $\mathbf{T}(n)$ we may write

$$\mathbf{T}(n) = \lim_{K\to\infty} \left\{ \sum_{k=0}^{K} \mathsf{A}(n)\mathsf{A}(n + 1) \cdots \right.$$

$$\times \cdots \mathsf{A}(n + k - 1)\mathbf{U}(n + k)$$

$$\left. + \left[\prod_{k=0}^{K} \mathsf{A}(n + k) \right] \mathbf{T}(n + K + 1) \right\} \qquad (7)$$

where $\mathbf{U}(n)$ is a column vector each of whose elements equals $\tau(n)$.

In almost every physically realistic situation it will be true that

$$\lim_{K\to\infty} \prod_{k=0}^{K} \mathsf{A}(n + k) \rightarrow \mathbf{0} \qquad (8)$$

where 0 is the matrix of all zeroes. (We have not been able to prove this generally.) When (8) holds, we may write

$$\mathbf{T}(n) = \lim_{K\to\infty} \sum_{k=0}^{K} \mathsf{A}(n) \cdots \mathsf{A}(n + k - 1)\mathbf{U}(n + k) \qquad (9)$$

$\mathbf{T}(n)$ may be found straightforwardly by calculating successive terms in this sum, although this will usually be a lengthy process. When $\mathsf{A}(n)$ and $\mathbf{U}(n)$ are independent of n, the solution (9) for $\mathbf{T}(n)$ becomes identical with the earlier solution (2).

Thus far we have considered the problem of calculating residence times from the procedural point of view of dividing the region of space under consideration into a set of boxes. Particles move from box to box, and when they leave the region, they also exit from the set of boxes. However, in many problems it is convenient to alter this picture slightly. Let us add to the set of N boxes which partition the physical region some additional boxes to correspond to the sinks where the particles go upon exiting from the physical region. These additional boxes may be labeled $N + 1, \cdots, L$. If we are calculating stratospheric residence times, the N boxes partition the stratosphere. The additional boxes $N + 1, \cdots, L$ will represent the sinks for the particles in the stratosphere, for example, regions of the troposphere or symbolic repositories for chemically transformed particles. The probabilities B_i for removal from the set of N boxes will now become transition probabilities to the additional boxes which correspond to sinks. Naturally, on reaching a physical sink a particle may not return to the physical region; therefore the transition probabilities from the additional boxes to boxes corresponding to the physical region must equal zero.

Mathematically, this situation may be represented as follows. Let P_{ij}, $i, j = 1, \cdots, L$ be the transition probabilities between the augmented set of L boxes. Then

$$\begin{aligned} P_{ij} &= A_{ij} && i, j = 1, \cdots, N \\ \sum_{j=N+1}^{L} P_{ij} &= B_i && i = 1, \cdots, N \\ P_{ij} &= 0 && i = N + 1, \cdots, L \\ & && j = 1, \cdots, N \end{aligned} \qquad (10)$$

$$\sum_{j=N+1}^{L} P_{ij} = 1 \qquad i = N+1, \cdots, L$$

For example, if there is a single sink, $L = N + 1$, then

$$\mathsf{P} = \begin{vmatrix} \mathsf{A} & \mathbf{B} \\ 0 & 1 \end{vmatrix} \tag{11}$$

where $\mathbf{B}$ is a column vector of the B_i and $\mathbf{0}$ is a row vector of zeroes. When modeling the stratosphere with the transition probabilities in (11), all particles exiting from the stratosphere will be transferred to the single box labeled $N + 1$. Additional boxes corresponding to sinks may be added if we wish to distinguish where or how a particle exited from the physical region, for example, which part of the troposphere a particle entered.

In problems involving residence and transfer times the addition of extra boxes corresponding to sinks allows utilization of useful results from the theory of matrices. Since each row sum of P equals one and each element is nonnegative, P is by definition a stochastic matrix (see for example *Gantmacher* [1959] or *Feller* [1968]). The boxes $i = 1, \cdots, N$ which correspond directly to the physical region under consideration are called transient states or inessential states. The boxes $i = N + 1, \cdots, L$ which correspond to sinks are called persistent states or essential states. This new picture of our problem will be used to good effect in the next section, which is devoted to transfer times.

TRANSFER TIMES

We define a transfer time to be the average time it takes a particle in a given box to move to one of a set B' of boxes, the average taken over only those particles that do not first reach one of a set B'' of boxes. We may think of transfer times in terms of a particular example: the average time for a particle to move from a particular place in the northern stratosphere to anywhere in the southern stratosphere (or vice versa), when permanent transfer to the troposphere may also occur. Our set of N boxes will correspond to the stratosphere, and the boxes $N + 1, \cdots, L$ will correspond to regions of the troposphere to which particles may move. We wish to calculate the average time a particle in the northern stratosphere takes to move to the southern stratosphere, ignoring those particles that reach the troposphere before reaching the southern stratosphere. Thus the set B' consists of those boxes corresponding to the southern stratosphere, and the set B'' consists of those boxes corresponding to the troposphere. Note again that in calculating these transfer times, when taking the average over particles, we must exclude those particles that reach the troposphere first, since they may never reach the southern stratosphere. The inclusion of such particles in the average obviously would lead to infinite transfer times.

