

## DIFFUSION AND MIXING

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### DIFFUSION

Diffusion is the movement of a substance within another, the diffusing phase being in solution or suspension within the dispersing phase. The term Diffusion is also applied to the migration of some property of a substance such as its temperature. Diffusion is one of the most basic of all the processes in nature, being one of the essential processes of life itself. The living cell obtains its food and eliminates its waste products by diffusion through the cell wall.

Diffusion takes place whenever there is a gradient of the concentration of the dispersed phase or intensity of the property which migrates. The dispersing phase may be in the solid, liquid or gaseous state. If it is in the solid state, the diffusion takes place as a result of molecular motion; if it is in the fluid state, diffusion can take place as a result of either the molecular movements alone or the combined effect of molecular motion and the movements of macroscopic masses of the fluid. In a turbulent flow regime, the diffusion which results from the macroscopic turbulent movements is very much greater than that due to the molecular motions. Since most of the problems of concern to hydraulic engineers deal with turbulent flow, turbulent diffusion is generally of more importance than molecular diffusion. However, there are some situations in which both processes play an important role, an example of which will be presented later.

### BASIC LAWS OF DIFFUSION

The basic equations of diffusion were first given by the physiologist, Fick, and have become known as Fick's Laws of Diffusion. Fick's first law is given by the equation

$$\frac{1}{A} \frac{dm}{dt} = -D \frac{dc}{dx} \quad (1)$$

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in which  $\frac{dm}{dt}$  is the rate of mass transfer by diffusion in the direction of  $x$  across an area,  $A$ , normal to  $x$ ,  $\frac{dc}{dx}$  is the gradient of the concentration of the diffusing substance and  $D$  is a proportionality constant. Fick's second law is given by

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad (2)$$

where  $\frac{\partial c}{\partial t}$  is the rate of change of concentration at a point where the concentration gradient is  $\frac{\partial c}{\partial x}$ . Equation (1) is intuitively acceptable, and equation (2) is readily derived from equation (1). Considering a stream tube of cross section  $A$ , and length  $dx$ , the rate of increase of the mass of diffusing substance within this element would be equal to the rate of diffusion into the element at  $x$  less the rate of diffusion out of the element at  $x + dx$ , or

$$\begin{aligned} \frac{dm}{dt} &= -AD \frac{\partial c}{\partial x} - \left[ -AD \left( \frac{\partial c}{\partial x} + \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} \right) dx \right) \right] \\ &= AD \frac{\partial^2 c}{\partial x^2} dx \end{aligned}$$

From this it follows that

$$\frac{\partial c}{\partial t} = \frac{dm}{A dx dt} = D \frac{\partial^2 c}{\partial x^2}$$

These equations may be applied to both molecular diffusion and turbulent diffusion, by use of the appropriate values of  $D$ . For molecular diffusion,  $D$  is known as the "Diffusivity" or the "Coefficient of Molecular Diffusion"; in the turbulent case,  $D$  is commonly known as the "Coefficient of Turbulent Diffusion." The values of the Diffusivity vary with the substances involved and with the temperature. For the diffusion of substances dissolved in water at ordinary temperatures, the molecular Diffusivity is of the order of magnitude of  $10^{-5}$   $\text{cm}^2/\text{sec}$ . The turbulent Diffusion Coefficient varies with the scale and intensity of the turbulence and is many orders of magnitude larger than the molecular Diffusivity.

Equation 2 can be applied to the flow of heat in a solid when  $C$  is taken as the temperature, and  $D$  as the Thermal Conductivity divided by the product of density and the specific heat of the substance. The constant,  $D$ , in this case, was called by Kelvin the "Diffusivity" of the substance.

Equation (2) is for the case of one dimensional diffusion with a constant value of  $D$ . For the more general three dimensional case, with variable values of  $D$ , the equation is

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_x \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial c}{\partial z} \right) \quad (3)$$

In many practical cases, the three components of  $D$  will be constants and the equation will be

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} \quad (3a)$$

#### DIFFUSION AND CONVECTION

In most cases of interest, the movement of a dispersed substance with reference to a fixed coordinate system will be the combined result of the diffusion of the substance within the fluid and the movement of the fluid itself. The rate of transfer of a dispersed substance with concentration,  $c$ , by the movement of the fluid across an area,  $A$ , is equal to  $cA$  multiplied by the component of the fluid velocity normal to  $A$ . With  $U$ ,  $V$  and  $W$  representing the three components of the average velocity of the fluid, the equation for the rate of change of concentration at a fixed point due to the combined effect of diffusion and convection will be given by

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_x \frac{\partial c}{\partial x} - U_c \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial c}{\partial y} - V_c \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial c}{\partial z} - W_c \right) \quad (4)$$

In many cases, each of the velocity components and the components of the diffusion coefficient are constants. Equation (4) then reduces to

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - U \frac{\partial c}{\partial x} - V \frac{\partial c}{\partial y} - W \frac{\partial c}{\partial z} \quad (4a)$$

Equation 4 is the basic differential equation for the movement of a conservative substance.

#### MOVEMENT OF NON-CONSERVATIVE SUBSTANCES

In many cases of practical interest, notably problems dealing with the dispersal of pollutants in water or in the atmosphere, the substance is non-conservative, i.e. its concentration decreases with time in accordance with some known law. Examples are the natural decay of radioactivity, the removal of a substance by sedimentation, the removal of organic matter by biological oxidation and the removal, by death, of bacteria. Most of these removal rates are simple first order reaction rates, in which the rate of removal is proportional to the amount present. This is fortunate, since it makes it possible to obtain many solutions which would be impossible with more complicated removal mechanisms.

