

REAERATION IN FLOWING SYSTEMS

REAERATION IN FLOWING SYSTEMS

by

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SCOPE AND CONTENTS:

The literature on stream reaeration was reviewed. A recirculating loop open channel system was designed and experiments were performed to study the effects of average stream velocity and temperature on the mass transfer coefficient for oxygen dissolution into "clean" water. The applicability of the apparatus to the study of the effects of surfactants was also investigated.

The velocity ranged from 0.1 to 0.9 ft/sec and the temperature from 5.0 to 25.0°C. The results indicated that the mass transfer coefficient varies approximately linearly with average stream velocity and that the temperature coefficient is a variable which depends on mixing conditions. Furthermore, it was found that the temperature dependency of the mass transfer coefficient could be expressed as either a linear or power function. Correlations expressing the mass transfer coefficient in terms of easily measurable stream parameters were developed and compared to those found in the recent literature.

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CHAPTER 1

Introduction

Man has "polluted" natural water courses to such an extent that in many cases the oxygen reserves necessary to maintain the normal plant-animal balance have been seriously depleted. Oxygen depletion occurs directly through chemical reaction when reducing agents are allowed to enter a stream or indirectly through the oxygen demand of micro-organisms which thrive on the organic material in effluents. Many situations could be alleviated by controlling the quantity and quality of effluent discharged into a river. Before such control can be effectively established the two parts of the problem must be understood: the nature and quantity of pollutants added, and the nature and quantitative effects of the factors governing the mass transfer process of atmospheric oxygenation.

It was the purpose of the present work to design a flowing aeration system which would hopefully simulate natural stream conditions, and to investigate some of the factors affecting the mass transfer process of oxygen dissolving into "clean" water. This would establish a base case for further study on the effects of surface active agents, wind velocity, air temperature, and other factors on the reaeration process. The effects of average stream velocity and temperature were to be investigated in some detail. Experiments were also performed to test the applicability of the apparatus to studies on the effects of surfactants.

CHAPTER 2

Literature Review

(A) Theoretical Developments

Adeney and Becker (1919) demonstrated that the rate of oxygen transfer into water is directly proportional to the dissolved oxygen deficit:

$$\frac{dD}{dt} = - K_2 D \quad (1)$$

where: K_2 is the overall mass transfer coefficient, and

D is the difference between the oxygen concentration present and the concentration at saturation.

The Adeney and Becker equation may be written in terms of oxygen concentrations:

$$\frac{dC}{dt} = K_2 (C_s - C) \quad (2)$$

where: C is the concentration of dissolved oxygen, and

C_s is the oxygen concentration at saturation.

The two-film gas absorption theory of Lewis and Whitman (1924) postulated the existence of adjacent, stagnant gas-liquid films at the

interface formed by the two phases. They reasoned that the surface of the liquid film was substantially saturated with the solute gas and that it was this liquid film which controlled the mass transfer process in the form of steady state molecular diffusion. The equation describing the mass transfer across the liquid film may be written:

$$N = \frac{1}{A_s} \frac{dm}{dt} = K_L (C_s - C) \quad (3)$$

or expressed in terms of concentration change:

$$\frac{dC}{dt} = K_L \frac{A_s}{V} (C_s - C) \quad (4)$$

where: N is the rate of mass transfer per unit time per unit area,

A_s is the area across which the mass transfer can take place,

K_L is the mass transfer coefficient (which must be distinguished from K_2),

V is the volume of the liquid, and

m is the mass of solute gas.

The Lewis and Whitman two-film theory results in the relationship:

$$K_L = \frac{D_m}{L} \quad (5)$$

where: D_m is the molecular diffusivity of the gas, and

L is the thickness of the stagnant liquid film.

It is, perhaps, at this point that a matter of apparent confusion among past authors as to the basic parameter to be evaluated in aeration systems should be noted. Consider the relationship which follows from equations (2) and (4):

$$K_2 = K_L \frac{A_s}{V} = K_L a = \frac{K_L}{H} \quad (6)$$

where: a is the specific area given by $a = \frac{A_s}{V}$, and
 H is the mean depth given by $H = \frac{V}{A_s}$

Further, many authors have found it convenient to convert integrated forms of equations to terms of common logarithms, lower case letters then being used to define coefficients. Then:

$$k_2 = K_2/2.303 \quad (7)$$

$$\text{and} \quad k_L = K_L/2.303 \quad (8)$$

where: k_2 and k_L are the respective coefficients to the base 10.

Throughout the literature researchers have expressed mathematical models, and developed theories of mass transfer in terms of k_2 or K_2 which implicitly encompass the surface to volume ratio. Repeatedly, in the discussions of these papers one or more of the critics have pointed out that the basic parameter is K_L . In particular, Dobbins (1964) noted that the literature indicates a variation in k_2 values of approximately five hundred fold, while in K_L the variation is of the order of ten fold. However, it must be recognized that, in many instances, especially in stream reaeration studies

the surface to volume ratio cannot be evaluated accurately; consequently k_2 or K_2 must be utilized.

Higbie (1935) abandoned the Lewis and Whitman film concept and proposed a model in which the interface is continuously replaced by eddies. The problem then became one of unsteady state molecular transfer controlled by molecular diffusivity and the time of exposure of the elements at the interface. Fick's law is the basic equation for the rate of transfer of a gas into solution by molecular diffusion. It may be written as:

$$\frac{\partial m}{\partial t} = - D_m \frac{\partial C}{\partial y} \quad (9)$$

where: $\partial C/\partial y$ is the concentration gradient in the direction normal to the interface.

For the case of unsteady state where the concentration gradient is also changing with y , the rate of concentration increase within an elemental volume is then given by:

$$\frac{\partial m}{\partial y \partial t} = \frac{\partial C}{\partial t} = - D_m \frac{\partial^2 C}{\partial y^2} \quad (10)$$

With the assumptions that the diffusivity was constant, the liquid depth, infinite, and that heat, surface, and dilatation effects were negligible, Higbie showed that the solution to equation (10) resulted in the relationship:

$$K_L = 2 \left(\frac{D_m}{\pi t} \right)^{\frac{1}{2}} \quad (11)$$

where: t is the time of exposure of a surface element.

Danckwerts (1951) took Higbie's hypothesis one step further by defining the age distribution of the liquid surface. The average rate of absorption was assumed to be uniform over the surface area and the liquid surface elements were assumed to be randomly and continuously replaced by those arising from the turbulent motion of the body of the fluid. Then for any given unit area of surface the age distribution ranges from zero to infinity. The age distribution is defined by a function $f(t)$ in which $f(t)dt$ is the fraction of area having ages between t and $t + dt$. It was shown that:

$$f(t) = re^{-rt} \quad (12)$$

where: r is the average rate of surface renewal with dimension time^{-1} .

Using this approach Danckwerts found that when the dissolved oxygen concentration throughout the body of water of infinite depth is uniform one could derive the following relationship:

$$K_L = (D_m r)^{1/2} \quad (13)$$

The disparity between the two-film concept of Lewis and Whitman (K_L varies directly with D_m) and the penetration theories of Higbie and Danckwerts (K_L varies directly with $\sqrt{D_m}$) was apparently resolved by Dobbins (1956). He suggested that the stagnant liquid film may be assumed to maintain its existence in a statistical sense no matter what the mixing conditions. The film is considered to be always present but its composition

is continuously changed by the eddies rising to the interface from the bulk fluid. Dobbins incorporated the age distribution function of Danckwerts for the surface film and substituting this function for the unit area implied in Fick's law -- equation (9), with subsequent integration between the limits $t = 0$ and $t = \infty$, he obtained:

$$\frac{\partial m}{\partial t} = - D_m r \int_0^{\infty} e^{-rt} \left(\frac{dC}{dy} \right)_{y=0} dt \quad (14)$$

and

$$\frac{\partial m}{\partial t} = - D_m r \left(\frac{\bar{C}}{dy} \right)_{y=0} \quad (15)$$

where: $\bar{C}$ is the Laplace transform of C .

For unsteady state the basic equation is Fick's law -- equation (10):

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial y^2}$$

The boundary conditions which are applied during the time of oxygen transfer are:

when: $t = 0$	$C = C_0$	at: $0 < y < L$
$t > 0$	$C = C_s$	$y = 0$
$t > 0$	$C = C_0$	$y = L$

where: C_0 is the initial oxygen concentration in the bulk liquid.

In the distance $y = 0$ to $y = L$ the diffusion is molecular; below $y = L$ eddy diffusion controls. When equation (10) is multiplied by e^{-rt}

and integrated with respect to t between $t = 0$ and $t = \infty$ the result is:

$$\frac{\partial \bar{C}}{\partial t} = D_m \frac{\partial^2 \bar{C}}{\partial y^2} \quad (16)$$

Applying the boundary conditions it was shown that:

$$\frac{\partial \bar{C}}{\partial t} = (D_m r)^{1/2} \coth \left(\frac{rL^2}{D_m} \right)^{1/2} \frac{A_s}{V} (C_s - C) \quad (17)$$

Comparing equations (17) and (4) we have:

$$K_L = (D_m r)^{1/2} \coth \left(\frac{rL^2}{D_m} \right)^{1/2} \quad (18)$$

The significant property of this equation is that at low values of the average rate of renewal (stagnant surface) K_L approaches the Lewis and Whitman model:

$$K_L = D_m / L$$

At high rates of surface renewal (turbulent conditions) the mass transfer coefficient, K_L , approaches the Danckwerts' description:

$$K_L = (D_m r)^{1/2}$$

The implicit assumption to this point has been that the control of the mass transfer process under consideration is at the surface of the liquid. This can be justified by examining the continuity equation:

$$\frac{\partial m}{\partial t} = D_G \left(\frac{\partial C}{\partial y} \right)_1 = D_m \left(\frac{\partial C}{\partial y} \right)_2 = D_E \left(\frac{\partial C}{\partial y} \right)_3 \quad (19)$$

where: $\left(\frac{\partial C}{\partial y}\right)_1$ is the concentration gradient through the gas film at the interface,

$\left(\frac{\partial C}{\partial y}\right)_2$ is the concentration gradient through the liquid film,

$\left(\frac{\partial C}{\partial y}\right)_3$ is the concentration gradient through the body of the liquid below the film,

D_G is the molecular diffusivity of the gas through the gas film,

D_m is the molecular diffusivity of the gas through the liquid film, and

D_E is the eddy diffusivity of the gas through the body of the liquid.

For sparingly soluble gases such as oxygen it has been shown that both D_G and D_E are ordinarily larger than D_m by a factor of approximately 10^6 . Thus the resistances of the gas film and the body of the liquid may be considered negligible.

An entirely different physical mechanism for the mass transfer problem has been proposed by Kishinevski (1955). Abandoning the film concept completely he asserted that the absorption process is controlled by turbulent diffusion, assuming that the surface layer is completely and instantaneously saturated with solute gas. Although Kishinevski states that molecular diffusion plays no part in the process, the proposed formula:

$$\frac{1}{A} \frac{\partial m}{\partial t} = \frac{1}{\Delta t} \int_0^{\Delta t} D_i \left(\frac{\partial C}{\partial y}\right)_{y=0} dt \quad (20)$$

includes an effective diffusivity, D_i , that must include the effects of molecular diffusion at the interface.

(B) Models for K_L , and the Influence of Temperature and Surface Contamination

With the aid of the physical theories developed since the time of Adeney and Becker (1919) researchers have developed mathematical models for K_L in terms of readily measurable stream parameters to assess the assimilative capacity of streams. Along with these models in terms of hydraulic characteristics, the influence of temperature, organic pollution and surface active agents on the mass transfer coefficient also required definition.

Streeter and Phelps (1925) were the first to apply the principles developed by Adeney and Becker (1919) in the study of stream reaeration. Equation (1) was extended to the form:

$$\frac{dD}{dt} = K_1 B - K_2 D \quad (21)$$

which when integrated gives:

$$D = \frac{K_1 B_0}{K_2 - K_1} (e^{-K_1 t} - e^{-K_2 t}) + D_0 e^{-K_2 t} \quad (22)$$

where: B is the remaining oxygen demand,

B_0 is the ultimate first stage or carbonaceous oxygen demand,

K_1 is the deoxygenation coefficient, and

D_0 is the initial oxygen saturation deficit.

It is to be noted that equation (22) cannot be used to predict reaeration rates although field data can be used to calculate the overall reaeration coefficient K_2 . As pointed out by Streeter (1926) the value of K_2 from equation (22) will probably be too low when applied to streams which have dissolved oxygen deficits due to organic pollution which has collected on the stream bed. A large portion of the oxygen absorbed will be withdrawn from the solution almost immediately and thereby fail to be accounted for in terms of reserve oxygen or biochemical oxygen demand. Also, as noted by Churchill et al (1962) other serious sources of error in the application of equation (22) include experimental measurement of velocity within the stretch of stream, determination of the dissolved oxygen applicable to each mass of water studied, and the determination of the carbonaceous oxygen demand.

Streeter and Phelps (1925) also suggested a form of mathematical model to predict the mass transfer coefficient from hydraulic considerations alone. Working with data of 1914, 1915 from the Ohio River the writers found that the observed data was closely approximated by the equation:

$$K_2 = \frac{C' U^n}{h^2} \quad (23)$$

where: U is the average velocity of the stream in feet per second,

h is the mean depth of the stream above extreme low water level in feet,

C' is a proportionality constant,

n is a constant, and

K_2 has units of days^{-1} .

The values of C' and n are constants only for a given stretch of river and depend on the turbulent flow regime. Although the empirical relationship is valid for a given situation, a reaeration coefficient must be determined in situ to define the constants of the relationship. Consequently the practical application of the equation is limited. Many of the subsequently established relationships have the same form as equation (23). Krenkel and Orlob (1962) questioned this form of relationship, explaining that velocity alone cannot account for the absorption phenomenon since systems of the same average velocity might have completely different turbulence characteristics and thus entirely different mass transfer properties.

Streeter (1926) utilized the substantial body of laboratory data available to estimate the effect of temperature on the mass transfer coefficient and developed the formulation:

$$K_2(T^{\circ}\text{C}) = K_2(20^{\circ}\text{C}) \theta^{T-20} \quad (24)$$

where: T is the temperature in degrees Centigrade, and

$\theta = 1.0159$, is the temperature coefficient.

The relationship indicates a geometric increase in K_2 at a rate of 1.59 percent per degree Centigrade.

To substantiate the earlier theory, Streeter, Wright and Kehr (1936) set up two lab scale recirculation channels. Equation (24) was substantiated in form but the constants were found to be vastly different. In the larger of the two systems, recirculation was effected by a boat propeller in one region of the channel.

Krenkel and Orlob (1962) noted that much of the oxygen transfer would probably have taken place at the point of energy input to the system. In this study by Streeter et al (1936) the temperature effect was re-evaluated and the value of θ was found to be 1.047. In the Progress Report of the A.S.C.E. (1961) it was noted that the data of these experiments showed little basis for their use in the determination of the temperature coefficient θ . For instance the data for experiments in which the temperature varied between 10°C and 20°C were plotted as 15°C. The paper also noted that surface contaminants in aeration systems apparently lowered the mass transfer coefficient.

From this time, 1935, onward many extensive studies were carried out on the effect of surface active agents (surfactants) on the mass transfer coefficient. Notable among these were studies by Kehr (1938), Holroyd and Parker (1952), Lynch and Sawyer (1954), Downing and Truesdale (1955), Downing et al (1957), and Mancy and Barlage (1968). Kehr (1938) found that severe depressions in K_2 resulted when 30 percent sewage was added to water and that varying degrees of depression occurred with the addition of different surfactants. Lynch and Sawyer (1954) reported that the different American synthetic detergents displayed vastly different frothing characteristics and varying degrees of mass transfer suppression when added to water in concentrations of 50 mg/l. Holroyd and Parker (1952) concluded that at very high and very low turbulence levels surfactants had little effect on the mass transfer process while in the middle ranges of turbulence drastic reductions in K_L resulted when the surfactant

concentration was approximately 100 mg/l. These writers further suggested that the effect of surfactants may be thought of as resulting from the additional resistance added to the resistance of the surface film of clean water. This suggested an expression of the form:

$$R = \frac{1}{K_{LT}} = \frac{1}{K_{LC}} + \frac{1}{K_{LS}} \quad (25)$$

where: $R = 1/K_{LT}$ is the total resistance to oxygen transfer,
 $1/K_{LC}$ is the resistance due to the surface film of
 clean water, and
 $1/K_{LS}$ is the resistance due to the surfactant layer.

Downing and Truesdale (1955) and Downing et al (1957) reported drastic reductions in K_L with additions of very small quantities of surfactants. For example, the reduction was in the order of 50 percent with the addition of 1.0 mg/l of alkylbenzenesulphonate. In these reports the general conclusions were that surfactants decrease K_L by an amount which depends on their concentration, on the initial mass transfer coefficient in clean water, and on the manner in which the water is agitated. Mancy and Barlage (1968) discussed the surface chemistry involved when surfactants are added to aqueous systems. The reduction in mass transfer is explained as resulting from two distinct mechanisms:

- (1) covering of the surface film layer thereby blocking dissolution sites at the interface or distorting intermolecular forces between the gas and water surface molecules, and

- (2) increasing surface viscosity, depressing hydrodynamic interface activity and forming a viscous hydration layer.

The mechanism responsible in a given situation was reported to depend on the physicochemical characteristics of the surfactant molecule. Extensive well-controlled laboratory experiments were carried out to support their thesis.

A paper of major influence in the study of the reaeration was presented by O'Connor and Dobbins (1958). Based on theoretical considerations of turbulence and the Dobbins (1956) equation for K_L :

$$K_L = (D_m r)^{1/2} \coth \left(\frac{rL^2}{D_m} \right)^{1/2}$$

these writers developed a semi-mechanistic model for the prediction of K_L in terms of easily measurable stream parameters. They assumed that for practical cases the coth term of equation (18) was equal to unity; thus reducing equation (18) to Danckwerts equation (13):

$$K_L = (D_m r)^{1/2}$$

O'Connor and Dobbins reasoned that the rate of surface renewal at the interface could be written

$$r = \frac{\sqrt{v^2}}{l} \quad (26)$$

where: $\sqrt{v^2}$ is the root mean square of the vertical velocity fluctuations, and

z is the Prandtl's mixing length near the surface.

Then for non-isotropic turbulence (the case in which definite shear and velocity gradients exist) the writers showed that, with the use of Prandtl's mixing length hypothesis and von Karman's universal logarithmic velocity law for pipes one could write:

$$r = \frac{\sqrt{v^2}}{f} = \frac{du}{dy} = \frac{(HgS)^{1/2}}{k'H} \quad (27)$$

where: S is the slope of the channel,

k' is von Karmon's constant,

g is the acceleration due to gravity, and

$\frac{du}{dy}$ is the velocity gradient of the flow.

Substituting the value of r from equation (27) into equation (13), results in:

$$K_L = C' \frac{D^{1/2} S^{1/2}}{H^{1/2}} \quad (28)$$

where: $C' = [g^{1/2}/(k')^{1/2}]$.

For isotropic turbulence (the case in which shear and velocity gradients are negligible) the writers assumed that the measurements of Kalinske (1943) were generally applicable. That is that:

$$\frac{\sqrt{v^2}}{z} = \frac{0.1 U}{0.1 H}$$

Then:

$$r = \frac{U}{H} \quad (29)$$

Substituting into equation (13) one obtains:

$$K_L = \left(\frac{D_m U}{H} \right)^{1/2} \quad (30)$$

As pointed out later by O'Connor (1958) equation (30) was the most generally applicable and equation (23) could be discarded. To verify the physical theory as described by equations (18) and (13) the writers conducted experiments in which water in a fixed vessel was agitated by a vertically oscillating lattice-work of screens. They found that the overall reaeration coefficient k_2 varied linearly with the square root of the frequency of oscillation. The average rate of surface renewal, r , was presumed to be proportional to the frequency of oscillation (rpm).

Experiments by Downing and Truesdale (1955) and Metzger and Dobbins (1967) indicated that the reaeration mass transfer coefficient varied linearly with frequency (rpm) of agitation. The results of the latter study were obtained from an apparatus which was apparently very similar to the equipment of O'Connor and Dobbins (1958).

Another significant contribution to the literature was made by Churchill, Elmore and Buckingham (1962). These writers reasoned that the development of the O'Connor and Dobbins (1956) relationship for the average rate of surface renewal:

$$r = \frac{du}{dy}$$

is fundamentally incorrect because:

"equal velocity gradients do not necessarily indicate equal states of turbulence".

The writers also noted that in previous stream studies:

- (1) the oxygen deficits in the reaches investigated were due to decomposing organic material,
- (2) the contributions of oxygen from photosynthesis were neglected,
- (3) some of the streams may have contained surfactants, and
- (4) stream geometries and flow rates were variable.