Now let us consider how to solve for transfer times. (*Hewitt and Martin* [1973] incorrectly noted that it is not easy to solve for transfer times. In their Appendix 1 the second equation and the statement following it are incorrect.) Let T_i now be the average time for a particle in box i to reach a box in B', the average being taken over particles that reach a box in B' before reaching one in B''. We rearrange the rows and columns of P so that rows and columns labeled $i, j = 1, \cdots, N'$ correspond to boxes not in B''. In calculating times to move from the northern to the southern stratosphere, boxes in B'' correspond to the troposphere, and in this particular example $N' = N$. To calculate transfer times, we must eliminate from consideration particles which move to boxes in B''. Let us denote by A_{ij}' probabilities which describe the transitions between the boxes for those particles that do not move directly to a box in B''. A_{ij}' will be the fraction of particles in box i which move during a time interval to a box j from which a set of transitions passing through boxes not in B'' and terminating at a box in B' is possible. For example, consider a particle in box i in the northern stratosphere, which moves during a time interval to any box also in the stratosphere (i.e., not to a box in B'' corresponding to the troposphere); A_{ij}' is the probability that such a particle moves to box j, representing part of the stratosphere, and from which eventual transfer to the southern stratosphere is possible. Mathematically,

$$A_{ij}' = \frac{P_{ij}}{\sum_{j=1}^{N'} P_{ij}} \qquad i, j = 1, \cdots, N' \tag{12}$$

(Remember the boxes labeled $1, \cdots, N'$ are those not in B''.)

In the above we have assumed that any particle in the stratosphere has a nonzero chance of reaching the southern hemisphere before reaching the troposphere. Mathematically, this is equivalent to the assumption that all sinks or persistent states are in B' or B'', so that for each box i not in B' or B'' there is at least one box j such that $P_{ij} \neq 0, j = 1, \cdots, N'$.

Of the transitions represented by A' between the boxes not in B'', those in B' act like sinks. That is, in following a particle from box to box we stop incrementing the time T_i when it reaches a box in B'. As we follow a particle released in the northern stratosphere as it moves from place to place, we note the time elapsed when the particle moves into the southern stratosphere. For the purpose of calculating these stratospheric transfer times the southern stratosphere thus acts like a sink. To model the effective role of B' as a set of sinks in calculating T_i, we merely set $T_i = 0$ if box i is in B'. We can easily write down equations for T_i similar to (1):

$$\begin{aligned} T_i &= \sum_{j=1}^{N'} A_{ij}'T_j + \tau \qquad i = 1, \cdots, N' \qquad i \notin B' \\ T_i &= 0 \qquad i \in B' \end{aligned} \tag{13}$$

To solve for T_i, we note that the specification $T_i = 0$ for $i \in B'$ effectively deletes rows and columns corresponding to boxes in B' from the matrix A'. Denote the matrix which results from deleting from A' rows and columns corresponding to B' by A''. Then analogous to (2), the transfer times are given by

$$\mathbf{T} = (\mathsf{I} - \mathsf{A}'')^{-1}\mathbf{U} \tag{14}$$

where the order of I is the same as that of A'' and is equal to the number of elements in $\mathbf{T}$ and $\mathbf{U}$.

To summarize the procedure for obtaining transfer times:

1. Normalize the elements of each row of P corresponding to boxes not in B'', giving A' (equation (12)).
2. Delete rows and columns corresponding to boxes in B' from A', giving A''.
3. Solve for the transfer times $\mathbf{T}$ using (14).

If we wish to determine how long a particle beginning in box i spends on the average in box j on its way to a box in the set B', ignoring particles that first reach a box in B'', we may use the method presented earlier. It is easy to show that this time is equal to τ times the i, jth element of $(\mathsf{I} - \mathsf{A}'')^{-1}$.

One may also wish to know the actual probability that a particle in box i will reach a box in B' before reaching one in B''. As well as determining the time for a particle at a given place in the northern stratosphere to move to the southern stratosphere (averaged over particles that make the transfer), one very likely would wish to know the probability that this transfer eventually takes place. For a particle in box i let this probability, which we call a transfer probability, be denoted by R_i. We may write

$$R_i = \sum_{j=1}^{N'} P_{ij}R_j \qquad i = 1, \cdots, N' \qquad i \notin B'$$
$$R_i = 1 \qquad i \in B' \tag{15}$$

To solve (15), first form P' by deleting rows and columns of P corresponding to boxes in B' or B''. Then multiply $(\mathsf{I} - \mathsf{P}')^{-1}$ by the column vector whose ith component is $\sum_{j\in B'} P_{ij}$.