It is also possible to have various sources or sinks which supply or remove the substance under variously defined conditions. Examples of the latter are the addition of pollutants along the path of flow of a stream, the addition of oxygen by reaeration at the surface of a stream, and the removal of oxygen by plant respiration. In general, these sources or sinks will supply or remove the substance along some axis or surface in accordance with some definable function of time. From these considerations, the general equation for the rate of change of concentration at a point can be written as

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left( D_x \frac{\partial c}{\partial x} - U c \right) + \frac{\partial}{\partial y} \left( D_y \frac{\partial c}{\partial y} - V c \right) + \frac{\partial}{\partial z} \left( D_z \frac{\partial c}{\partial z} - W c \right) - \phi(c) + \psi(t) \quad (5)$$

and in the case of constant components of velocity and diffusion coefficient as

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + D_z \frac{\partial^2 c}{\partial z^2} - U \frac{\partial c}{\partial x} - V \frac{\partial c}{\partial y} - W \frac{\partial c}{\partial z} - \phi(c) + \psi(t) \quad (5a)$$

In equations (5) and (5a),  $\phi(c)$  represents the rate of removal of the substance at some decay rate which is a function of  $c$  and  $\psi(t)$  represents the net rate of increase of  $c$  due to sources and sinks. In many practical cases  $\phi(c)$  can be taken as  $Kc$ ,  $K$  being a constant and  $\psi(t)$  can be taken as a constant along some line or plane.

#### SOLUTIONS FOR CASES OF PRACTICAL INTEREST

The differential equation for any particular case must be solved subject to particular boundary conditions. In most cases the general equation (5) can be greatly simplified because many of the terms vanish. One and two dimensional cases are of great practical interest, but use of the general three dimensional equation is only rarely necessary. Solutions to a great many problems can be found in treatises dealing with heat conduction. The book, "Conduction of Heat in Solids," by Carslaw and Jaeger (1) is a catalogue of solutions for particular boundary conditions. Solutions to some of the most important cases are given below:

I(a) *One Dimensional Diffusion*—No convection—Instantaneous release at time  $t = 0$  and  $x = 0$ , of a conservative substance in an amount,  $m$ , per unit cross-sectional area.

$$\begin{aligned} \text{Differential equation: } & \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} \\ \text{Solution: } & c = \frac{m}{\sqrt{4 \pi D_x t}} \exp\left(-\frac{x^2}{4 D_x t}\right) \end{aligned} \quad (6)$$

This condition would be approximated by the release of a slug of tracer in a long narrow, completely mixed, estuary of uniform cross-section in which the fresh water inflow is so low as to make  $U$  negligible. The concentration at any time,  $t$ , would be spread out as a Gaussian curve with its center at the point of release. As time went on, the concentration would approach zero at all values of  $x$ .

I(b) *One Dimensional Diffusion*—Convection along  $x$  axis—Instantaneous release as in I(a).

$$\text{Differential equation: } \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} - U \frac{\partial c}{\partial x}$$

$$\text{Solution: } c = \frac{m}{\sqrt{4\pi D_x t}} \exp \left[ -\frac{(x - Ut)^2}{4 D_x t} \right] \quad (7)$$

This would represent a completely mixed narrow estuary in which the seaward velocity is  $U$ . The distribution will be Gaussian as in I(a), with the center moving downstream at velocity,  $U$ .

I(c) *One Dimensional Diffusion*—No convection—Continuous release of conservative tracer at  $t = 0$  and  $x = 0$  at rate  $m$  per unit cross-sectional area per unit time.

Differential equation: same as in I(a)

$$\text{Solution: } c = \frac{mt^{1/2}}{\sqrt{\pi D_x}} \exp \left[ -\frac{x^2}{4 D_x t} \right] - \frac{mx}{2 D_x} \operatorname{erfc} \left( \frac{x}{2 \sqrt{D_x t}} \right) \quad (8)$$

This would represent the continuous release of a tracer, or pollutant, into a long narrow, completely mixed, estuary. The equation implies that the concentration would continue to increase indefinitely at all values of  $x$ . Physically, this result would have no meaning since the volume of the tracer fluid would increase the volume of the dispersing fluid and would continue to build up until a net outflow developed at a rate equal to the inflow. The concentration of any particular substance would then reach an equilibrium, as is indicated by the next case, I(d).

I(d) *One Dimensional Diffusion*—Convection along  $x$  axis—Continuous release as in I(c).

Differential equation: same as in I(b)

$$\text{Solution: } c = \frac{m}{\sqrt{4\pi D_x}} \int_0^t \frac{1}{\sqrt{t-t'}} \exp \left[ -\frac{[x - U(t-t')]^2}{4D_x(t-t')} \right] dt' \quad (9)$$

For the steady state  $c = m/U$  for all values of  $x > 0$   
 ( $t = \infty$ ) (downstream)

$$\text{and } c = \frac{m}{U} \exp \left[ -\frac{Ux}{D_x} \right] \text{ for } x < 0$$

(upstream)

II(a) *Two Dimensional Diffusion*—No convection—Instantaneous release of a conservative tracer in amount  $m$  per unit depth.

$$\text{Differential equation: } \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2}$$

$$\text{Solution: } c = \frac{m}{4\pi \sqrt{D_x D_y t}} \exp \left[ -\frac{x^2}{4 D_x t} - \frac{y^2}{4 D_y t} \right]$$

(10)

The distributions along the  $x$  and  $y$  axes would be Gaussian and the iso-concentration lines would be ellipses. The maximum concentration would be centered around the point of release and would gradually decrease to zero. If  $D_x$  and  $D_y$  were equal, the equation would be

$$c = \frac{m}{4\pi Dt} \exp \left[ -\frac{r^2}{4Dt} \right]$$

(10a)

where  $r^2 = x^2 + y^2$

This condition represents, approximately, the dispersal of a slug of tracer released in a large body of water like the ocean. However, as will be discussed later, this condition is not too well represented by equation (10a) since the value of  $D$  will actually be a function of  $r$ .