To eliminate these sources of error the writers studied reaches of rivers in which the water was relatively unpolluted, the oxygen deficits resulting from prolonged storage at depth in reservoirs. The flows from the reservoirs were controlled at constant rates and only reaches where the river geometries remained approximately constant were investigated. Using dimensional analysis and multiple regression techniques Churchill et al (1962) developed nineteen predictive equations for the mass transfer coefficient which had approximately the same correlation coefficient. The favored expression was:

$$k_2 = 5.026 \frac{U^{0.969}}{H^{1.673}} \quad (31)$$

or approximately, in terms of K_L :

$$K_L = 11.565 \ U/H^{2/3} \quad (32)$$

It should be noted however, that equation (32) is dimensionally incorrect, and that even within the reaches studied by the writers, geometric variations in stream cross-section were inevitable. In their work the authors reported the temperature coefficient, θ , to be 1.0241 -- based on extensive laboratory studies. Another point of merit in the work of Churchill et al is that the values of the oxygen saturation concentration were determined in situ, thus avoiding errors caused by assuming the "Standard Methods" (1965) saturation values which have since been shown to be in error (Isaacs and Gaudy (1968) and Douglas (1964)).

Proctor (1969) and Isaacs and Gaudy (1968) applied dimensional analysis and multiple regression techniques on data obtained from different types of laboratory scale channels to derive predictive equations for the mass transfer coefficient. When reduced to terms of K_L Proctor's (1969) equation can be written:

$$K_L = 2.650 \left(\frac{D_n \sqrt{v^2}}{R'} \right)^{1/2} \quad (33)$$

where: R' is the hydraulic radius.

It should be noted that the practical application of this equation would be limited, due to the difficulties in evaluating $\sqrt{v^2}$. Isaacs and Gaudy (1968) reported:

$$K_L = 7.031 \frac{U}{H^{3/2}} \quad (34)$$

in which the constant represents the functional group:

$$C' (D_m^{1/2} \nu^{-1/6} g^{-1/6}) \text{ at } 20^\circ\text{C}$$

where: ν is the kinematic viscosity.

The exponents for D_m , ν and g were assigned so that the functional group would describe the effects of temperature according to Churchill's (1962) value of the temperature coefficient ($\theta = 1.0241$). The writers also presented a correlation for the data of Churchill et al (1962):

$$K_L = 8.611 \frac{U}{H^{1/2}} \quad (35)$$

which they believed was valid for natural stream data.

In the paper presented by Isaacs, McCorkle and Lorang (1970) it was reported that Isaacs, Chulavachana and Bogart (1969) obtained:

$$K_L = 6.524 \frac{U}{H^{1/2}} \quad (36)$$

Equation (36) was developed using an experimental apparatus similar to that of Isaacs and Gaudy (1968) and resulted from a composite analysis of data obtained by varying the degree of channel roughness. Further, the paper (Isaacs et al (1970)) reported that a study by Isaacs and Maag (1969) employing the data of Churchill et al (1962) recommended the following relationship:

$$K_L = 6.863 \phi_s \phi_v \frac{U}{H^{1/2}} \quad (37)$$

where: $\phi_s = 1.05$, is a dimensionless velocity coefficient for their channel, and

$\phi_v = 1.16$, is a dimensionless cross-section shape coefficient.

The experimental work of Isaacs et al (1970) resulted in the following equation for K_L :

$$K_L = 6.750 \phi_s \phi_v \frac{U}{H^{1.5}} \quad (38)$$

where: $\phi_s \phi_v = 1.0907$ for their channel.

Equations (35), (37) and (38) were apparently developed with the a priori assumption that the functional form of equation (34) was the most suitable. The approximate agreement between equations (37) (from stream data) and (38) (from laboratory data) suggests that the factors ϕ_s and ϕ_v may account for geometry and velocity profile variations.

As can be seen from these studies, the nature of the temperature dependency of K_L is uncertain. While Streeter (1926) showed that the dependency could be written in the form of equation (24), writers who have agreed with this formulation (geometric increase with temperature) have differed in the value which they have assigned to the temperature coefficient θ :

Streeter (1926): $\theta = 1.016$

Streeter et al (1936): $\theta = 1.047$

Churchill et al (1962): $\theta = 1.0241$

Other writers reported the temperature dependency to be linear (Downing and Truesdale (1955), Downing et al (1957)) and variable with mixing conditions. The A.S.C.E. report (1961) resulted in endorsement for the geometric relationship and, based on well-controlled laboratory experiments,

reported the temperature coefficient θ to be 1.0241. Since this report (1961) other writers (Dobbins (1964), Metzger and Dobbins (1967)) have suspected that θ is not a constant at all but varies with the level of turbulence and temperature. Metzger (1968) showed that based on the experiments of Metzger and Dobbins (1967) and on the author's own results, the suspected variation was indeed true. Metzger also demonstrated that this variation in the temperature coefficient is predicted by Dobbins' equation (18). Metzger (1967, 1968) and Dobbins (1964, 1967) have proposed mechanisms to explain the Dobbins equation (18):

$$K_L = (D_m r)^{1/2} \coth \left(\frac{rL^2}{U_m} \right)^{1/2}$$

Theoretical models for r and L were developed through consideration of turbulence-energy relationships. Dobbins (1964) reasoned that turbulent eddies are created at the channel bottom and drift into the main body of the stream where they are broken to a smaller size by inertial forces. The upper limit of the eddy size is equal to the scale of the main flow (depth of flow) and the lower limit is determined by rate of dissipation of energy and viscosity. It is mainly through the small eddies that kinetic energy is converted into heat. Larger eddies transfer most of their energy to the smaller eddies of higher frequency; the process being repetitive until the limiting small scale is reached. Within the smallest eddies the flow is no longer turbulent and the predominant forces are molecular. According to the Kolmogoroff Similarity Principle (considering possible variables involved and satisfying dimensional requirements) the lower limit of the scale of turbulence is proportional to $(\nu^3/E)^{1/4}$ and

is independent of the initial eddy size. E represents the rate of energy loss per unit mass of water, and ν is the kinematic viscosity. By similar reasoning the velocity scale for the smallest eddies is proportional to $(\nu E)^{1/4}$ and by combining the previous two expressions the frequency of the smallest eddies is shown to be proportional to $(E/\nu)^{1/2}$. The source of energy for the flow process as a whole is equal to the rate of loss of potential energy per unit mass of liquid. Mathematically:

$$E = S U g$$

Although the above relationships for the limiting size, velocity, and frequency may hold for the body of the fluid, they must be modified when applied to surface layers. Additional molecular forces and specifically surface tension σ , must be overcome in order to accomplish surface overturn. The rate of energy expenditure per unit mass required to overcome surface tension should be proportional to $\sigma L^2 / \rho L^3$. This energy must be supplied by, and may be assumed to be proportional to, the turbulent energy per unit mass of liquid in the vicinity of the surface: E_s . Transforming proportionalities into equation form the following relationships can be written:

$$r = C_1 \frac{\rho L E_s}{\nu} \quad (39)$$

If E_s can be assumed proportional to the rate of energy dissipation of the fluid as a whole:

$$E_s = C_2 E \quad (40)$$

$$L = C_3 \left(\frac{v^3}{E_s} \right)^{1/4} \quad (41)$$

or

$$L = C_4 \left(\frac{v^3}{E} \right)^{1/4} \quad (42)$$

In equation (42) L is shown proportional to the size of the smallest eddies. Consequently L cannot be considered an invariable but rather an effective film thickness, that is, the effective value which offers the same resistance to gas transfer as occurs in the actual process.

Further:

$$r = C_1 C_2^{3/4} C_3 \frac{\rho v^{3/4} E^{3/4}}{\sigma} \quad (43)$$

$$\text{or} \quad r = \frac{C_5}{(C_4)^3} \frac{\rho v^{3/4} E^{3/4}}{\sigma} \quad (44)$$

$$rL^2 = \frac{C_5}{C_4} \frac{\rho v^{3/4} E^{1/4}}{\sigma} \quad (45)$$

$$rL^3 = C_5 \frac{\rho v^3}{\sigma} \quad (46)$$

where: ρ is the density of the water.

It is important to note that rL^3 depends only on fluid properties and thus is a constant for a given temperature and pressure no matter what the mixing conditions. As previously stated, the basic differential equation describing the mass transfer process is equation (4):

$$\frac{dC}{dt} = K_L \frac{A_s}{V} (C_s - C)$$

However, if the surface area cannot be evaluated the following relationship is used to facilitate the handling of experimental data:

$$A_s = C_A A_0 \quad (47)$$

where: A_0 is the horizontal projection of the actual surface area and

C_A is the proportionality constant.

The following equations follow from equations (4) and (47):

$$K_L = K_L' / C_A \quad (48)$$

$$r = r' / C_A^2 \quad (49)$$

$$L = C_A L' \quad (50)$$

$$rL^2 = r'(L')^2 \quad (51)$$

$$rL^3 = r'(L')^3 / C_A \quad (52)$$

The values designated by the primes are apparent values of the corresponding variables. To verify the proposed theory, experiments were carried out with a number of different gases. The absorption vessel was cylindrical with agitation provided by a vertically oscillating mechanism. By running the absorption experiment under identical conditions of temperature and agitation for two gases of different diffusivities the values of r' and L'

could be calculated from equation (18):

$$K_L = (D_m r)^{1/2} \coth \left(\frac{rL^2}{D_m} \right)^{1/2}$$

The calculations were carried out by inserting measured values of K_L' and the known diffusivities into equation (18) for nitrogen and helium and then solving the two equations simultaneously. The result of this analysis indicated a consistent relationship between r' and L' independent of the mixing conditions, that is, a given value of r' was always accompanied by the same value of L' . This demonstrated that they were both controlled by the same factors as is indicated by equations (39) through (46). From the experimental results Dobbins (1964) obtained $C_5 = 14.3$, and from analysis of available laboratory and stream data:

$$C_4 = 0.65 + 15000 \left(\frac{(v^3/E)^{1/4}}{H} \right)^2 \quad (53)$$

when C_A is given by:

$$C_A = 1.0 + 0.3 F^2 \quad (54)$$

where: F is the Froude number.

Equation (54) is an empirical equation based on the "experience" of the author. With these values of C_5 , C_4 and C_A the numerical values of r and L can be calculated and substituted into equation (18) to predict K_L . Dobbins showed this correlation to be superior to the equations of Churchill et al (1962) and O'Connor and Dobbins (1958) for a wide range of stream and laboratory data.

The work of Dobbins (1964) was extended by Metzger and Dobbins (1967). Equations (44), (45) and (46) were modified to account for the presence of surfactants, which decrease the surface tension σ , and generally also depress the value of K_L . The equations as proposed by Dobbins (1964) actually predict an increase in K_L with a decrease in surface tension. To revise the equations the writers introduced the concept of surface elasticity. The surface pressure p , (two dimensional, in the plane of the surface) was given as:

$$p = \sigma_0 - \sigma' \quad (55)$$

where: σ_0 is the surface tension of the clean portion, and
 σ' is the surface tension of the portion contaminated with adsorbed molecules.

It is this surface pressure or the associated surface force which has a definite effect on surface renewal. When the value of surface pressure is used in conjunction with surface concentrations a two-dimensional compressional modulus M_s (dynes per centimeter) relative to clean water can be obtained from force-area curves. With a development similar to that of Dobbins (1964) the writers derived the following expressions:

$$\rho v^2 = \frac{M_s}{x} \quad (56)$$

$$r = C_1 \frac{v}{x} = C_1 \frac{\rho v^3}{M_s} \quad (57)$$

$$v = C_3 (v E_s)^{1/4} \quad (58)$$

$$r = \frac{C_1 C_3^3 \rho E_s^{3/4} v^{3/4}}{M_s} \quad (59)$$

$$E_s = C_2 E \quad (60)$$

$$r = \frac{C_1 C_2^{3/4} C_3^3 \rho v^{3/4} E^{3/4}}{M_s} \quad (61)$$

$$L = C_4 (v^3/E)^{1/4} \quad (62)$$

$$rL^3 = C_5 \frac{\rho v^3}{M_s} \quad (63)$$

where: v is the vertical component of eddy velocity, and

x is the depth of the surface region and must be distinguished from L , the effective film thickness.

The value x represents the depth where resistance to surface overturn is extant and could be much less than the size of eddy. The coefficients C_2 and C_4 are the same as those used by Dobbins (1964). The others are analagous to but numerically different than those of Dobbins. Equations (62) and (60) are identical with (42) and (40) respectively. Equation (61) is the same as Dobbins equation (43) with one notable exception -- M_s is found in the denominator of (61) while σ is found in (43). This is in qualitative

agreement with the observations that surfactants lower the rate of surface renewal $r \propto M_s$ increasing with decreases in surface tension. Absorption experiments with an apparatus similar to Dobbins' were carried out, again with different gases (nitrogen, argon and oxygen) in order to calculate the values of r' and L' from equation (18). When K_L' was plotted against the frequency of oscillation (rpm) a straight line relationship held until the frequency reached the value at which the surface visibly rippled. Accordingly, it was concluded that up to this critical value of frequency the apparent mass transfer coefficient K_L' was in actuality identical to the true value K_L and that the deviation from linearity, after the critical frequency, was due only to increases in surface area given by the value C_A ($C_A = A_s/A_o$). A plot of C_A versus rpm yielded a straight line for each mixing condition and a plot of C_A versus K_L' resulted in a single curve. Consequently it was concluded that a value of K_L' is always associated with a certain value of C_A regardless of mixing condition. The values $r'(L')^3$ were found to be a constant ($8.1 \times 10^{-5} \text{ cm}^3/\text{min}$) for a given temperature until the surface began to ripple. The deviation from constancy was again attributed to the increase in surface area. Plots of $r'(L')^3$, L' and r' versus temperature were in qualitative agreement with equations (57) through (63).

Metzger (1968) reported that the value C_5/M_s in equation (63) could be taken as equal to $1.3 \text{ sec}^2/\text{gm}$ for distilled water as well as for water with surfactants in the concentration range reported for natural streams. Then the only impediment to the use of equation (18) as a predictive equation for K_L is the determination of C_4 in equation (62). C_4 is a constant which should be determined by the system or by a relationship such as equation (53).

(C) Summary

The development of theories to describe the mass transfer process of oxygen dissolution into a stream of water has culminated in the search for predictive models for the mass transfer coefficient K_L . The following is a list of some of the previously cited models proposed for K_L :

1. O'Connor and Dobbins (1958):

$$K_L = \left(\frac{D_m U}{H} \right)^{1/2} \quad (30)$$

2. Churchill et al (1962):

$$K_L = 11.57 \frac{U}{H^{2/3}} \quad (32)$$

3. Proctor (1969):

$$K_L = 2.65 \left(\frac{D_m \sqrt{v^2}}{R^1} \right)^{1/2} \quad (33)$$

4. Isaacs and Gaudy (1968) (for laboratory data):

$$K_L = 7.031 \frac{U}{H^{1/2}} \quad (34)$$

5. Isaacs and Gaudy (1968) (for stream data):

$$K_L = 8.611 \frac{U}{H^{1/2}} \quad (35)$$

6. Isaacs et al (1969):

$$K_L = 6.524 \frac{U}{H^{1/2}} \quad (36)$$

7. Isaacs and Maag (1969):

$$K_L = 6.863 \phi_s \phi_v \frac{U}{H^{1/2}} \quad (37)$$

8. Isaacs et al (1970):

$$K_L = 6.750 \phi_s \phi_v \frac{U}{H^{1/2}} \quad (38)$$

9. Dobbins (1956, 1964, 1967) and Metzger (1967, 1968):

$$K_L = (D_m r)^{1/2} \coth \left(\frac{rL^2}{D_m} \right)^{1/2} \quad (18)$$

when used with:

$$rL^3 = C_5 \frac{\rho v^3}{M_s} \quad \text{and} \quad L = C_4 (v^3/E)^{1/4}$$

It is interesting to note that only equations (30), (33) and (18) are dimensionally correct and only equations (30) and (18) were mechanistic in their derivation. Furthermore, equation (30) is only a special case of equation (18). Accordingly it must be noted that in equations (32) to (38) the units which must be used are:

U: feet per second,

H: feet, and

K_L : feet per day.

Equations (34) through (38) can be presented in a dimensionally correct form when the relationships are written as:

$$K_L = C' (U_m^{1/3} \nu^{-1/6} g^{-1/6}) \frac{U}{H^{1/2}} \quad (64)$$

It must also be noted that equations (30), and (32) through (38), are correctly expressed only when the mean depth is the ratio of the actual surface area to volume. Except for equations (30), (33) and (18) K_L is expressed as a linear function of average stream velocity. Metzger and Dobbins (1967) showed that as long as a linear dependence holds, the increase in surface area due to agitation can be assumed negligible. Accordingly, the transformation of the equations from terms of k_2 to terms of K_L , the more fundamentally important parameter, appears to be rational.

Some reasons for the variation in results of the studies on the problem under consideration should be mentioned. In the early stream studies biological action of oxygen production and depletion were not fully accounted for (Churchill et al, 1962), surfactants may have been present, oxygen concentrations were determined by the Winkler method (about 10% variability), flow rates and stream geometries were variable, temperature control was lacking, and incorrect values of oxygen saturation concentration were used (see Isaacs and Gaudy (1968) for the importance of correct oxygen saturation values). The work of Churchill et al (1962) apparently

overcame most of these difficulties, however variabilities in stream geometry could not have been completely eliminated. In laboratory work with mechanically agitated fixed bodies of water, conditions were so remotely related to natural streams that their application to the latter is questionable. Furthermore, some studies with laboratory scale flowing systems such as those of Isaacs and Gaudy (1968) and Streeter, Wright and Kehr (1936) have been thought to inadequately represent stream conditions (Thackston and Krenkel, 1969, and Krenkel and Orlob, 1962).

Another type of correlation has been presented by Krenkel and Orlob (1962) and Thackston and Krenkel (1966) in which K_L is related to the coefficient of longitudinal dispersion which is determined by tracer concentration studies. The design of the apparatus used in the present work could not be adapted to such procedures because of its small scale. Consequently these correlations were not considered.

CHAPTER 3

Experimental Apparatus and Techniques

(A) The Equipment

The apparatus employed was basically a small scale open channel with a closed recycle loop and was erected in a controlled temperature room. A photograph of the essential features of the equipment is given in Figure 1. Since the apparatus was designed for future application in the study of the effects of surfactants special care was taken in choosing the materials of construction. These included nylon, viton, teflon, 316 stainless steel, glass (pyrex and Q.V.F. borosilicate), epoxy, neoprene and black rubber. With the exception of epoxy, neoprene and rubber the above materials have been shown by Topp (1966) to be extremely resistant to chemical breakdown. The only components composed of neoprene and rubber were bottle stoppers which could be replaced by newly marketed teflon-coated stoppers. The head chamber and impeller of the recirculation pump and the adhesive used in the entrance section were composed of epoxy. There is a continuing search for more chemically inert materials for these applications.