A residence time is also a transfer time. In our example the set B' consists of the boxes corresponding to the troposphere, and B'' is the empty set. In general, the set B' may contain any particular box out of the full set of L boxes. For example, a transfer time may be calculated from a given box to one of a set which contains boxes corresponding to regions of the troposphere. The set B'' will always contain all boxes corresponding to sinks which are not in B' but may contain other boxes as well. In calculating stratospheric transfer times, B'' will always contain all boxes not in B' which correspond to regions of the troposphere and perhaps boxes corresponding to regions of the stratosphere as well. Since all boxes corresponding to sinks are either in B' or B'', every particle will eventually reach a box in B' or B'', and therefore transfer times will always exist.

EXACT FORMULATION FOR RESIDENCE TIMES IN A ONE-DIMENSIONAL PROBLEM

One simple and convenient way to determine the transition probabilities A is to write the mass transfer equation in the numerical form (3) and note the coefficients of $m_j(n)$ on the right-hand side. Although the transition probabilities obtained in this way will usually serve adequately in determining residence and transfer times, they are not guaranteed to give good results. Here we investigate the form of the transition probabilities in a one-dimensional transfer problem in which an analytical expression may be obtained for the residence times.

Let us stop thinking about transition probabilities for movement from one box to another during a fixed finite time interval and reconsider what the idea of a residence time means. In a diffusion process a particle starting at the center of a given box i moves in a random walk toward neighboring boxes, back toward the center of the given box, and so forth. We note that a particle has probability one of eventually reaching some contiguous box (a neighboring box with a boundary common with box i or a box corresponding to a sink that may be reached directly from box i). Furthermore, there is a certain probability for each contiguous box j that the particle from box i reaches it before reaching any other contiguous box. Call this probability f_{ij}. We set $f_{ij} = 0$ if j is not a box contiguous to box i. By definition $f_{ii} = 0$ and by conservation of particles, $\sum_{j=1}^{L} f_{ij} = 1$.

Now since we are determining residence times, we may also note that for the fraction f_{ij} of particles first reaching box j from box i there is an average time for the movement from box i to box j. Denote by τ_{ij} the average time that a particle in box i takes to reach box j, the average taken over those particles which reach box j before reaching any other box k, $k \neq i$, $k \neq j$. Then our formula (1) for residence times may be written in terms of the quantities f_{ij} and τ_{ij} as

$$T_i = \sum_{j=1}^{N} f_{ij}T_j + \sum_{j=1}^{L} f_{ij}\tau_{ij} \qquad i = 1, \cdots, N \tag{16}$$

(In the second sum in (16) no summation over i is implied.) Physically, this formula indicates that the average time for a particle in box i to escape from the system to a sink equals the weighted sum of times to escape from boxes $j = 1, \cdots, N$ corresponding to the physical system and to which direct transfer from box i may be made, plus the weighted sum of times for direct transfer to any box $j = 1, \cdots, L$ whether corresponding to the physical region or to a sink. The solution to (16) may be written

$$\mathbf{T} = (\mathsf{I} - \mathsf{F})^{-1}\mathbf{V}$$
$$V_i = \sum_{j=1}^{L} f_{ij}\tau_{ij} \qquad i = 1, \cdots, N \tag{17}$$

where the rows and columns of I and F and the elements of $\mathbf{T}$ and $\mathbf{V}$ refer to the boxes $i = 1, \cdots, N$ which correspond to the physical system. The advantage of the formulation (17) over (1) is that the fractions f_{ij} and the average times τ_{ij} may be calculated exactly for a particular one-dimensional problem, which we now consider.

Let the movement of particles in one dimension be described by the equation

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}\left(K\frac{\partial c}{\partial z} - Vc\right) \tag{18}$$

For example, we may imagine a one-dimensional model of atmospheric diffusion in which z is the altitude coordinate (positive upward) and in which the time and space variation in the concentration c of some tracer particles is described by (18). The residence time at height z is the average time it takes a particle released at height z to reach the ground. In such a problem, K would be the vertical eddy diffusion coefficient, and $V = w - K/H$, where w is the mean vertical wind speed and H is the scale height. Of course this model of atmospheric diffusion is more or less idealized, depending on the diffusing species and the physical circumstances, because processes such as the horizontal divergence of particles and rainout are ignored. Even this one-dimensional problem is not easy to solve analytically if K, w, and H vary with z.

Divide the altitude coordinate into a series of boxes, labeled $1, \cdots, N$ from the ground up. Box $N + 1$ corresponds to the surface of the earth, which is the sink for the problem. $f_{i\,i+1}$ is the probability that a particle in box i reaches the next higher box $i + 1$ before reaching the next lower box $i - 1$, and $\tau_{i\,i+1}$ is the average time required for this movement. The box $N + 1$ corresponding to the surface of the earth will have $f_{N+1\,i} = \delta_{N+1\,i}$.

