104. R. Bartha and D. Pramer, *Bull. Environ. Contam. Toxicol.*, 4, 240 (1969).

105. K. Hurle and B. Rademacher, *Weed Res.*, 10, 159 (1970).

106. K. A. Sund, *J. Agr. Food Chem.*, 4, 57 (1956).

107. F. M. Ashton, *Weeds*, 11, 167 (1963).

108. J. Monod, *Ann. Rev. Microbiol.*, 3, 371 (1949).

109. P. G. Moe, *Environ. Sci. Tech.*, 4, 429 (1970).

AP-42 Section 9.2.2
Reference 10
Report Sect.
Reference

Chapter 5

DIFFUSION AND VOLATILIZATION

J. W. Hamaker

Ag-Organics Department
The Dow Chemical Company
Walnut Creek, California

I. INTRODUCTION

The process of diffusion is involved in all movement of chemical substances through the soil and, therefore, plays a role in all the various processes by which organic substances meet their fate in the soil. In some instances, the movement is directly due to diffusion, while in others it is an indirect influence. We list a few of the important soil phenomena involving diffusion:

Loss by Volatilization. Vapors which are lost from the surface of the soil must reach that surface from the body of the soil. This will involve diffusion.

The Action of Fumigants in the Soil. The diffusion of gases and vapors is necessary to reach the pest that is to be controlled, be it plant, fungus, or a nematode.

Nonvolatile Pesticides in Soil. In like manner, nonvolatile, soluble pesticides must also reach the pest and, in this process, diffusion through the soil solution plays a part.

Dispersion. Diffusion contributes to the many instances in which the organic chemical disperses to a larger volume of soil than its original placement. This includes such varied situations as the large-scale movement of fumigants, the micromovement to the interior of soil crumbs, or the broadening of adsorption bands during leaching. This latter, obviously, overlaps with mass movement which is dealt with in another chapter.

Decomposition. Where the site of degradation is localized, as may be the case for microorganisms, or catalysis at soil surfaces, movement of the chemical to the active site is an essential factor. Since diffusion is inevitably involved, it will relate to kinetics, which is treated in another chapter.

If these and the many other phenomena occurring in the soil are studied without attention to the diffusion processes, they will not be fully understood. This is evident in a number of published empirical studies, both as to conclusions drawn and to the experimental designs used.

In a qualitative sense, diffusion is very simple: Diffusion always occurs from a higher concentration to a lower concentration; and the greater the difference, the greater the diffusion rate. This is exactly similar to the flow of heat from hot to cold. In fact, the mathematics of heat flow was first worked out and it was followed in the development of the mathematics of diffusion. The mathematical techniques are thoroughly presented in several standard works, including Crank [1], Jost [2], and Jacobs [3], and the reader is referred to them for a fuller treatment of diffusion in general. The review, "Movement of Nutrients to Plant Roots" by Olsen and Kemper [4] has an excellent presentation of diffusion of dissolved materials in soils. The following presentation is naturally oriented to soil phenomena but will attempt to provide a conceptual basis and an introduction to mathematical tools for dealing with diffusion in the soil environment.

II. GENERAL THEORY

A. Fick's Laws of Diffusion

The basic relationships governing diffusion are usually stated mathematically as Fick's two laws, but it is helpful also to relate them to simple physical systems. Fick's first law, for example, may be visualized in terms of a uniform tube of unit area cross section containing a fluid with a dissolved material having a constant concentration gradient. This concentration gradient is attained by maintaining a constant concentration at one end (e. g., a saturated solution) and zero concentration at the other. This system is illustrated by Fig. 1.

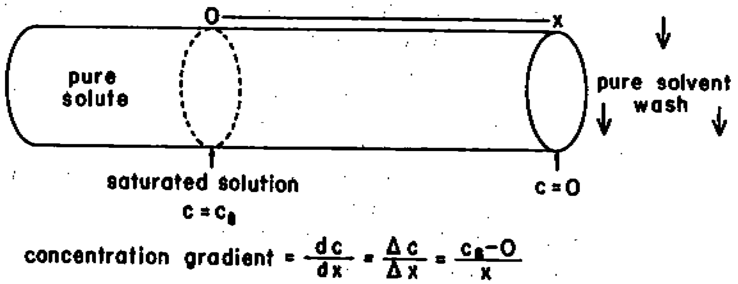

Fig. 1. One dimensional case of steady-state illustrating Fick's first law of diffusion.

Fick's first law simply says that the rate of transfer of material down this tube by diffusion will be directly proportional to the concentration gradient or rate of concentration change with respect to distance. This can be represented symbolically as follows:

$$\text{Flux} = \frac{dq}{dt} = -D\left(\frac{\partial c}{\partial x}\right)_t \qquad (1)$$

where dq/dt is the rate that material moves past a given point per unit cross-sectional area, c is the concentration, x is the distance measured along the tube, and D is the constant of proportionality or diffusion constant. (It is always a positive number. The negative sign is essential since diffusion occurs in the opposite direction from the concentration gradient, i.e., from high to low concentration.)

The illustrative physical system shown in Fig. 1 is in a condition known as steady state; that is, although actually diffusion is occurring constantly to transfer material from one end of the tube to the other, the concentration at any point along that tube remains constant and unchanging with time. Thus, although the system is in constant dynamic flux, it appears to be static. Diffusion in systems of this sort is relatively easy to treat for two reasons: First, Fick's first law can normally be applied, and the resulting first-order differential equations are comparatively easy, mathematically speaking. Second, diffusion rates and concentration gradients are frequently easy to determine. For example, in the one-dimensional case of Fig. 1, the flux must be constant throughout the system. Furthermore, if the diffusion constant D is truly constant throughout the system, the concentration gradient will also be constant since, otherwise, the flux would not be constant according to the equation for Fick's first law. As will be seen later, steady-state systems are often used to measure diffusion coefficients. However, it needs to be kept in mind that diffusion constants may not be independent of concentration or position, particularly for ionic solutes.

In many cases, however, systems are not in a steady state and it is extremely difficult to apply Fick's first law, so that Fick's second law is employed. The second law is not actually a different law from the first, but only a modification of it, in which the rate of flow or the flux has been transformed into the rate of change of concentration with time. This is accomplished by applying the principle of material balance; namely, that the rate of change in the concentration at a given region represents the difference between the rates of diffusion into and out of the region, also called the law of continuity. The transformation is relatively straightforward and will be described in detail later in connection with diffusion in porous media. It leads to Eqs. (2) and (3) for diffusion in one dimension:

$$\left(\frac{\partial c}{\partial t}\right)_x = \left(\frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right)\right)_t \tag{2}$$

If D is a constant, independent of concentration and position, this equation becomes (3), which is the form usually encountered:

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right) \tag{3}$$

Visualization of the second law is more difficult than that of the first law, since the second law deals with gradients of concentration gradients. The second law deals with the phase of the diffusion process which ends either in a steady state or cessation of diffusion. In either case, final concentration gradients are uniform (in relation to any nonuniformities of the medium, of course), so the second derivatives are zero.

The precise pattern of concentration as it changes with time can be determined by solving the partial differential equation for diffusion [Eq. (2) or (3)]. However, the equation alone is insufficient, since it is only a description of rates of change from point to point and from time to time. There must also be a description of a particular system, since any one partial differential equation can represent any number of different particular systems. This information is in terms of "boundary conditions," which are simply times or places where the condition of the system is specifically known.

B. Boundary Conditions

Boundary conditions can be conveniently classified into three categories:

The initial or final state or some other specific state of the system.

The existence of real or virtual boundaries in the system.

Some constraint on the system such as constant amount of material in the total system.

With these types of information, it is then possible to obtain a specific answer from the differential equation for a given diffusion system. An example of the first type could be a salt solution overlayered with pure water. Here, the initial condition of the system is defined as two regions of constant concentration separated by a sharp boundary. Thus, having obtained a general solution of the differential equation, we then need to substitute time = zero, and concentration = zero, for coordinate values greater than those represented by the boundary, and concentration = C_0 for values less than those of the boundaries. With these two fixes on the system, it should be possible to evaluate exactly the distribution of concentration in the system at any other time afterwards, if the value of D is known. Another variant of this type of boundary condition sometimes used is the state of the system when final equilibrium is reached, i.e., when time is infinite.

The second type of boundary condition is illustrated by the top and bottom of the container for the overlayered salt solution. These real physical boundaries also serve to define the special solution of the diffusion equation that fits this particular system. Another instance of the second type of boundary condition would be the surface of a fumigated soil with enough air movement to maintain an essentially zero concentration. If an impervious tarp is thrown over the surface, it becomes a further example in which the gradient is considered to be zero at the interface: $(\partial c/\partial x) = 0$.

The third type of restriction or constraint on the system is much more individual with the particular situation and needs to be evaluated in each case. It is obvious that enough boundary conditions must be recognized and utilized to evaluate all the arbitrary constants in the general solution, and part of the art of applying mathematics to diffusion systems lies in recognizing these boundary conditions.

C. Diffusion Constants

1. General Considerations

The fundamental relationships of diffusion were originally derived by analogy to the mathematics of heat transfer, and Fick then provided experimental verification. It is, however, possible to derive these relationships from physicochemical first principles as was done by Nernst and Einstein. The reader is referred to Jacobs [3, p. 11], for a description of the derivation which, in essence, depends on relating diffusion to osmotic pressure and ends with the following interesting relationship involving the rate of change of the osmotic pressure with concentration:

$$\frac{dq}{dt} = -\frac{1}{Nf}\left(\frac{\partial P}{\partial C}\right)\left(\frac{\partial C}{\partial x}\right) \tag{4}$$

where N is the number of molecules per mole; f is the frictional force on a molecule moving at unit velocity; and P is the osmotic pressure. If Vant Hoff's law for osmotic pressure holds: $P = CRT$, where R is the gas constant and T is the absolute temperature, then $\partial P/\partial C$ is RT, which is constant at a constant temperature. All factors except $\partial C/\partial x$ are thus constant, and the result is Fick's first law with the diffusion coefficient represented by

$$D = \frac{RT}{Nf} \tag{5}$$

According to this theory, D should be constant for dilute solutions of a specific solute molecule in a specific solvent (this determines the frictional force, f) and directly proportional to the absolute temperature. However, Vant Hoff's law is an approximation that holds only for dilute solutions, so Fick's first law should more accurately be written as

$$\frac{dq}{dt} = -D(C)\left(\frac{\partial C}{\partial x}\right)_t \tag{6}$$

where D(C) is a function of the concentration.

This complicates the solution of the equation greatly, both mathematically and because the exact nature of the function D(C) needs to be determined. It is fortunate, therefore, that the solutions in soil (gaseous or liquid) are very dilute and it is generally safe to ignore any inconstancy in D. An exception to this is the diffusion of ions, in which case interionic attraction causes deviation from "ideal behavior," as it is called, at quite low concentrations.

Diffusion constants have been determined for a large number of substances by a variety of methods. The reader is referred to general texts such as Jost [2] for descriptions of method, development of theory, and tabulation of data.

Diffusion coefficients of some substances which may appear in soil are listed for gases in Table 1 and for liquids in Table 2. A comparison of these tables shows immediately that at comparable concentration gradients diffusion in gases proceeds 1,000 to 10,000 times more rapidly than in the liquid phase (e.g., O_2 in air, $D = 0.178$; O_2 in 1% NaCl solution, $D = 1.98 \times 10^{-5}$ cm^2/sec). Two values of diffusion coefficients in solids given in Table 2 show them to represent so slow a process as to be certainly negligible in soil.

Table 1 also makes the point that whether the term "interdiffusion" should actually be used for the diffusion coefficient depends on all substances involved. Thus, the interdiffusion of O_2 and N_2 is definitely more rapid than interdiffusion of O_2 and CO_2. This can also be regarded as resulting from the effect of concentration upon the diffusion constant as is indicated by diffusion of hydrogen from H_2-CO_2 mixtures into pure CO_2. Fortunately, gaseous diffusion in soil air volume is generally for very dilute vapors and a single, limiting value for the diffusion coefficient. It is noted, however, that soil air contains higher CO_2 content due to microbiological activity and slow diffusion of oxygen into the soil. The possible small effect of this on diffusion in soil does not appear to have been studied. Diffusional movement in a uniform, homogenous solution with no concentration changes is known as self-diffusion and can be measured with radioactive isotopes. This will be discussed in connection with diffusion in the soil solution.

TABLE 1

Gaseous Diffusion Constants at 1 atm Pressure

Gas pair		D	Temp.				
1 into	2	(cm^2/sec)	(°C)	m^a	Mol. wt.	$D/\overline{M}$	Ref.
O_2	Air	0.178	0	1.75	32	1.01	[5]
O_2	N_2	0.181	0	1.75	32	1.02	[5]
O_2	CO_2	0.132	0	2.0	32	0.79	[5]
$H_2(+CO_2)$	CO_2						
3:1		0.594	0	—	2	1.19	[2]
1:1		0.605	0	—	2	1.21	[2]
1:3		0.633	0	—	2	1.27	[2]
H_2O	Air	0.219	0	1.75	18.02	0.929	[2]
CO_2	CO_2	0.113	23	—	44.01	0.75	[6]
Ethylene dibromide	Air	0.07042	0	1.95	187.86	0.967	[7]
Chloropicrin	Air	0.088	25	(2.0)	164.4	0.947	[8]
CCl_4	Air	0.0828	0	—	153.82	1.03	[9]
CS_2	Air	0.0892	0	2.0	76.14	0.778	[5]
Biphenyl	Air	0.0610	0	2.0	154.2	0.758	[5]

---

[a] m is defined by the equation $D = D_{std} (T/273.2)^m 760/P$, where D_{std} is the diffusion coefficient at 0°C and 760 mm.