II(b) *Two Dimensional Diffusion*—Convection along  $x$  axis—Instantaneous release as in II(a).

$$\text{Differential equation: } \frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} - U \frac{\partial c}{\partial x}$$

$$\text{Solution } c = \frac{m}{4\pi \sqrt{D_x D_y t}} \exp \left[ -\frac{(x - Ut)^2}{4 D_x t} - \frac{y^2}{4 D_y t} \right]$$

(11)

This would represent the movement and spread of a substance in a large body of water with a current velocity  $U$ . As in case II(a), the

solution is only approximate since  $D_x$  and  $D_y$  would increase with the extent of the spread of the substance.

II(c) *Two Dimensional Diffusion*—No convection—Continuous release of conservative substance at  $t = 0$  and  $x = 0$ , at rate  $m$  per unit depth per unit time.

Differential equation: same as in II(a)

$$\text{Solution: } c = \frac{m}{4 \pi D} \int_{\frac{x^2}{4Dt}}^{\infty} \frac{e^{-\theta}}{\theta} d\theta \tag{12}$$

This solution is for the symmetrical case in which  $D_x = D_y = D$ .

Equation (11) indicates a concentration which would increase indefinitely. As in the case of I(c), this result could not take place physically since the release of the tracer fluid would ultimately result in a radial outflow from the point of release. The maximum concentration would obviously be the actual concentration of the tracer substance, itself, in its carrier fluid.

II(d) *Two Dimensional Diffusion*—Convection along  $x$  axis—Continuous release of conservative substance as in II(c).

Differential equation: same as in II(b)

Solution: The steady state concentration for the case where  $D_x = D_y = D$  is given by

$$c = \frac{m}{2 \pi D} \exp\left[-\frac{Ux}{2D}\right] K_0\left(\frac{Ur}{2D}\right) \tag{13}$$

where  $K_0$  is the modified Bessel Function of the second kind of order zero.

*Dispersion of Non-Conservative Substances*—The cases considered above show that the continuous release of a fluid containing a highly concentrated conservative tracer substance into a turbulent field with no convection would result in the gradual build up of the tracer substance to a very high concentration. However, if the substance is non-conservative and decays at a rate proportional to  $Kc$ , the concentrations in all cases will be less than the values given by the previous equations. For the instantaneous releases, the concentrations will be as given by the previous equations, multiplied by  $e^{-Kt}$ . For the continuous releases, the solutions are more complicated. The effect of



natural decay of the diffusing substance has been discussed by Diachisian (2), who concluded that a steady state condition would be reached, even in those cases of continuous release into a turbulent field with no convection.

*Coefficient of Longitudinal Dispersion*—In case I(b) the assumption is that the velocity,  $U$ , is uniform across the section of flow. Under these conditions  $D_x$  is the true coefficient of turbulent diffusion, which results from the turbulent fluctuations of velocity. In the turbulent shear flow which occurs in conduits and channels, there is a variation in  $U$  across the section which results in an apparent value of  $D_x$  which is much larger than the value due to the velocity fluctuations alone. This apparent value is referred to as the longitudinal dispersion coefficient,  $D_L$ . Taylor (3) has analyzed this problem and derived the equation for  $D_L$  in a circular pipe as

$$D_L = 10.1 r U_* \quad (14)$$

where  $r$  is the pipe radius and  $U_*$  is the friction velocity  $\sqrt{\tau_o/\rho}$ . Elder (4) considered this for channel flow and presented the equation

$$D_L = 20.2 R \sqrt{R S g} \quad (15)$$

where  $R$  is the hydraulic radius and  $S$  is the slope of the energy gradient. If the Manning equation is used for  $S$ , equation (14) becomes

$$D_L = 77 R^{5/6} n U \quad (15a)$$

The vertical component of the eddy diffusion coefficient for a channel is given by

$$D_y = 0.0667 R \sqrt{R S g} \quad (16)$$

and  $D_x$  is thought to be of the same order of magnitude. From this, it follows that  $D_L$  is several hundred times as large as  $D_x$ . Equation (7) is still applicable for turbulent shear flow, but  $D_x$  must be replaced by  $D_L$  and  $U$  is to be taken as the average velocity. In many natural channels, the effective value of  $D_L$  will be greater than that given by equation (15) because of the influence of bends, obstructions, etc. Methods of computing  $D_L$  from measured dispersion curves have been discussed by Parker (5), Krenkel and Orlob (6), Diachisian (2) and others.