For our special problem, K and V are constants. Furth's formula for first passages [*Feller*, 1968, p. 359] is an expression for the probability $u(t, \xi)\,dt$ that in a diffusion process in one dimension described by (18) a particle released at time zero and position $\xi > 0$ will reach 0 before reaching $\alpha > \xi$ and that this event will occur in an infinitesimal time interval dt centered on t:

$$u(t, \xi) = 2\pi K\alpha^{-2} \exp\left[-\tfrac{1}{4}(Vt + 2\xi)V/K\right] \times \sum_{\nu=1}^{\infty} \nu \exp\left(-\nu^2\pi^2 Kt/\alpha^2\right) \sin \pi\xi\nu/\alpha \tag{19}$$

(Note that our K corresponds to $\frac{1}{2}D$ in *Feller*'s [1968] notation and our V to his c; see his formula (6.12), p. 358.) Furth's formula (19) may be used to calculate the values of f_{ij} and τ_{ij} to be used in (17). Let the center of box i be denoted by z_i. If we set $z_i - z_{i-1} = \xi$ and $z_{i+1} - z_i = \alpha - \xi$, thus being concerned with passage from the center of one box to the center of another, then

$$f_{i\ i-1} = \int_0^\infty u(t, \xi)\, dt$$

$$f_{i\ i+1} = \int_0^\infty \tilde{u}(t, \alpha - \xi)\, dt = 1 - f_{i\ i-1} \tag{20}$$

$$f_{ij} = 0 \qquad j = 1, \cdots, N \qquad j \neq i - 1 \qquad j \neq i + 1$$

where $\tilde{u}$ is the function u with $V \to -V$. The mean times τ_{ij} for the two transfers, weighted by the respective probabilities of making the transfer, are given by

$$f_{i\ i-1}\tau_{i\ i-1} = \int_0^\infty tu(t, \xi)\, dt$$

$$f_{i\ i+1}\tau_{i\ i+1} = \int_0^\infty t\tilde{u}(t, \alpha - \xi)\, dt \tag{21}$$

$$f_{ij}\tau_{ij} = 0 \qquad j = 1, \cdots, N \qquad j \neq i - 1 \qquad j \neq i + 1.$$

To give an idea of the typical form of the probabilities f_{ij} and the average times τ_{ij}, we calculate expressions for a specific case. First assume uniform box sizes, so that $z_{i+1} - z_i = z_i - z_{i-1} = \xi = \frac{1}{2}\alpha$. We may then easily perform the integrals in (20) and obtain

$$f_{i\ i-1} = C_f \exp(-\xi V/2K) \tag{22}$$

$$f_{i\ i+1} = C_f \exp(\xi V/2K) \tag{23}$$

$$C_f = \frac{2}{\pi} \sum_{\nu=0}^{\infty} \frac{(-1)^\nu (2\nu + 1)}{(2\nu + 1)^2 + (\xi V/\pi K)^2} \tag{24}$$

Since C_f in (24) does not depend upon the sign of V, we may replace its calculation by the normalization expression $f_{i\ i-1} + f_{i\ i+1} = 1$. Equations (22) and (23) become

$$f_{i\ i-1} = \exp(-\xi V/2K)/[\exp(-\xi V/2K) + \exp(\xi V/2K)] \tag{25}$$

$$f_{i\ i+1} = 1 - f_{i\ i-1}$$

As expected, particles are more likely to move to the box toward which the effective wind V is blowing; when $V = 0$, each probability equals $\frac{1}{2}$, as is required by symmetry.

For the probability f_{ij} multiplied by the average time τ_{ij} the integrals (21) with $\alpha = 2\xi$ give

$$f_{i\ i-1}\tau_{i\ i-1} = C_\tau \exp(-\xi V/2K) \tag{26}$$

$$f_{i\ i+1}\tau_{i\ i+1} = C_\tau \exp(+\xi V/2K) \tag{27}$$

$$C_\tau = \frac{8}{\pi^3} \frac{\xi^2}{K} \sum_{\nu=0}^{\infty} \frac{(-1)^\nu (2\nu + 1)}{[(2\nu + 1)^2 + (\xi V/\pi K)^2]^2} \tag{28}$$

The sum in (28) converges rapidly if the effective wind is not too dominant over diffusion, that is, if $\xi V/\pi K$ is not large in comparison with one.