TABLE 2

Diffusion Coefficients in Aqueous Solutions

Solute	Solution	Temp. (°C)	D x 10^5 (cm^2/sec)	Ref.
O_2	1% $NaCl^a$	18	1.98	[5]
CO_2	H_2O	18	1.46	[2]
KCl	0.01 M	25	1.917	[10]
	0.1 M	25	1.844	[10]
	0.1 M	18.5	1.513	[10]
Urea	2.0 M	20	1.14	[5]
	0.25 M		1.18	[5]
Glucose	0.39%	25	0.673	[10]
NH_4Cl	1.0 M	20	1.64	[5]
$ZnSO_4$	0.05 M	20	0.54	[5]
$CaCl_2$	1.0 M	20	1.16	[5]
Allyl alcohol	0^a	15	0.9	[5]
Nicotine	0.1 M	20	0.53	[5]
Na in permutite[b]		20	1.30 x 10^{-3} (cm^2/day)	[5]
Air-lead[b]		100	0.23 x 10^{-3} (cm^2/day)	[5]

---

[a] Very dilute solution of solute; D approaches limiting value for infinite dilution.

[b] Solid-state diffusion.

The dependence of gaseous diffusion coefficients upon temperature and pressure can best be understood in the light of the molecular theory of gases. A complete development of this is, of course, far beyond the scope of this text and the reader is referred again to works on diffusion such as Jost [2], who will further refer to the classics in the area such as Chapman and Cowling [11]. The basic model for all these treatments is that the diffusion rate depends upon the average velocity of the molecular motion and the average distance the molecules travel between collisions (mean free path). The former is determined primarily by temperature and the latter by density, which depends on both pressure and temperature. Equation (7) is an approximate relationship given by Jost [2]:

$$D_{12} \cong \frac{1}{3} \lambda_1 \overline{V}_1 \tag{7}$$

where D_{12} is the diffusion coefficient of gas No. 1 into gas No. 2, λ_1 is the mean free path for molecules of gas No. 1, and $\overline{V}_1$ is the mean velocity of the molecules of gas No. 1. Simple molecular theory of gases relates average velocity directly to temperature:

$$\overline{V} = \left(\frac{8\,RT}{\Pi\,(\text{Mol. wt.})}\right)^{1/2} \tag{8}$$

and the mean free path inversely to the density:

$$\lambda = \frac{B}{\text{Density}} = B\left(\frac{RT}{P}\right) \tag{9}$$

where T is the absolute temperature, P the pressure, R the gas constant, and B the constant of proportionality by the perfect gas law. When combined with Eq. (7), these allow us to compare diffusion rates at different temperatures and pressures:

$$\frac{\left(D_{12}\right)_a}{\left(D_{12}\right)_b} = \frac{P_b}{P_a}\left(\frac{T_a}{T_b}\right)^m \tag{10}$$

where m is 3/2 by the approximate theory, but has been measured to be in the range of 1.75 to 2.0 and to estimate the effect of molecular weight:

$$\frac{D_{13}}{D_{23}} = \left(\frac{(MW)_2}{(MW)_1}\right)^{1/2} \tag{11}$$

As indicated by values for the exponent, m (1.75 or 2.0 instead of 1.5), and also the values for $D/\sqrt{M}$ in Table 1, these relationships are only approximate. The pressure proportionality is quite accurate for the normal atmospheric pressures since it depends on neglecting molecular diameters relative to distances between molecules. This does not become a significant error until the pressure well exceeds several atmospheres. The deviations of the simple relationships for temperature [Eq. (10)] and molecular weight [Eq. (11)] are due to ignoring intermolecular attraction in the simple theory. More exact theory requires molecular constants of this nature which are not generally available. However, Eq. (10) with the empirical value for the exponent, m (1.75 to 2.0), is useful for the relatively limited temperature range of the soil environment. The rough comparisons of gaseous diffusion coefficients that are possible with Eq. (11) can be useful guides but are subject to considerable error.

The complexity of the liquid state causes a more complex theory for liquid state diffusion which is generally less helpful than that for gases. Temperature dependence, for example, needs to be determined experimentally in each case. Some illustrative values for diffusion coefficients in water solutions appear in Table 2, and several points should be noted: Comparing KCl with urea, the greater effect of concentration on the ionic materials can be seen. The values differ less as a group than is noted with gaseous diffusion. Finally, temperature effects are larger than with gases. All these, and particularly the last, arise because interaction energies are so much larger and more important in the liquid state than for gases.

2. Diffusion Constants for Soils

Soil is a porous medium, and the diffusion is modified appropriately. First, it will be seen that the diffusion coefficient in soil, on the basis of the total soil mass, should be smaller than the diffusion coefficient for unobstructed fluid, simply because the solid portion of the soil will interfere with the flow of material. Moreover, there are interactions with soil, such as adsorption and solution, which would further reduce the diffusional flow. Some experimental values for diffusion coefficients in soil are given in Table 3, and it will be seen that, indeed, they are lower than corresponding values in Tables 1 and 2.

The ratio D/D_0, given where it is known, indicates decrease by a factor of 3 or more for gaseous diffusion. The ratio for aqueous diffusion of the anion Cl is approximately the same (0.23); but cation diffusion is greatly hindered as shown by the diminished ratio (0.01-0.0005). This is an obvious consequence of the cation exchange of the soil whereby most of the ions are bound to the clay and, hence, immobile. This point will receive further discussion at a later point.

TABLE 3

Representative Diffusion Coefficients in Soils, Clays, and Porous Materials

Solute - Solution		D (cm^2/sec)	D/D_o[b]	Temp. (°C)	Soil conditions	Method[c]	Ref.
A. Gaseous Diffusion							
CO_2 (g)[a]	CO_2	0.043	0.38	23	Dry	U-3	[6]
CS_2 (g)	Air	0.193	0.248	15.4	Dry sand, $\theta^d = 0.374$	S-1	[12]
Ethanol (g)	Air	0.0415	0.589	21.3	Dry quartz sand, $\theta = 0.415$	S-1	[13]
O_2 (g)	Air	0.105	0.469	25	32.7% moisture, $\theta = 0.38$	U-2	[24]
		0.056	0.250	25	45.3% moisture, $\theta = 0.27$		
B. Liquid Diffusion							
Sr^{2+} (l) (10^{-3} M as Cl^-)	Aq.	1.09×10^{-7}	0.014	25	Sandy soil - saturated (upper green sand soil)	U-3	[19]
Sr^{2+} (l) (0.010 M as I^-)	Aq.	1.21×10^{-7}	0.0027	21	Lower green sand soil (bulk density = 1.68)	U-1	[20]
K^+ (l) (0.002 M as Cl^-)	Aq.	2.22×10^{-7}	0.011	21	Lower green sand soil (bulk density = 1.68)	U-1	[20]
K^+ (l)	Aq.						
(0.0334 M as $H_2PO_4^-$)		1.4×10^{-7}	0.0071		% H_2O = 15 (upper green)	U-5	[21]
(0.0334 M as $H_2PO_4^-$)		2.7×10^{-7}	0.013		% H_2O = 35 sand soil)		
(0.017 M as $H_2PO_4^-$)		0.1×10^{-7}	0.0005		% H_2O = 15		
(0.017 M as $H_2PO_4^-$)		0.4×10^{-7}	0.002		% H_2O = 35		
R_b^{2+} (l)	Aq.				Lower green sand soil	U-1	[20]
(0.002 M as Cl^-)		0.028×10^{-7}	—	3.5	Bulk density = 1.34		
		0.18×10^{-7}	—	21.0	= 1.34		
		0.58×10^{-7}	—	3.5	= 1.64		
		0.81×10^{-7}	—	21.0	= 1.64		
Cl^- (l)	Aq.						
(0.1–0 as NaCl)		36.9×10^{-7} (25-60 range)	0.23	25	Na-bentonite - saturated	S-2	[22]
Na^+	Aq.	8.1×10^{-7}		-1	Exch Na^+ = 0.96 mg/g	U-5	[23]
(as Na bentonite equilibrated with NaCl = 10^{-4} M)		4.0×10^{-7}		-3.1			
		2.0×10^{-7}		-10			
		1.7×10^{-7}		-15			

[a] Indicates diffusion is in the gaseous phase (g), liquid phase (l), or both (g, l).

[b] D/D_0 is the ratio of diffusion coefficient in soil to nearest equivalent diffusion coefficient in bulk (homogeneous) diffusion medium.

[c] See Table 5 for description of method.

[d] Soil porosity as a fraction of total soil volume.

Another general feature in Table 3 which is worthy of mention is the effect of temperature. An indication of temperature effect may be noted in the $RbCl_2$ diffusion results obtained by Graham-Bryce [20] (6.5 and 1.4-fold for 7.5° temperature change) and the diffusion of NaCl through Na-bentonite by Dutt and Low [22] and by Murrmann et al. [23] (~2X between -1°C and -3°C and ~4X between ambient and -1°C). The results of Murrmann et al. are particularly interesting since they show that diffusion may continue even in frozen soil. The likely explanation is that the water near the clay surfaces is subject to attractive forces which prevent it from assuming the crystalline structure of ice. This effect has not been demonstrated for soil with organic chemicals and is of sufficient significance that such experiments should be done. In fact, the general lack of data on the temperature effect for the few organic chemicals reported is a handicap for the possible practical usefulness of the studies.

Much of the available data on diffusion coefficients of pesticides in soil are summarized in Table 4. These data include cases of both gaseous and aqueous diffusion. The results of Graham-Bryce [16] with disulfoton and dimethoate show rather clearly the opposite effect of moisture content upon gaseous and aqueous diffusion. Diffusion coefficients for dimethoate show a dramatic increase (over 40-fold) as the water content changes from 10 to 43%. On the other hand, disulfoton shows little change in diffusion coefficient with moisture content from 7.7 to 40.8%. The explanation for this behavior is that dimethoate, having high solubility and low vapor pressure, diffuses in the liquid phase while disulfoton has such a balance of solubility and vapor pressure that it diffuses about equally in both phases. Lindane [14, 15] shows quite a high degree of constancy for the diffusion constant as the moisture content changes from field capacity to saturation. Oxygen represents a case of a highly volatile, slightly soluble material, and its diffusion would be decreased as water displaces the air through which the greatest part of diffusional flow occurs. A practical example of this phenomenon is the suffocation and death of plant roots in waterlogged soil. Papendick and Runkles [24] obtained diffusion coefficients (see Table 3) showing this to be true for even a relatively narrow range of moisture contents.

At very low moisture contents, diffusion constants tend to decrease for another reason: increase in sorption. This phenomenon is illustrated in Table 4 by lindane and dieldrin. Apparently, many adsorption sites exist in soil which preferentially adsorb water, and these will adsorb other substances only when the amount of water falls below the saturation value. As adsorption increases, the mobility, and therefore diffusion rates, are decreased. This is discussed further at a later point in this chapter. The chapter on sorption should also be consulted.

TABLE 4

Diffusion Coefficients of Pesticides in Soils, Clays, and Porous Materials

Solute-Solution		D (cm^2/sec)	D/D_o[b]	Temp. (°C)	Soil conditions	Method[c]	Ref.
A. Gaseous Diffusion							
Ethylene dibromide (g)[a]	Air	0.01507	0.187	20	Garden soil, θ^e = 0.389	S-1	[7]
		0.005058	0.626	20	Ashhurst soil, θ = 0.199	S-1	
		0.01121	0.1383	20	θ = 0.303	S-1	
					(Above 3 at field capacity)		
B. Gaseous and/or Aqueous Diffusion							
Lindane (g,1) (80 ppm)[d]	Aq.	0	0	20	Gila silt loam, 0% H_2O	U-1	[14, 15]
		1.88×10^{-7}	—	30	Gila silt loam, 10% H_2O	U-1	
Dieldrin (g,1) (35 ppb)	Aq.	0.058×10^{-7}	—	20	Gila silt loam, 53% r.h.[f] (2.01% H_2O)	U-1	[58]
		0.096×10^{-7}	—	20	Gila silt loam, 75% r.h. (2.67% H_2O)	U-1	
		1.06×10^{-7}	—	20	Gila silt loam, 94% r.h. (3.93% H_2O)	U-1	
Disulfoton (g, 1) (2-14 ppm)	Aq.	0.28×10^{-7}	—	20	7.7% H_2O	U-2	[16]
		0.25×10^{-7}	—	20	16.4% H_2O	U-2	

TABLE 4 (continued)

Solute-Solution		D (cm^2/sec)	D/D_o[b]	Temp. (°C)	Soil conditions		Method[c]	Ref.
Disulfoton (contd.)		0.20×10^{-7}	—	20	21.6% H_2O		U-2	[16]
		0.21×10^{-7}	—	20	23.0% H_2O		U-2	
		0.23×10^{-7}	—	20	30.1% H_2O		U-2	
		0.18×10^{-7}	—	20	31.9% H_2O		U-2	
		0.29×10^{-7}	—	20	39.3% H_2O		U-2	
		0.30×10^{-7}	—	20	40.8% H_2O		U-2	
Dimethoate (1) (10 ppm)	Aq.	0.34×10^{-7}	—	20	10.4% H_2O		U-2	[16]
		1.17×10^{-7}	—	20	17.4% H_2O		U-2	
		2.18×10^{-7}	—	20	23.4% H_2O		U-2	
		4.69×10^{-7}	—	20	31.6% H_2O		U-2	
		5.46×10^{-7}	—	20	32.8% H_2O		U-2	
		9.22×10^{-7}	—	20	35.6% H_2O		U-2	
		14.13×10^{-7}	—	20	42.9% H_2O		U-2	
2,4-D (1) (1.26 ppm)	Aq.				% Organic matter	% Clay	U-4	[17]
		0.38×10^{-7}	—	25	2.6	14		
		0.14×10^{-7}	—	25	6.9	33.3		
		0.70×10^{-7}	—	25	29.0	12.6		
		0.19×10^{-7}	—	25	4.7	63.7		
		0.41×10^{-7}	—	25	0.9	7.2		
		0.020×10^{-7}	—	25	4.1	—		
		0.030×10^{-7}	—	25	15.1	13.1		
		0.52×10^{-7}	—	25	1.1	17.0		
		1.61×10^{-7}	—	25	Quartz sand			
					(All the above saturated with H_2O)			
Atrazine (1) (424 ppm)	Aq.	1.52×10^{-7}	—	25	(An average over eight soil types, two pH's, two moisture contents, and two concentrations)		U-1	[18]
Simazine (1) (224 ppm)	Aq.	4.5×10^{-7}	—	25				
Propazine (1) (342 ppm)	Aq.	2.4×10^{-7}	—	25				

[a-c] See Table 3.