The absorption or control section was a four foot length of Q.V.F. borosilicate glass pipe with four inch internal diameter through which water was recirculated at the half-diameter depth. It was set in a nearly horizontal position. The entrance and exit sections are shown in the photographs of Figure 2. Quarter-inch teflon sheet and viton O-ring material

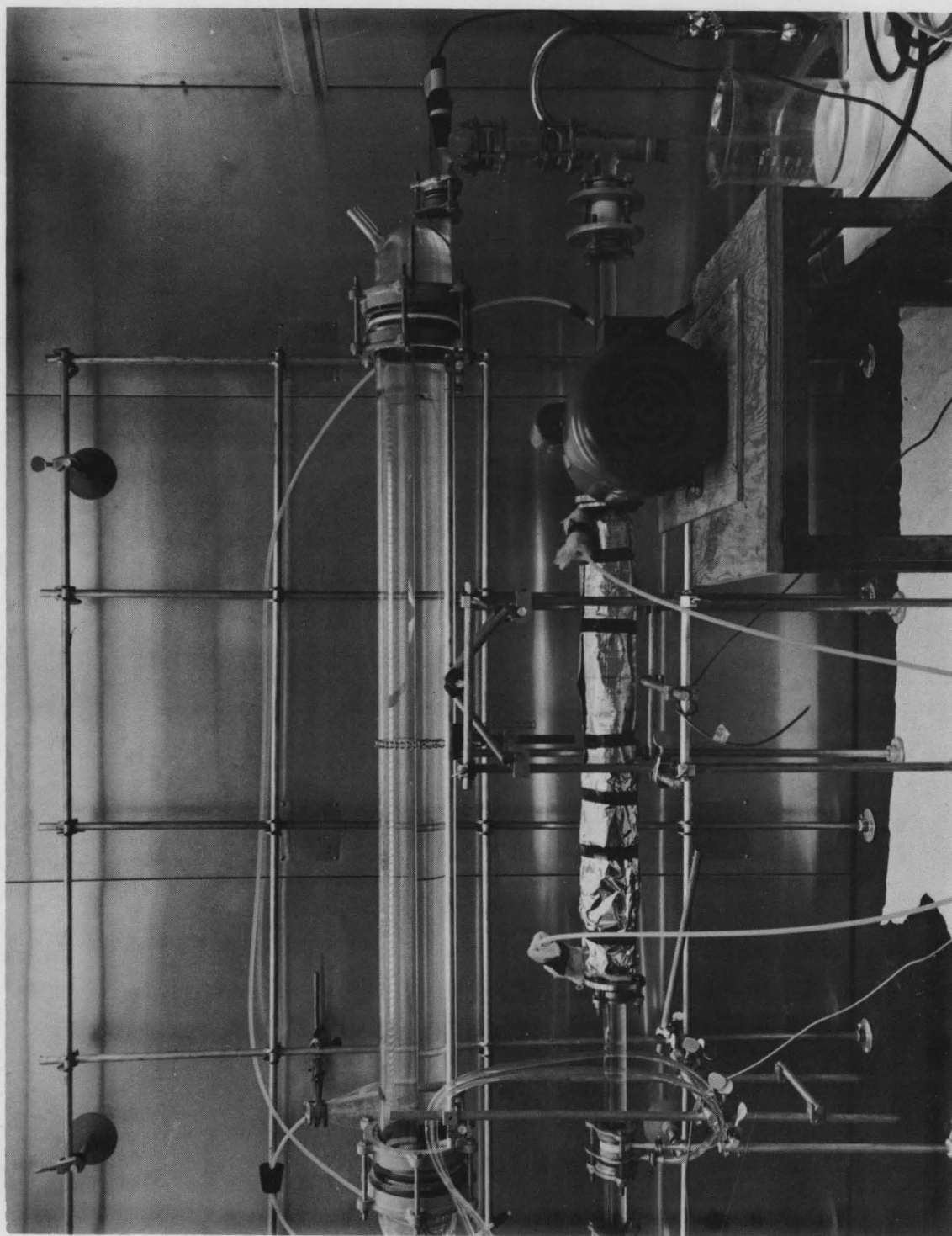
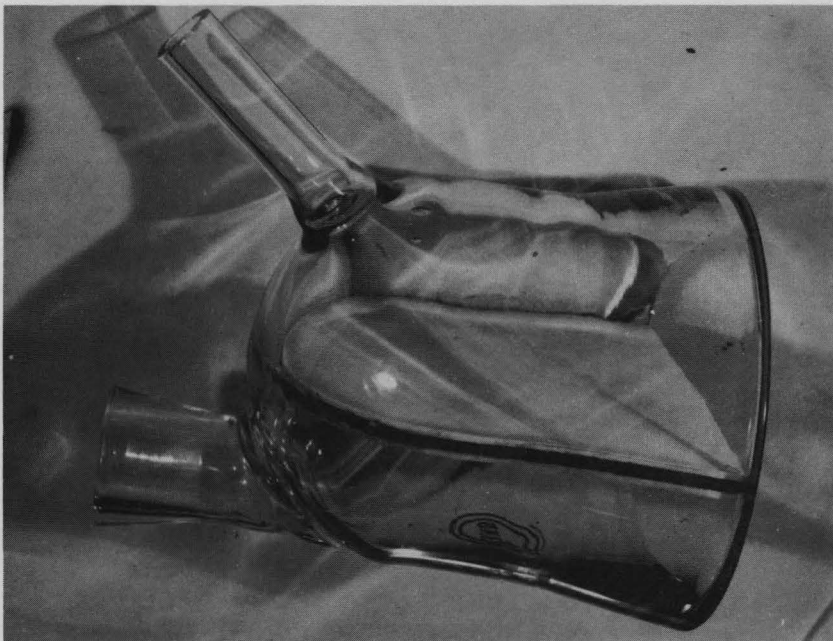


FIGURE 1: The Apparatus



Entrance Section



Exit Section

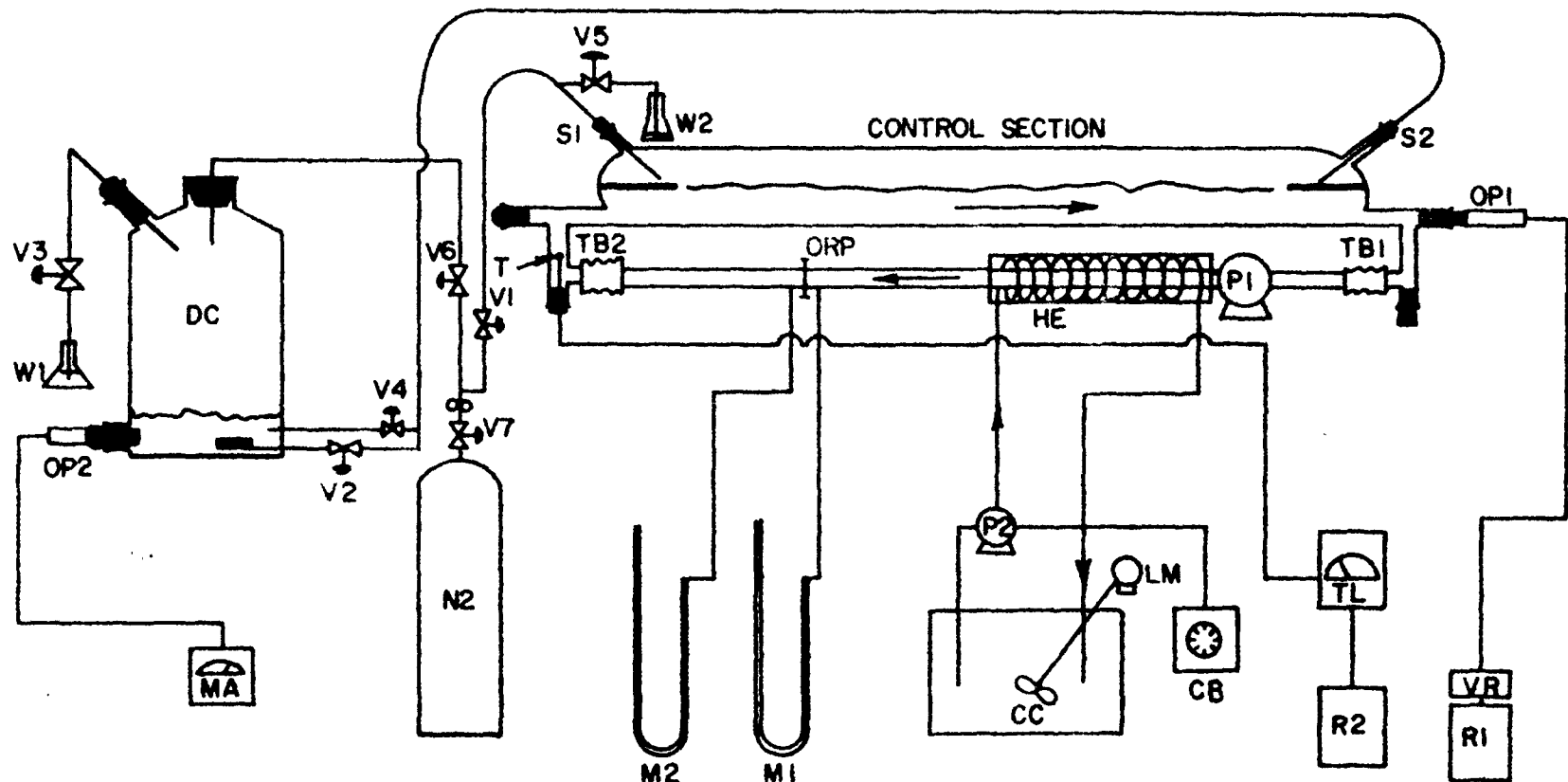
were used as dividers to restrict the water flow and to prevent the formation of an air-water interface outside of the control section. In both the entrance and exit sections a half-inch diameter opening allowed atmospheric air to enter the control section. The liquid flow was uniformly dispersed at the entrance by means of a "pack" of ten millimeter glass tubes about four inches in length. The tubes were held in place by a stainless steel mesh.

The major portion of the recirculation loop was a Q.V.F. borosilicate glass pipe of one inch internal diameter. A twenty-six inch section of one inch outside diameter stainless steel tube was utilized to provide a heat exchange surface. The circuit as a whole is shown in the schematic flow diagram of Figure 3.

The flow was provided by a variable discharge positive displacement pump (marketed by Cole-Parmer, maximum discharge: 23 U.S. gal/min at 5 ft. head). Pump vibrations were isolated from the control section by means of teflon bellows inserted in the recirculation loop on both sides of the pump. In addition, vibrations were absorbed by quarter-inch rubber cushions placed under the feet of the pump stand which was not itself in contact with the recirculation loop.

In experiments a single stainless steel orifice plate ($1/8$ inch thickness) with a $1/2$ inch orifice diameter was utilized for flow measurement. This was found inadequate at very low flow rates -- when the average stream velocity in the control section was 0.1 ft/sec, the pressure differential across the plates was only 0.7 cm of mercury. A $5/16$ inch orifice provided a pressure drop of 4.0 cm and was used for the low velocity runs. Single

FIGURE 3
SYSTEM FLOW DIAGRAM



CB: PUMP SPEED CONTROLLER
CC: COLEMAN COOLER
DC: DEOXYGENATION CHAMBER
HE: HEAT EXCHANGER
LM: LAB MIXER
M1, M2: MERCURY MANOMETERS
MA: MICROAMMETER
N2: NITROGEN GAS CYLINDER
S1, S2: AIR OPENING STOPPERS
OP1, OP2: OXYGEN PROBES
ORP: ORIFICE PLATE

P1, P2: PUMPS
R1, R2: RECORDERS
T: THERMISTOR
TB1, TB2: TEFLON BELLOWS
TL: TELETHERMOMETER
V1, V2, V3, V4, V5, V6, V7: VALVES
W1, W2: WATER SEALS
VR: VARIABLE RESISTANCE VOLTAGE DIVIDER

mercury filled U-tubes were connected to the manometer openings via teflon nipples inserted in short teflon sections which formed part of the recirculation loop on both sides of the orifice plate. The orifice plate calibration curves are presented in Appendix A.

The heat exchanger consisted of $\frac{1}{4}$ inch O.D. soft copper tubing wound around the stainless steel tube of the recirculation loop. The coolant was contained in a plastic cooler (about one cubic foot capacity) and was kept at a low temperature by either ice or solid carbon dioxide. For all runs above five degrees centigrade ordinary ice and water provided sufficient cooling. At five degrees centigrade and at the highest flow rate it was found necessary to employ a glycol-based antifreeze solution as a coolant to absorb the generated heat. For the other flow rates at five degrees centigrade, brine and ice were used. The cooler contents were continuously agitated by a variable speed high torque laboratory mixer.

A thermistor-based scanning "tele-thermometer" (Model 47, Yellow Springs Instrument Co.) was utilized in combination with a millivolt recorder to provide continuous monitoring of temperature. In preliminary experiments three channels of the automatic scanning feature were used with two of the teflon-coated thermistor probes being inserted through neoprene stoppers in tee sections on either side of the heat exchanger and one near the center of the controlled temperature room. The ambient room temperature was also indicated on a rotating circular recorder -- part of the original room equipment. No temperature difference was detected between the two points in the recirculation loop, and the room's temperature recorder was found to give accurate readings although it responded rather slowly to temperature changes. Consequently the scanning mechanism of the tele-thermometer was

not used with the temperature being monitored at one point only -- upstream of the control section. Appendix B gives some details of the thermistor tele-thermometer as well as calibration curves.

In preliminary experiments the coolant flow was controlled by a needle valve and short circuit throttling system. This required repeated opening and closing of the door to the controlled temperature room for valve adjustments during the experimental runs. The temperature variations within the loop could be kept to within $\pm 0.5^{\circ}\text{C}$, and the ambient room temperature within $\pm 5.0^{\circ}\text{C}$. This flow control system was replaced by a variable speed pump, which was electrically controlled from outside of the constant temperature room. The temperature control improved considerably. The smallest scale division on the tele-thermometer recorder represented about 0.045°C and the temperature within the loop did not vary more than half a scale division and never more than one and a half divisions during a run. The room temperature variations were normally less than 1.0°C and always less than 2.5°C .

Other experimental difficulties encountered included bubble formations at bends and under the entrance and exit flow divider plates, and gradual decreases in the flow velocity. Both conditions occurred only during experimental runs in which the average velocity in the control section was 0.1 ft/sec. The latter problem was overcome by adjustments of the recirculation pump impeller during a run and the former was assumed to have a negligible effect.

The dissolved oxygen was continuously monitored with a lead-silver galvanic cell oxygen probe (Precision Scientific Co.) which has been described by Mancy et al (1962). The probe which generates up to 15 microamps (when used with a standard polyethylene membrane) was connected to a variable

resistance voltage divider (zero to one thousand ohms). The voltage across the variable resistance which is directly proportional to the dissolved oxygen content was measured on a millivolt recorder. By adjustment of the variable resistance any degree of scale deflection could be obtained on the recorder for a given concentration of dissolved oxygen.

(B) Operating Techniques

All of the components of the recirculation loop were thoroughly cleaned before assembling the apparatus; all glass, teflon, and viton pieces being rinsed several times in chromic acid. The assembled apparatus was also rinsed several times with distilled water before initiating the experimental runs.

All reaeration experiments were continued until the oxygen concentration remained unchanged for a period of about twenty minutes, at which time a condition of saturation was assumed. The completion of one experiment marked the start of the calibration procedure for the next. The thermostat of the controlled temperature room was set at the value specified for the subsequent experiment and the temperature of the water was adjusted to the specified value by continuing the recirculation under an increased or decreased flow rate of coolant. When thermal equilibrium was reached at the specified temperature the apparatus could be "turned off" and the experiment continued at a later time or the calibration of the oxygen probe could be started immediately. In either case, the water was recirculated until a saturated condition was again established for the specified temperature and the D.O. probe recorder deflection was set at 90 percent of full scale by adjusting the variable resistance of the voltage divider. The current output of the probe was checked to insure that the minimum value recommended by the manufacturer was equaled or exceeded. When the current output was too low, the probe was cleaned and the membrane replaced as outlined in the manufacturer's manual. Next the water was emptied from the apparatus and the oxygen probe placed in a beaker of distilled water to prevent it from drying

out during the deoxygenation procedure.

In the following description of the deoxygenation procedure and experimental run the alphanumeric symbols refer to Figure 3.

Initially all valves except valve V7 were closed, isolating the interior of the entire system from the atmosphere. Approximately nine liters of distilled water were added to the deoxygenation chamber. Valves V1, V2 and V3 were opened allowing nitrogen gas (regular grade) to flow through the entire apparatus and bubble into the deoxygenation chamber through a fritted glass diffuser. This deoxygenation process was continued for approximately twenty minutes giving a residual oxygen concentration of less than 1.0 mg/l. Another lead-silver oxygen probe OP2, in the deoxygenation chamber indicated relative decreases in oxygen concentration during the deoxygenation process. This probe was neither calibrated nor periodically reconditioned. Before stopping the flow of nitrogen the oxygen probe OP1, was replaced in the tee fitting. In removing the stopper in the tee fitting some nitrogen escaped but this outflow prevented the inflow of significant amounts of air. Valves V1, V2 and V3 were closed. Valves V4 and V5 were opened and with the subsequent opening of valve V6 the water was discharged under pressure, from the deoxygenation chamber into the recirculation loop. The displaced gas was forced out through valve V5 and water seal W1. When the water level reached mid-diameter depth in the control section the valves were closed. Pump P1 was started at a high flow rate to drive out any bubbles which may have accumulated at the bend fittings or under the teflon divider plates of the entrance and exit sections. The pump was stopped and the water level was readjusted to exactly the half-diameter depth by

adding a small additional amount of water from the deoxygenation chamber. The pump was restarted and the flow rate adjusted to provide the desired average velocity in the control section. The variable speed peristaltic coolant pump, P2, was started and its speed adjusted to bring the temperature of the water to the desired level. When thermal equilibrium was established at the desired temperature by readjustments of the coolant pump speed, the stoppers S1 and S2 were removed exposing the liquid surface in the control section to the atmosphere. The concentration of oxygen in the water was continuously monitored on recorder R1, as was the temperature on recorder R2. During the run, the temperature recorder was continually observed and when the temperature plot began to show a deviation from desired level the flow rate of the coolant was adjusted by rheostatic control of coolant pump speed to bring the temperature back to the required level. The pump speed control box CB, and recorders R1 and R2 were situated outside the controlled temperature room so that once the experiment had been started the door of the room could usually be kept closed and the room isolated from exterior thermal conditions. As mentioned previously, the experiment was continued until the saturation level was reached.

After the run a 100 ml sample was removed from the recirculation loop for measurement of surface tension and organic carbon content. Then the temperature conditions were changed and the oxygen probe recorder was calibrated for the next run.

The initial startup of the system was accomplished by merely saturating distilled water in the recirculation system at the desired temperature and velocity level as was done with the "used" water following

subsequent experiments. The water did not become significantly contaminated during the experiments and thus the system water of one experiment was used for the calibration procedure of the subsequent run. No effort was made to completely empty out the recirculation loop after an experimental run -- about 280 ml of saturated water was then remaining in the system from the previous run.

After the 100 ml sample had reached exterior room temperature the surface tension was measured utilizing a DuNouy Tensiometer. The surface tension of a control sample of distilled water was also determined at the same time. The tensiometer was calibrated before each set of determinations. A portion of the sample (about 80 ml) was acidified using 2 drops of concentrated hydrochloric acid and stored for determination of organic carbon content. A blank of distilled water was also acidified and stored in like manner. After all experimentation was completed, the organic carbon level of all samples was measured using a Beckman infrared carbon analyzer.

For the two experimental runs performed with surfactants, solutions of sodium lauryl sulphate (U.S.P. grade) were made up to yield concentrations of 50 and 100 mg/l when added to the aeration system contents. The concentrated solutions were siphoned from a beaker through the air opening of the exit section into the deaerated distilled water in the system. The remainder of the experiment was carried out in the normal manner.

CHAPTER 4

Experimental Results and Discussion

(A) Introduction

Twenty-four experiments (excluding preliminary runs) were performed in all. Two experiments were performed to investigate the applicability of the apparatus to the study of the effects of surfactants. Twenty-two experiments were run with temperature and average velocity as the only variables. The velocity ranged from 0.1 to 0.9 ft/sec and the temperature from 5.0 to 25.0°C within a "3² factorial" experimental design. From the five replicates at the center point (15.0°C, 0.5 ft/sec) estimates of the coefficient of variation and standard deviation for K_L values were calculated to be 5.4 percent and 0.017 cm/min, respectively.

A typical oxygen concentration and temperature curve is reproduced in Figure 4. All data derived from such curves are presented in Appendix C. The value of K_2 was determined as the slope of the "least squares" straight line drawn through the plot of the natural log of $(C_s - C)$ versus time. The value of K_L was calculated by multiplying K_2 by the volume to interfacial area ratio. These results are presented in Table 1.