*Effect of Scale on the Value of the Diffusion Coefficients*—Many observers have noted that the value of the turbulent diffusion coefficient

increases with the scale of the phenomenon. This was first reported by Richardson (7), who suggested that the diffusion coefficient in the atmosphere is proportional to  $L^{4/3}$ , where  $L$  is some measure of the scale of the system. Although there is no simple way of defining  $L$  in all cases, for ocean diffusion it can be taken as the size of the patch of the diffusing substance. That the "four-thirds law" seems to be valid is shown by Fig. 1, which was compiled by Pearson (8).

That the effective diffusion coefficient should increase with the size

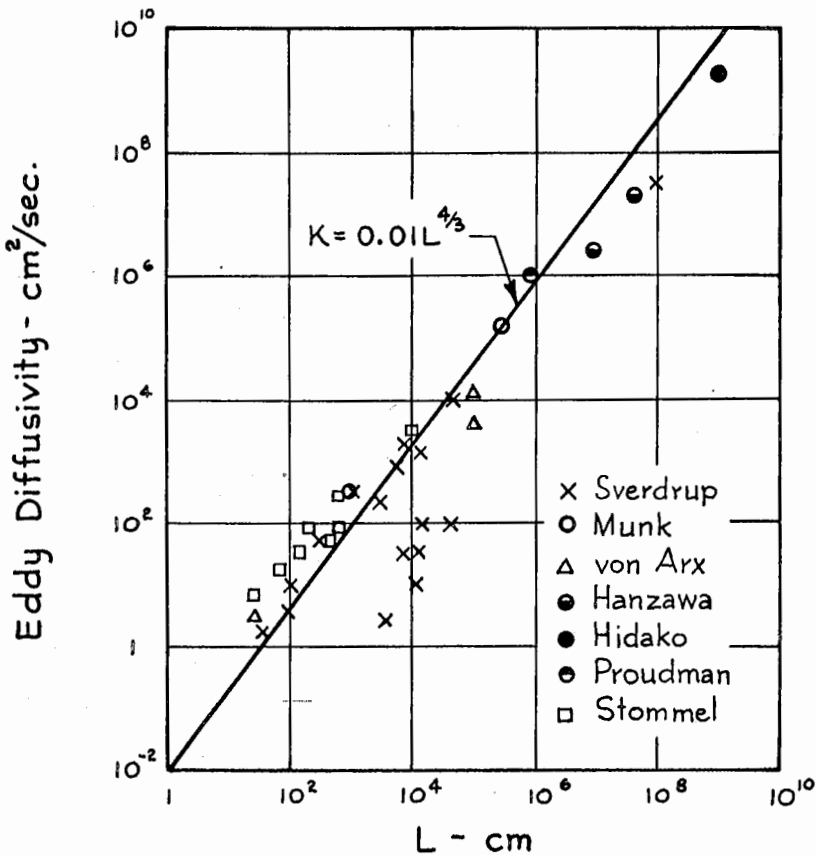


FIG. 1 VARIATION OF EDDY DIFFUSIVITY WITH SCALE (AFTER PEARSON)

of the patch is readily understood when one considers the nature of the structure of turbulence. Turbulence is considered to be the superposition of eddies of all sizes varying from the largest ones which are of the order of the size of the system to the smallest ones in which the dissipation of the kinetic energy into heat takes place.

It is obvious that the effect of the largest eddy would be convection which would move the whole patch without having any effect on its shape or size. The diffusion within the patch is influenced only by those eddies of the scale equal to or less than the size of the patch itself. As the patch grows the influence of still larger eddies increases the effective value of the diffusion coefficient. It is noted from Fig. 1 that the four-thirds law seems to be applicable over a very wide range of  $L$  from less than one foot to over several hundred miles.

Since the diffusion coefficient should be influenced by the turbulent energy as well as the scale of the phenomenon, it could be considered as being proportional to some power of  $E$  multiplied by  $L^{4/3}$ . By dimensional considerations, this leads to

$$D = \alpha E^{1/3} L^{4/3} \quad (17)$$

where  $E$  is the rate of dissipation of turbulent energy per unit mass of fluid. Orlob (9) found a value of 0.0136 for  $\alpha$  in a laboratory channel. Values in the same order of magnitude have been reported for lateral diffusion in the oceans. Orlob (9) and Okubo (10) have discussed this subject in detail.

Because of the variation of  $D$  with the scale of the phenomenon, the Fickian solutions, based on constant values of  $D$ , are not strictly applicable. A number of investigators have proposed alternate solutions for the diffusion of substances in the ocean. Okubo (10) presented a detailed review and analysis of these alternate solutions.

#### SEDIMENT TRANSPORT

The transport of suspended sediment in rivers is of very great interest to hydraulic engineers and a great deal of research has been done in this area. Most of the work has been done on the equilibrium distribution of sediment across the section of flow. The one dimensional diffusion—convection equation can be applied to the transient condition, in the form

$$\frac{\partial c}{\partial t} = D_x \frac{\partial^2 c}{\partial x^2} + D_y \frac{\partial^2 c}{\partial y^2} + \left( w + \frac{\partial D_y}{\partial y} - U \right) \frac{\partial c}{\partial y} \quad (18)$$

where  $D_x$ , the longitudinal component of the diffusion coefficient, is assumed to be constant; the vertical component,  $D_y$ , is assumed to be a function of  $y$  and where  $w$  is the settling velocity of the sediment particles. An analytical solution to a certain simplified case of equation (18) has been obtained by the writer and the application of this solution to estimating the removal of grit in a channel has been discussed by Camp (11).