[d] On a whole soil basis.

[e] θ = Soil porosity as a fraction of total soil volume.

[f] Relative humidity.

Lindstrom and co-workers' work with 2,4-D [17] shows quite clearly that the organic matter of the soil most definitely affects the diffusion coefficient for saturated soil, i.e., liquid diffusion. Quartz sand, having no organic matter, shows the highest diffusion coefficient and one which is somewhat comparable to many values obtained for other anions. Other than that, there is a general trend that the higher the organic matter, the lower the diffusion coefficient. A correction was derived for sorption of organic matter in soil; and when this was applied, the residual diffusion was roughly comparable for all soils of the series.

3. Methods of Measurement

A variety of methods have been used to estimate diffusion coefficients in soil, including both steady state and unsteady state methods. A full review of the methodology is beyond the purposes of this chapter, but a brief delineation of general types is presented in Table 5. For details, the reader should consult the references also provided in the table. This list is, of course, not intended to be exhaustive, and other variants or modifications may be found in the literature, but these basic types seem to cover most of the literature.

One thing that is apparent in all cases is that the method is chosen to minimize the complexity of mathematical treatment as far as possible. Steady-state methods were used earliest because of the simple mathematical evaluation. Most of the unsteady-state methods are designed to make use of the fact that the amount of material diffused from one layer to another is related, sometimes linearly, to the variable $(Dt/L^2)^{1/2}$ where L is the thickness of this layer. This tendency of the amount diffused, depending on the $(\text{time})^{1/2}$, has been used to distinguish diffusion-controlled processes. An example is a study by Weber and Gould [27] on sorption of organic pesticides by activated charcoal where the rate of sorption was directly proportional to the $(\text{time})^{1/2}$. This was taken as evidence that intraparticle transport, i.e., diffusion controlled the rate.

The variety of soil environments suggested in Tables 3 and 4 indicates quite clearly that a purely empirical approach would be wastefully large. Efforts that have been made to understand the quantitative relationships between diffusion constants in air or water and those in soil are, therefore, quite justified. The factors that have been considered include: (a) the porous structure of soil, (b) sorption by soil surfaces, (c) gas solubility in the water phase, and (d) decomposition.

D. Diffusion Laws for Porous Media

1. Tortuous Tube Model

The diffusion coefficient is usually based on the flow through a homogeneous fluid across a unit area. However, in the porous medium, this unit area is partially blocked, so the flux is only a fraction of that for the pure fluid. This fraction or factor has been the subject of considerable discussion and investigation without complete unanimity. In order to limit consideration to the geometrical aspect, the analysis that follows immediately will consider an inert, stationary phase and, thus, will put interactions such as sorption, reaction, or solution temporarily aside to receive later consideration. The diffusion phase is considered to be homogeneous, so a corresponding real system would be sand, either dry or completely waterlogged, depending upon whether gaseous or liquid diffusion is being considered.

Following the initial work by Buckingham [28], a number of investigators used the model (see Penman [12] and Call [7]) involving the following quantities:

Porosity. Considering the cross section only, the maximum attainable diffusion will be determined by the fraction of open area. This can be taken to be the fraction of open volume in the mass or porosity: θ.

Blocked Pores. Correction must be applied for the portion of this open area b representing blocked pores which do not contribute to the diffusion paths. This can be subtracted: $\theta - b$.

Tortuosity. The diffusion paths are not straight, but twist and turn, so this distance traveled is increased. This is called tortuosity and is corrected for by a factor often symbolized as α.

According to this model, we can write Fick's first law for diffusion in an inert, porous material:

$$\text{Flux} = -D\left(\frac{\partial c}{\partial x}\right) = -\alpha(\theta - b)D_o\left(\frac{\partial c}{\partial x}\right) \qquad (12)$$

$$D = \alpha(\theta - b)D_o$$

where the symbols are as previously defined. The experimental values for α and b, which have been reviewed by Currie [29, 30] and by Call [7], are quite varied, with possible best values: $\alpha = 0.66$ (0.6-0.7) and

TABLE 5

Representative Methods for Determining Diffusion Coefficients in Soils and Porous Materials

Method	Physical arrangement	Mathematical treatment	Examples
S-1	Evaporation of a volatile solvent through a soil column	$\left(\frac{dq}{dt}\right)_{exp} = -D\left(\frac{\text{Vapor Conc.}}{\text{Length}}\right)$	Penman [12]; Van Bavel [13]; Call [7]
(The mathematical treatment and measurements, usually weighing, are simple but equilibrium is achieved slowly. An integral diffusion coefficient is given.)			
S-2	Diffusion between two reservoirs maintained at different concentrations	$\left(\frac{dq}{dt}\right)_{exp} = -D\left(\frac{\text{Conc. diff.}}{\text{Length}}\right)$	Dutt and Low [22]
(Very small pressure differences between the two reservoirs produce errors. With liquids, equilibrium times are long: 44 days for clay [22]. End effects and nonuniform concentration gradients are possible.)			
U-1	Split cell (preferably with separator). (a) Analysis of each half for transfer	$\left(\frac{Qt}{Q_\infty}\right) = \frac{2}{L}\left(\frac{DT}{\Pi}\right)^{1/2}$ (Valid if equal to 0.5)	Schofield and Graham-Bryce [25]; Rowell et al. [26]; Ehlers et al. [14, 15]
(Matching moisture, porosity, etc., of the two halves is difficult. Results tend to be variable–30%, according to Mott and Nye [19]. An integral or "averaged" diffusion coefficient is given.)			
U-2	(b) Sectioning and analysis of increments	Boltzman-Matano method: $D = \frac{1}{2t}\ \frac{dx}{d(C/C_o)} \int dx(C/C_o)$ Plot C/C_o vs x and measure appropriate slopes and areas.	Graham-Bryce [16]
(Slopes are particularly difficult to read from graph. The method yields a series of integral diffusion coefficients of different concentration ranges and, hence, indicates variation of D with concentration.)			
U-3	A stirred reservoir in contact with the soil. (a) Analysis for amount transferred at time t	$\frac{Qt}{Q_\infty} = \text{Func.}\left(\frac{Dt}{L^2}\right)^{1/2}$	Mott and Nye [19]
(Chosen by Nye for its accuracy compared with other methods. The mathematical expression is not directly solvable for D but susceptible to numerical solution of an integral diffusion constant.)			
U-4	(b) Solid phase is sectioned and increments are analyzed. Large reservoir or equivalent short time simplifies mathematics as indicated	$C(xt) = C_o \operatorname{erfc}\left[x/2(Dt)^{1/2}\right]$ (For a description of the erfc function, see Crank's, Jost's, or other mathematical methods sources.)	Lindstrom et al. [17]
(Again, D must be solved by indirect methods.)			
U-5	(c) A "sink" used to absorb the diffused materials. Ion exchange paper for K+ as an example	$D = \frac{\Pi}{4}\ \frac{M_t^2}{c^2 t}$, M_t = loss to sink	Vaidyanathan et al. [21]
U-6	Diffusion from a line source analysis by sectioning	$\frac{C}{C_o} = \left(\frac{1}{2(\Pi Dt)^{1/2}}\right) \exp\left(-\frac{x^2}{4Dt}\right)$ Plot log C/C_o vs x^2	Murrmann et al. [23]

---

[a] S — steady state; U — unsteady state.

b = 0.1 (0-0.25). This relationship has validity over only a limited range of porosity: approximately 0.2-0.7; and experimental values in the literature are quite variable, particularly for b. Actually, b, the blocked pore volume, was earlier identified as the residual air porosity remaining after water addition had caused gaseous diffusion to cease. This has the obvious weakness of probably not being equivalent to porosities obtained by compaction. It appears that this relationship might be sufficiently valid for the porosity ranges found in soil but is probably not to be considered as theoretically sound.

The idea of blind or blocked pore volume has another significance in the case of non-steady-state diffusion. Here it refers to that portion of the porosity which does not contribute directly to the diffusion pathways through the medium. This volume comprises a "storage" reservoir into which material moves by diffusion, and it acts to slow down diffusional movement. Some references have appeared on the determination of blind pore volume in soil: Jackson and Klute [31], Philip [32], and Turner [33]; but an effective application of this concept to soil diffusion has not yet appeared. The theory using this concept is well developed in chemical engineering and geological applications and should be able to give useful insights for soil diffusion, as Turner suggests. Goodnight and Fatt [34], for example, developed a differential equation based on the picture of a blind pore as a cavity with a single, constricted opening and applied it to a sandstone. As would be expected, the differential equation is much more difficult to handle: i.e., it contains $\partial^2 C/\partial t^2$. It is again clear that this is closely allied to flow through the porous medium since the same process of diffusion into the cavity will occur. This will be discussed somewhat further in connection with diffusion to plant roots.

Nye [35, 36] has used this model for the treatment of diffusion of ions in the soil solution. He proposes the following relationship for the diffusion coefficient in soil:

$$\begin{aligned} D &= D_L\theta_L\alpha_L\frac{dC_L}{dC} + D_S\theta_S\alpha_S\frac{dC_S}{dC} \\ &= D_L\theta_L\alpha_L\frac{dC_L}{dC} \quad (D_S = 0) \end{aligned} \qquad (13)$$

where L and S refer to liquid and solid states, respectively, and D is the total diffusion coefficient for the soil, D_L is the diffusion coefficient in the liquid phase, and D_S is the diffusion coefficient in the solid soil. This last has been shown to be probably zero (as would be expected). C and C_L have the anticipated meanings of total exchangeable and dissolved ion concentrations; θ and α have the usual meanings of fraction of soil volume and tortuosity factor. The derivative dC_L/dC is particularly interesting as being the fractional change in soil solution concentration for a small change in total soil concentration, the difference being ions taken out of solution by exchange. It simply is the slope at a point on the ion exchange isotherm or plot of soil solution concentration against total soil concentration. Since the exchange isotherm is far easier to determine than are direct measurements of diffusion coefficients, this method could be very useful. It should also be applicable to reversible sorption of neutral materials.

An important problem with ionic substances is that diffusion coefficients are strongly dependent upon the kind and concentration of salts in the soil solution. Thus, a necessary distinction is drawn between conditions where concentration differences produce a significant difference in diffusion coefficients and where they do not. Several terms are used in making this distinction and also two sorts of diffusion coefficients are described in the literature:

Self-Diffusion. Diffusion under conditions of negligible concentration difference: i.e., diffusion of a substance against itself. This is accomplished experimentally with radioactive isotopes as, for example, the diffusion of a trace of ^{14}C-labeled 2,4-D from a solution of inactive 2,4-D into an otherwise identical solution of inactive 2,4-D.

Differential Diffusion Coefficient. Measured under condition of self-diffusion.

Bulk Diffusion. Diffusion between two concentrations for which differential diffusion coefficients are significantly different. (Used by Nye [36].)

Integral Diffusion Coefficient. Measured under conditions of bulk diffusion.

Diffusion coefficients are strictly valid only for the system in which they were measured or the exact equivalent. Thus, use of differential diffusion coefficients at other concentrations or integral diffusion coefficients at other concentration differences always has an element of risk.

Nye [36] points out in his analysis that, for self-diffusion, $dC_L/dC = C_L/C$ can be determined by analysis in any given case. However, for bulk diffusion, this relationship is normally not true and dC_L/dC must be evaluated. He proposes an expression due to Crank [1]:

$$\overline{D} = \frac{1}{C_1 - C_2}\int_{C_2}^{C_1} D\,dC \qquad (14)$$

Crank examined diffusion into a plane sheet for a number of functions relating D and C and found less than 25% discrepancy. An expression can then be written for the "bulk" or integral diffusion coefficient:

$$\begin{aligned}\overline{D} &= \theta_L \alpha_L \overline{D}_L \frac{\left(C_{L_1} - C_{L_2}\right)}{(C_1 - C_2)} + \theta_S \alpha_S \overline{D}_S \frac{\left(C_{S_1} - C_{S_2}\right)}{(C_1 - C_2)} \\ &= \theta_L \alpha_L \overline{D}_L \frac{\left(C_{L_1} - C_{L_2}\right)}{(C_1 - C_2)}\end{aligned} \tag{15}$$

Nye points out further that $\overline{D}$, where $C_2 = 0$, closely approximates the self-diffusion coefficient at concentration C where normal soil liquid concentrations are used.