In comparing (16) with (1) it is not hard to show that the equations will be identical if

$$1 - A_{ii} = \frac{\tau}{\sum_{j=1}^{L} f_{ij}\tau_{ij}} \qquad i = 1, \cdots, N \tag{29}$$

$$A_{ij} = (1 - A_{ii})f_{ij} \qquad i, j = 1, \cdots, N \qquad i \neq j \tag{30}$$

The formulation (16) uses average times τ_{ij}, while the formulation (1) uses rates of transfer (transfer of a mass fraction A_{ij} in time τ). Since dimensionally a rate is the inverse of a time, the relations (29) and (30) make sense physically. From these expressions one may also note that $\mathbf{I} - \mathbf{A}$ is proportional to τ, with the proportionality factor independent of τ. Therefore the solution (2) found using (29) and (30) is completely independent of τ, as indeed must be the case if use of these expressions is to give the same results as (17), which does not involve τ.

In Figure 1 we illustrate the form of the transition probabilities found using formulas (25)-(30). The results are given in terms of the parameters $r = \xi V/K$ and $\alpha_{ij} = (\xi^2/K\tau) \cdot |\delta_{ij} - A_{ij}|$. The results presented in Figure 1 for smaller r are quite close to those obtained by approximating the derivatives in (18) by the simple finite difference forms

$$\frac{c(z_i, n+1) - c(z_i, n)}{\tau} = K\frac{c(z_{i+1}, n) - 2c(z_i, n) + c(z_{i-1}, n)}{\xi^2} - V\frac{c(z_{i+1}, n) - c(z_{i-1}, n)}{2\xi}$$

where $c(z_i, n)$ is the value of c at position z_i and at the nth time interval. However, for large r (say, $r \gtrsim 1$) the form of the transition probabilities differs from the form obtained from any standard numerical representation of (18). This is only to be expected, since a numerical representation designed to represent mass transfer is not necessarily accurate when used to obtain the times taken for the transfer.

Just as we have here calculated mathematically exact residence times for a one-dimensional problem, so may transfer times be calculated exactly. This is done by generalizing (16) as (1) was generalized in the previous section. In fact, the requirements that probabilities be normalized and that rows and columns be deleted may be seen to be equivalent to

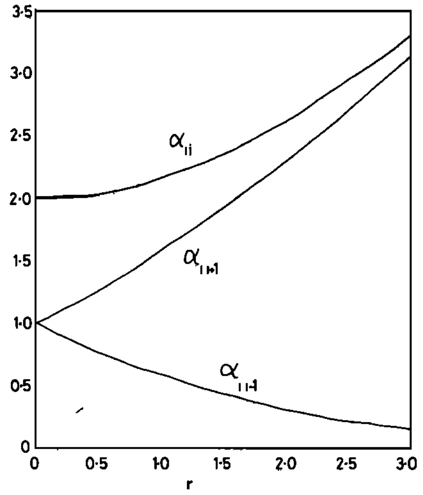

Fig. 1. Normalized transition probabilities α_{ij} as a function of the dimensionless ratio $r = \xi V/K$. As r increases, the influence of V relative to that of K becomes larger, and the rate of transfer from box i to the box $i + 1$ toward which the effective wind is blowing becomes more and more dominant.

the boundary conditions given by *Feller* [1968, equation (2.2), p. 344, equation (7.4), p. 362] for random walks.

There would seem at first sight to be no reason not to always use the formulation (16) to calculate residence and transfer times, since in practice it is only a matter of choosing the correct transition probabilities as from Figure 1. And indeed this is true in one-dimensional problems with constant K and V. But with more complicated problems, difficulties arise.

If the diffusion parameters vary in space, it seems unlikely that mathematically exact transfer times can be obtained even in one dimension. In cases when the diffusion parameters vary in space, it is easiest to use the local values of the parameters to calculate the transition probabilities out of each box. If the parameters do not vary significantly from box to box, the transfer times resulting from this procedure should closely approximate the exact values.

Exact formulations of random walk problems in more than one dimension usually assume that particles can only move parallel to the coordinate axes in integral steps. But in physical space, particles can move in any direction, and rigorously formulating the problem is probably not easy, not to mention solving it. In particular, it is not obvious how to treat anisotropic diffusion arising from a nondiagonal tensor K of diffusion coefficients.

Given the problem of calculating residence times in a problem in more than one dimension and having anisotropic diffusion terms, one of two approaches might be used:

1. Take the transition probabilities to be used in (1) from a numerical representation of the diffusion equation.
2. Calculate the transition probabilities in each direction from (29) and (30), ignoring anisotropic diffusion.

On the basis of our previous discussion it may be recommended that approach 1 be used if mean motions do not dominate (if $r \lesssim 1$) and anisotropic diffusion terms are important and that approach 2 be used in the converse situation. Note that since r is proportional to ξ, the relative effect of the mean motions within the numerical representation can be reduced by decreasing the box sizes.