#### ANALYSIS OF RIVER AND ESTUARY POLLUTION

For the rate of change of concentration of an organic pollutant at some cross section of a river or estuary, the diffusion-convection equation would take the form

$$\frac{\partial L}{\partial t} = D_L \frac{\partial^2 L}{\partial x^2} - U \frac{\partial L}{\partial x} - (K_1 + K_3)L + L_a \quad (19)$$

in which  $L$  is the first stage BOD,  $K_1$  is the rate constant for the removal of BOD by biochemical oxidation,  $K_3$  is the rate constant for removal of BOD by sedimentation or adsorption and  $L_a$  is the rate of addition of BOD by the local runoff or by the resuspension of organic matter from a bottom sludge deposit. For the steady state condition in which the BOD is changing only with  $x$ , the equation would be

$$D_L \frac{d^2 L}{dx^2} - U \frac{dL}{dx} - (K_1 + K_3)L + L_a = 0 \quad (19a)$$

Applied to a stretch of a stream in which  $U$ ,  $K_1$ ,  $K_3$  and  $L_a$  can be taken as constants and in which the BOD at the upper end is  $L_A$ , the equation (19a) can be integrated to give the variation of  $L$  along the stretch, as

$$L = L_A \exp(mx) + \frac{L_a}{K_1 + K_3} (1 - \exp(mx)) \quad (20)$$

where

$$m = \frac{U - \sqrt{U^2 + 4(K_1 + K_3)D_L}}{2D_L}$$

The differential equation for the oxygen profile for the steady state condition is given by

$$D_L \frac{d^2c}{dx^2} - U \frac{dc}{dx} - K_1 L + K_2 (C_s - C) - D_B = 0 \quad (21)$$

where  $C$  represents the concentration of dissolved oxygen,  $C_s$  is the saturation concentration,  $K_2$  is the reaeration constant and  $D_B$  represents the net rate of removal of oxygen by all processes other than the oxidation of the flowing BOD load.  $D_B$  could be positive if the predominant processes were the removal of oxygen by plant respiration and the oxygen demand of the bottom sludge; it could be negative if the addition of oxygen by photosynthesis predominated.

Equation (21) can be integrated by using the expression for  $L$  as given in equation (20) and taking  $C = C_0$  at the beginning of the stretch, to give

$$D = \frac{K_1 \left( L_A - \frac{L_a}{K_1 + K_3} \right) \left( \exp(mx) - \exp(rx) \right)}{K_2 - (K_1 + K_3)} + D_0 \exp(rx) + \left( \frac{D_B}{K_2} + \frac{K_1 L_a}{K_2 (K_1 + K_3)} \right) \left( 1 - \exp(rx) \right) \quad (22)$$

in which the concentration,  $C$ , has been replaced by the saturation deficit,  $D = C_s - C$ , and in which

$$r = \frac{U - \sqrt{U^2 + 4 K_2 D_L}}{2 D_L}$$

A simplified version of equation (22), which omitted the factors,  $K_3$ ,  $L_a$  and  $D_B$ , was presented by O'Connor (12). A detailed discussion of the application of equation (22) in stream pollution analysis has been presented elsewhere (13).

*Reaeration in Streams*—The absorption of atmospheric oxygen by a natural stream is a process that is controlled by both molecular diffusion and turbulent mixing. The principal resistance to the absorption process is due to the existence of a laminar film at the surface of the water, through which the oxygen must pass by molecular diffusion. Beneath the film the gas is so rapidly dispersed by the turbulent mixing that the concentration of gas in solution is essentially uniform throughout the depth.

The rate of mass transfer of oxygen across a surface area,  $A_s$ , can be expressed by the general equation

$$\frac{dm}{dt} = K_L A_s (C_s - C) \quad (23)$$

and the rate of change of concentration within the body of water by

$$\frac{dc}{dt} = K_L \frac{A_s}{V} (C_s - C) \quad (23a)$$

where  $V$  is the volume and  $K_L$  is variously known as the "absorption coefficient," the "transfer coefficient" or the "liquid film coefficient." For a river, the interfacial area is commonly taken as the horizontal projection,  $A_o$ , although the actual interfacial area will be greater in most cases. In these notes the interfacial area will be defined as

$$A_s = C_A A_o \quad (24)$$

where  $C_A$  is a coefficient whose value will depend upon the flow characteristics and the magnitude of any surface disturbances created by wind, etc. In the absence of wind or other disturbances, the value of  $C_A$  will probably be related to the Froude No.,  $U/\sqrt{gH}$ . As applied to a river, the absorption equation becomes

$$\frac{dc}{dt} = \frac{K_L C_A A_o}{V} (C_s - C) = \frac{K_L C_A D}{H} = \frac{K_L' D}{H} = K_2 D \quad (25)$$

where  $K_2$  is the reaeration constant previously referred to. Equation (25) emphasizes that the reaeration constant,  $K_2$ , is equal to the apparent absorption coefficient,  $K_L'$ , divided by the depth and that  $K_L'$  is equal to the true absorption coefficient,  $K_L$ , multiplied by the factor,  $C_A$ .