All these treatments of the porous mass look at it as if it were a bundle of tubes or channels of uniform diameter. As such, it is related to the Kozeny-Carman permeability equation (16) which is a relationship much used in permeability of porous media:

$$\text{Permeability const} = \frac{\theta^3}{(\text{Area})^2} B \tag{16}$$

where B is the empirical constant (~5), and Area is the total surface area of the particles in centimeters squared per cubic centimeter.

Particular difficulty occurs for media where the pore size is variable, such as is probably the case with soil. Furthermore, it is not reasonable to consider the tortuosity and the blind pore volume to be independent of the porosity, whether changed by compaction or by water saturation.

2. Random Pore Model

A more recent approach looks "at the hole rather than the doughnut" by regarding soil as a system of pores connected by small openings or necks. Originated by Childs and Collis-George [37] for the treatment of permeability, this approach has been applied to diffusion by Marshall [38] and Millington and Quirk [39, 40]. The basic assumption of this theory is that the area of the "necks" between pores controls the rate of diffusion (and permeation) through the porous matter. Marshall estimates this area by considering random joining of two cut faces. The fraction of "open" space on any one face is simply θ, the porosity; but the fraction of open space "shared" in common will be by $\theta \times \theta$ or θ^2. From this he derives the relationship

$$D/D_0 = \theta^{3/2} = \theta^{1/2} \times \theta = \theta^{1.5} \tag{17}$$

A simple visualization will show that intersections of pores are variously oriented in space and that the area is greater than the projection onto the cut face. Thus, the area of the necks will be larger than θ^2 or, because θ is less than 1, represented by a lower power of θ than the square. Millington and Quirk derive an equation:

$$D/D_0 = S^{4/3} = S^{1.3} \tag{18}$$

A very successful aspect of this theory is the simple treatment of gaseous diffusion of porous media containing a wetting fluid, e.g., wet soil. Millington [32] derives the following relationship:

$$\frac{D}{D_0} = \frac{\theta^{10/3}}{\theta_t^{2}} \tag{19}$$

where θ is the air-filled porosity and θ_t the total porosity of water and air.

Currie [29, 30] has studied the diffusion of hydrogen gas through a large variety of granular materials, both wet and dry, including soils. He concluded that for dry materials his data fitted the empirical equation

$$D/D_0 = a\theta^b \tag{20}$$

where a and b depend on the material. He found that a varied between 0.8 and 1, while b was less than 2 for soils and sand. This has obvious similarity to the equations of Marshall and Millington. In his study of diffusion through wet materials, Currie considered both solid particles and porous particles. The latter would represent normal soils which have a crumb structure (bimodal pore distribution, i.e., a group of small pores and a second group of large pores) while the former might represent soil in a "puddled" condition. He found for the condition where the larger pores are being drained (crumbs fully saturated and solid particles), that the empirical equation fitting his data was

$$\frac{D}{D_0} = \left(\frac{\theta}{\theta_v}\right)^{\sigma} \tag{21}$$

where θ is the air-filled porosity, θ_v the large-pore porosity, and $\sigma = 4$.

This is only partially equivalent to Millington's equation. He was unable to find any simple relationship for the condition of partial saturation of soil crumbs, pumice particles, or the equivalent. It would appear likely that the present theoretical foundation for diffusion is basically sound when applied to disturbed or puddled soils. The theoretical treatments probably use an overly simplified model for soil but may be close enough for practical use with these soil conditions. Undisturbed soils containing enough clay to develop a crumb structure are another matter and are not fully understood. All analyses thus far studied assume a continuous distribution of pore size, not bimodal distribution as is actually the case for such soils.

3. Fick's Laws Modified for a Porous Medium

The previous section developed the difference between diffusion constants in homogeneous and in porous (heterogeneous) media. Fick's first law requires only that the diffusion coefficient and concentration be on the basis of the porous medium rather than the diffusing phase. The required diffusion coefficient can be estimated from the normally more available diffusion coefficients in pure solvent and the data or relationship discussed in the previous section. Concentrations are frequently on a whole soil basis or can be converted thereto.

In contrast, the second law takes a slightly different form in inert, porous media because diffusion flux is, in fact, controlled by the concentration gradients in the diffusion fluid. This will be seen in the following derivation: Visualize a uniform tube of porous material of unit cross-sectional area, the pores of which are completely filled with a "diffusion fluid," e.g., water or air. Consider a thin slice of it as indicated in Fig. 2. The change in concentration on the basis of the diffusion fluid in the slice is clearly the change in the amount of material divided by the volume of the slice. On the basis of rates, this is the rate of inflow at point x less the rate of outflow at (x + dx), all divided by the volume of the fluid in the slice:

$$\frac{dC}{dt} = \frac{(dq/dt)_x - (dq/dt)_{(x+dx)}}{dV'} \tag{22}$$

where dV' is the volume of diffusion fluid in the slice and is determined by area, width, and porosity:

$$dV' = \theta\,(A\,dx) = \theta\,dx \tag{23}$$

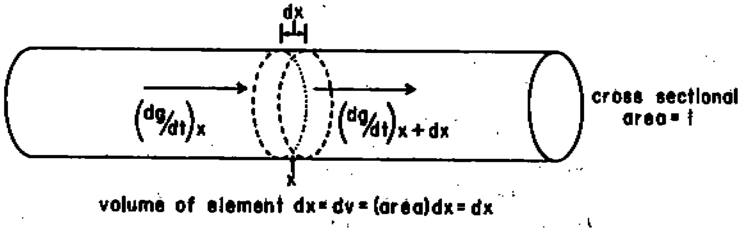

Fig. 2. Diffusion through a porous medium.

(since A = 1 by construction). Noting that the numerator of Eq. (22) is the negative of the rate of change of material in the slice, this can be transformed to

$$\left(\frac{dC}{dt}\right)_x = -\frac{1}{\theta}\left(\frac{\partial dq/dt}{\partial x}\right)_x \tag{24}$$

Finally, substituting for dq/dt from Fick's first law [Eq. (1)]:

$$\theta\left(\frac{dC}{dt}\right)_x = \frac{\partial}{\partial x}\left(D\,\frac{\partial C}{\partial x}\right)_t = D\,\frac{\partial^2 C}{\partial x^2} \tag{25}$$

(if D is independent of C) where D is the diffusion coefficient for the total porous medium and will be related to the diffusion coefficient in pure fluid, D_0, as discussed previously. C is the concentration in the diffusion fluid or any quantity linearly proportional to it. Thus, concentration on a whole soil basis can be used including sorbed and dissolved material if they are also linearly related to the concentration of the diffusing material. That is, if the concentration can be represented as a constant times the solution concentration (C' = AC), the constant will disappear by cancellation. A little consideration will show that this will be the case only if the amount of material fixed by the immobile phase is linearly related to the concentration in the mobile phase. Comparison of Eqs. (2) and (3) for diffusion in homogeneous media with Eq. (25) shows the factor θ to be the difference.

E. Interactions with the Soil

1. Sorption and Solution

Soil is not an inert, porous medium and there will be interactions which must be considered. Three interactions and their effects on the diffusion equations are generally recognized as important: (a) sorption by the solid soil, (b) solution in the water phase in the case of a gas, and (c) disappearance of the chemical by chemical reaction. Where steady-state diffusion is occurring, the first two are normally at equilibrium so that they produce no obvious effect on the diffusion. The immobile phases simply retain a constant amount of material which does not affect the diffusion flow, as such. Any irreversible loss as in factor (c) will, of course, increase the diffusion flow and will have to be considered separately. The reason for the long time required for the establishment of steady-state diffusion is that it includes the time for distribution and storage of what may be a major portion of the material. One important advantage of the application of the study of steady-state diffusion is that these interactions can be ignored, which makes things very much simpler.

In the case of nonsteady or transient diffusion, interactions with the porous medium cannot be ignored since the concentration is continually changing at every point, producing corresponding changes in the sorption and solution of solute. Reversible sorption of chemical on the immobile phase of soil and solution in the aqueous phase can be incorporated into Fick's second law without difficulty. The term $\theta(\partial C/\partial t)$ in Eq. (25) can be interpreted as the rate of increase of material per unit of diffusing fluid volume at point x, as supplied by the diffusion represented by the right-hand side of the equation. If, however, part of this incoming material is lost from solution as adsorbed (ads), dissolved (sol), and decomposed (dec), additional terms will be needed on the left side of the equation to represent the material thus lost from the solution:

$$\theta\left(\frac{\partial C}{\partial t}\right) + \left(\frac{\partial C(\mathrm{ads})}{\partial t}\right) + \left(\frac{\partial C(\mathrm{sol})}{\partial t}\right) = D\left(\frac{\partial^2 C}{\partial x^2}\right) \qquad (26)$$

The new symbols represent the concentration of these amounts calculated on the volume of diffusing fluid, i.e., as if they had not yet been adsorbed. These new terms can be evaluated in terms of their relationship to the solution (or gaseous) concentration C as follows:

$$\left(\frac{\partial C(\mathrm{ads})}{\partial t}\right) = \left(\frac{\partial C(\mathrm{ads})}{\partial C}\right)\left(\frac{\partial C}{\partial t}\right) \qquad (27)$$

$$\left(\frac{\partial C(\mathrm{sol})}{\partial t}\right) = \left(\frac{\partial C(\mathrm{sol})}{\partial C}\right)\left(\frac{\partial C}{\partial t}\right) \qquad (28)$$

Substituting and rearranging yields

$$\frac{\partial C}{\partial t} = \frac{D}{\theta + (\partial C(\mathrm{ads})/\partial C) + (\partial C(\mathrm{sol})/\partial C)}\left(\frac{\partial^2 C}{\partial x^2}\right) \qquad (29)$$

whose exact form will depend on the relationships for sorption and solution. It is assumed that sorption and solution are reversible and rapid enough that they can keep up with changes in concentration produced by diffusion.

Three relationships are commonly encountered for the isothermal equilibrium between adsorbed and dissolved material: linear partition (distribution law), Freundlich, and Langmuir. These relationships and the associated derivatives follow:

Linear partition: $C(\mathrm{ads}) = KC \qquad \frac{\partial C(\mathrm{ads})}{\partial C} = K$ (30)

Freundlich: $C(\mathrm{ads}) = KC^n \qquad \frac{\partial C(\mathrm{ads})}{\partial C} = KnC^{n-1}$ (31)

Langmuir: $C(\mathrm{ads}) = \frac{K_1 C}{K_2 + C} \qquad \frac{\partial C(\mathrm{ads})}{\partial C} = \frac{K_1 K_2}{(K_2 + C)^2}$ (32)

It can be seen immediately why the first relationship for sorption is universally used: The differential equation is much easier to solve. There is, however, experimental justification for this simplification; although for sorption in soil the Freundlich isotherm appears to be most accurate, the value of n is quite close to unity in many cases. This was discussed in the chapter on sorption.

With regard to solubility, two possibilities exist: (a) solubility from water solution into waxes, organic materials, etc., of the soil, or (b) of gases in the soil water. The former of the two is generally lumped in with adsorption, which is fine if the linear partition approximation can be used for adsorption. If the more exact laws for sorption are used, this solubility term should be entered separately if it can be identified, which seems doubtful at present.

Solubility in water as a hindrance to diffusion applies, of course, to gaseous diffusion. In this case, at the dilute concentrations that were obtained in soil treatments with gases, we are quite justified to assume that the concentration in water is directly proportional to the concentration or pressure of gas in the air of the soil. This, of course, is known as Henry's law in physical chemistry. As with the direct proportion or distribution relationship for sorption, this means that the derivative of the concentration in solution, with respect to concentration in the gas, is a constant which we denote appropriately in this case as $K_{(sol)}$. Thus, in its simplest form, the diffusion equation becomes the following:

$$\left(\frac{\partial C}{\partial t}\right) = \frac{D}{\theta_A + K'_{(sorp)} + K'_{(sol)}} \frac{\partial^2 C}{\partial x^2} \tag{33}$$

where the constants are computed on the basis of concentration in the "diffusing phase," i.e., the air volume, and θ_A is the fraction of air space in the soil. It is customary to state adsorption on the basis of weight per weight of soil vs volume concentration, the dissolved concentration on the basis of volume of soil water (θ_W), and the "primes" on the constants indicate this. With the indicated changes, the equation becomes

$$\left(\frac{\partial C}{\partial t}\right) = \frac{D}{\theta_A + BK_{(sorp)} + (\theta_w/\theta)\, K_{(sol)}} \left(\frac{\partial^2 C}{\partial x^2}\right) \tag{34}$$

where B is a factor for conversion to volume concentration units.

As has been pointed out previously, it is universally assumed that the establishment of sorption and solution equilibrium is rapid compared with diffusion; but, in fact, this is not apparently always true of sorption. At lease one reference exists in the literature [41] which indicates that sorption by soil can be slow, taking even months to establish equilibrium. Full discussion of the significance of this phenomenon and its occurrence belongs, of course, in the chapter devoted to sorption, particularly on its kinetics; but mention should be made of the possible need for its inclusion in the diffusion equations. This is, in theory, readily accomplished by simply noting that the sorption constant in the equation indicated last will be a function of time and probably of concentration. Thus, in theory, the incorporation of this relationship would make an equation very difficult but not impossible to solve. However, at the present time, there does not appear to be sufficient, basic understanding of the change of the sorption with time to permit really meaningful incorporation of this factor. It would only be possible to incorporate some empirical relationship which would, of course, hold only for specific pesticide soil, etc., and this would have limited usefulness. This particular consideration awaits further data and work.