SAMPLE CALCULATION: TRANSFER TIMES FROM NORTHERN TO SOUTHERN STRATOSPHERE

The method outlined above based on using the quantities f_{ij} and τ_{ij} has been used to determine transfer times for movement from the northern to the southern stratosphere and the probabilities for making the transfer. A grid was assigned in the two dimensions of latitude and altitude, and boxes formed by sweeping this grid around the earth longitudinally along lines of latitude. In latitude there were 25 boxes at each altitude spaced evenly between the north and south poles, and in altitude, 25 boxes at each latitude, each of height 1 km, and centered at altitudes from 15 to 39 km. Thus the stratospheric region considered was partitioned into a total of 625 boxes.

Escape from the set was permitted only by downward movement from the boxes at 15 km. Particles moving toward the poles and upward above 39 km in effect met reflecting barriers, and there were no chemical sinks. Thus the set B'' of boxes represented the region below 15 km. For the particles in the northern stratosphere the set B' of boxes consisted of those boxes above the equator, since on reaching the center of such a box a particle may be considered to have reached the southern hemisphere. Thus the matrices inverted, $\mathsf{I} - \mathsf{A}''$ and $\mathsf{I} - \mathsf{P}'$, were of order $12 \times 25 = 300$.

It may be noted that some of the particles that move below 15 km will eventually move to the southern stratosphere and that these particles have been excluded from the averaging process. They cannot be easily included except by enlarging the model to include the troposphere, since within the model as given an indeterminate fraction will be permanently absorbed on the surface of the earth. Our calculation is primarily meant to illustrate the technique involved. However, the model may not be physically unrealistic if, for example, we envisage a fairly complete process of rainout below 15 km.

The transition probabilities were determined using mean winds and eddy diffusion coefficients interpolated from values given by *Gudiksen et al.* [1968] (see also *Reed and German* [1965]). Procedure 2 described above was used. For example, the vertical transport parameters at a horizontal face between two boxes were used in (25)–(30) to obtain the transition probability up from the lower box and down from the upper box. The validity of the neglecting of the anisotropic diffusion terms in the use of procedure 2 is discussed later.

Transfer times from the northern to the southern stratosphere are presented in Figures 2 and 3 for different sets of velocities and eddy diffusion coefficients. The contours on each side of the equator in each of the figures refer to transfer times for the northern stratosphere, calculated with the transport parameters for the indicated times of the year. In Figures 4 and 5 are presented the corresponding probabilities for making the transfer to the southern stratosphere.

Transfer times are presented only up to 27 km for two reasons: (1) the data of Gudiksen et al. extend only to 27 km; the parameters used above this height, equal to those at 27 km, lack a detailed physical basis and (2) the reflecting barrier at 39.5 km truncates the trajectories of many particles released higher than 27 km. These influences do not affect the times significantly at 27 km, however, especially since the effect of vertical motions is rather small.

Of greatest importance in determining the magnitude of the transfer times are the values of the winds and eddy diffusion coefficients. If all of the transport parameters are multiplied by an identical factor, then the transfer times are divided by the same factor, and the probabilities for making the transfer are unaltered. This scaling property is apparent, for example, in formulas (26)–(28): if $r = \xi V/K$ is a constant, then the times τ_{ij} vary as $1/K$.

The transfer times presented in Figures 2 and 3 are based on data for particular times of the year. Transfer times based on the time-varying parameters are likely to give results intermediate to these figures. It will normally be the case that transfer times based on time-varying parameters are bounded

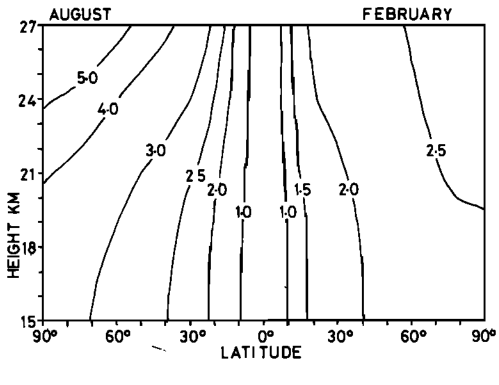

Fig. 2. Contours of times for transfer from the northern to the southern stratosphere, based on transport coefficients of Gudiksen et al. for August (left half) and February (right half). The times are in years.

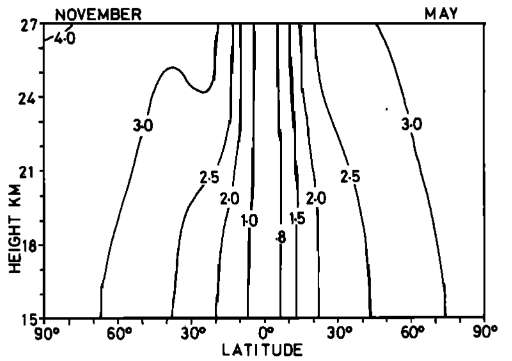

Fig. 3. Contours of times for transfer from the northern to the southern stratosphere, based on transport coefficients of Gudiksen et al. for November (left half) and May (right half). The times are in years.