If the liquid film were considered to be stagnant, the value of  $K_L$  would be equal to the molecular diffusivity,  $D_M$ , divided by the film thickness,  $L$ . This follows directly from equation (1). Such a concept was first proposed by Whitman (14). This theory has now been largely abandoned because of the fact that the film cannot be considered stagnant. Danckwerts (15) proposed that the film concept should be abandoned and introduced a different physical model of the process. By Danckwerts' model, the liquid is assumed to remain quiescent for a

period of time,  $t'$ , during which the gas penetrates the liquid by molecular diffusion and the entire depth of liquid is then instantaneously mixed, this sequence being repeated indefinitely. To take into account the stochastic nature of the mixing process, Danckwerts proposed that the mixing should not be considered to be taking place at the same time over the entire surface but that there would be a random distribution of ages over the surface area, the age at each point representing the time elapsed since the previous mixing at that point. Danckwerts' age distribution function is given by the expression

$$\psi(t) = r \exp(-rt) \quad (26)$$

where  $\psi(t) dt$  would represent that portion of the interface that had ages between  $t$  and  $t + dt$ , and  $r$  would be the average rate of surface exchange,  $1/\sqrt{t'}$ . From these considerations, and assuming that the liquid depth was infinite, Danckwerts derived the expression for  $K_L$  as

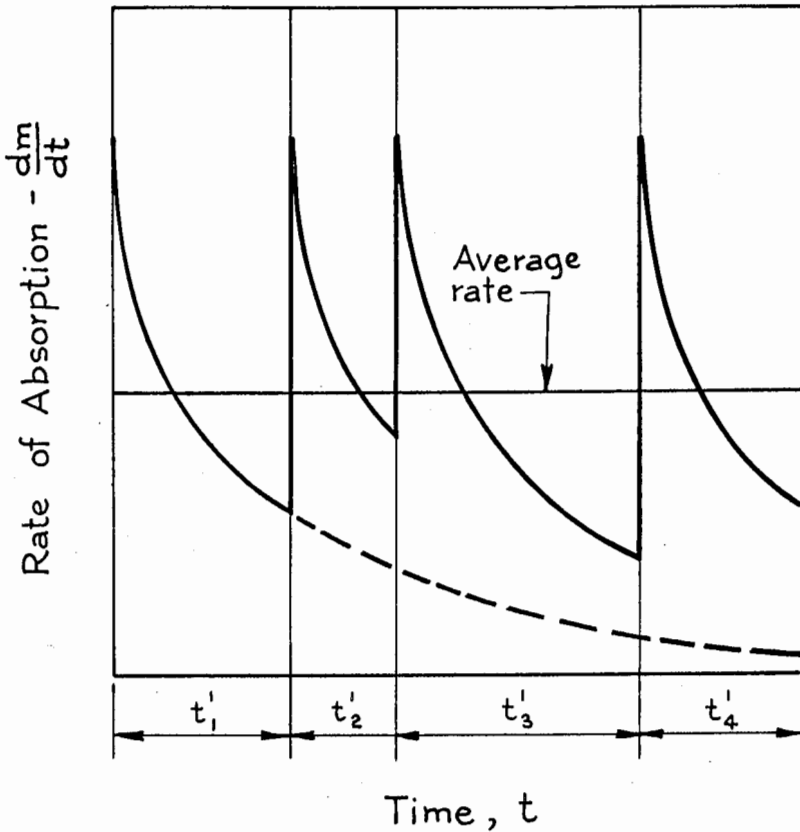
$$K_L = \sqrt{D_M r} \quad (27)$$

Danckwerts' development was intended for application to industrial process equipment, such as absorption towers, in which the liquid flows in layers over various types of packings. In such applications, the flow might well be entirely laminar and the abandonment of the film concept be, thereby, justified. However, for a natural stream, the film concept must be closer to the actual physical conditions. The film can maintain its existence in the statistical sense, i.e. it is always present but the liquid content is being continuously exchanged for liquid from the main body. Kanwisher (15) has reported on experiments in which the surface film at the interface between the atmosphere and a turbulent mass of water has been observed and actually sampled.

Using the Danckwerts age distribution function, but applying it to a film of finite thickness,  $L$ , with uniform concentration below the film, the writer (16) obtained the equation

$$K_L = \sqrt{D_M r} \coth \left( \sqrt{\frac{rL^2}{D_M}} \right) \quad (28)$$

Fig. 2 shows how the rate of absorption of oxygen would vary with time at some particular point at the surface in accordance with the film replacement model. With reference to Fig. 2, the time,  $t = 0$ , represents some instant at which the film at the point had just been replaced.



**FIG. 2 RATE OF ABSORPTION OF OXYGEN AT A FIXED POINT ON THE SURFACE (BY FILM REPLACEMENT MODEL)**

The concentration of dissolved oxygen at that instant would be uniform across the film and equal to the concentration in the main body of water. The concentration would immediately become that of saturation at the very interface and the process of absorption would commence at an infinite initial rate and decline with time as indicated by the curve. At time,  $t'$ , replacement would occur and the process would start all over again. Such a process would continue indefinitely, with the period between replacements being a random variable. The average



rate of absorption would be given by equation (23) with  $K_L$  as in equation (28). The acceptability of equation (28) has been demonstrated by experiments conducted at New York University using various gases, principally helium and nitrogen (17). These experiments indicate that the effective values of  $r$  and  $L$  depend upon the intensity of the surface turbulence and that a given value of  $r$  is always accompanied by the same value of  $L$ , thus demonstrating that they are both controlled by the same conditions.