2. Chemical Decomposition

One further factor that needs to be incorporated is the degradation or decomposition of the chemical in the soil, for, obviously, if the chemical is decomposing at a rate comparable to the rate of diffusion, the diffusion pattern will reflect the decomposition. At any point in the medium, the rate of change of concentration is due not only to the diffusion in and out of material, as influenced by sorption or solution, but must also be diminished by the rate of decomposition or disappearance:

$$\frac{\partial C}{\partial t} = \frac{D}{\theta + BK_{(sorp)} + (\theta_w/\theta)K_{(sol)}} \left(\frac{\partial^2 C}{\partial x^2}\right) - \left(\frac{\partial C}{\partial t}\right)_{(decomp)} \tag{35}$$

Rates of decomposition in soil are a subject for discussion in another chapter, but it can be pointed out that textbook chemical kinetics will usually not apply. However, so little is known of the kinetics of decomposition in soil that arbitrary assumptions such as first-order are usually applied. One cautionary note here is that one may freely flip from concentration on a diffusing volume basis to a total bulk basis in the equation, where it is assumed that sorption is linear with concentration. It is most convenient to express it this way, since the rate of change of concentration may be most conveniently expressed on a soil volume basis. However, should it turn out that the sorption or even solution constants are replaced by some function of concentration, as with the Freundlich equation, then it could not be so readily done, in that proper factors would have to be incorporated. This poses no insurmountable problem, but it will cause error if not considered.

3. Biological Effects

With the proper boundary conditions, the solution of the diffusion differential equations yields a picture of the concentration pattern through the soil profile at any given time. This is useful for questions relating to residual amounts of chemical, but does not provide an adequate guide to the biological effects from the chemical because it ignores time of exposure. A low concentration for a very long period may have more effect than a high concentration for a short period. Since purposeful or accidental effects on life forms are an important consideration regarding use of organic chemicals in soil, this question must be examined. Goring [42] has used three terms to structure the problem:

Intensity — actual toxicant concentration experienced by the organism.

Capacity — a measure of the amount of toxicant effect an organism can tolerate.

Dose — the joint effect of intensity and time.

Dose and capacity are related concepts with the first referring to the external environment and the second to an internal environment. When an organism is exposed to an external concentration, i.e., intensity, it will take in the chemical to some extent and by detoxifying, ignoring, or simply tolerating it, live with it. Dose measures the amount of exposure that the organism has received, while the maximum amount of internal punishment that it can absorb is its capacity. The capacity is, of course, associated with the lethal dose. Dose, as the combined effect of concentration and time, is actually a complex of many factors such as absorption rate by the organism, detoxification, water content, etc.; but, as Goring pointed out, it has been found that a summation of the product of concentration and increments of time is a reasonably good measure of dosage. This assumes that a dosage of 2000 ppm achieved by a 4-h exposure at 500 ppm concentration has the same effect as an 8-h exposure to 250 ppm. The expression is obviously not exact because the scale is limited at both ends: at the lower end by a threshold below which the organism is capable of detoxifying or challenging the exposure indefinitely, and at the high end because it cannot be any deader than dead. Within these limitations, however, the summation is generally accepted as a useful approximation. The determination of the amount of dosage is easy if the concentration is constant; but it becomes difficult if the concentration is varying, as in a case of unsteady-state diffusion. In such a case, the methods of integral calculus can be applied:

$$\text{Dose} = \int_{t_1}^{t_2} C\,dt = \int_{t_1}^{t_2} f(t)\,dt \tag{36}$$

The solution of the diffusion equation will give a relationship, $C = f(t)$, so dose for any time period can be determined by performing the integration and evaluating the result. In the case of nonintegratable expressions, numerical methods are well known. For experimental data, the area under a concentration-time plot is the accumulated dose. Thus, one way or another, dosage can be estimated and a distribution of dosage constructed where a concentration distribution is known.

III. APPLICATIONS

A. Gaseous Diffusion

1. Soil Fumigation

A very practical example of gaseous diffusion is soil fumigation, and the extensive investigations of the subject are reviewed in the corresponding chapter. However, mathematical analysis in terms of diffusion laws is appropriate here. Perhaps the most complete mathematical analysis of the fumigation process is that due to Hemwall [43-45]. Since many of the points thus far made are illustrated and drawn together in his treatment, we will present this analysis in some detail. An important consideration is that he makes two significant contributions that do not occur elsewhere: (a) dealing with the normal fumigation geometry consisting of injection in lines spaced in the field, and (b) a description of the manner in which electronic computers were used for the solution and evaluation of the diffusion differential equations. This last point is of particular importance, since it can enable us to get around the often formidable mathematical difficulties posed by the differential equations of diffusion and in applying them to very complex situations (see the chapter on fumigation).

Mathematical analysis of soil fumigation has otherwise been limited to simplified models, as, for example, in the work of Call [46] which considered radial diffusion from a point of injection. Hemwall considers the typical injection pattern in parallel lines and analyzes it as basically a two-dimensional pattern on the cross section of the field, perpendicular to the lines of injection. Diffusion is, therefore, from points spaced regularly across the field, as shown in Fig. 3 which is taken from his work [45].

As indicated, symmetry allows this to be reduced to a single, small area which repeats itself throughout the field, one side of which passes (as will be seen) through the injection point and, the other, midway between two injection points. Again, by these symmetry considerations, one can consider that the barriers thus conceptually constructed in the diffusion field actually act as impervious barriers reflecting diffusion. Another way of looking at it is that diffusion out of the space is exactly counterbalanced by diffusion into the space from the other injection points on either side.

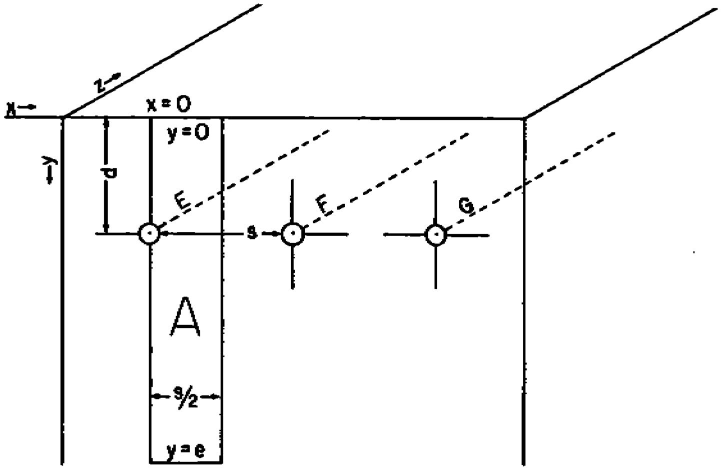

Fig. 3. Cross section of a fumigated field perpendicular to the fumigant injection lines E, F, and G. (x and y are the coordinates perpendicular to the injection lines, d is the injection depth, and s is the spacing between adjacent injection lines; area A is one of a series of identical mirror images which can be drawn through the field and E is the depth of these mirror images.) (Reprinted from Hemwall [45].)

He used an equation (37) derived, as was Eq. (35), with two modifications: (a) diffusion in two dimensions and (b) assuming first-order kinetics — $(dC/dt) = -k_1C$:

$$\left(\frac{\partial C}{\partial t}\right) = D'\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2}\right) - k_1 C \tag{37}$$

where

$$D' = \frac{0.66\ \theta_A D_o}{\theta_A + BK_{(\mathrm{sorp})} + (\theta_w/\theta_A)\,K_{(\mathrm{sol})}}$$

C is the concentration in the air space, A the air space, and w the water-filled space. The term $0.6\ \theta_A D_o$ is based on Penman's tortuosity value and ignores the change of tortuosity with porosity or the existence of blind-end pores. In the light of later work already discussed, the equation and diffusion constant could probably be changed, but the method of mathematical treatment would remain the same as probably would the general conclusions.

The numerical method of solution, which was used, is based on approximating the derivatives as ratio of small finite increments, i.e., $dC/dt = \Delta C/\Delta t$.

The diffusion field is imagined as divided into a square grid of small cells (10 x 90 = 900 for this case) and the increments computed between adjacent cells as indicated in Fig. 4. Diffusional flow from or into the central square from each of the surrounding eight squares is computed for the small time difference, Δt. Hemwall uses the finite difference method of Milne [47] to get the following difference equation:

$$\begin{aligned} C_{(x,y,t+\Delta t)} = (1-k_r\,\Delta t)\Big\{\big[1-(10/3)\alpha\big]C_{(x,y)} + (\alpha/6)\Big(4C_{(x+\Delta x,y)} \\ + 4C_{(x-\Delta x,y)} + 4C_{(x,y+\Delta y)} + 4C_{(x,y-\Delta y)} \\ + C_{(x+\Delta x,y+\Delta y)} + C_{(x+\Delta x,y-\Delta y)} \\ + C_{(x-\Delta x,y+\Delta y)} + C_{(x-\Delta x,y-\Delta y)}\Big)\Big\}_t \end{aligned} \tag{38}$$

$$\alpha = \frac{D'\,\Delta t}{(\Delta x)^2} \quad \text{for} \quad \Delta x = \Delta y$$

The computer is programmed to run through the entire grid of cells using the difference equation and, thus, advancing to the pattern after the small time differential. Provision is made for boundary conditions in the edge cells. The answer is obviously approximate because of the finite size of the cells and of the time interval; but if these are made small enough, it can lead to an answer which is reasonably representative of the true answer. The parameter α determines the accuracy of the answer; and, thus, for a given mesh size and for a desired accuracy, the time increment Δt that must be used is determined. The accumulated dose at every point is calculated by the equation

$$\mathrm{Dose}_{(x,y,t)} = \sum_{t=o}^{t=t} C_{x,y}\,\Delta t \tag{39}$$

Using this mathematical technique and its definition of dose, Hemwall compared the zone of control for nematodes under a variety of fumigation conditions. He used the vapor pressure of ethylene dibromide which had been determined by Call [49], a representative range of soil properties,

$C_{(x-\Delta x, y+\Delta y, t)}$	$C_{(x, y+\Delta y, t)}$	$C_{(x+\Delta x, y+\Delta y, t)}$
$C_{(x-\Delta x, y, t)}$	$C_{(x,y,t)}$ $\downarrow$ $C_{(x,y,t+\Delta t)}$	$C_{(x+\Delta x, y, t)}$
$C_{(x-\Delta x, y-\Delta y, t)}$	$C_{(x, y-\Delta y, t)}$	$C_{(x+\Delta x, y-\Delta y, t)}$

Fig. 4. Operation of the finite difference equation for diffusion.

and the figure of 2000 ppm h for the lethal dose value of ethylene dibromide on nematodes. The zone of control is, of course, simply the volume within which the dose exceeds the lethal dose value. An example of his analysis is shown in Fig. 5 where the comparative effect of different depths of injection was computed. These seem to indicate a definite advantage as might be expected for a deeper injection and is interesting in view of the current swing toward the practice of injecting fumigants at greater depth for better control. In general, his conclusions are in agreement with the results of the extensive studies that have been made in this area of fumigation factors. A thorough discussion of the principles of fumigation as applied in the field will be found in the chapter on fumigation.

Whereas Hemwall's treatment was theoretical and lacked experimental data to confirm his predictions, other studies in this area, contrarily, have been theoretically incomplete. An example of this is the study by Call [46] of the diffusion of ethylene dibromide through soil. In this case, the material was injected in the center of a cylindrical mass of soil at a depth of 6 in. and the concentration of ethylene dibromide in the air measured experimentally. The diffusion was treated according to the diffusion equations, and much valid information was obtained; but, in the absence of data on solubility, adsorption, and decomposition for his soil, the full analysis which Hemwall demonstrates cannot be carried out.

2. Soil Aeration

Aeration of soil is an important phenomenon which is now generally recognized as a diffusion process (see Van Bavel [13] for a brief summary).

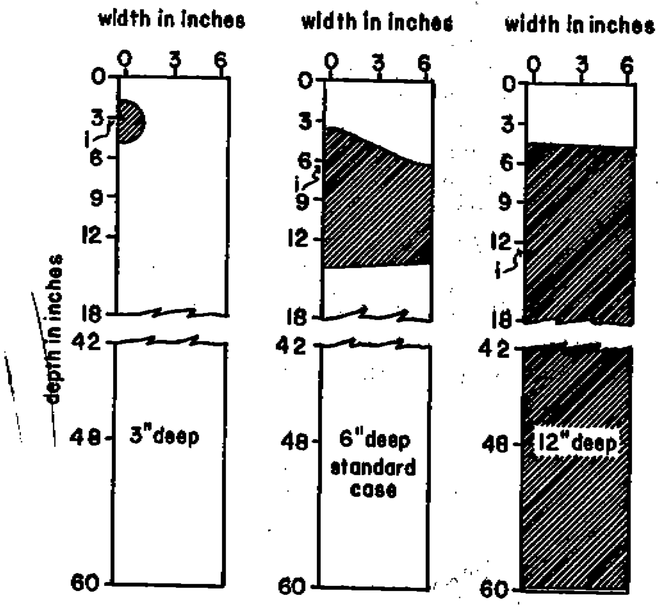

Fig. 5. Biological control patterns for various injection depths for a soil fumigant. (Reprinted from Hemwall [45].)