The measurements of surface tension and organic carbon on water samples taken after each experiment revealed that contamination could not be detected by these methods. The average value of the surface tension for the samples taken from the twenty-two experiments (66 determinations) was

FIGURE 4: Typical Data Record

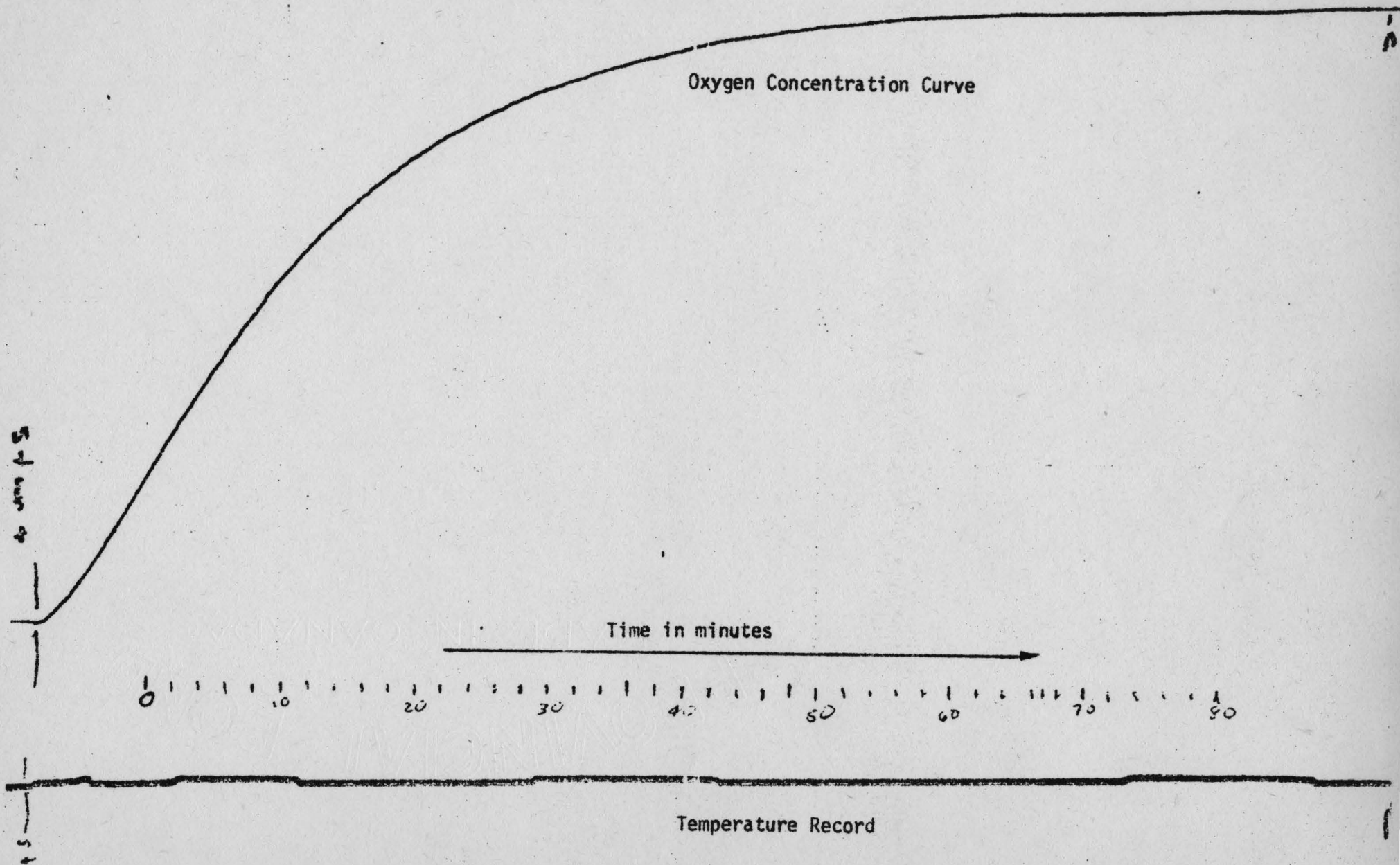


TABLE 1

Experimental Results

	<u>Temperature</u>	<u>Velocity</u>		<u>k₂ (Base 10)</u>	<u>K_L (Base e)</u>
	°C	ft/sec	cm/sec	per day	cm/min
1	25	0.90	27.432	63.092	0.6233
2	25	0.50	15.240	38.336	0.3787
3	25	0.50	15.240	37.757	0.3730
4	25	0.10	3.048	9.456	0.0934
5	20	0.50	15.240	36.143	0.3570
6	20	0.50	15.240	33.144	0.3274
7	20	0.50	15.240	35.815	0.3538
8	15	0.90	27.432	53.950	0.5330
9	15	0.75	22.860	44.200	0.4366
10	15	0.50	15.240	32.135	0.3174
11	15	0.50	15.240	34.782	0.3436
12	15	0.50	15.240	32.172	0.3178
13	15	0.50	15.240	31.835	0.3145
14	15	0.50	15.240	30.858	0.3048
15	15	0.35	10.668	20.256	0.2001
16	15	0.10	3.048	7.702	0.0761
17	10	0.50	15.240	27.624	0.2729
18	10	0.50	15.240	28.155	0.2781
19	5	0.90	27.432	46.280	0.4572
20	5	0.50	15.240	27.618	0.2728
21	5	0.50	15.240	27.249	0.2692
22	5	0.10	3.048	6.254	0.0618

71.25 dynes/cm with a standard deviation of 0.235 dynes/cm. For the control samples of distilled water the average value was 71.16 dynes/cm with a standard deviation of 0.369 dynes/cm. As expected, the measurements of organic carbon gave a random sequence of readings between 3 and 7 mg/l for both the samples and distilled water controls. It is generally accepted that infrared carbon analysis does not give meaningful results for carbon concentrations less than 10 mg/l.

(B) The Effect of Velocity

Figure 5 shows that the dependence of K_L upon average velocity was found to be approximately linear throughout the range of velocities used. Metzger and Dobbins (1967) stated that increases in surface area with increased agitation are negligible until the degree of agitation is such that a linear relationship no longer holds. Accordingly, increases in interfacial area were considered to be negligible for all experimental conditions and therefore the results are presented in terms of K_L as well as k_2 . Actual observation of the interface revealed rippling of the water surface which was barely detectable at an average velocity of 0.5 ft/sec and more pronounced at a velocity of 0.9 ft/sec.

Multiple regression procedures were used to fit the data to functional forms found in the recent literature. These results are given in Table 2. Equations (65) through (68) were obtained using the data from the nine experiments at 15°C. The data from all twenty-two experiments were used to obtain equations (69) and (70) in which β_2 is the temperature co-

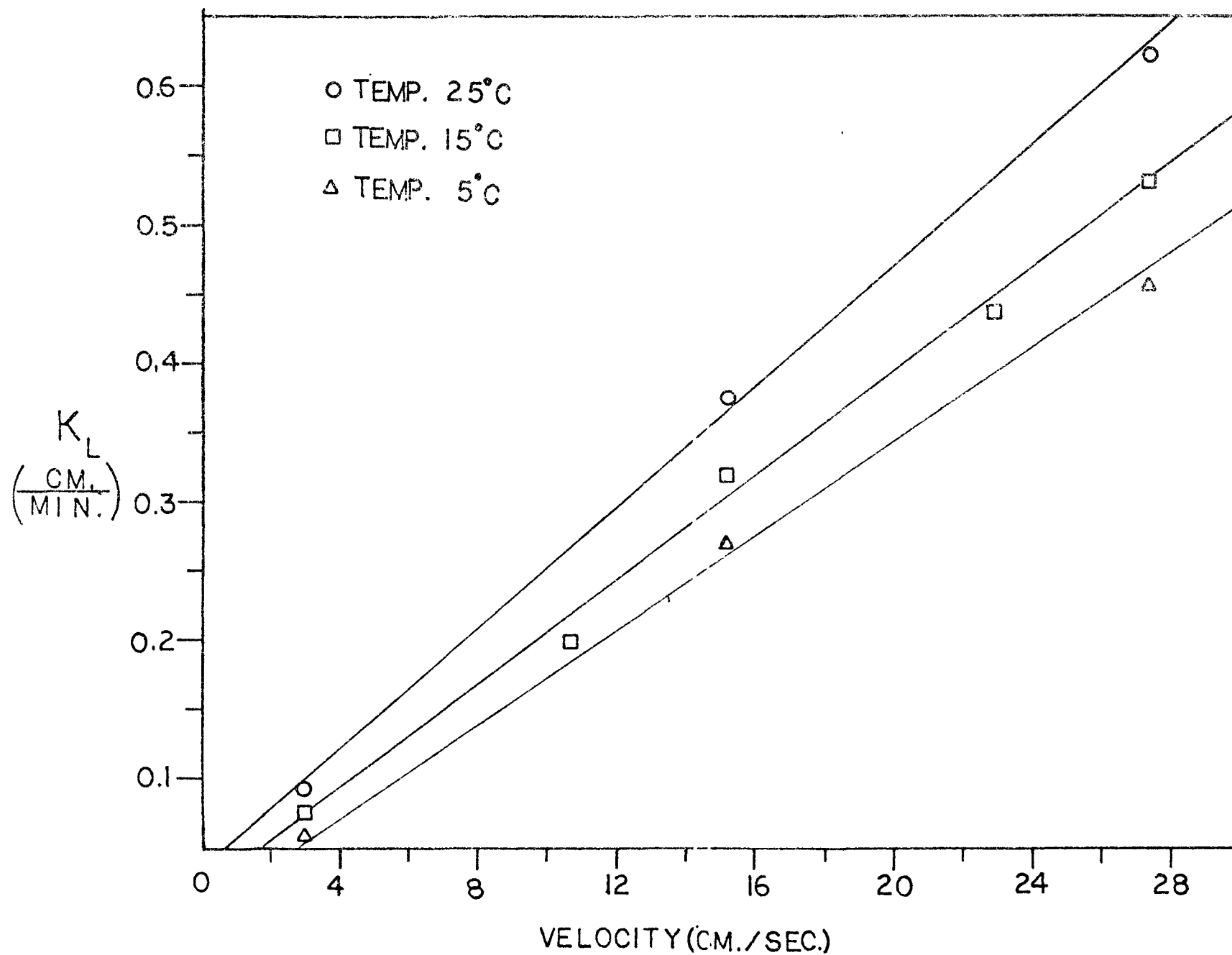


TABLE 2

Correlations Showing the Effect of Velocity on K_L

<u>General Form</u>	<u>Experimental Results</u>	<u>Number of Experiments</u>	<u>Correlation Coefficient</u>	<u>Equation Number</u>
$k_2 = \beta_0 \frac{U}{H^{3/2}}$	$k_2 = 2.930 \frac{U}{H^{3/2}}$ or $K_L = 10.447 \frac{U}{H^{1/2}}$	9 (at 15°C)	0.998	(65) (66)
$k_2 = \beta_0 \frac{U^{\beta_1}}{H^{3/2}}$	$k_2 = 2.777 \frac{U^{0.893}}{H^{3/2}}$ or $K_L = 9.901 \frac{U^{0.893}}{H^{1/2}}$	9 (at 15°C)	0.994	(67) (68)
$k_2 = \beta_0 \frac{U^{\beta_1}}{H^{3/2}} \beta_2^{(T-20)}$	$k_2 = 3.049 \frac{U^{0.874}}{H^{3/2}} (1.018)^{T-20}$ or $K_L = 10.871 \frac{U^{0.874}}{H^{1/2}} (1.018)^{T-20}$	22	0.997	(69) (70)

Note: k_2 is to base 10, and K_L is to base e.

efficient. Isaacs and Gaudy (1968) reported a correlation similar to equation (69):

$$k_2 = 3.053 \frac{U}{H^{3/2}} (1.0241)^{T-20} \quad (71)$$

and Isaacs et al (1970) a correlation similar to equation (65):

$$k_{20^{\circ}\text{C}} = 2.931 \phi_s \phi_v \frac{U}{H^{3/2}} \quad (72)$$

where the product $\phi_s \phi_v$ was equal to 1.0907.

It might be concluded that the mass transfer characteristics for the apparatus used in this study were very similar to those which led to equations (71) and (72). Equations (34) and (38) give the relationships of equations (71) and (72) respectively, in terms of K_L :

$$K_{L20^{\circ}\text{C}} = 7.031 \frac{U}{H^{1/2}}$$

and

$$K_{L20^{\circ}\text{C}} = 6.750 \phi_s \phi_v \frac{U}{H^{1/2}}$$

On the basis of K_L the coefficients obtained in the studies of Isaacs and Gaudy (1968) and Isaacs et al (1970) are between 30 and 40 percent less than those obtained in the present work. The general agreement in terms of k_2 and disagreement in terms of K_L results from the trans-

formation of k_2 values to K_L which has been previously discussed. In the experimental system employed, the volume to surface area ratio is not equivalent to the mean depth H as in streams since only the control section was exposed to the atmosphere.

A possible explanation for the relatively high K_L values obtained is that small scale turbulence of high intensity may have been caused by the entrance conditions. This would cause a higher rate of surface renewal than would normally be expected for a given average velocity.

Although the K_L values obtained appear to be significantly higher than those obtained in lab scale studies with rectangular cross sections (Isaacs and Gaudy, 1968, Isaacs et al, 1969, Isaacs and Maag, 1969 and Isaacs et al, 1970) the values given by equation (35):

$$K_L = 8.611 \frac{U}{H^{1/2}}$$

which was obtained by Isaacs and Gaudy (1968) for the stream data of Churchill et al (1962) are less than 21 percent lower than the K_L values obtained in the present study. Since a natural stream cross section usually lies somewhere between a rectangular and semi-circular shape the present data suggest that channel geometry might have a significant effect on K_L .

Another possible explanation is that K_L values are significantly larger in a truly "clean" system -- a condition which may have been approached in the present work.

(C) The Effect of Temperature

The data obtained was compared to the predictions of the film penetration model advanced by Dobbins (1956) and refined by Dobbins (1964), Metzger and Dobbins (1967) and Metzger (1968). Equation (18) gives:

$$K_L = (D_m r)^{\frac{1}{2}} \coth \left(\frac{rL^2}{D_m} \right)^{\frac{1}{2}}$$

and equation (63):

$$rL^3 = \frac{C_5 \rho v^3}{M_s}$$

where $C_5/M_s = 1.3 \text{ sec}^2/\text{gm}$ (Metzger, 1968)

An initial estimate of the surface renewal rate, r , was obtained by assuming the coth term equal to unity. Then using an iterative procedure with equations (18) and (63) the values of r and effective film thickness, L , were calculated for each experimental value of K_L . The values for the density viscosity of water were obtained from The Handbook of Chemistry and Physics (49th Ed. 1968-69). The value of diffusivity of oxygen into water was taken as $2.14 \times 10^{-5} \text{ cm}^2/\text{sec}$ at 20°C and the Stokes-Einstein equation was used to correct to other temperatures. The results of these calculations are shown in Table 3.

The relationship of r and L to temperature was given by equations (61) and (62) respectively:

TABLE 3

Rate of Surface Renewal, r and Effective Film Thickness, L

	Temperature $^{\circ}\text{C}$	Velocity (cm/sec)	K_L (cm/min)	rL^3 $\text{cm}^3/\text{sec} \times 10^6$	r 1/min	L $\text{cm} \times 10^3$
1	25	27.43	0.6233	0.923	257.33	5.99
2	25	15.24	0.3759	0.923	90.58	8.49
3	25	3.05	0.0934	0.923	5.31	21.85
4	20	15.24	0.3461	1.313	90.98	9.53
5	15	27.43	0.5330	1.924	255.24	7.68
6	15	22.86	0.4366	1.924	171.05	8.77
7	15	15.24	0.3197	1.924	91.31	10.81
8	15	10.67	0.2001	1.924	35.36	14.84
9	15	3.05	0.0761	1.924	4.76	28.94
10	10	15.24	0.2755	2.902	79.40	12.99
11	5	27.43	0.4572	4.556	270.04	10.04
12	5	15.24	0.2710	4.556	94.87	14.23
13	5	3.05	0.0618	4.556	4.89	38.25

$$r = \frac{C_1 C_2^{3/4} C_3^3 \rho v^{3/4} E^{3/4}}{M_s}$$

$$L = C_4 \left(\frac{v^3}{E} \right)^{1/4}$$

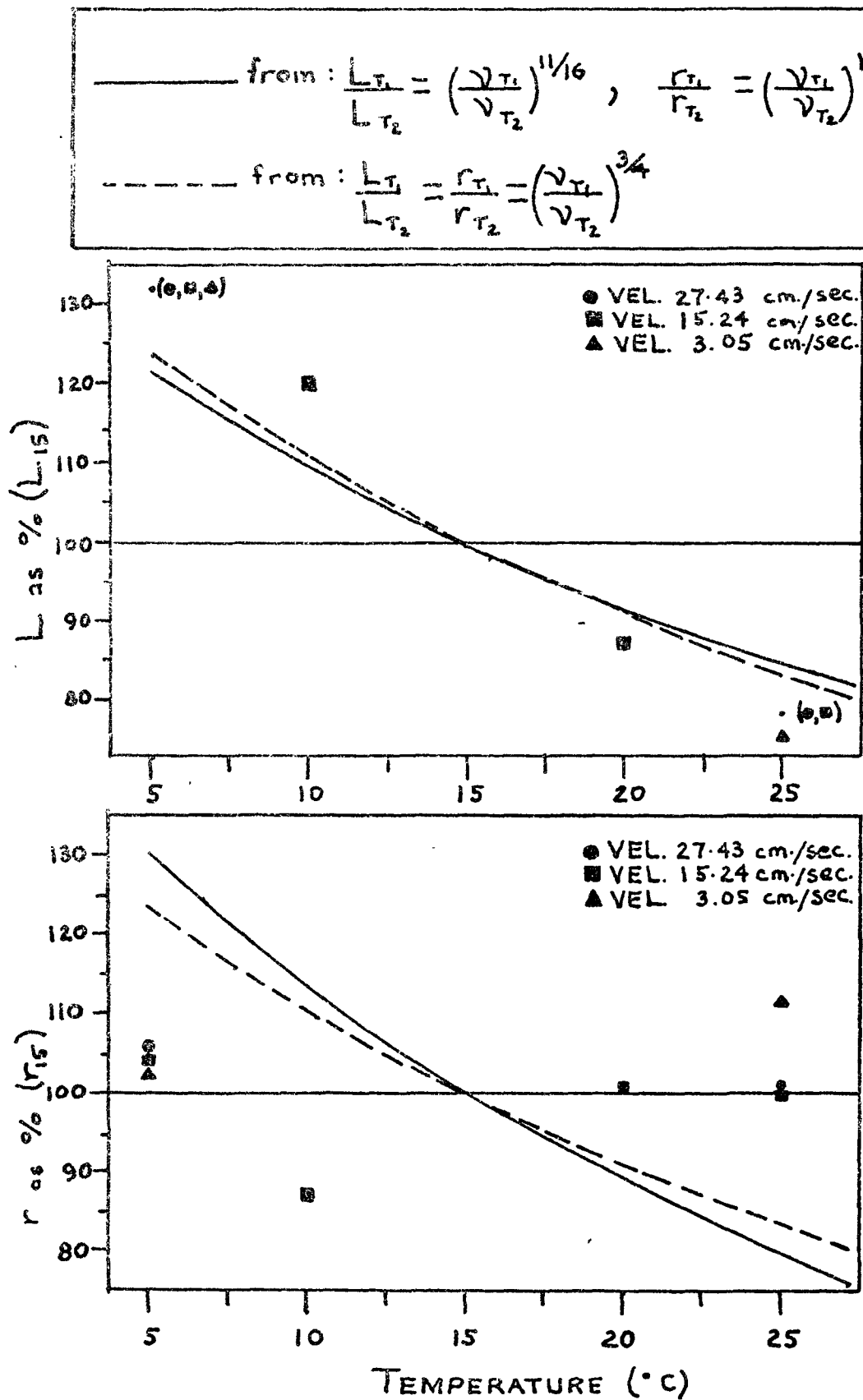
Assuming as Metzger (1968) does, that the effects of temperature on r and L are due mainly to the $v^{3/4}$ term in equations (61) and (62) the ratios of the two quantities at any two given temperatures T_1 and T_2 may be written:

$$\frac{r_{T_1}}{r_{T_2}} = \frac{L_{T_1}}{L_{T_2}} = \left(\frac{v_{T_1}}{v_{T_2}} \right)^{3/4} \quad (73)$$

Figure 6 shows the relationship of r and L to temperature obtained from equation (73) and also the experimental points calculated from the data of Table 3. Although the data indicates that the relationship of L might be correctly expressed in a form such as equation (73) no correlation is apparent for r -- which appears to be independent of temperature.

While the assumption that the energy dissipation per unit mass of water, E , is relatively independent of temperature may have been correct for the mechanical aeration system used by Metzger (1968) -- for flowing systems this is probably not the case. For open channel flow, E is defined by the relationship:

$$E = S U g \quad (74)$$

FIGURE 6: EFFECT OF TEMPERATURE ON r AND L 

and friction slope may be expressed:

$$S = \frac{f}{4R^1} \frac{U^2}{2g} \quad (75)$$

where f , the friction factor for smooth, fully turbulent flow may be defined by the Blassius equation:

$$f = \frac{0.316}{Re^{1/4}} \quad (76)$$

where Re is the hydraulic radius Reynold's number which is normally written as:

$$Re = \frac{4R^1 U}{\nu} \quad (77)$$

The Chezy-Manning equation has also been used to calculate the slope of the energy grade line which is then given by:

$$S = \left(\frac{UN}{1.486 (R^1)^{2/3}} \right)^2 \quad (78)$$

where N is the Manning coefficient and is taken to be 0.01 for glass in further calculations. The limited applicability of the Chezy-Manning equation has been described by Morris (1963). Table 4 gives the values of E calculated using both equations (75) and (78) for the experimental conditions used. The tabulation indicates that the two equations yield results which can differ by a factor as high as 1.7. Since equation (75) takes into account the effects of temperature it appears to be the more

TABLE 4

Energy Dissipation

	Temperature °C	Velocity (cm/sec)	Energy Dissipation (Chezy-Manning Equation) $\frac{\text{dyne} - \text{cm}}{\text{gm} - \text{sec}}$	Energy Dissipation (Blassius Friction Factor) $\frac{\text{dyne} - \text{cm}}{\text{gm} - \text{sec}}$
1	25	27.432	27.0919	23.4996
2	25	15.240	4.6454	4.6673
3	25	3.048	0.0372	0.0558
4	20	15.240	4.6454	4.9384
5	15	27.432	27.0919	25.6672
6	15	22.860	15.6787	15.5464
7	15	15.240	4.6454	5.0978
8	15	10.668	1.5934	1.9116
9	15	3.048	0.0372	0.0610
10	10	15.240	4.6454	5.2750
11	5	27.432	27.0919	27.5767
12	5	15.240	4.6454	5.4770
13	5	3.048	0.0372	0.0655

generally applicable. When equations (74) through (77) are combined with equations (61) and (62) the temperature dependency of r and L may be expressed in terms of kinematic viscosity as:

$$\frac{r_{T_1}}{r_{T_2}} = \left(\frac{v_{T_1}}{v_{T_2}} \right)^{15/16} \quad (79)$$

$$\frac{L_{T_1}}{L_{T_2}} = \left(\frac{v_{T_1}}{v_{T_2}} \right)^{11/16} \quad (80)$$

The solid lines in Figure 6 were obtained using equations (79) and (80) which appear to be more appropriate than equation (73) for flowing systems. However, the use of equations (79) and (80) does not improve the agreement between the predicted and actually observed values of r and L .