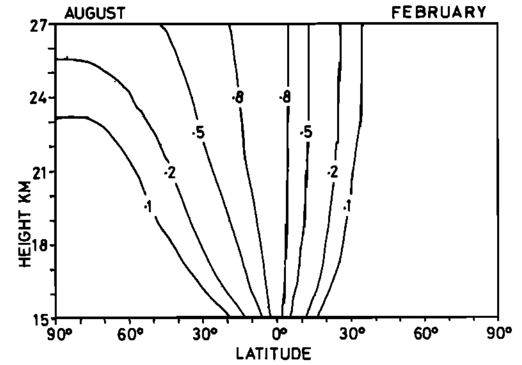

Fig. 4. Contours of the probability of making the transfer from the northern to the southern stratosphere, based on transport coefficients of Gudiksen et al. for August (left half) and February (right half).

by the sets of transfer times obtained using as constant parameters the time-varying parameters at particular times. Only in certain special situations, as when a particle is blown back and forth between two points, will this not be true. Such a situation is unlikely in a natural system such as the stratosphere, where turbulence plays a major role.

Interhemispheric mixing times presented in the literature (see *Pressman and Warneck* [1970] and references therein) are typically in the range of 3-5 years. Transfer times representative of the ones found here (either values for a mid-latitude and medium altitude position or values averaged over the entire hemisphere) are roughly of this size. This agreement may be somewhat fortuitous. The parameters of Gudiksen et al., especially the horizontal eddy diffusion coefficients, are probably too large. If other data, say, those of *Reed and German* [1965], had been used, the transfer times obtained would be several times smaller than the ones obtained here. A possible contribution to the agreement is that a stratospheric transfer time as defined here may be a somewhat different quantity than an interhemispheric mixing time; this point will be discussed further in the next section.

To check the validity of neglecting the anisotropic diffusion terms in using procedure 2 for calculating the transition probabilities, procedure 1 was twice used to calculate the transfer times and probabilities, once including and once omitting the anisotropic terms. It was found that neglecting the anisotropic terms typically changed the transfer times by a few percent or less, although for the times near the bottom of the region, large fractional changes (of a few tens of percent) sometimes occurred. Neglecting the anisotropic terms usually changed the transfer probabilities only by small amounts but sometimes by up to 0.05 (in the probability itself, not a fractional change), which was most significant when it affected the small transfer probabilities near the bottom of the region. There was no clear pattern of increase or decrease in the transfer times or probabilities due to the neglect of the anisotropic diffusion terms.

The net effect of using procedure 2 instead of procedure 1 is a combination of the loss of accuracy due to neglect of the anisotropic diffusion terms and the improvement of accuracy over finite difference methods in treating the horizontal and vertical diffusion terms. The size of this second effect was determined by comparing the results obtained using procedure 2 with those obtained applying procedure 1 with the anisotropic terms omitted. The magnitude and extent of the differences were found to be rather less than the differences, described in the preceding paragraph, resulting from neglecting the anisotropic terms. Therefore with the parameters of Gudiksen et al. and the box sizes used, procedure 1 is actually somewhat superior to procedure 2. Procedure 2 would be superior if Reed and German's data had been used, since then the relative size of the anisotropic diffusion terms would be smaller. Procedure 2 also would be called for if the box sizes were larger. Furthermore, the errors due to having finite box sizes are probably as large as those arising from either the limitations of finite difference approximations or the neglect of the anisotropic diffusion terms in this context, especially in the lower stratosphere, where the diffusion parameters vary rapidly in space. Be all this as it may, the calculation here is meant primarily to illustrate the application of the technique described here for calculating transfer times and probabilities.

REMARKS ON INTERPRETING RESIDENCE AND TRANSFER TIMES

When calculating residence or transfer times, one should be careful to include in the averaging process all the time trajectories of all particles that make a significant contribution to the average. If this is not done, then one should be careful to note which particle trajectories have been excluded or truncated. Otherwise, a false impression may be imparted as to the average time for a particular movement. For example, in calculating times for transfer from the northern to the southern hemisphere one should mention that the times refer only to those particles that eventually make the transfer;

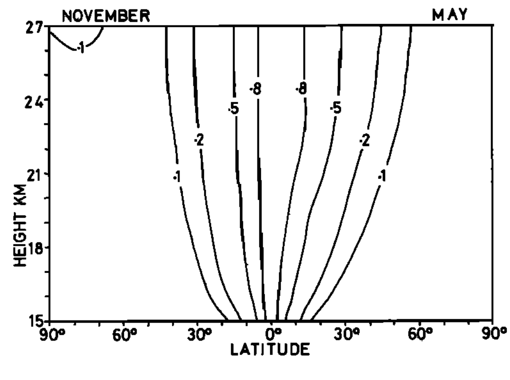

Fig. 5. Contours of the probability of making the transfer from the northern to the southern stratosphere, based on transport coefficients of Gudiksen et al. for November (left half) and May (right half).

otherwise, this transfer time might sometimes give an incorrect impression as to the dominant physical processes occurring (for example, that transfer to the troposphere or chemical destruction is unimportant).