The oxygen content of soil is important to the growth of plant roots and to the metabolism of microorganisms in the soil. The former aspect is not directly pertinent to this book, and the reader is referred to the review by Grable [48] for a summary and references. Since, however, microorganisms play such an important rôle in the decomposition of many chemical substances, the oxygen content of soil is an important factor. When the oxygen falls below a critical value (1-5%), the metabolic pattern changes from aerobic to anaerobic; and the degradation pattern for organic chemical, likewise, can be radically changed. One example is DDT which is degraded relatively rapidly to DDD under anaerobic conditions while aerobic decomposition is very slow. This is discussed more fully in the chapters on chemical transformation in soil.

Van Bavel [50] has developed a soil aeration theory based on diffusion in which he assumes a rate of consumption of oxygen which is constant and a steady-state condition of the soil. In order to simplify the mathematical treatment, he also has assumed that the soil occurs in horizons with constant porosity and other properties and also cases where impervious layers or zones occur. These conditions represent a rather artificial situation; and, furthermore, the soil may not be in a condition of steady state if soil conditions are changing. Penman [12] has concluded that a 40- to 100-min period may be required for a steady state to be established in a 1-in. soil sample so that, for a layer of soil many feet deep, many days may be necessary. For this reason, Papendick and Runkles [24] developed an aeration theory based on non-steady-state diffusion which, of course, is convertible to steady-state diffusion conditions by the extension of time to infinite value. In a second paper [51], they treat unsteady-state diffusion with the added condition that the consumption of oxygen is not constant, but changes with time, using an empirical equation for the rate:

$$\frac{dC}{dt} = a + be^{kt} \tag{40}$$

where a, b, and k are constants. This leads to an equation for diffusion of oxygen into soil:

$$\frac{\partial C}{\partial t} = D' \frac{\partial^2 C}{\partial x^2} - (a + be^{kt}) \tag{41}$$

which is solved explicitly for concentration. Using Millington's relationship between diffusion in a porous medium compared to that in air, they find their theory fits their data reasonably well for shallow depths and short times. For deeper penetration and consequent longer times, deviations are noted in the direction of less oxygen than anticipated. Although not perfect, this model appears to represent a definite step toward dealing with soil as a dynamic system that is subject to change. This is particularly true when dry soil has been recently wetted as would occur naturally in the rain cycle. An ultimate value of such work is, of course, to develop the ability to determine depth beyond which anaerobic patterns of decomposition must occur and, thus, to better understand the decomposition pattern of pesticides and organic materials in soil profiles. However, there is a conspicuous need to consider the dynamics of soil in treating all aspects of the fate of chemicals in soil.

B. Liquid Phase Diffusion

Because it is so much slower than gaseous diffusion, liquid diffusion is significant for a much smaller scale of movement in soil. As will be seen later, the order of magnitude of movement in soil is a few centimeters per month. An excellent review bearing on this subject is that by Olsen and Kemper [4], "Movement of Nutrients to Roots." If we but substitute the word "pesticides" or "organic chemicals" for "nutrients," we find that much of the discussion is generally pertinent. Their general discussion of the principles of diffusion is soil is recommended.

Diffusion serves to redistribute applied chemicals on a microscale and thus to provide for the delivery of the chemical to active sites of decomposition or sorption, or other aspects of soil activity besides movement to roots.

One of the complexities in liquid phase diffusion is that most salts are ionized but the ions have only partial independence of movement. If, for example, a herbicide is a sodium salt of an acid (e.g., 2,4-D), the sodium cation and the anion will diffuse partially independently. They are subject to the condition that the electrical neutrality of the solution must be maintained. Thus, the rate of diffusion or the diffusion coefficient for the anion will depend upon the associated cation, i.e., sodium, potassium, etc., as well as other salts in the solution. Another way of looking at this is in terms of the counterdiffusion. Thus, when an organic ion such as 2,4-D anion diffuses in a given direction, electrical neutrality can be maintained by counterdiffusion of other anions or by diffusion of cations in the same direction. Thus, SO_4^{2-} or Cl^- ions could diffuse to exchange places with 2,4-D anion in place of "parallel" diffusion of Na^+. This means, again, that the other ions present in the solution, as well as the particular counterions which accompany the organic molecular ion, will make a difference in the diffusion rate and, therefore, the value of the diffusion coefficient.

The clay in the soil plays a role as an immobile electrolyte based on its cation exchange capacity, which further complicates the diffusion of ions. In the case of large organic cations like paraquat or diquat, it is likely that they are held so firmly as to be essentially immobile. It is expected that organic anions, such as 2,4-D, would diffuse more than the organic cations. Here again, the size and polarizability of organic anions make them more subject to adsorption than inorganic anions like Cl. An interesting study of ionic diffusion through clay is provided by Dutt and Low [22] (see Table 3). They established a steady-state diffusion through Na-bentonite from 0.1 M NaCl to distilled water. When the plug of Na-bentonite was sectioned, it was found that not only was the Cl gradient unconstant but there was an apparent discontinuity in concentration at the two surfaces, e.g., a 0.1 M solution reservoir was associated with a 0.07 M solution in the clay. Although there was controversy (involving Bolt and De Haan [52]) on interpretation, there was no challenge to the experimental results. Lindstrom and co-workers [17] use a large reservoir (essentially infinite) over a column of water-saturated soil which was then sectioned and analyzed for ^{14}C-labeled 2,4-D (Method No. 4, Table 4); it is noted that, although the reservoir is 1.26 ppm, the highest concentration shown in soil is about 1.07 ppm. It is interesting to speculate that this could be a discontinuity, although it may be an artifact of their experimental method such as sorption. Information provided in the paper does not permit clarification of this latter factor. The diffusion coefficient was obtained from the concentration-distance profile by the standard error function equation (Crank [1], p. 30), so that integral diffusion coefficients to any given depth can be calculated. Single values for D are obtained, so it cannot be determined if there is any trend in the coefficient as observed with Dutt and Low's work [22]. Graham-Bryce [16] found no meaningful trend in a sectioning experiment using dimethoate and disulfoton.

An important potential application of diffusion theory is in studies of uptake of pesticides by plant roots. The reader is again reminded of the review by Kemper and Olsen [4].

Graham-Bryce [16] has assembled the necessary basic information (diffusion coefficient, adsorption coefficient, soil properties, vapor pressure, and solubility) needed to estimate the rate at which the insecticides, dimethoate and disulfoton, would diffuse to the root surface. This he has compared with uptake by plants through the roots, and he concludes that the limiting factor is root absorption rather than soil diffusion. Thus, for example, he calculates that the observed uptake of insecticide, in one case, should require no more than 0.9 cm of root length, which is to say the diffusion oversupplies the root surface with chemical.

Lavy [53] has qualitatively studied the uptake and transfer of three symmetrical triazines through soil: atrazine, propazine, and simazine. Using radioautographs, he found that atrazine tended to concentrate in the soil around the root, simazine tended to become deficient, and propazine was intermediate in character, with its behavior depending upon the soil. This was consistent with the higher water solubility of atrazine which would tend to make more of it available for movement. Quantitative calculations are not possible since the basic information on the soil, the pesticides, and their interaction is not available. Lavy [18] has studied the diffusion coefficients of these three chemicals in the same soils but reports only grand averages which cannot be used for specific calculation. Lavy [53] puts the same interpretation upon this phenomenon as Barber [54] in his work with Rb^+, which is that, where deficiency occurs, diffusion is the primary mechanism, and, conversely, concentration results from mass flow being the primary mechanism. It would seem to be more fundamental to look at the relative rates of uptake of water and solute at the root in relation to the concentration of the soil solution. If the ratio of rate of solute absorption to rate of water uptake is greater than the concentration, there will be deficiency, and vice versa. Nye and Spiers [55] point out that it is not really valid to treat the movement to the root as the sum of diffusion of the solute and mass movement of solution, since the standard diffusion equations are not valid if there is solvent flux. Water will also diffuse rapidly since it has a small molecule. They derive an equation based only on the flux of water and of solute and deduce that for steady state a critical index is

$$\frac{r_o V_o}{D'} - 2 \tag{42}$$

where r_o is the radius at the root surface, V_o the inward radial velocity of water at the root surface, $D' = D\,dC'/dC$, D the diffusion coefficient of the solute, and dC'/dC the rate of change of soil solution concentration with total soil concentration. This compares the inward movement of water with the diffusion of the solute as a condition for a steady-state concentration gradient of solute.

C. Solid Phase Diffusion

What is referred to as diffusion in the solid phase, if it exists, is more likely to be diffusion along the solid surface and refers to possible contribution to the diffusion by movement of adsorbed material along the surface. As noted in the earlier discussion of diffusion coefficients, those representing diffusion through solids are so low that diffusion in the solid particles of soil should be negligible in comparison with movement through the liquid. It is interesting to note that this type of diffusion has been studied in connection with gaseous flow. Winterbottom and Hirth [56] have discussed the diffusional flow in a Knutsen vapor pressure cell where a very dilute gas ($<10^{-2}$ mm) escapes through an orifice. Although diffusion is far less rapid than effusion or direct molecular escape, the increase in concentration of gas near the surface due to adsorption may be great enough to partially compensate. Thus, particularly with very small orifices, a significant fraction of the total flux through the hole may be due to diffusion. In a similar way, the possibility exists that chemical adsorbed to the soil particles may contribute to diffusion through the soil.

It has not been fully resolved as to whether "solid phase" diffusion is significant in soil. Nye and co-workers have studied soil diffusion for evidence of contribution by adsorbed cations, considering that the diffusion process can be considered to be a sum of the liquid diffusion flow and "solid" diffusion flow and is represented by Eq. (13). They have found no evidence that "solid" diffusion made a significant contribution. The most accurate experiment by Mott and Nye [19] with self-diffusion of Sr^{2+} (10^{-2}-10^{-4} M) indicated a liquid diffusion contribution of about 130X that of any possible solid diffusion. Vaidyanathan et al. [21] found no significant solid diffusion for potassium ion. Gast [57], on the other hand, has concluded from a study of diffusion in bentonite that the diffusion current is greater than can be accounted for by electroconductivity of the clay systems and discusses diffusion of "bound" cations. Graham-Bryce [20] also discusses indications that diffusion by the exchangeable cations may occur in soil. However, the work of Nye and co-workers is more complete and appears to be less subject to experimental uncertainty than any other published reports. In soil, a high proportion of many organic chemicals adsorb in apparent association with the organic matter, so the possibility exists that this solid sorption is contributing to diffusion. The existing data provide no indication.

D. Liquid-Gaseous Diffusion

There is no similar uncertainty about cases where diffusion occurs simultaneously in both liquid and vapor phases of soil. One example already has been shown in connection with the insecticide, disulfoton. According to the data of Graham-Bryce [16] (Table 3), the diffusion rate of this material is largely independent of water content. This can only mean that the rates of diffusion in the two phases, liquid and gas, are comparable; so that changing the proportion of the two phases does not change the total rate of diffusion. This is reasonable, in view of the partition coefficient which has a value of 5.5×10^3. The partition coefficient represents the ratio of the equilibrium concentration in the liquid phase to that in the vapor phase. This ratio of 5.5×10^3 is the same order of magnitude as the ratio of diffusion coefficients in gas to liquid, and so the faster diffusion in the gaseous phase is balanced by the proportionally lower concentration in that phase. This, of course, is only a rough rule-of-thumb, since the factors of sorption will enter here as well. A listing of this factor for a number of pesticides is given in Table 6.

Another case which has been studied with great care by Ehlers and co-workers [14, 15] is the diffusion of lindane in soil. In this case, again, the diffusion coefficient is essentially unchanged over a wide range of water:air ratios for the soil. We reproduce, at this point, as Fig. 6, their data which shows that, indeed, for most of the range of water content the diffusion coefficient does not change. The drop of diffusion coefficient to zero at very low water contents is interpreted as strong adsorption of the lindane when the water is no longer present in quantities sufficient to compete for adsorption by surfaces. Thus, the lindane will be immobilized in very dry soil. A similar behavior for dieldrin is indicated by the work of Farmer and Jensen [58] and the calculated value for the partition coefficient of 4.4×10^3 (see Table 6).

The effect of temperature upon this diffusion is shown by Table 7, taken from the work of Ehlers et al. In the use of activation energies, Table 7 represents an exponential relationship between diffusion and temperature ($e - \Delta H/RT$) which might appear to be inconsistent with the relation described in Sec. II, C. 1.

$$\frac{D_1}{D_2} = \left(\frac{P_2}{P_1}\right)\left(\frac{T_1}{T_2}\right)^m , \quad m = 1.75 - 2 \qquad (10$$

The reason for this apparent discrepancy is that the ratio P_2/P_1 depends on the changes of vapor pressure and solubility of the chemical, which are exponential. Change in the ratio P_2/P_1 is so large that it quite overshelms the second factor: $(T_1/T_2)^m$.