Figures 7 and 8 show that K_L may be expressed as either a linear or geometric function of temperature.

Figure 7 is reproduced on a larger scale in Figure 9 for the 5 data points which include replicates (16 experiments) at a velocity of 15.24 cm/sec. The geometric curve of Figure 8 is superimposed showing that both the linear and geometric fit lie within the standard deviation of 0.017 cm/min estimated from the five replicates at the center point. When this procedure was applied to the other 6 data points the geometric curve did give a better fit but both curves were well within one estimated standard deviation of the data points. This indicates that although the geometric

FIGURE 7: EFFECT OF TEMPERATURE ON K_L

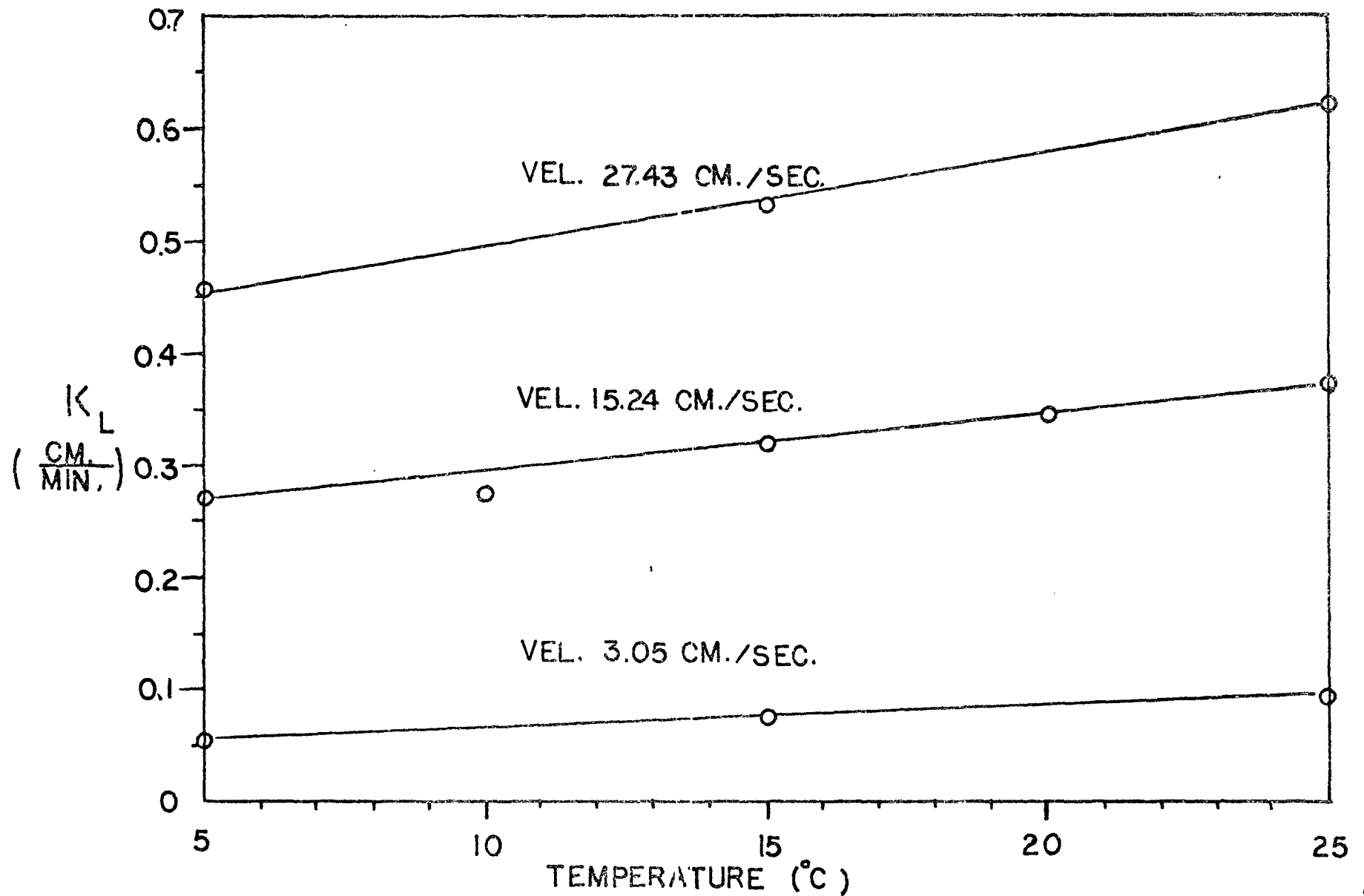


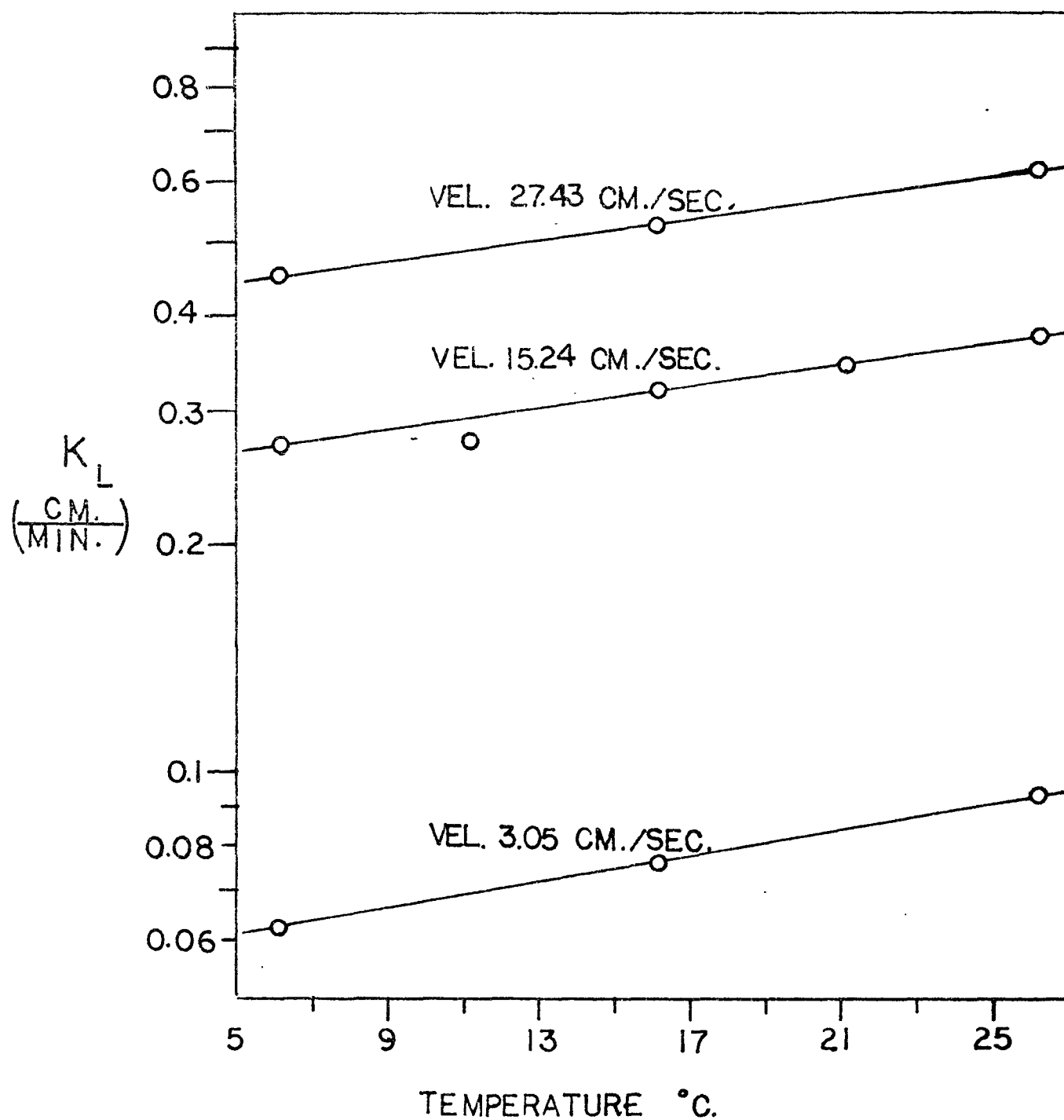
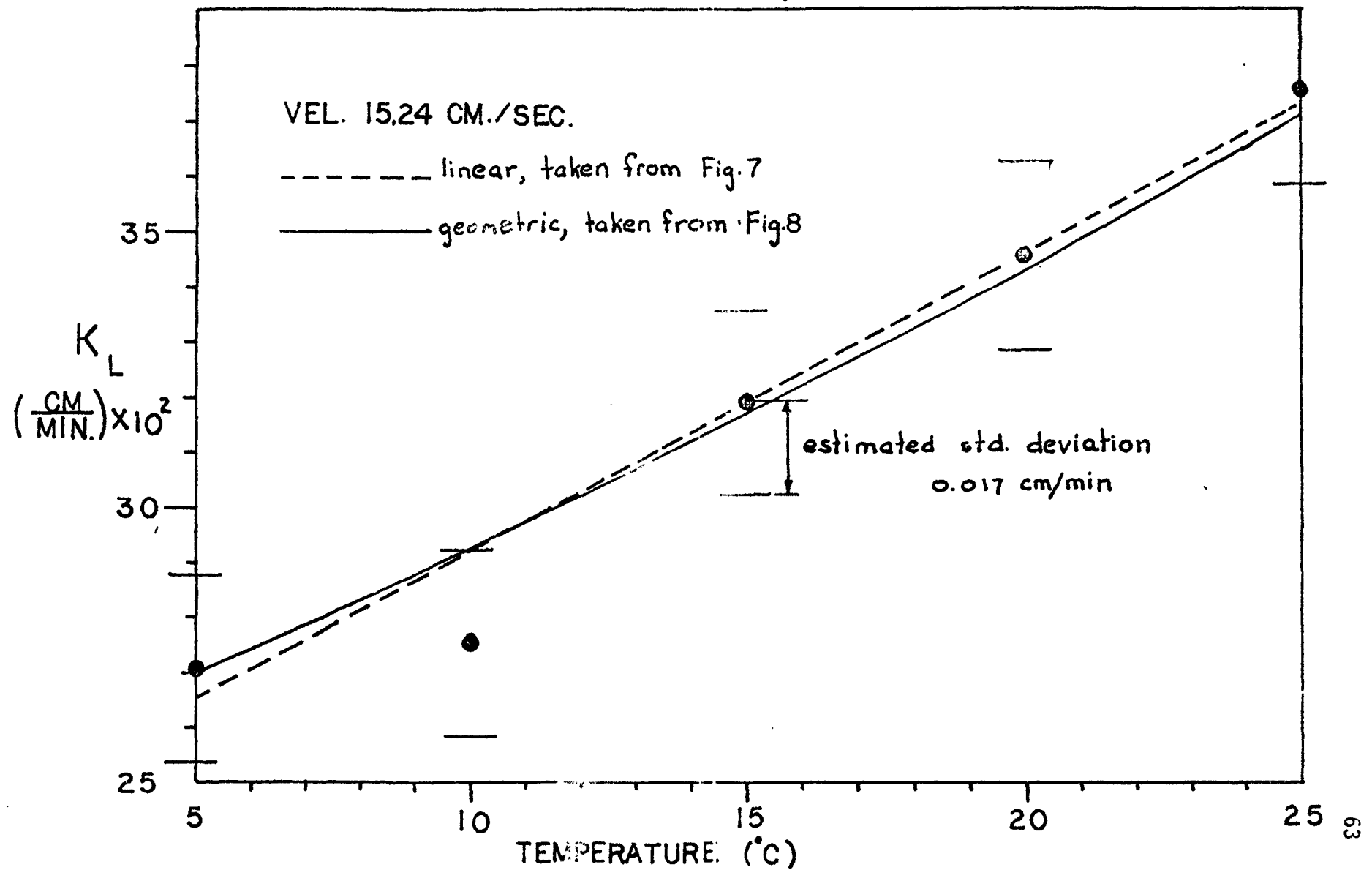
FIGURE 8 : EFFECT OF TEMPERATURE ON K_L 

FIGURE 9: EFFECT OF TEMPERATURE ON K_L
(LINEAR AND GEOMETRIC)

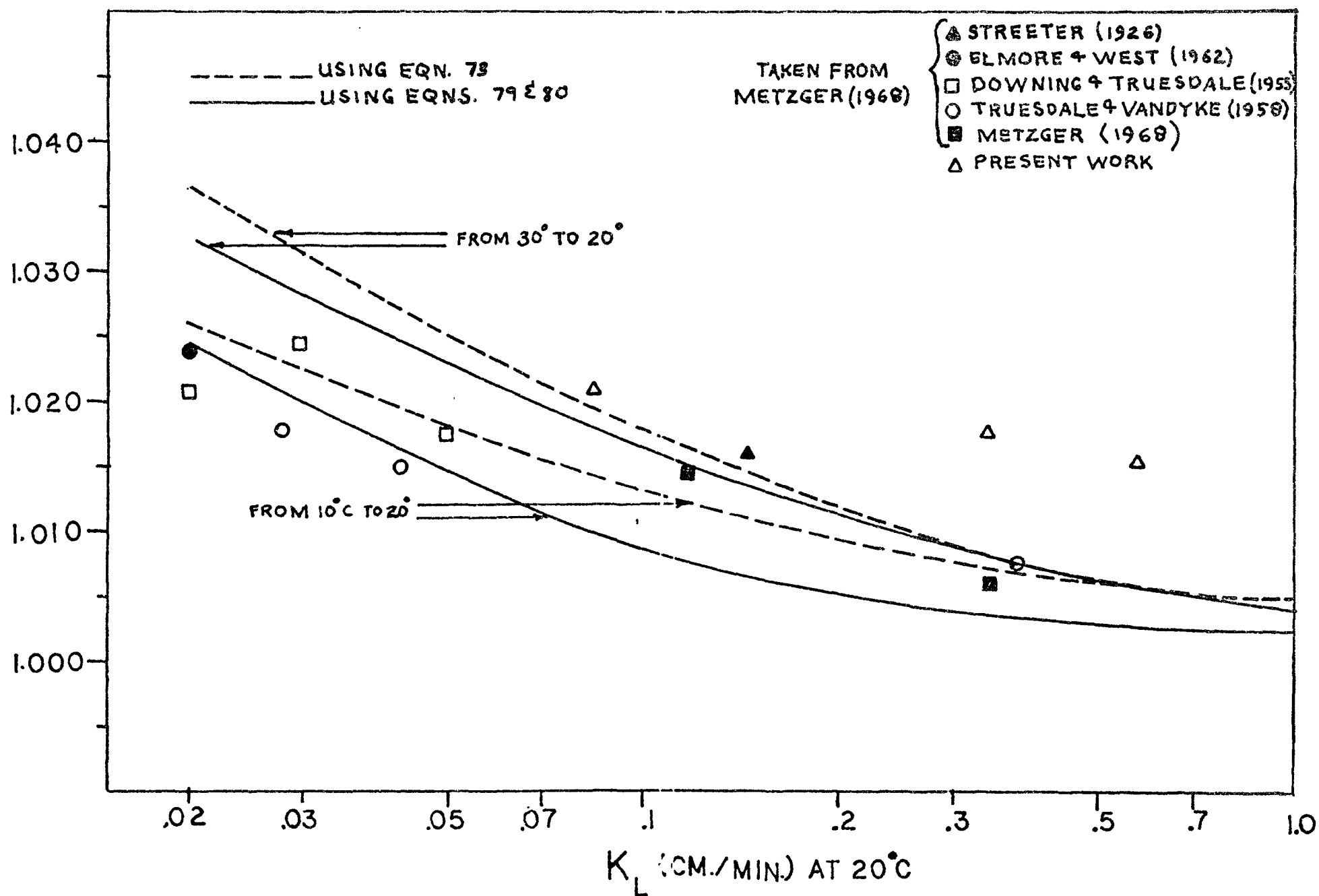


curve (which is generally accepted in the recent literature) may give a slightly better fit, the arithmetic relationship may be used for practical cases, especially in the light of the experimental error in calculating K_L .

The overall value of the temperature coefficient, θ for all twenty-two experiments as calculated by multiple regression techniques was given by equation (67) as 1.018. A linear least squares fit was applied to each set of data at velocities 3.05, 15.24 and 27.43 cm/sec and the values θ , from the slopes of the straight lines, were calculated to be 1.0209, 1.0178 and 1.0157, respectively. These results confirm the contention of Metzger and Dobbins (1967) that θ varies with mixing intensity. The values of θ obtained in this study have been superimposed on the curves taken from Metzger (1968) and those obtained using equations (79) and (80) instead of Metzger's equation (73). These are shown in Figure 10 along with the θ values obtained by other investigators. The data appear to indicate that neither set of curves apply for the experimental system used, at least in the range of high K_L values (K_L greater than about 0.1 cm/min).

It should be noted that a disparity exists between the methods of calculating the temperature coefficient θ and the comparison of θ to the theoretical values of Figure 10. When θ is calculated by taking the slope of a geometric plot of K_L versus temperature, as is the general practice, one must assume that θ is independent of level of temperature. The theoretical curves of Figure 10 indicate that θ does depend on temperature level. Then to compare observed θ values to theoretical values, θ should be calculated from individual points rather than using the slope method. To do this accurately a large number of replicates at individual points would be re-

FIGURE 10: TEMPERATURE COEFFICIENT AS A FUNCTION OF THE LEVEL OF K_L



quired because the experimental error would probably be at least 5 percent.

(D) The Effect of Surfactants

In an attempt to qualitatively evaluate the effect of surfactants on the mass transfer coefficient in flowing systems, two runs were carried out at 15.0°C and a velocity of 0.5 ft/sec with additions of concentrated solutions of sodium lauryl sulphate which had been calculated to produce overall concentrations of 50 and 100 mg/l. The values of K_L were observed to be depressed to 34.3 and 21.5 percent of the "clean" water values, respectively. The results are given in Table 5 below.

TABLE 5

Effect of Surfactants

Overall Concentration of Sodium Lauryl Sulphate (mg/l)	Surface Tension of Sample from Bulk (dynes/cm)	K_L (cm/min)
0	71.2	0.3197
50.0	67.1	0.1097
100.0	56.9	0.0688

These experiments, which were only of a preliminary nature, have produced results which are in qualitative agreement with the general consensus that surfactants usually reduce the rate of mass transfer of oxygen dissolving into flowing water.

CHAPTER 5

Conclusions and Recommendations

(A) Conclusions

1. The temperature coefficient θ depends on mixing intensity or level of turbulence (indicated by the average velocity of the stream). However, the dependency observed in this study did not follow the relationships proposed by Metzger (1968).
2. With modifications to facilitate the introduction of additives to the liquid phase, the apparatus appears to be suitable for studying the effects of surfactants on the mass transfer process of oxygen dissolution into water.
3. The observed values of the mass transfer coefficient varied approximately linearly with the average velocity of the stream for the range of velocities used. The values of K_L obtained were greater than those reported in the recent literature for rectangular cross-sections, with these values being 30 to 40 percent less than those observed in this study for equal values of average stream velocity.

(B) Recommendations

1. If this apparatus is to be used in further work investigations on the turbulence regime should be carried out. Hot wire anemometry techniques may be appropriate for this. Because these probes are available in minute sizes it is conceivable that they will not disturb the flow pattern to a significant extent. The anemometer probes should be placed in two or three positions along the control section well below the surface in order to leave the interface undisturbed. Such an investigation may provide an explanation for the rather high mass transfer rates observed.
2. A system of automatic temperature control within the recirculation loop should be incorporated into the apparatus. A thermistor controlled solenoid valve as the coolant flow regulator might accomplish this purpose.
3. Air exit valves at the bends would be desirable. Such devices would allow removal of bubbles which tend to accumulate in these locations during low velocity runs.
4. Further study with varying depths of flow would indicate the dependence of K_L on mean depth in correlations such as equations (65) through (70).
5. A study with surfactants should be carried out to develop quantitative expressions for their effect on the mass transfer coefficient.