A proposed theory which relates  $r$  and  $L$  to the stream flow parameters and the liquid properties has been given in detail elsewhere (13) and will be presented very briefly here. It was reasoned that the effective film thickness,  $L$ , would be related to the smallest of the turbulent eddies, in which the forces are predominantly molecular and in which most of the dissipation of kinetic energy into heat takes place. The size of these eddies was given by Kolmogoroff as  $(\nu^3/E)^{1/4}$ , where  $\nu$  is the kinematic viscosity and  $E$  is the rate of loss of energy per unit mass of fluid. The molecular forces which are responsible for surface tension act to oppose the surface overturn and energy must be expended in opposition to these forces in order to break the surface. It was reasoned that the rate of expenditure of energy required to oppose the surface tension must be proportional to the product of the frequency,  $r$ , the surface tension,  $\sigma$ , and the square of some length factor,  $L$ , which is related to the eddy size. The rate of expenditure of energy per unit mass of fluid would then be given by the expression

$$\frac{r \sigma L^2}{\rho L^3} = \frac{r \sigma}{\rho L}$$

This energy would have to be supplied by the turbulence and was assumed to be equal to  $C_1 E_s$ , where  $E_s$  is the turbulent energy per unit mass in the vicinity of the surface and  $C_1$  is a proportionality constant.  $E_s$  was in turn assumed to be equal to  $C_2 E$  where  $E$  is the energy per unit mass for the flow as a whole and  $C_2$  is a factor whose value depends upon the dynamics of the system. These considerations lead to the following expressions for  $r$  and  $L$  and their interrelationships.

$$L = C_3 \left( \frac{\nu^3}{E_s} \right)^{1/4} = \frac{C_3}{(C_2)^{1/4}} \left( \frac{\nu^3}{E} \right)^{1/4} = C_4 \left( \frac{\nu^3}{E} \right)^{1/4} \quad (29)$$

$$r = C_1(C_2)^{3/4} C_3 \frac{\rho(vE)^{3/4}}{\sigma} = \frac{C_5}{(C_4)^3} \frac{\rho(vE)^{3/4}}{\sigma} \quad (30)$$

$$rL^3 = C_1(C_3)^4 \frac{\rho v^3}{\sigma} = C_5 \frac{\rho v^3}{\sigma} \quad (31)$$

Equation (31) indicates that  $rL^3$  should be independent of the system dynamics and should depend only upon the properties of the liquid. This was quite closely complied with in the results of the laboratory experiments and a value of 6.70 was obtained for  $C_5$ .

In order to apply the proposed theory to stream flow conditions it was necessary to establish the relationships between the various stream flow parameters and the factors  $C_A$  and  $C_4$ . Based purely on judgment,  $C_A$  was taken as

$$C_A = 1.0 + 0.3 F^2 \quad (32)$$

where  $F$  is the Froude Number. For the purpose of evaluating  $C_4$ , the equations were assembled in the form

$$\frac{K_L'(C_4)^{3/2}}{C_A \sqrt{C_5 D_M \theta}} = \coth \left( \sqrt{\frac{C_5 \psi}{C_4 D_M}} \right)$$

in which

$$\theta = \frac{\rho(vE)^{3/4}}{\sigma}$$

and

$$\psi = \frac{\rho v^{9/4} E^{1/4}}{\sigma}$$

In these expressions,  $\rho$ ,  $v$ ,  $\sigma$  and  $D_M$  are functions of the temperature of the water.  $E$  is equal to  $SUg$ , where  $S$  is the slope of the energy gradient,  $U$  is the mean velocity and  $g$  is the gravitational constant. With  $C_5$  taken as 6.70,  $C_A$  computed from equation (32) and  $K_L'$  computed from the logarithmic absorption equation or the oxygen sag equation,  $C_4$  is the only unknown. Although it cannot be expressed as an explicit function of the other variables, the value of  $C_4$  was readily computed for a number of reported stream flow conditions by a process of iteration using a digital computer. Fig. 3 shows the computed values of  $C_4$  plotted against the ratio of  $(v^3/E)^{1/4}$  to the depth  $H$ . The laboratory channel data were reported by Krenkel and Orlob (18),