E. Volatilization

1. With Diffusion

With respect to soil, volatilization is obviously a matter of migration to a surface followed by removal. This, of course, occurs normally in fumigation where, unless the surface is tarped, the escape of fumigant vapor from the soil surface causes a loss in biological control for the surface layers. In models of diffusion in soil such as have already been discussed, one of the boundary conditions is that the concentration at the surface of the soil be maintained essentially at zero. In the case of less volatile materials and fumigants, loss from the soil by vaporization involves vaporization from a water or a soil surface. It appears that in most cases the dry soil surfaces hold organic chemicals very tenaciously and may in many instances prevent loss for extended periods of time. This was already pointed out in the discussion of lindane diffusion in soil and has been reported for many of the soil-applied herbicides. This has been reported for propham and chlorpropham by Parochetti and Warren [59], for EPTC by Fang et al. [60], and by Gray and Weierich [61], and also for CDAA by Deming [62], to mention a few cases. In all these and other instances, it is observed that the losses of chemical from moist soil are considerably greater than from dry soil.

This factor can be approximately quantized based on the fact that the amounts of pesticides applied are much less, in general, than the amount required to saturate the water phase of the soil. Thus, volatilization in a moist soil is from a dilute water solution; and an important quantity, as was pointed out by Hartley [63], is the partition coefficient between water and air. A number of these have been listed in Table 6, and a further

TABLE 6

Vapor Pressure and Solubility of a Number of Soil Applied Pesticides

	Vapor pressure (mm Hg)	Water solubility (ppm)	Distribution ratio (Vol. Conc.) (Liquid-Gas)	Ref.
Propham ($C_{10}H_{13}NO_2$) MW 179.2	—	250 at 25°C	—	[64]
Chlorpropham ($C_{10}H_{12}ClNO_2$) MW 213.7	Est 10^{-5} at 25°C	80 at 25°C	7×10^5	
EPTC ($C_9H_{19}NOS$) MW 189.3	1.62×10^{-2} at 23°C	636 at 3°C		
	1.97×10^{-2} at 24°C	375 at 25°C	1.86×10^3	
	2.77×10^{-2} at 28°C			
	6.2×10^{-2} at 40°C			
CDAA ($C_8H_{12}ClNO$) MW 173.6	9.4×10^{-3} at 20°C	19,700 at 25°C	2.21×10^5	
Dinoseb ($C_{10}H_{12}N_2O_5$) MW 240.2	6×10^{-4} at 20°C (for acetate)	52 at 25°C	6.6×10^3	
CDEC ($C_8H_{14}ClNS_2$) MW 223.8	2.2×10^{-3} at 20°C	92 at 25°C	3.42×10^3	
Trifluralin ($C_{13}H_{16}F_3N_3O_4$) MW 335.3	1.0×10^{-4} at 25°C	0.58 at 25°C	3.22×10^2	
Dichlobenil ($C_7H_3Cl_2N$) MW 172.0	5.5×10^{-4} at 20°C	18 at 20°C	3.48×10^3	
Disulfoton ($C_8H_{19}O_2PS_3$) MW 274.2	1.8×10^{-4} at 20°C	15 at 20°C	5.56×10^3	[16]
Dimethoate ($C_5H_{12}NO_3PS_5$) MW 229.1	8.5×10^{-6} at 20°C	30,000 at 20°C	2.81×10^8	
Aldrin ($C_{12}H_8Cl_6$) MW 364.9	6.0×10^{-6} at 25°C	0.2 at 25°C	2.26×10^3	[65]
Lindane ($C_6H_6Cl_6$) MW 290.8	3.2×10^{-5} at 20°C	10	1.96×10^4	[70]
DDT ($C_{14}H_9Cl_5$) MW 354.5	1.9×10^{-7} at 20°C	1.2 ppb	3.26×10^2	
Dieldrin ($C_{12}H_8Cl_6O$) MW 380.9	2.7×10^{-6} at 20°C	0.25	4.44×10^3	[64] [58]

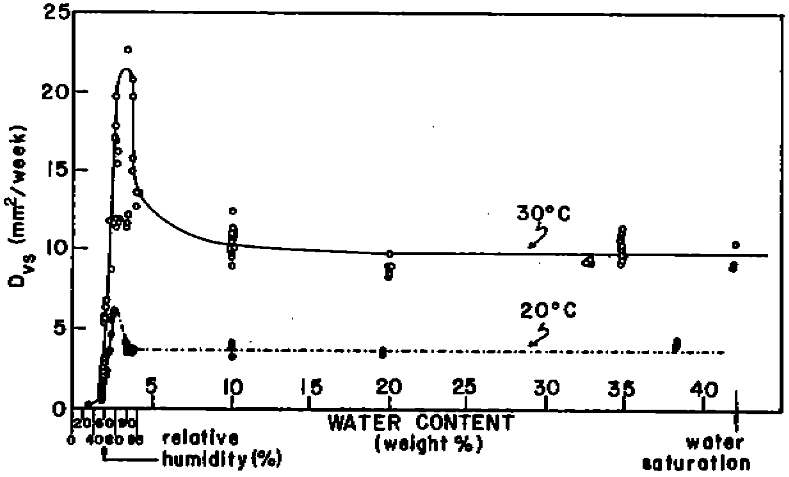

Fig. 6. Effect of soil water content on the diffusion of lindane in gila silt loam. (The equivalent relative humidities were determined at 20°C.) (Reprinted from Ehlers et al. [15].)

TABLE 7

Influence of Temperature on Apparent Diffusion Coefficients of Lindane Calculated from Relative Energies of Activation[a]

Temperature (°K)	D_{vapor}' (mm^2/week)	D_{soln}' (mm^2/week)	D_{vs} (mm^2/week)
293	1.6	2.1	3.7
303	5.6[b]	5.8[b]	11.4[b]
313	18.1	15.1	33.2
E calc.[c]	2.0		20.0

[a] Reprinted from Ehlers et al. [15].

[b] Experimentally determined values.

[c] E_{vs} = 20 K_{cal}/mole, $E_v = \Delta H_{vap.}$ = 24.1 K_{cal}/mole, and E_s = 16.1 K_{cal}/mole.

source is Goring's review [42]. The coefficient indicates to us what proportion of chemical is in the vapor and, thus, gives some idea of the potential for volatilization. For example, the coefficient for trifluralin in Table 6 (3.2×10^2) suggests that something in the order of 3% of the trifluralin in solution is in the vapor phase where volumes of soil:air and water are equal. We hasten to add that this is an extremely rough measure, since adsorption will occur and tend to decrease the amount of material in the vapor phase and because the water:air ratio in the soil is not very often equal to 1.

Since diffusion is a significant factor in this volatilization process, the depth of soil through which the chemical is dispersed has a very large effect upon the rate of volatilization. It is on this basis, of course, that volatile materials of this nature can be successfully used as soil-applied herbicides if they are immediately incorporated or mixed into the soil. An examination of the operation of diffusion laws in such a case gives a better appreciation of the incorporation factor, so the following, more detailed examination is to be presented: Let us then visualize soil into which chemical has been uniformly mixed to a given depth and consider that the vapor is in equilibrium with the dissolved and adsorbed material throughout the soil mass. It is further assumed that the chemical is largely adsorbed and immobile so that at any moment only a minor fraction is free to move by diffusion or leaching. It should be clear, then, that as the vaporization from the surface occurs, depletion will develop a concentration gradient for the material in all phases: air, water, and soil surfaces; and this concentration gradient will, in turn, be the driving force for further diffusion. However, as the diffusion proceeds, this concentration gradient will diminish because of a greater path over which diffusion takes place; and the rate of volatilization will fall off with time. The mathematics of this system are, as previously noted, somewhat complex; but are much simplified where the impregnated soil layer can be considered to be semi-infinite, namely, that its total depth is large compared to the depth significantly depleted by diffusion and volatilization. In this case, there is a simple relationship for the total amount of loss (see Crank [1, p. 31]):

$$Q_t = 2C_0 (Dt/\Pi)^{1/2} \tag{43}$$

where Q_t is the total loss per unit area, D the diffusion coefficient of the vapor through soil, C_0 the initial soil concentration, and t the time. In case the loss has proceeded far enough to significantly affect the bottom of the layer, a reasonably accurate answer should be obtainable by Crank's formula for evaporation from a surface [1, p. 57] with assistance from the graph of a family of solutions [1, Figs. 4 and 7]. This ignores the diffusion downward through the soil, which will change the bottom boundary. However, where the incorporation occurs in somewhat compacted soil, one might expect this to be minimized.

The application of the approximate formula (43) is illustrated by Table 8 which contains data from Lichtenstein and Schultz [66] treated to yield estimates of diffusion coefficients. The fact that the calculated diffusion rate is smaller than might be expected from Table 4 is probably due to soil factors ignored and other approximations. It will be noted, for example, also that the estimated diffusion coefficients decrease with increasing amounts of organic matter, reaching a minimum with the muck soil. This is quite evidently due to sorption which lowers the amount of available material in the solution and, thus, the concentration of vapor in the soil air. The value for pure sand is reasonably close to the diffusion coefficients for pesticides listed in Table 4, i.e., $\sim 10^{-7}$ cm^2/sec. It is freely admitted that such treatment is quite approximate in these cases for two reasons: (a) that the amount lost, at least in the case of the quartz sand, became quite substantial; and (b) there was a concurrent decomposition occurring so that the total concentration was decreasing at the same time as diffusion took place. The numbers, therefore, can only be considered as very approximate indicators of this diffusion process.

Approximation notwithstanding, it is of interest to make some further rough calculations on the simplified formula for a semi-infinite system to show the effect of time and depth of incorporation upon the loss rate. Using the formula and the data from Table 8, we can calculate for a 4-1/2-in. layer of Carrington silt loam that (a) with the same total dosage, 0.89% volatilization would be expected in 56 days while 16% was observed, and (b) that if the soil concentrations were the same in the deeper layer, then it would take 43 years to achieve the 16% loss by volatility achieved in 56 days for the thinner layer, 0.31 cm = 0.1 in. Farmer and Jensen [58] have treated a similar case for dieldrin (1 lb/acre incorporated in 15 cm to give 7.4×10^{-7} g/cm^3) using the diffusion coefficients they determined (see Table 4). Noting that diffusion was much slower through dry than wet soil (e.g., tenfold difference), they treated the system as if it were "tarped" with a thin layer of dry soil (0.1 cm) and assumed that diffusion was rapid up to that bed. They predicted 20% loss in 1 year. If, however, the same problem is treated by Eq. (43) using the highest value for the diffusion coefficient, 17 months is predicted; while the diffusion coefficient for drier soil (75% relative humidity or $D = 0.096 \times 10^{-7}$ cm^2/sec) computes 294 months! Drying of the soil surface should yield a value intermediate to these two. What was overlooked was that, because of the square root, a sixteenfold difference in diffusion coefficient produces only a fourfold difference in amount of loss per unit area (Q_t).

TABLE 8

Aldrin Volatility by Diffusion from Soil[a]

Soil	Organic matter (%)	Loss		Time (days)	C_o (μg/cm^3)	$D = \frac{\Pi}{4t}\left(\frac{M}{C_o}\right)^2$ (cm^2/sec)
		% of Total	μg/cm^2 (M)			
Quartz sand[b]	0.0	52	1.027	3.5	6.43	8.44×10^{-8}
		79	1.561	7	6.43	9.74×10^{-8}
Plainfield sand[c]	0.8	61.7 - 38.2 = 23.5[d]	1.437	56	8.86	0.427×10^{-8}
Carrington silt loam[b]	4.3	70.2 - 53.9 = 16.3[d]	0.865	56	7.68	0.206×10^{-8}
Muck[b]	40.0	75.8 - 67.0 = 8.8[d]	2.604	56	29.6	0.126×10^{-8}

[a] Data from Lichtenstein and Schultz [66].

[b] 3.07 mm layer at 10 ppm with concentration at 37°C.

[c] 6.9 mm layer at 10 ppm with concentration at 37°C.

[d] Difference in loss from closed and open bottles.

These discrepancies suggest further work for experimental verification. Existing data do not permit distinguishing between loss by volatilization and by chemical degradation, so specially designed experiments are indicated. It appears quite likely, however, that in the majority of cases soil decomposition processes will probably be more important for the loss of semivolatile materials than volatility, providing they are distributed through a large enough soil mass. In fact, adequacy of incorporation is likely to be a limiting factor.

2. Codistillation

At this point, some discussion seems advisable in relation to the idea that "steam distillation" or codistillation will hasten volatilization of chemicals from the soil or water surfaces. Acree et al. [67] proposed this explanation for work on the loss of DDT from water solution. They placed a dilute suspension of DDT in water on a hot water bath and left it overnight to determine the amount of water and DDT that were lost. They found that the ratio of DDT loss to water loss was larger than would be predicted from the vapor pressures of the two substances and invoked the idea that DDT codistilled with the water, i.e., the evaporation of the water increased the volatilization of the DDT. Hartley [63] has commented on this notion in his paper, "Evaporation of Pesticides," and this writer shares his opinion that there is no need, thus, to repeal the laws of classical physical chemistry. First, the use of the term "steam distillation" is an unfortunate semantic error since, strictly speaking, steam distillation requires boiling water and an actual sweeping of vapor by mass transport. Second, diffusion in the gaseous state is, by classical physicochemical theory, due to the largely independent motion of individual molecules, so it is most difficult to see any basis for the degree of molecular interaction implied in "codistillation." As a matter of fact, since molecular velocities depend inversely upon the square root of the molecular weight, the speed of diffusion of DDT to that of water should be even less than the proportion of vapors in the air. Assuming that diffusion rates are inversely proportional to the (molecular weight)$^{1/2}$, we would expect the water vapor rate to be 4.4X that of DDT vapor on the basis of moles per second. When this is corrected for the difference in molecular weights to a weight basis (grams per second), DDT vapor is calculated to diffuse 23% slower than water vapor, other things being equal, including gaseous partial pressure.