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APPENDIX A

ORIFICE PLATE CALIBRATION CURVES

FIGURE 11: ORIFICE PLATE CALIBRATION (1/2 INCH DIA. ORIFICE)

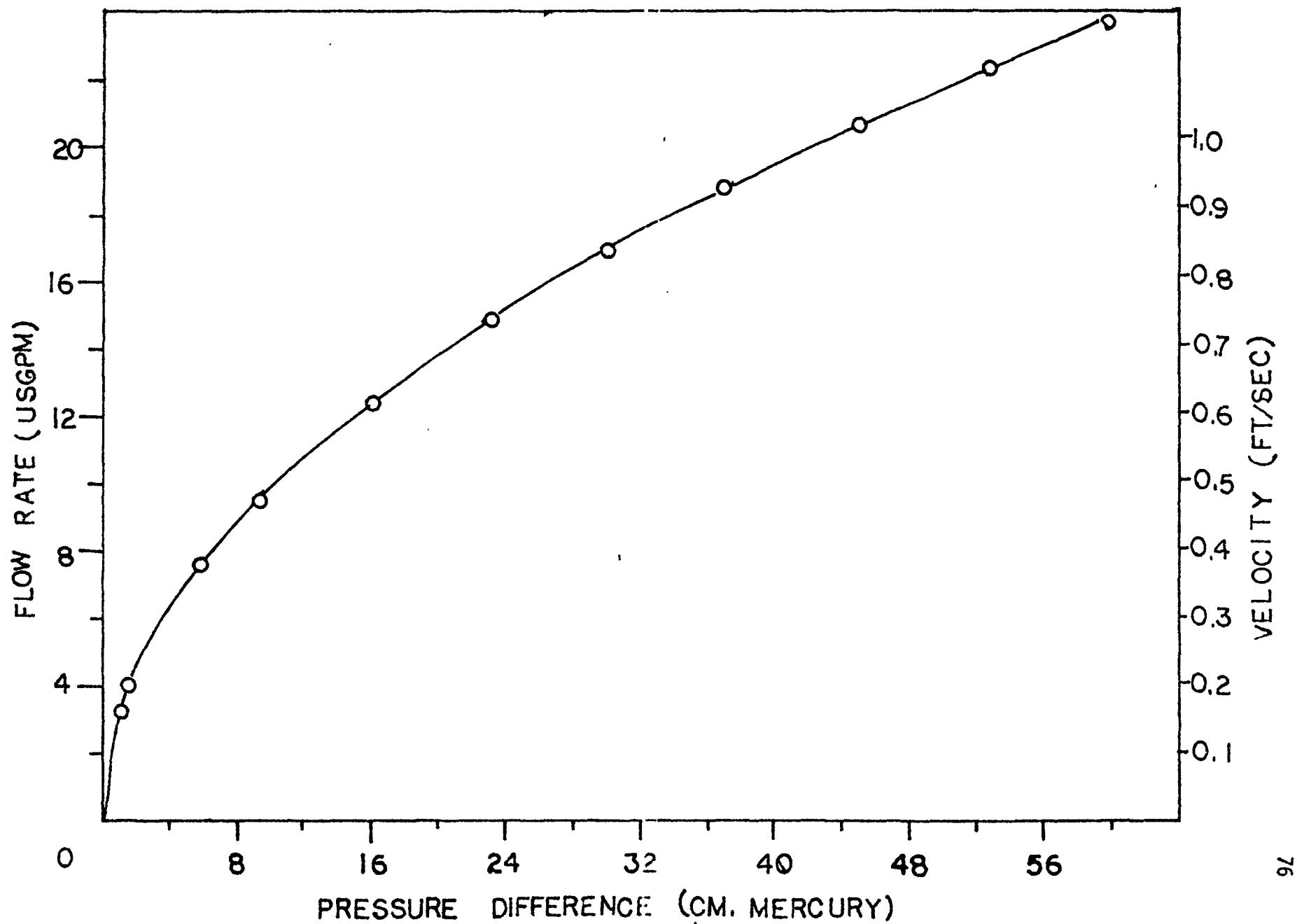
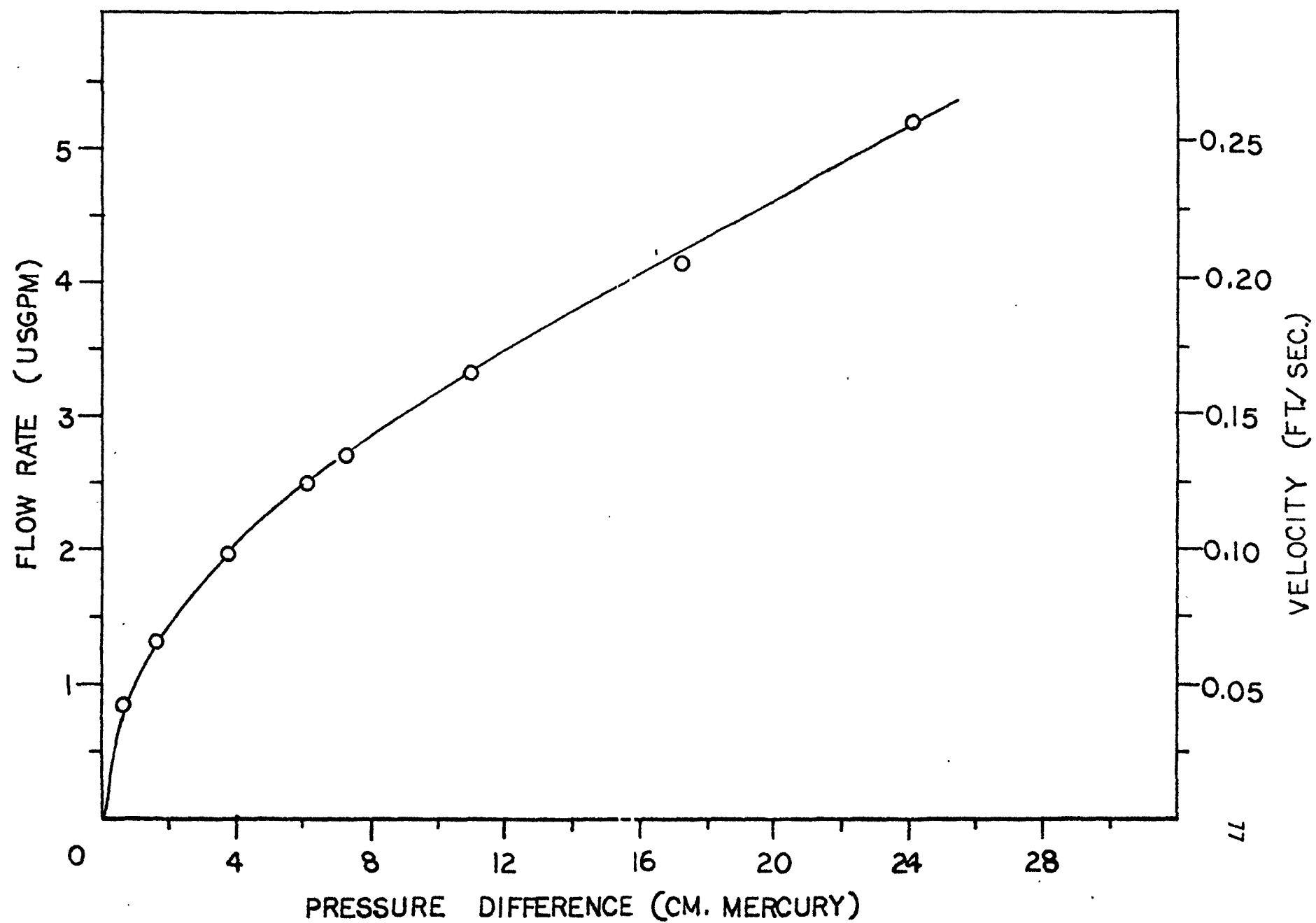


FIGURE 12: ORIFICE PLATE CALIBRATION (5/16 INCH ORIFICE DIA.)



APPENDIX B

TELE-THERMOMETER SPECIFICATIONS AND CALIBRATION CURVES

YSI Model 47 Scanning Tele-Thermometer

Specifications

1. Temperature range: 0.0 to 50.0°C.
2. Accuracy: (a) 1% of scale span at 25°C ambient temperature
(b) at ambient temperature of 5°C to 50°C, additional error will not exceed 1% of scale span
3. Readability: approximately ½% of scale span.

The calibration of the tele-thermometer increased the accuracy to the limits of readability for the entire temperature range used.

When connected to the recorder each scale division represented between 0.040 and 0.050°C, depending on the level of temperature. During experiments the temperature variations usually did not exceed 0.025°C and never exceeded 0.075°C.

FIGURE 13: TELE-THERMOMETER CALIBRATION
(4 TO 14°C)

80

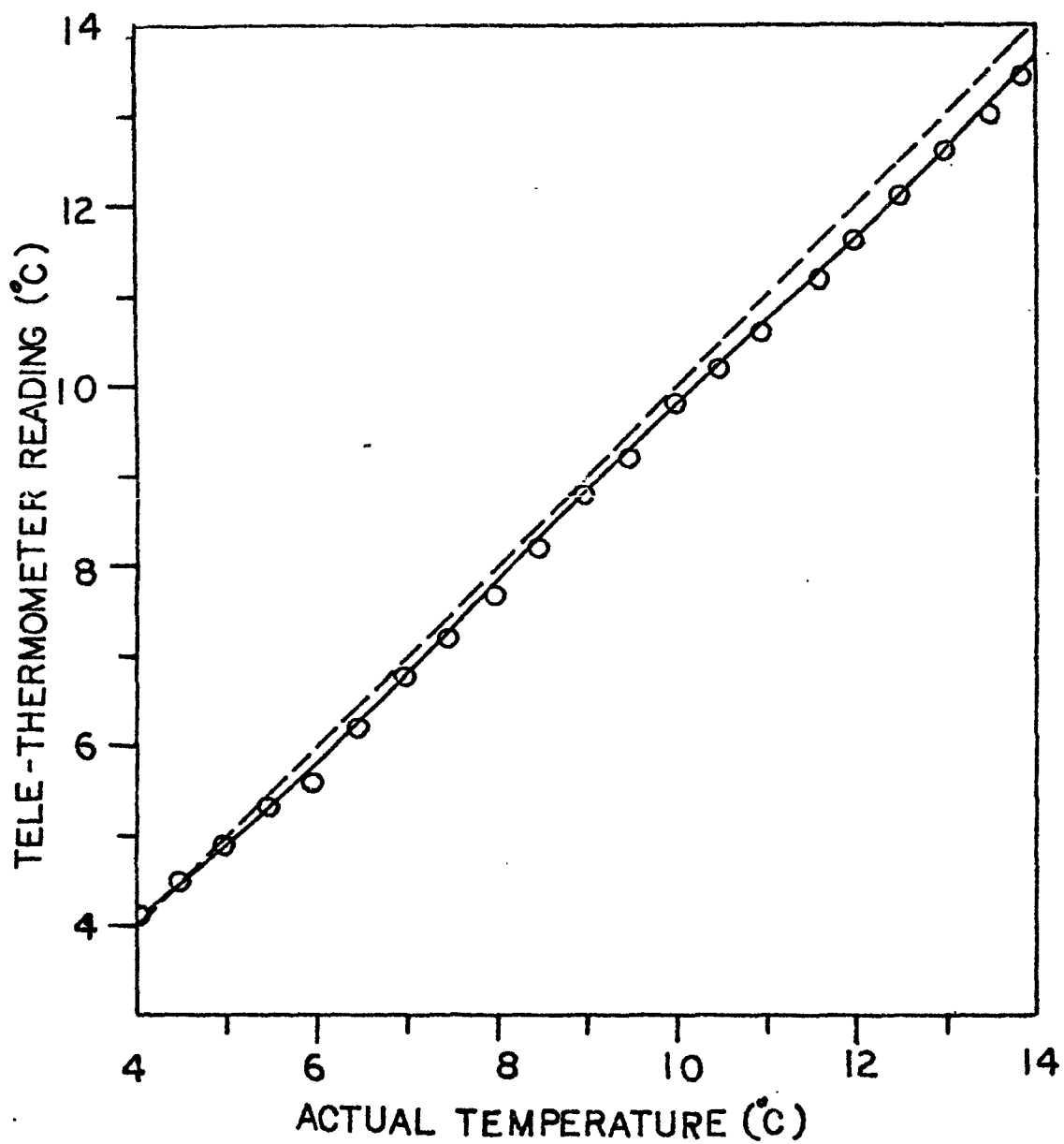
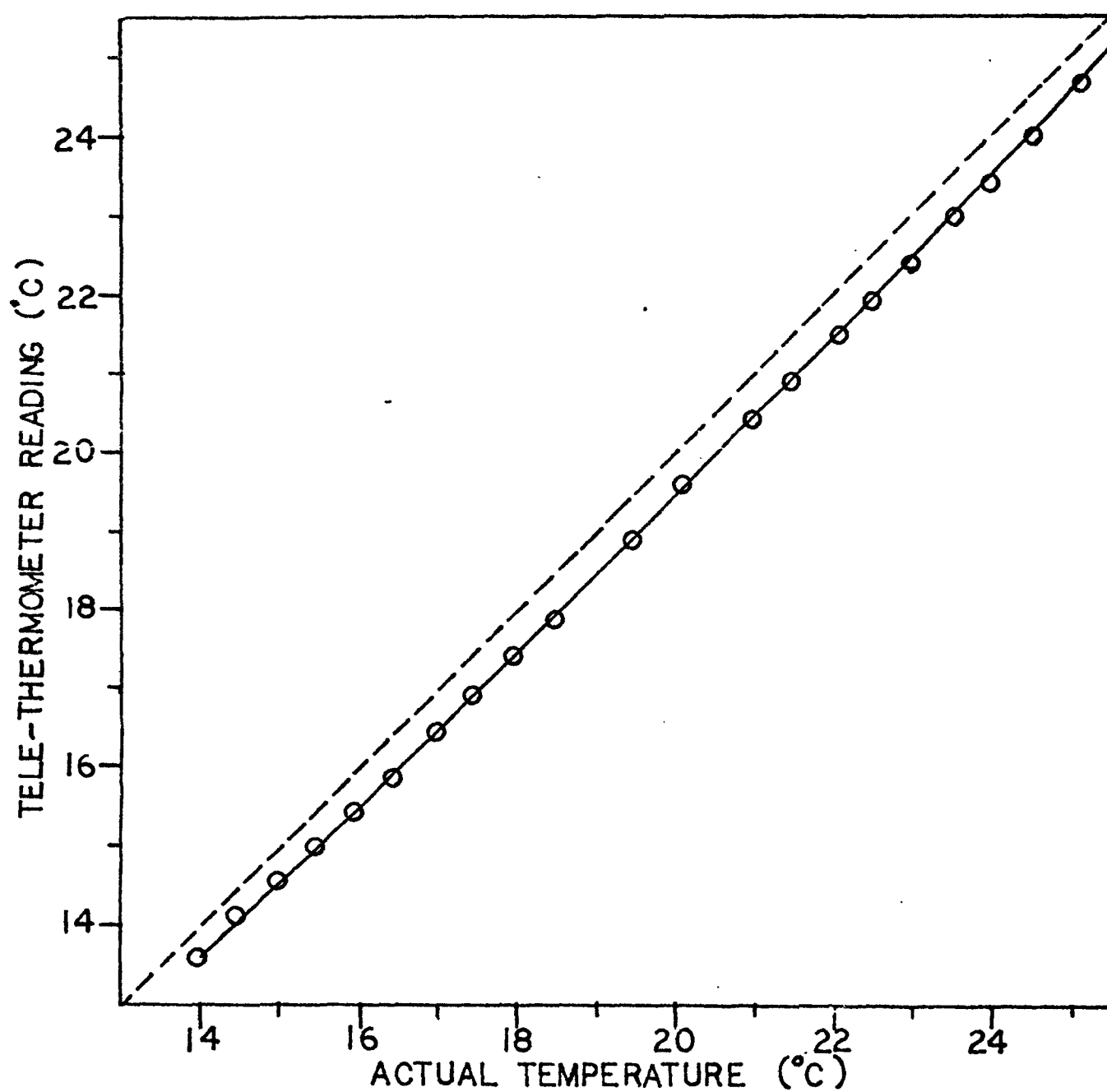


FIGURE 14: TELE-THERMOMETER CALIBRATION
(14 TO 25°C)



APPENDIX C

EXPERIMENTAL DATA

(A) Choosing Points of the Data Record

At the beginning of each experiment a lag period of between six to eight minutes preceded the normal first order oxygen absorption process. This was due, in part, to the time required for the complete change of the atmosphere within the control section from nitrogen to atmospheric air. It was also noted that when the oxygen saturation deficit became less than 0.2 mg/l considerable "scatter" occurred on the plot of natural log ($C_s - C$) versus time. This was due to semilogarithmic spacing - the "scatter" of observed values of equal arithmetic error increase towards the lower end of the semilog scale. Consequently, these low values of the saturation deficit are less useful for the accurate determination of the slope of the line. Accordingly, the portion of the oxygen concentration curve used for analysis was taken from the reading at eight minutes (called zero time in Table 6.) to a reading at which the deficit was still greater than 0.2 mg/l.

Thirty points at equal time intervals were read off the data record within this region of interest. In some preliminary runs fifteen, thirty and sixty points were used in the calculations but no significant differences were observed in the K_L values obtained. Taking sixty data points for the experiments at a velocity 0.9 ft/sec was rather inconvenient because these runs were completed in less than one hour. It was decided to take thirty points for all experiments because only a small amount of additional work was required in using thirty rather than fifteen

points. The data are presented in Table 6.

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
25.00000	.90000	0.00000	3.25000	1.59534	
25.00000	.90000	1.00000	3.65000	1.51172	.08462
25.00000	.90000	2.00000	3.99000	1.43270	.07802
25.00000	.90000	3.00000	4.35000	1.34286	.08984
25.00000	.90000	4.00000	4.68000	1.25276	.09010
25.00000	.90000	5.00000	5.03000	1.14740	.10536
25.00000	.90000	6.00000	5.29000	1.06126	.08615
25.00000	.90000	7.00000	5.55000	.96698	.09427
25.00000	.90000	8.00000	5.79000	.87129	.09569
25.00000	.90000	9.00000	6.04000	.76681	.11049
25.00000	.90000	10.00000	6.26000	.65233	.10848
25.00000	.90000	11.00000	6.43000	.55962	.09271
25.00000	.90000	12.00000	6.60000	.45742	.10219
25.00000	.90000	13.00000	6.73000	.37156	.08586
25.00000	.90000	14.00000	6.88000	.26236	.10920
25.00000	.90000	15.00000	7.00000	.16551	.09685
25.00000	.90000	16.00000	7.13000	.04879	.11672
25.00000	.90000	17.00000	7.22000	-.04682	.08961
25.00000	.90000	18.00000	7.31000	-.13926	.09844
25.00000	.90000	19.00000	7.42000	-.27444	.13517
25.00000	.90000	20.00000	7.49000	-.37106	.09663
25.00000	.90000	21.00000	7.56000	-.47804	.10697
25.00000	.90000	22.00000	7.61000	-.56212	.08408
25.00000	.90000	23.00000	7.67000	-.67334	.11123
25.00000	.90000	24.00000	7.72000	-.77653	.10318
25.00000	.90000	25.00000	7.77000	-.89160	.11507
25.00000	.90000	26.00000	7.82000	-1.02165	.13005
25.00000	.90000	27.00000	7.84000	-1.07881	.05716
25.00000	.90000	28.00000	7.87000	-1.17118	.09237
25.00000	.90000	29.00000	7.90000	-1.27297	.10178

1

KL= -.6232565067

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
25.00000	.50000	0.00000	2.40000	1.75440	
25.00000	.50000	2.00000	2.92000	1.66613	.09427
25.00000	.50000	4.00000	3.40000	1.56444	.09569
25.00000	.50000	6.00000	3.88000	1.45862	.10583
25.00000	.50000	8.00000	4.32000	1.35667	.10795
25.00000	.50000	10.00000	4.72000	1.24127	.10940
25.00000	.50000	12.00000	5.36000	1.03674	.20453
25.00000	.50000	14.00000	5.44000	1.00796	.02878
25.00000	.50000	16.00000	5.78000	.87547	.13249
25.00000	.50000	18.00000	6.06000	.75142	.12405
25.00000	.50000	20.00000	6.33000	.61519	.13623
25.00000	.50000	22.00000	6.53000	.50078	.11441
25.00000	.50000	24.00000	6.72000	.37844	.12234
25.00000	.50000	26.00000	6.88000	.26236	.11607
25.00000	.50000	28.00000	7.02000	.14842	.11394
25.00000	.50000	30.00000	7.17000	.00995	.13847
25.00000	.50000	32.00000	7.29000	-.11653	.12648
25.00000	.50000	34.00000	7.38000	-.22314	.10661
25.00000	.50000	36.00000	7.47000	-.34249	.11935
25.00000	.50000	38.00000	7.55000	-.46204	.11955
25.00000	.50000	40.00000	7.63000	-.59784	.13580
25.00000	.50000	42.00000	7.70000	-.73397	.13613
25.00000	.50000	44.00000	7.76000	-.86750	.13353
25.00000	.50000	46.00000	7.80000	-.96758	.10008
25.00000	.50000	48.00000	7.85000	-1.10866	.14108
25.00000	.50000	50.00000	7.89000	-1.23787	.12921
25.00000	.50000	52.00000	7.93000	-1.38629	.14842
25.00000	.50000	54.00000	7.96000	-1.51413	.12783
25.00000	.50000	56.00000	7.99000	-1.66073	.14660
25.00000	.50000	58.00000	8.01000	-1.77196	.11123