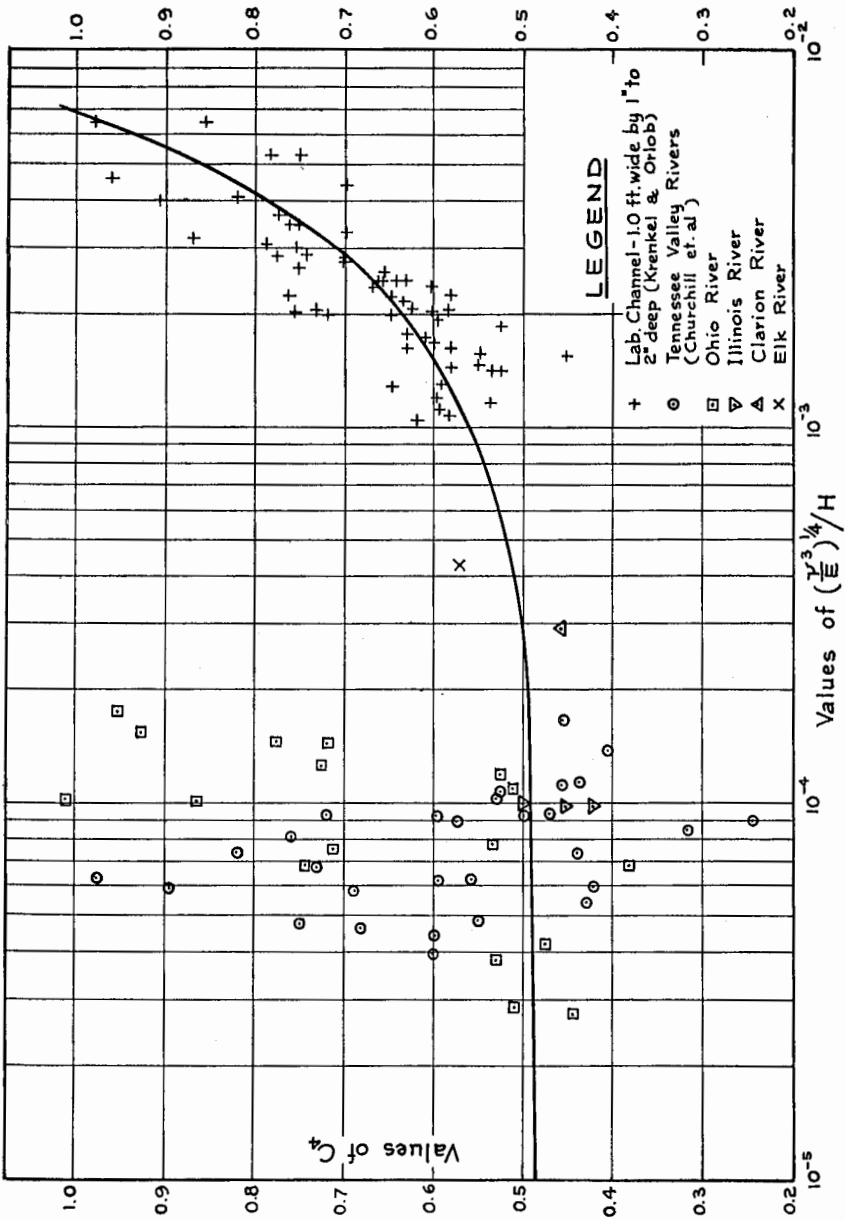


FIGURE 3

the data on the Tennessee rivers by Churchill, Elmore and Buckingham (19), and the data for the Ohio and other rivers were previously assembled by O'Connor and Dobbins (20). The curve which is drawn on Fig. 3 can be represented by the equation,

$$C_4 = 0.485 + 75 \frac{(v^3/E)^{1/4}}{H} \quad (33)$$

This is actually a linear relationship although it appears as a curve on the semi-logarithmic plot. With  $C_A$  from equation (32) and  $C_4$  from

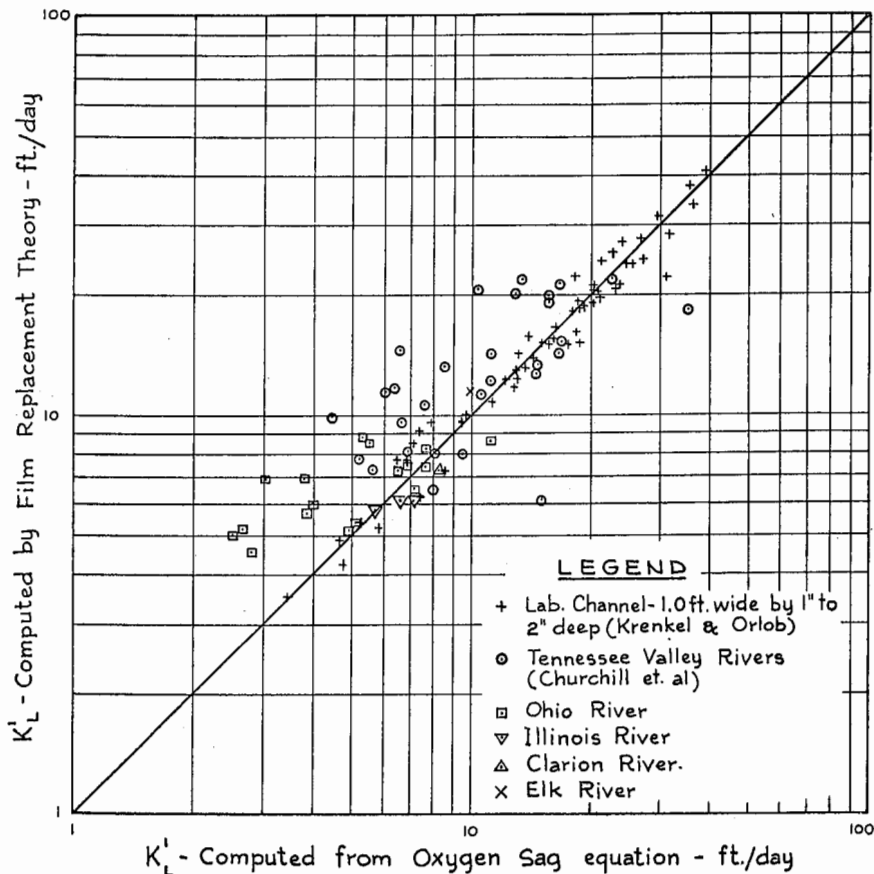


FIG. 4 . OXYGEN ABSORPTION COEFFICIENTS

equation (33) the theoretical values of  $K_L'$  were then computed and compared to the reported values, the results being shown by Fig. 4. It is seen that there is excellent agreement between the computed and reported values for the small channel and for the majority of the rivers. For some of the rivers, the predicted values are somewhat greater than the reported values, a fact which can be attributed to the presence of pollutants which are known to reduce the oxygen transfer or to the effect of various conditions which were not taken into account in the field evaluations.

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