Bowman and Acree suggest that intermolecular interactions tend to concentrate the DDT at the water surface but overlook the fact that the same processes would tend to concentrate the DDT from the vapor phase, so that the same vapor pressure could be anticipated. Hartley has proposed that the suspensions of DDT in Acree and Bowman's experiments were in a condition of super-cooled liquid, and he estimates that the vapor pressure would be ninefold greater in such a case. He points out the work of Feichtmeir [68] wherein acetone solutions of DDT evaporated on glass slides did, indeed, yield liquid drops which required days to crystallize. Certainly, we would hardly expect the situation in soils to be similar to the experiments of Bowman, since the large surfaces would tend to adsorb or crystallize the DDT. Spencer et al. [69, 70] found no evidence to support codistillation of dieldrin in soil or water, i.e., the vapor density was the same over crystalline dieldrin or excess dieldrin in moist soil (≥100 ppm apparently required to saturate soil water and sorption capacity). The method used was saturation of air. Lichtenstein and Schultz [66] concluded that soil surfaces had to be wet to achieve maximum evaporation of aldrin but that the amount of water evaporated had no significant effect on the persistence of either DDT or aldrin. There does not seem to be any reason to continue the use of the idea of codistillation in the volatilization of pesticides.

Hartley has also pointed out that the mass movement of soil solution to the surface by capillary action accelerates the evaporation of dissolved chemicals because it is much more rapid than vapor diffusion; and he dubs this "wicking," since soil behaves as a wick. It is well recognized that water evaporates from soil much more rapidly when the surface is wet than when it is dry. The mass movement of water in soil is treated in Chapter 6, and the reader is referred to it for further discussion.

The previous treatment of volatilization from soil, in terms of diffusion only, ignored mass transfer and could, therefore, tend to give somewhat low estimates of loss. A more accurate estimate of loss might be obtained from the total water loss, particularly if the latter could be divided into loss due to water vapor diffusion and loss due to mass transfer of soil solution. The ratio of diffusion rates for water vapor and for chemical vapor would predict the calculation of an estimated loss for the chemical from the first component, while the mass transfer component and the concentration in the soil solution would yield a figure for the loss of chemical by this route. Thus, as a first approximation, we could write for the loss of a dissolved, volatile chemical:

$$Q_t = \frac{VP}{VP_{H_2O}} \times \frac{D}{D_{H_2O}} \times \left(Q_{H_2O}\right)_V + C \times \left(Q_{H_2O}\right)_L \qquad (44)$$

where Q represents amount of loss per unit area, Q_t represents the total amount of loss per unit area, C is the concentration of chemical in the soil solution, and V and L designate loss as vapor and liquid, respectively. This simple expression would immediately be in need of refinements to achieve precision but might well give useful estimates of volatilization to expected under-field conditions using rainfall data. Concentration in the soil solution could be estimated from solubility and sorption measurements or directly as by Green and Obien [71] or Grover and Hance [72]. The diffusion transfer of water through soil has been studied in detail [73, 74]; it cannot be estimated properly from the diffusion coefficient of water vapor in air and porosity because of the phenomenon of "leap-frogging," i.e., condensation on one end of a pore filled with water and almost immediate vaporization from the other end, thus gaining time over the diffusion process. Hartley [63] has used this approach in a simplified form. Using the ratio of vapor pressures of pesticide and of water, and the evaporation rate for water (6 tons/acre per day), he calculated an estimated evaporation rate for the pesticide.

IV. PERSPECTIVE

The mathematical and theoretical bases of diffusion are well established, and their application to soil is quite advanced. However, two factors have held back progress toward a fuller understanding of the diffusion phenomena of organic chemicals in the soil, namely: (a) mathematical complexity of the differential equations, and (b) a paucity of basic physicochemical data such as diffusion constants, etc. Recent papers in this field, fortunately, have begun to correct the second deficiency as the studies of pesticides are beginning to supplement the data we already have for inorganic ions. Model examples include lindane diffusion in soil by Ehlers et al. [14, 15], root uptake of disulfoton and dimethoate by Graham-Bryce [16], and the classical work of Call [7] on ethylene dibromide. Needless to say, this should be only a beginning.

The potential of the computer to overcome the first hindrance was clearly shown by Hemwall [43-45] in his papers on fumigation, and it is disappointing that nothing further has appeared since that time. Much of the work that has thus far appeared on diffusion in soil has been on simplified systems for the purpose of determining diffusion coefficients and the effect of various soil factors such as porosity, sorption, solubility, vapor pressure, etc. Much progress has been made in unraveling the basic factors, and it is high time that they be applied to realistic situations by utilizing the really enormous capacity of the modern computer to deal with complex and time-consuming mathematical operations. Even in existing literature, there are many instances where, with reasonable assumptions and mathematical analysis, published work could be made more meaningful. This was perhaps suggested by the analysis just outlined for volatilization from soil. It seems likely that this has not been undertaken because of the mathematical complexity involved. However, the increased availability of computers and of professional assistance should correct this.

Certainly a great opportunity exists in bridging the gap between exact, simplified laboratory studies and the complex reality of the field, which has been dealt with only approximately and empirically. The finite difference method used by Hemwall to solve his partial differential equation is well suited to contribute, particularly with regard to the inhomogeneity of soil in situ, a consideration so well delineated in Chapter 1. The mesh or grid used in that method permits assignment of different constants for soil properties at different locations in the soil profile. Thus, while Van Bavel [50] was forced to introduce discrete strata and impervious soil layers to make his treatment of the aeration process somewhat realistic, this use of the computer would handle a gradation of soil properties through the profile. The present challenge presented by environmental problems is certain to generate intensive effort in just this direction: a more exact treatment of the real-life behavior of chemicals in soil. We are hopeful that there will be rapid progress in the near future.

REFERENCES

1. J. Crank, Mathematics of Diffusion, Oxford, London, 1956.
2. W. Jost, Diffusion, 3rd ed., Academic, New York, 1960.
3. M. H. Jacobs, Diffusion Processes, Springer-Verlag, New York, 1967.
4. S. R. Olsen and W. D. Kemper, Adv. in Agron., 20, 91-151 (1968).
5. International Critical Tables, Vol 5, McGraw-Hill, New York, 1929, pp. 61-63.
6. R. H. Rust, A. Klute, and J. E. Geiseking, Soil Sci., 84, 453-463 (1957).
7. F. Call, J. Sci. Food Agri. 8, 143-150 (1957).
8. I. M. Klotz and D. K. Miller, J. Am. Chem. Soc., 69, 2557-2558 (1947).
9. G. A. Lugg, Anal. Chem., 40, 1072-1077 (1968).
10. Handbook of Chemistry and Physics, 49th ed., The Chemical Rubber Company, Cleveland, Ohio, 1968.
11. S. Chapman and T. G. Cowling, The Mathematical Theory of Non-Uniform Gases, Cambridge Univ. Press, London, 1939.

12. H. L. Penman, J. Agr. Sci., 30, 437-462 (1940).

13. C. H. M. Van Bavel, Soil Sci., 73, 91-104 (1952).

14. W. Ehlers, J. Letey, W. F. Spencer, and W. J. Farmer, Soil Sci. Soc. Am. Proc., 33, 501-504 (1969).

15. W. Ehlers, W. J. Farmer, W. F. Spencer, and J. Letey, Soil Sci. Soc. Am. Proc., 33, 505-508 (1969).

16. I. J. Graham-Bryce, J. Sci. Food Agr., 20, 489-494 (1969).

17. F. T. Lindstrom, L. Boersma, and H. Gardiner, Soil Sci., 106(2), 107-113 (1968).

18. T. L. Lavy, Weed Sci., 18, 53-56 (1970).

19. C. J. B. Mott and P. H. Nye, Soil Sci., 105, 18-23 (1968).

20. I. J. Graham-Bryce, J. Soil Sci., 14, 188-194 (1963).

21. L. V. Vaidyanathan, M. C. Drew, and P. H. Nye, J. Soil Sci., 19, 94-107 (1968).

22. G. R. Dutt and P. F. Low, Soil Sci., 93, 233-240 (1962).

23. R. P. Murrmann, P. Hoekstra, and R. C. Bialkowski, Soil Sci. Soc. Am. Proc., 32, 501-506 (1968).

24. R. I. Papendick and J. R. Runkles, Soil Sci., 100, 251-261 (1965).

25. R. K. Schofield and I. J. Graham-Bryce, Nature, 188, 1048-1049 (1960).

26. D. L. Rowell, M. W. Martin, and P. H. Nye, J. Soil Sci., 18, 204-222 (1967).

27. W. J. Weber and J. P. Gould, Adv. in Chem., Ser. 60, 280-304 (1966).

28. E. Buckingham, U.S. Dept. of Agr. Bur. Soils Bulletin 25, 1904.

29. J. A. Currie, Brit. J. Appl. Physics, 11, 318-324 (1960).

30. J. A. Currie, Brit. J. Appl. Physics, 12, 275-281 (1961).

31. R. D. Jackson, and A. Klute, Soil Sci. Soc. Am. Proc., 31, 122-123 (1967).

32. J. R. Philip, Soil Sci. Soc. Am. Proc., 31, 711-712 (1967).

33. G. A. Turner, Soil Sci. Soc. Am. Proc., 32, 604-605 (1968).

34. R. C. Goodnight and I. Fatt, J. Phys. Chem., 65, 1709-1712 (1961).

35. P. H. Nye, J. Soil Sci., 17, 16-23 (1966).

36. P. H. Nye, Trans. 9th Intern. Cong. Soil Sci., 1, 117-126 (1968).

37. E. C. Childs and N. Collis-George, Proc. Roy. Soc. (London), A201, 392-405 (1950).

38. T. J. Marshall, J. Soil Sci., 10, 79-82 (1959).

39. R. J. Millington and J. P. Quirk, Trans. Faraday Soc., 57, 1200-1207 (1961).

40. R. J. Millington, Science, 130, 100-102 (1959).

41. J. W. Hamaker, C. A. I. Goring, and C. R. Youngson, Adv. in Chem., Ser. 60, 23-37 (1966).

42. C. A. I. Goring, Ann. Rev. Phytopath., 5, 285-318 (1967).

43. J. B. Hemwall, Soil Sci., 88, 184-190 (1959).

44. J. B. Hemwall, Soil Sci., 90, 157-168 (1960).

45. J. B. Hemwall, Phytopath., 52, 1108-1115 (1962).

46. F. Call, J. Sci. Food Agr., 8, 591-596 (1957).

47. W. F. Milne, Numerical Solutions of Differential Equations, Wiley, New York, 1953.

48. A. R. Grable, Adv. in Agron., 18, 57-106 (1966).

49. F. Call, J. Sci. Food Agr., 8, 86-89 (1957).

50. C. H. M. Van Bavel, Soil Sci., 72, 33-46 (1951).

51. R. I. Papendick and R. J. Runkles, Soil Sci., 102, 223-230 (1966).

52. A. H. Bolt and F. A. M. De Haan, Soil Sci., 94, 344-349 (1964).

53. T. L. Lavy, Soil Sci. Soc. Am. Proc., 32, 377-380 (1968).

54. S. A. Barber, Soil Sci., 93, 39-49 (1962).

55. P. H. Nye and J. A. Spiers, Trans. 8th Intern. Cong. Soil Sci. Bucharest, 3, 535-542 (1964).

56. W. L. Winterbottom and J. P. Hirth, J. Chem. Phys., 37, 784-793 (1964).

57. R. G. Gast, J. Colloid Sci., 17, 492-500 (1962).

58. W. J. Farmer and C. R. Jensen, Soil Sci. Soc. Am. Proc., 34, 28-31 (1970).

59. J. V. Parochetti and G. F. Warren, Weeds, 14, 281-285 (1966).

60. S. C. Fang, P. Theisen, and V. H. Freed, Weeds, 9, 569-574 (1961).

61. R. A. Gray and A. J. Weierich, Weeds, 13, 141-147 (1965).

62. J. M. Deming, Weeds, 11, 91-96 (1963).

63. G. S. Hartley, Adv. in Chem., Series 86, 115-134 (1969).

64. Herbicide Handbook of the Weed Society of America, 1st ed., W. F. Humphrey Press, Geneva, New York, 1967.

65. Guide to Chemicals Used in Crop Protection (E. Y. Spencer, ed.) Canada Dept. of Agr., London, Ontario, Canada, 1968.

66. E. P. Lichtenstein and K. R. Schultz, J. Econ. Ent., 54, 517-522 (1961).

67. F. Acree, Jr., M. Beroza, and M. C. Bowman, J. Agr. Food Chem., 11, 278-280 (1963).

68. E. C. Feichtmeir, Phytopath., 42, 200-202 (1952).

69. W. F. Spencer, M. M. Cliath, and W. J. Farmer, Soil Sci. Soc. Am. Proc., 33, 509-511 (1969).

70. W. F. Spencer and M. M. Cliath, Environ. Sci. Tech., 3(7), 670-674 (1969).

71. R. E. Green and S. R. Obien, Weed Science, 17, 514-519 (1969).

72. R. Grover and R. J. Hance, Soil Sci., 109, 136-138 (1970).

73. J. R. Philip and D. A. DeVries, Trans. Am. Geophys. U., 38, 222-232 (1957).

74. D. K. Cassel, D. R. Nielsen, and J. W. Biggar, Soil Sci. Soc. Am. Proc., 33, 493-500 (1969).