2

KL= -.3787058867

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
25.000000	.500000	0.000000	2.530000	1.73166	
25.000000	.500000	2.000000	3.050000	1.53511	.09655
25.000000	.500000	4.000000	3.550000	1.53256	.10255
25.000000	.500000	6.000000	4.020000	1.42552	.10704
25.000000	.500000	8.000000	4.450000	1.31641	.10911
25.000000	.500000	10.000000	4.860000	1.19996	.11644
25.000000	.500000	12.000000	5.220000	1.08519	.11478
25.000000	.500000	14.000000	5.560000	.96317	.12201
25.000000	.500000	16.000000	5.840000	.85615	.11302
25.000000	.500000	18.000000	6.100000	.73237	.11778
25.000000	.500000	20.000000	6.360000	.59884	.13353
25.000000	.500000	22.000000	6.570000	.47623	.12260
25.000000	.500000	24.000000	6.760000	.35166	.12558
25.000000	.500000	26.000000	6.910000	.23902	.11164
25.000000	.500000	28.000000	7.060000	.11333	.12569
25.000000	.500000	30.000000	7.180000	0.00000	.11333
25.000000	.500000	32.000000	7.280000	-.10536	.10536
25.000000	.500000	34.000000	7.380000	-.22314	.11778
25.000000	.500000	36.000000	7.470000	-.34249	.11935
25.000000	.500000	38.000000	7.550000	-.46204	.11955
25.000000	.500000	40.000000	7.630000	-.59784	.13580
25.000000	.500000	42.000000	7.710000	-.75502	.15719
25.000000	.500000	44.000000	7.740000	-.82093	.06596
25.000000	.500000	46.000000	7.790000	-.94161	.12063
25.000000	.500000	48.000000	7.830000	-1.04982	.10821
25.000000	.500000	50.000000	7.880000	-1.20397	.15415
25.000000	.500000	52.000000	7.920000	-1.34707	.14310
25.000000	.500000	54.000000	7.950000	-1.46968	.12260
25.000000	.500000	56.000000	7.990000	-1.66073	.19106
25.000000	.500000	58.000000	8.020000	-1.83258	.17185

KL= -.3729879689

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
25.000000	.100000	0.000000	1.800000	1.85317	
25.000000	.100000	5.000000	2.240000	1.78171	.07146
25.000000	.100000	10.000000	2.640000	1.71199	.06971
25.000000	.100000	15.000000	3.020000	1.64194	.07106
25.000000	.100000	20.000000	3.370000	1.57170	.07024
25.000000	.100000	25.000000	3.690000	1.50185	.06834
25.000000	.100000	30.000000	4.000000	1.43031	.07154
25.000000	.100000	35.000000	4.260000	1.36609	.06422
25.000000	.100000	40.000000	4.530000	1.29473	.07135
25.000000	.100000	45.000000	4.770000	1.22671	.06801
25.000000	.100000	50.000000	5.020000	1.15057	.07614
25.000000	.100000	55.000000	5.240000	1.07841	.07216
25.000000	.100000	60.000000	5.450000	1.00430	.07411
25.000000	.100000	65.000000	5.650000	.92622	.07608
25.000000	.100000	70.000000	5.830000	.85442	.07380
25.000000	.100000	75.000000	6.000000	.77932	.07509
25.000000	.100000	80.000000	6.160000	.70310	.07623
25.000000	.100000	85.000000	6.300000	.63127	.07183
25.000000	.100000	90.000000	6.440000	.55389	.07739
25.000000	.100000	95.000000	6.570000	.47623	.07765
25.000000	.100000	100.000000	6.690000	.39878	.07746
25.000000	.100000	105.000000	6.800000	.32208	.07669
25.000000	.100000	110.000000	6.910000	.23902	.08307
25.000000	.100000	115.000000	7.020000	.14842	.09060
25.000000	.100000	120.000000	7.110000	.06766	.08076
25.000000	.100000	125.000000	7.210000	-.03046	.09012
25.000000	.100000	130.000000	7.290000	-.11653	.08607
25.000000	.100000	135.000000	7.360000	-.19845	.08192
25.000000	.100000	140.000000	7.410000	-.26136	.06291
25.000000	.100000	145.000000	7.450000	-.31471	.05335

KL= -.0934135907

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
20.000000	.500000	0.000000	2.640000	1.85317	
20.000000	.500000	2.000000	3.190000	1.76302	.09015
20.000000	.500000	4.000000	3.740000	1.66393	.09909
20.000000	.500000	6.000000	4.220000	1.56862	.09531
20.000000	.500000	8.000000	4.700000	1.46326	.10536
20.000000	.500000	10.000000	5.090000	1.36864	.09462
20.000000	.500000	12.000000	5.480000	1.26413	.10451
20.000000	.500000	14.000000	5.820000	1.16315	.10098
20.000000	.500000	16.000000	6.170000	1.04732	.11583
20.000000	.500000	18.000000	6.420000	.95551	.09181
20.000000	.500000	20.000000	6.660000	.85866	.09685
20.000000	.500000	22.000000	6.880000	.76081	.09786
20.000000	.500000	24.000000	7.130000	.63658	.12423
20.000000	.500000	26.000000	7.340000	.51879	.11778
20.000000	.500000	28.000000	7.500000	.41871	.10008
20.000000	.500000	30.000000	7.670000	.30610	.11861
20.000000	.500000	32.000000	7.800000	.19885	.10125
20.000000	.500000	34.000000	7.920000	.09531	.10354
20.000000	.500000	36.000000	8.030000	-.01105	.10536
20.000000	.500000	38.000000	8.120000	-.10536	.09531
20.000000	.500000	40.000000	8.210000	-.21072	.10536
20.000000	.500000	42.000000	8.270000	-.28768	.07696
20.000000	.500000	44.000000	8.350000	-.40048	.11280
20.000000	.500000	46.000000	8.420000	-.51083	.11035
20.000000	.500000	48.000000	8.490000	-.63488	.12405
20.000000	.500000	50.000000	8.550000	-.75502	.12014
20.000000	.500000	52.000000	8.610000	-.89160	.13658
20.000000	.500000	54.000000	8.650000	-.99425	.10265
20.000000	.500000	56.000000	8.690000	-1.10866	.11441
20.000000	.500000	58.000000	8.730000	-1.23787	.12921

KL= -.3274163324

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
20.000000	.500000	0.000000	2.730000	1.83896	
20.000000	.500000	2.000000	3.320000	1.74047	.09849
20.000000	.500000	4.000000	3.880000	1.63705	.10341
20.000000	.500000	6.000000	4.410000	1.52823	.10883
20.000000	.500000	8.000000	4.880000	1.42070	.10753
20.000000	.500000	10.000000	5.380000	1.29198	.12871
20.000000	.500000	12.000000	5.790000	1.17248	.11950
20.000000	.500000	14.000000	6.130000	1.06126	.11123
20.000000	.500000	16.000000	6.430000	.95166	.10960
20.000000	.500000	18.000000	6.710000	.83725	.11441
20.000000	.500000	20.000000	6.980000	.71295	.12430
20.000000	.500000	22.000000	7.210000	.59333	.11962
20.000000	.500000	24.000000	7.400000	.48243	.11090
20.000000	.500000	26.000000	7.550000	.38526	.09716
20.000000	.500000	28.000000	7.720000	.26236	.12290
20.000000	.500000	30.000000	7.850000	.13700	.10536
20.000000	.500000	32.000000	7.970000	.04879	.10821
20.000000	.500000	34.000000	8.090000	-.07257	.12136
20.000000	.500000	36.000000	8.190000	-.18633	.11376
20.000000	.500000	38.000000	8.270000	-.28768	.10135
20.000000	.500000	40.000000	8.350000	-.40048	.11280
20.000000	.500000	42.000000	8.430000	-.52763	.12716
20.000000	.500000	44.000000	8.500000	-.65393	.12629
20.000000	.500000	46.000000	8.550000	-.75502	.10110
20.000000	.500000	48.000000	8.600000	-.86750	.11248
20.000000	.500000	50.000000	8.650000	-.99425	.12675
20.000000	.500000	52.000000	8.700000	-1.13943	.14518
20.000000	.500000	54.000000	8.740000	-1.27297	.13353
20.000000	.500000	56.000000	8.780000	-1.42712	.15415
20.000000	.500000	58.000000	8.810000	-1.56065	.13353

KL= -.3570455402

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
20.000000	.500000	0.000000	2.900000	1.81156	
20.000000	.500000	2.000000	3.510000	1.70656	.10500
20.000000	.500000	4.000000	4.100000	1.59331	.11326
20.000000	.500000	6.000000	4.600000	1.48614	.10717
20.000000	.500000	8.000000	5.070000	1.37372	.11242
20.000000	.500000	10.000000	5.500000	1.25846	.11525
20.000000	.500000	12.000000	5.900000	1.13783	.12063
20.000000	.500000	14.000000	6.240000	1.02245	.11538
20.000000	.500000	16.000000	6.540000	.90826	.11419
20.000000	.500000	18.000000	6.820000	.78846	.11980
20.000000	.500000	20.000000	7.080000	.66269	.12577
20.000000	.500000	22.000000	7.300000	.54232	.12036
20.000000	.500000	24.000000	7.500000	.41871	.12361
20.000000	.500000	26.000000	7.660000	.30748	.11123
20.000000	.500000	28.000000	7.800000	.19885	.10863
20.000000	.500000	30.000000	7.920000	.09531	.10354
20.000000	.500000	32.000000	8.030000	-.01105	.10536
20.000000	.500000	34.000000	8.140000	-.12783	.11778
20.000000	.500000	36.000000	8.220000	-.22314	.09531
20.000000	.500000	38.000000	8.310000	-.34249	.11935
20.000000	.500000	40.000000	8.400000	-.47804	.13555
20.000000	.500000	42.000000	8.480000	-.61619	.13815
20.000000	.500000	44.000000	8.530000	-.71335	.09716
20.000000	.500000	46.000000	8.580000	-.82098	.10763
20.000000	.500000	48.000000	8.620000	-.91629	.09531
20.000000	.500000	50.000000	8.670000	-1.04982	.13353
20.000000	.500000	52.000000	8.710000	-1.17118	.12136
20.000000	.500000	54.000000	8.740000	-1.27297	.10178
20.000000	.500000	56.000000	8.770000	-1.38629	.11333
20.000000	.500000	58.000000	8.790000	-1.46968	.08338

KL= -.3537987043

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.900000	0.000000	3.970000	1.80171	
15.000000	.900000	1.000000	4.420000	1.72455	.07716
15.000000	.900000	2.000000	4.850000	1.64481	.07975
15.000000	.900000	3.000000	5.260000	1.56235	.08246
15.000000	.900000	4.000000	5.850000	1.42792	.13443
15.000000	.900000	5.000000	6.000000	1.39377	.03415
15.000000	.900000	6.000000	6.340000	1.30563	.08814
15.000000	.900000	7.000000	6.670000	1.21194	.09369
15.000000	.900000	8.000000	6.990000	1.11186	.10008
15.000000	.900000	9.000000	7.290000	1.00796	.10390
15.000000	.900000	10.000000	7.530000	.91629	.09167
15.000000	.900000	11.000000	7.720000	.83725	.07904
15.000000	.900000	12.000000	7.910000	.75142	.08583
15.000000	.900000	13.000000	8.090000	.66269	.08873
15.000000	.900000	14.000000	8.250000	.57661	.08607
15.000000	.900000	15.000000	8.410000	.48243	.09419
15.000000	.900000	16.000000	8.550000	.39204	.09038
15.000000	.900000	17.000000	8.680000	.30010	.09194
15.000000	.900000	18.000000	8.800000	.20701	.09309
15.000000	.900000	19.000000	8.890000	.13103	.07599
15.000000	.900000	20.000000	8.980000	.04879	.08224
15.000000	.900000	21.000000	9.040000	-.01105	.05884
15.000000	.900000	22.000000	9.130000	-.10536	.09531
15.000000	.900000	23.000000	9.220000	-.21072	.10535
15.000000	.900000	24.000000	9.270000	-.27444	.06372
15.000000	.900000	25.000000	9.320000	-.34249	.06805
15.000000	.900000	26.000000	9.380000	-.43078	.08029
15.000000	.900000	27.000000	9.430000	-.51083	.08004
15.000000	.900000	28.000000	9.480000	-.59784	.08751
15.000000	.900000	29.000000	9.510000	-.65393	.05509

KL= -.5329520196

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
15.00000	.75000	0.00000	4.02000	1.79342	
15.00000	.75000	1.00000	4.38000	1.73166	.06177
15.00000	.75000	2.00000	4.74000	1.66582	.06584
15.00000	.75000	3.00000	5.07000	1.60141	.06441
15.00000	.75000	4.00000	5.39000	1.53471	.06669
15.00000	.75000	5.00000	5.70000	1.46557	.06915
15.00000	.75000	6.00000	6.01000	1.39128	.07429
15.00000	.75000	7.00000	6.27000	1.32442	.06686
15.00000	.75000	8.00000	6.52000	1.25562	.06880
15.00000	.75000	9.00000	6.78000	1.17865	.07696
15.00000	.75000	10.00000	7.04000	1.09527	.08338
15.00000	.75000	11.00000	7.29000	1.02245	.07282
15.00000	.75000	12.00000	7.43000	.95551	.06694
15.00000	.75000	13.00000	7.62000	.87963	.07588
15.00000	.75000	14.00000	7.76000	.81578	.05985
15.00000	.75000	15.00000	7.90000	.75612	.06366
15.00000	.75000	16.00000	8.04000	.68813	.06799
15.00000	.75000	17.00000	8.19000	.60977	.07837
15.00000	.75000	18.00000	8.33000	.53063	.07914
15.00000	.75000	19.00000	8.45000	.45742	.07320
15.00000	.75000	20.00000	8.57000	.37844	.07899
15.00000	.75000	21.00000	8.66000	.31481	.06363
15.00000	.75000	22.00000	8.75000	.24686	.06795
15.00000	.75000	23.00000	8.85000	.16551	.08135
15.00000	.75000	24.00000	8.93000	.09531	.07020
15.00000	.75000	25.00000	8.98000	.04879	.04652
15.00000	.75000	26.00000	9.05000	-.02020	.06899
15.00000	.75000	27.00000	9.12000	-.09431	.07411
15.00000	.75000	28.00000	9.18000	-.16252	.06821
15.00000	.75000	29.00000	9.23000	-.22314	.06062

KL= -.4366340047

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TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
15.00000	.50000	0.00000	2.98000	1.95303	
15.00000	.50000	2.00000	3.60000	1.86097	.09205
15.00000	.50000	4.00000	4.15000	1.77156	.08942
15.00000	.50000	6.00000	4.72000	1.66959	.10196
15.00000	.50000	8.00000	5.23000	1.56862	.10098
15.00000	.50000	10.00000	5.71000	1.46326	.10536
15.00000	.50000	12.00000	6.14000	1.35841	.10485
15.00000	.50000	14.00000	6.54000	1.24990	.10851
15.00000	.50000	16.00000	6.88000	1.14740	.10250
15.00000	.50000	18.00000	7.21000	1.03674	.11067
15.00000	.50000	20.00000	7.49000	.93216	.10457
15.00000	.50000	22.00000	7.75000	.82418	.10799
15.00000	.50000	24.00000	7.96000	.72755	.09663
15.00000	.50000	26.00000	8.17000	.62058	.10697
15.00000	.50000	28.00000	8.33000	.53063	.08995
15.00000	.50000	30.00000	8.50000	.42527	.10536
15.00000	.50000	32.00000	8.63000	.33647	.08080
15.00000	.50000	34.00000	8.77000	.23111	.10536
15.00000	.50000	36.00000	8.89000	.13103	.10008
15.00000	.50000	38.00000	9.02000	.00995	.12108
15.00000	.50000	40.00000	9.11000	-.08338	.09333
15.00000	.50000	42.00000	9.20000	-.18633	.10295
15.00000	.50000	44.00000	9.27000	-.27444	.08811
15.00000	.50000	46.00000	9.34000	-.37106	.09663
15.00000	.50000	48.00000	9.43000	-.51083	.13976
15.00000	.50000	50.00000	9.51000	-.65393	.14310
15.00000	.50000	52.00000	9.55000	-.73397	.08004
15.00000	.50000	54.00000	9.58000	-.79851	.06454
15.00000	.50000	56.00000	9.62000	-.89160	.09309
15.00000	.50000	58.00000	9.66000	-.99425	.10265

KL= -.3174454549

10

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.500000	0.000000	2.930000	1.96009	
15.000000	.500000	2.000000	3.640000	1.85473	.10536
15.000000	.500000	4.000000	4.270000	1.75094	.10380
15.000000	.500000	6.000000	4.830000	1.64666	.10228
15.000000	.500000	8.000000	5.380000	1.53687	.11179
15.000000	.500000	10.000000	5.840000	1.43270	.10417
15.000000	.500000	12.000000	6.230000	1.33500	.09770
15.000000	.500000	14.000000	6.640000	1.22683	.11417
15.000000	.500000	16.000000	7.010000	1.10526	.11557
15.000000	.500000	18.000000	7.340000	.98954	.11572
15.000000	.500000	20.000000	7.640000	.87129	.11825
15.000000	.500000	22.000000	7.910000	.75142	.11988
15.000000	.500000	24.000000	8.170000	.62058	.13084
15.000000	.500000	26.000000	8.350000	.51879	.10178
15.000000	.500000	28.000000	8.510000	.41871	.10008
15.000000	.500000	30.000000	8.660000	.31481	.10390
15.000000	.500000	32.000000	8.790000	.21511	.09970
15.000000	.500000	34.000000	8.900000	.12222	.09289
15.000000	.500000	36.000000	9.020000	.00995	.11227
15.000000	.500000	38.000000	9.150000	-.12783	.13778
15.000000	.500000	40.000000	9.260000	-.26136	.13353
15.000000	.500000	42.000000	9.350000	-.38566	.12430
15.000000	.500000	44.000000	9.440000	-.52763	.14197
15.000000	.500000	46.000000	9.500000	-.63488	.10725
15.000000	.500000	48.000000	9.560000	-.75502	.12014
15.000000	.500000	50.000000	9.600000	-.84397	.08895
15.000000	.500000	52.000000	9.640000	-.94161	.09764
15.000000	.500000	54.000000	9.670000	-1.02165	.08004
15.000000	.500000	56.000000	9.690000	-1.07881	.05716
15.000000	.500000	58.000000	9.710000	-1.13943	.06062

11.