The transfer times presented in the previous section are for movement from a particular place in the northern stratosphere to anywhere on the boundary between the northern and southern halves of the stratosphere. On the other hand, many of the interhemispheric mixing times in the literature are approximately twice as large as the corresponding transfer times, due to the method of calculation. (We hope to verify this observation in a later paper.) The method of calculation of interhemispheric mixing times perhaps selects different particle trajectories than for transfer times. This difference may partly explain the apparent agreement between the two sets of times, noted earlier. The point to be made here is that a transfer time is well defined, only if the original position of all particles, the positions of all sinks, and the positions of the set of places to which the particle transfer is made, are all specified.

Another case is worth mentioning. *Ehhalt* [1973] calculated tropospheric turnover times from observed steady state mass distributions. His turnover time is defined as the average time a particle released at height z spends below that height before moving to the surface of the earth (ignoring horizontal divergence). This turnover time is the residence time for a particle released at height z in a system in which there is a reflecting barrier at height z. To calculate the residence time in a system without this reflecting barrier, one must include those parts of particle trajectories which pass higher than z. The difference between the residence time and the turnover time is in general not negligible. For example, one may show that if the vertical eddy diffusion coefficient and scale height H are constant in altitude and there is no vertical wind or rainout, then the ratio of the turnover time to the residence time for a particle released at height z is $1 - (H/z)(1 - e^{-z/H})$. For example, since the scale height $H \sim 6$ km, according to this expression, a particle released at a tropopause height of $z \sim 12$ km spends nearly half its time in the stratosphere before reaching the surface of the earth. Of course, this result is highly idealized since it ignores spatial variation of the diffusion coefficient and H as well as horizontal motions and rainout; nevertheless, it indicates the possibility of a large contribution to residence times due to trajectories that might be thought to be unimportant.

Sometimes the average time a particle remains in a system is indicated by a quantity, such as the half-life, which implies that the mass of particles in the system decreases exponentially with time. However, the use of the approximation of exponential decay can be misleading when exit from the system occurs as a result of physical movement to a sink. Let us consider why.

If the only means by which a particle can be removed from the system is by a process that proceeds uniformly in time and space, then the particle mass decreases exponentially with time and the residence time T_t is related to a quantity such as the half-life $T_{1/2}$ by a simple expression, in this case, $T_t = T_{1/2}/\ln 2$. Now consider the possibility of physical escape which occurs at particular places and thus does not proceed uniformly in space. The fraction of the particles in the system which exits in a given increment of time is not necessarily a constant in time. Obviously, if a particle starts in the middle of the region away from sinks, then no exit will take place for a finite time. Or if winds dominate over diffusion, then all particles starting at a given place will exit at about the same time. In these and other cases the approximation of exponential decay is extremely poor. The application of this approximation to situations where exit from the system occurs as a result of physical movement gives results whose interpretation as a residence or transfer time may not be meaningful. In practice, times calculated using the assumption of exponential decay are only safely interpreted pragmatically as being the results of the procedure used to obtain them, as their relation to times for a particle to move from one place to another may be difficult to ascertain.

Acknowledgments. I would like to thank Jos Beunen and George Vorlicek for helpful comments and Robert G. Hewitt for much valuable advice and criticism. Suggestions by the referee were also very useful. Support for this work was received from H. Messel and the Science Foundation for Physics at Sydney University, and personal support from a Commonwealth Postgraduate Studentship.

REFERENCES

Ehhalt, D. H., Turnover times of ^{137}Cs and HTO in the troposphere and removal rates for natural aerosol particles and water vapor, *J. Geophys. Res., 78*, 7076–7086, 1973.

Feller, W., *An Introduction to Probability Theory and Its Applications*, vol. 1, 3rd ed., John Wiley, New York, 1968.

Gantmacher, F. R., *Applications of the Theory of Matrices*, Interscience, New York, 1959.

Gudiksen, P. H., A. W. Fairhall, and R. J. Reed, Roles of mean meridional circulation and eddy diffusion in the transport of trace substances in the lower stratosphere, *J. Geophys. Res., 73*, 4461–4473, 1968.

Hewitt, R. G., and B. Martin, A method for calculating residence times, *J. Geophys. Res., 78*, 6212–6217, 1973.

Pressman, J., and P. Warneck, The stratosphere as a chemical sink for carbon monoxide, *J. Atmos. Sci., 27*, 155–163, 1970.

Reed, R. J., and K. E. German, A contribution to the problem of stratospheric diffusion by large-scale mixing, *Mon. Weather Rev., 93*, 313–321, 1965.

(Received October 8, 1974;
revised April 15, 1975;
accepted April 15, 1975.)