KL= -.3436027664

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.500000	0.000000	2.820000	1.97547	
15.000000	.500000	2.000000	3.410000	1.89010	.08537
15.000000	.500000	4.000000	4.050000	1.78842	.10167
15.000000	.500000	6.000000	4.590000	1.69378	.09464
15.000000	.500000	8.000000	5.080000	1.59939	.09439
15.000000	.500000	10.000000	5.500000	1.49290	.10648
15.000000	.500000	12.000000	5.960000	1.40364	.08926
15.000000	.500000	14.000000	6.370000	1.29746	.10618
15.000000	.500000	16.000000	6.720000	1.19695	.10051
15.000000	.500000	18.000000	7.030000	1.09861	.09834
15.000000	.500000	20.000000	7.360000	.98208	.11653
15.000000	.500000	22.000000	7.620000	.87963	.10245
15.000000	.500000	24.000000	7.840000	.78390	.09573
15.000000	.500000	26.000000	8.050000	.68310	.10080
15.000000	.500000	28.000000	8.230000	.58779	.09531
15.000000	.500000	30.000000	8.410000	.48243	.10536
15.000000	.500000	32.000000	8.550000	.39204	.09038
15.000000	.500000	34.000000	8.670000	.30748	.08456
15.000000	.500000	36.000000	8.790000	.21511	.09237
15.000000	.500000	38.000000	8.910000	.11333	.10178
15.000000	.500000	40.000000	9.030000	0.00000	.11333
15.000000	.500000	42.000000	9.130000	-.10536	.10536
15.000000	.500000	44.000000	9.240000	-.23572	.13036
15.000000	.500000	46.000000	9.340000	-.37106	.13534
15.000000	.500000	48.000000	9.430000	-.51083	.13976
15.000000	.500000	50.000000	9.500000	-.63488	.12405
15.000000	.500000	52.000000	9.550000	-.73397	.09909
15.000000	.500000	54.000000	9.580000	-.79851	.06454
15.000000	.500000	56.000000	9.610000	-.86750	.06899
15.000000	.500000	58.000000	9.640000	-.94161	.07411

12

KL= -.3178184957

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.500000	0.000000	2.710000	1.99061	
15.000000	.500000	2.000000	3.310000	1.90509	.08552
15.000000	.500000	4.000000	3.880000	1.81645	.08864
15.000000	.500000	6.000000	4.400000	1.72811	.08834
15.000000	.500000	8.000000	4.890000	1.63705	.09106
15.000000	.500000	10.000000	5.400000	1.53256	.10450
15.000000	.500000	12.000000	5.880000	1.42311	.10945
15.000000	.500000	14.000000	6.240000	1.33237	.09074
15.000000	.500000	16.000000	6.610000	1.22964	.10273
15.000000	.500000	18.000000	6.940000	1.12817	.10147
15.000000	.500000	20.000000	7.230000	1.02962	.09855
15.000000	.500000	22.000000	7.520000	.92028	.10934
15.000000	.500000	24.000000	7.790000	.80648	.11381
15.000000	.500000	26.000000	8.010000	.70310	.10338
15.000000	.500000	28.000000	8.210000	.59884	.10426
15.000000	.500000	30.000000	8.380000	.50078	.09806
15.000000	.500000	32.000000	8.530000	.40547	.09531
15.000000	.500000	34.000000	8.680000	.30110	.10536
15.000000	.500000	36.000000	8.800000	.20701	.09309
15.000000	.500000	38.000000	8.920000	.10436	.10265
15.000000	.500000	40.000000	9.020000	.00995	.09441
15.000000	.500000	42.000000	9.130000	-.10536	.11531
15.000000	.500000	44.000000	9.230000	-.22314	.11778
15.000000	.500000	46.000000	9.320000	-.34249	.11935
15.000000	.500000	48.000000	9.390000	-.44629	.10380
15.000000	.500000	50.000000	9.450000	-.54473	.09844
15.000000	.500000	52.000000	9.490000	-.61819	.07146
15.000000	.500000	54.000000	9.540000	-.71335	.09716
15.000000	.500000	56.000000	9.580000	-.79851	.08516
15.000000	.500000	58.000000	9.630000	-.91629	.11778

KL= -.3144910271

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.500000	0.000000	2.770000	1.98238	
15.000000	.500000	2.000000	3.350000	1.89912	.08326
15.000000	.500000	4.000000	3.930000	1.80829	.09083
15.000000	.500000	6.000000	4.480000	1.71380	.09449
15.000000	.500000	8.000000	4.970000	1.62137	.09243
15.000000	.500000	10.000000	5.450000	1.52170	.09967
15.000000	.500000	12.000000	5.870000	1.42552	.09618
15.000000	.500000	14.000000	6.220000	1.333763	.08789
15.000000	.500000	16.000000	6.570000	1.24127	.09536
15.000000	.500000	18.000000	6.890000	1.14422	.09705
15.000000	.500000	20.000000	7.210000	1.03674	.10749
15.000000	.500000	22.000000	7.480000	.93609	.10064
15.000000	.500000	24.000000	7.720000	.83725	.09885
15.000000	.500000	26.000000	7.930000	.74194	.09531
15.000000	.500000	28.000000	8.130000	.64185	.10008
15.000000	.500000	30.000000	8.320000	.53649	.10536
15.000000	.500000	32.000000	8.470000	.44469	.09181
15.000000	.500000	34.000000	8.610000	.35166	.09403
15.000000	.500000	36.000000	8.730000	.26236	.08829
15.000000	.500000	38.000000	8.860000	.15700	.10536
15.000000	.500000	40.000000	8.970000	.05827	.09873
15.000000	.500000	42.000000	9.070000	-.04182	.09909
15.000000	.500000	44.000000	9.170000	-.15082	.11000
15.000000	.500000	46.000000	9.260000	-.26136	.11054
15.000000	.500000	48.000000	9.340000	-.37106	.10970
15.000000	.500000	50.000000	9.410000	-.47804	.10697
15.000000	.500000	52.000000	9.470000	-.57982	.10178
15.000000	.500000	54.000000	9.510000	-.65393	.07411
15.000000	.500000	56.000000	9.560000	-.75502	.10110
15.000000	.500000	58.000000	9.600000	-.84397	.08895

KL= -.3048319814

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14

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.350000	0.000000	2.480000	2.02155	
15.000000	.350000	2.000000	2.920000	1.96150	.06005
15.000000	.350000	4.000000	3.330000	1.90211	.05939
15.000000	.350000	6.000000	3.710000	1.84372	.05839
15.000000	.350000	8.000000	4.110000	1.77834	.06538
15.000000	.350000	10.000000	4.500000	1.71619	.06815
15.000000	.350000	12.000000	4.880000	1.63900	.07119
15.000000	.350000	14.000000	5.210000	1.57277	.06622
15.000000	.350000	16.000000	5.500000	1.51072	.06205
15.000000	.350000	18.000000	5.780000	1.44692	.06380
15.000000	.350000	20.000000	6.040000	1.38379	.06313
15.000000	.350000	22.000000	6.280000	1.32176	.06204
15.000000	.350000	24.000000	6.510000	1.25846	.06329
15.000000	.350000	26.000000	6.740000	1.19689	.06757
15.000000	.350000	28.000000	6.940000	1.12617	.06272
15.000000	.350000	30.000000	7.170000	1.05682	.07735
15.000000	.350000	32.000000	7.370000	.97833	.07250
15.000000	.350000	34.000000	7.570000	.90016	.07816
15.000000	.350000	36.000000	7.700000	.84587	.05429
15.000000	.350000	38.000000	7.850000	.77932	.06654
15.000000	.350000	40.000000	8.030000	.69315	.08618
15.000000	.350000	42.000000	8.140000	.63658	.05657
15.000000	.350000	44.000000	8.240000	.58222	.05436
15.000000	.350000	46.000000	8.350000	.51879	.06342
15.000000	.350000	48.000000	8.420000	.47623	.04256
15.000000	.350000	50.000000	8.520000	.41211	.06412
15.000000	.350000	52.000000	8.600000	.35767	.05444
15.000000	.350000	54.000000	8.690000	.29267	.06500
15.000000	.350000	56.000000	8.760000	.23902	.05365
15.000000	.350000	58.000000	8.830000	.18232	.05670

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KL= -.2000980367

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
15.000000	.100000	0.000000	2.160000	2.06306	
15.000000	.100000	5.000000	2.600000	2.00553	.05753
15.000000	.100000	10.000000	3.060000	1.94162	.05391
15.000000	.100000	15.000000	3.480000	1.87947	.06215
15.000000	.100000	20.000000	3.880000	1.81645	.06301
15.000000	.100000	25.000000	4.250000	1.75440	.06205
15.000000	.100000	30.000000	4.600000	1.69194	.06246
15.000000	.100000	35.000000	4.910000	1.63315	.05878
15.000000	.100000	40.000000	5.230000	1.56862	.05454
15.000000	.100000	45.000000	5.530000	1.50408	.05454
15.000000	.100000	50.000000	5.790000	1.44456	.05951
15.000000	.100000	55.000000	6.040000	1.38379	.06077
15.000000	.100000	60.000000	6.280000	1.32176	.06204
15.000000	.100000	65.000000	6.480000	1.26695	.05481
15.000000	.100000	70.000000	6.670000	1.21194	.05501
15.000000	.100000	75.000000	6.870000	1.15657	.06137
15.000000	.100000	80.000000	7.050000	1.09192	.05865
15.000000	.100000	85.000000	7.230000	1.02962	.06230
15.000000	.100000	90.000000	7.400000	.96698	.06264
15.000000	.100000	95.000000	7.560000	.90422	.06277
15.000000	.100000	100.000000	7.700000	.84587	.05835
15.000000	.100000	105.000000	7.850000	.77932	.06654
15.000000	.100000	110.000000	7.990000	.71295	.06638
15.000000	.100000	115.000000	8.120000	.64710	.06585
15.000000	.100000	120.000000	8.220000	.59333	.05378
15.000000	.100000	125.000000	8.350000	.51879	.07453
15.000000	.100000	130.000000	8.460000	.45108	.06772
15.000000	.100000	135.000000	8.550000	.39204	.05903
15.000000	.100000	140.000000	8.640000	.32930	.06274
15.000000	.100000	145.000000	8.710000	.27763	.05167

16

KL= -.9760823393

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
10.000000	.500000	0.000000	2.870000	2.12823	
10.000000	.500000	2.000000	3.470000	2.05412	.07411
10.000000	.500000	4.000000	4.090000	1.97130	.08282
10.000000	.500000	6.000000	4.730000	1.87794	.09336
10.000000	.500000	8.000000	5.260000	1.79342	.08451
10.000000	.500000	10.000000	5.760000	1.70656	.08686
10.000000	.500000	12.000000	6.190000	1.62531	.08125
10.000000	.500000	14.000000	6.610000	1.53902	.08630
10.000000	.500000	16.000000	6.990000	1.45395	.08506
10.000000	.500000	18.000000	7.350000	1.36609	.08786
10.000000	.500000	20.000000	7.690000	1.27536	.09073
10.000000	.500000	22.000000	8.030000	1.17557	.09979
10.000000	.500000	24.000000	8.300000	1.08856	.08701
10.000000	.500000	26.000000	8.580000	.98954	.09902
10.000000	.500000	28.000000	8.800000	.90422	.08532
10.000000	.500000	30.000000	9.030000	.80648	.09774
10.000000	.500000	32.000000	9.200000	.72755	.07893
10.000000	.500000	34.000000	9.380000	.63658	.09097
10.000000	.500000	36.000000	9.530000	.55389	.08269
10.000000	.500000	38.000000	9.650000	.48243	.07146
10.000000	.500000	40.000000	9.780000	.39878	.08365
10.000000	.500000	42.000000	9.910000	.30748	.09129
10.000000	.500000	44.000000	10.020000	.22314	.08434
10.000000	.500000	46.000000	10.120000	.13976	.08338
10.000000	.500000	48.000000	10.230000	.03922	.10054
10.000000	.500000	50.000000	10.320000	-.05129	.09051
10.000000	.500000	52.000000	10.410000	-.15082	.09953
10.000000	.500000	54.000000	10.480000	-.23572	.08490
10.000000	.500000	56.000000	10.570000	-.35667	.12095
10.000000	.500000	58.000000	10.630000	-.44629	.08961

KL= -.2728914635

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
10.000000	.500000	0.000000	2.720000	2.14593	
10.000000	.500000	2.000000	3.340000	2.07065	.07528
10.000000	.500000	4.000000	3.960000	1.98924	.08141
10.000000	.500000	6.000000	4.540000	1.90658	.08267
10.000000	.500000	8.000000	5.070000	1.82455	.08203
10.000000	.500000	10.000000	5.580000	1.73871	.08584
10.000000	.500000	12.000000	6.040000	1.65441	.08430
10.000000	.500000	14.000000	6.480000	1.56653	.08783
10.000000	.500000	16.000000	6.860000	1.48387	.08266
10.000000	.500000	18.000000	7.230000	1.39624	.08763
10.000000	.500000	20.000000	7.590000	1.30291	.09333
10.000000	.500000	22.000000	7.910000	1.21194	.09097
10.000000	.500000	24.000000	8.190000	1.12493	.08701
10.000000	.500000	26.000000	8.450000	1.03674	.08819
10.000000	.500000	28.000000	8.690000	.94779	.08895
10.000000	.500000	30.000000	8.920000	.85442	.09337
10.000000	.500000	32.000000	9.120000	.76547	.08895
10.000000	.500000	34.000000	9.320000	.66783	.09764
10.000000	.500000	36.000000	9.490000	.57661	.09122
10.000000	.500000	38.000000	9.670000	.47600	.10661
10.000000	.500000	40.000000	9.800000	.38526	.08474
10.000000	.500000	42.000000	9.930000	.29267	.09259
10.000000	.500000	44.000000	10.040000	.20701	.08566
10.000000	.500000	46.000000	10.150000	.11333	.09369
10.000000	.500000	48.000000	10.230000	.03922	.07411
10.000000	.500000	50.000000	10.320000	-.05129	.09051
10.000000	.500000	52.000000	10.400000	-.13926	.08797
10.000000	.500000	54.000000	10.480000	-.23572	.09646
10.000000	.500000	56.000000	10.570000	-.35667	.12095
10.000000	.500000	58.000000	10.660000	-.49430	.13762

KL= -.2781287174

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
5.000000	.900000	0.000000	4.310000	2.13771	
5.000000	.900000	1.000000	4.810000	2.07694	.06077
5.000000	.900000	2.000000	5.240000	2.02155	.05539
5.000000	.900000	3.000000	5.710000	1.95727	.06427
5.000000	.900000	4.000000	6.160000	1.89160	.06567
5.000000	.900000	5.000000	6.620000	1.81970	.07191
5.000000	.900000	6.000000	7.040000	1.74920	.07050
5.000000	.900000	7.000000	7.450000	1.67923	.07397
5.000000	.900000	8.000000	7.790000	1.60944	.06579
5.000000	.900000	9.000000	8.130000	1.53902	.07042
5.000000	.900000	10.000000	8.460000	1.46957	.07345
5.000000	.900000	11.000000	8.760000	1.39377	.07180
5.000000	.900000	12.000000	9.050000	1.31909	.07468
5.000000	.900000	13.000000	9.320000	1.24415	.07493
5.000000	.900000	14.000000	9.580000	1.16827	.07788
5.000000	.900000	15.000000	9.810000	1.09192	.07435
5.000000	.900000	16.000000	10.030000	1.01523	.07669
5.000000	.900000	17.000000	10.230000	.94001	.07522
5.000000	.900000	18.000000	10.420000	.86289	.07712
5.000000	.900000	19.000000	10.590000	.78846	.07443
5.000000	.900000	20.000000	10.750000	.70804	.08042
5.000000	.900000	21.000000	10.910000	.63127	.07676
5.000000	.900000	22.000000	11.050000	.55389	.07739
5.000000	.900000	23.000000	11.180000	.47623	.07765
5.000000	.900000	24.000000	11.280000	.41211	.06412
5.000000	.900000	25.000000	11.380000	.34359	.06852
5.000000	.900000	26.000000	11.480000	.27003	.07356
5.000000	.900000	27.000000	11.610000	.19551	.10451
5.000000	.900000	28.000000	11.700000	.08618	.07934
5.000000	.900000	29.000000	11.780000	.00995	.07623

KL= -.4571809575

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN(CS-C)	CONSECUTIVE DIFFERENCES
5.000000	.500000	0.000000	3.160000	2.26488	
5.000000	.500000	2.000000	3.800000	2.19611	.06877
5.000000	.500000	4.000000	4.430000	2.12346	.07265
5.000000	.500000	6.000000	5.050000	2.04611	.07835
5.000000	.500000	8.000000	5.630000	1.96651	.07660
5.000000	.500000	10.000000	6.230000	1.88099	.08752
5.000000	.500000	12.000000	6.720000	1.80036	.07763
5.000000	.500000	14.000000	7.230000	1.71956	.08776
5.000000	.500000	16.000000	7.650000	1.63705	.07855
5.000000	.500000	18.000000	8.060000	1.55393	.08313
5.000000	.500000	20.000000	8.450000	1.46787	.08605
5.000000	.500000	22.000000	8.810000	1.38128	.08659
5.000000	.500000	24.000000	9.130000	1.29746	.08392
5.000000	.500000	26.000000	9.420000	1.21491	.08255
5.000000	.500000	28.000000	9.700000	1.12817	.08674
5.000000	.500000	30.000000	9.950000	1.04023	.08789
5.000000	.500000	32.000000	10.220000	.94391	.09637
5.000000	.500000	34.000000	10.440000	.85442	.08949
5.000000	.500000	36.000000	10.650000	.76081	.09361
5.000000	.500000	38.000000	10.820000	.67803	.08277
5.000000	.500000	40.000000	10.990000	.58779	.09025
5.000000	.500000	42.000000	11.140000	.50078	.08701
5.000000	.500000	44.000000	11.280000	.41211	.08867
5.000000	.500000	46.000000	11.430000	.30748	.10462
5.000000	.500000	48.000000	11.550000	.21511	.09237
5.000000	.500000	50.000000	11.680000	.10436	.11075
5.000000	.500000	52.000000	11.790000	0.00000	.10436
5.000000	.500000	54.000000	11.900000	-.11653	.11653
5.000000	.500000	56.000000	11.970000	-.19845	.08192
5.000000	.500000	58.000000	12.030000	-.27444	.07599

KL= -.2728240780

TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
5.000000	.500000	0.000000	3.330000	2.24707	
5.000000	.500000	2.000000	3.980000	2.17589	.07118
5.000000	.500000	4.000000	4.680000	2.09310	.08279
5.000000	.500000	6.000000	5.290000	2.01490	.07819
5.000000	.500000	8.000000	5.860000	1.93586	.07904
5.000000	.500000	10.000000	6.390000	1.85630	.07956
5.000000	.500000	12.000000	6.800000	1.79009	.06621
5.000000	.500000	14.000000	7.310000	1.70111	.08899
5.000000	.500000	16.000000	7.750000	1.61741	.08370
5.000000	.500000	18.000000	8.200000	1.52388	.09353
5.000000	.500000	20.000000	8.570000	1.43984	.08404
5.000000	.500000	22.000000	8.910000	1.35584	.08400
5.000000	.500000	24.000000	9.230000	1.26976	.08607
5.000000	.500000	26.000000	9.520000	1.18479	.08497
5.000000	.500000	28.000000	9.790000	1.09861	.08618
5.000000	.500000	30.000000	10.030000	1.01523	.08338
5.000000	.500000	32.000000	10.270000	.92426	.09097
5.000000	.500000	34.000000	10.490000	.83291	.09135
5.000000	.500000	36.000000	10.670000	.75142	.08149
5.000000	.500000	38.000000	10.830000	.67294	.07847
5.000000	.500000	40.000000	10.970000	.59684	.07411
5.000000	.500000	42.000000	11.110000	.51879	.08004
5.000000	.500000	44.000000	11.250000	.43178	.08701
5.000000	.500000	46.000000	11.380000	.34359	.08819
5.000000	.500000	48.000000	11.540000	.22314	.12045
5.000000	.500000	50.000000	11.670000	.11333	.10981
5.000000	.500000	52.000000	11.790000	0.00000	.11333
5.000000	.500000	54.000000	11.910000	-.12783	.12783
5.000000	.500000	56.000000	11.980000	-.21072	.08289
5.000000	.500000	58.000000	12.050000	-.30111	.09038

KL= -.2691795872

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TEMP (C)	VELOCITY (FT/SEC)	TIME (MIN)	CONC (MG/L)	LN (CS-C)	CONSECUTIVE DIFFERENCES
5.000000	.100000	0.000000	4.250000	2.14476	
5.000000	.100000	5.000000	4.610000	2.10169	.04307
5.000000	.100000	10.000000	4.970000	2.05668	.04501
5.000000	.100000	15.000000	5.310000	2.01223	.04445
5.000000	.100000	20.000000	5.650000	1.96571	.04652
5.000000	.100000	25.000000	6.000000	1.91545	.05026
5.000000	.100000	30.000000	6.330000	1.86563	.04982
5.000000	.100000	35.000000	6.600000	1.82294	.04269
5.000000	.100000	40.000000	6.880000	1.77665	.04629
5.000000	.100000	45.000000	7.140000	1.73166	.04499
5.000000	.100000	50.000000	7.360000	1.69194	.03972
5.000000	.100000	55.000000	7.600000	1.64673	.04521
5.000000	.100000	60.000000	7.860000	1.59534	.05139
5.000000	.100000	65.000000	8.110000	1.54330	.05204
5.000000	.100000	70.000000	8.330000	1.49515	.04815
5.000000	.100000	75.000000	8.570000	1.43984	.05531
5.000000	.100000	80.000000	8.800000	1.38379	.05604
5.000000	.100000	85.000000	9.000000	1.33237	.05143
5.000000	.100000	90.000000	9.190000	1.28093	.05143
5.000000	.100000	95.000000	9.330000	1.24127	.03967
5.000000	.100000	100.000000	9.530000	1.18173	.05954
5.000000	.100000	105.000000	9.690000	1.13140	.05033
5.000000	.100000	110.000000	9.840000	1.08181	.04960
5.000000	.100000	115.000000	10.000000	1.02604	.05576
5.000000	.100000	120.000000	10.140000	.97456	.05148
5.000000	.100000	125.000000	10.290000	.91629	.05827
5.000000	.100000	130.000000	10.430000	.85866	.05763
5.000000	.100000	135.000000	10.560000	.80200	.05666
5.000000	.100000	140.000000	10.680000	.74669	.05531
5.000000	.100000	145.000000	10.790000	.69315	.05354

KL= -.0617788701

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APPENDIX D

NOMENCLATURE

TABLE 7

Nomenclature

a	specific area, defined by A_s/V .
A_o	horizontal projection of actual surface area of gas-liquid interface.
A_s	actual surface area of the gas-liquid interface.
B	remaining biochemical oxygen demand.
B_o	ultimate first stage or carbonaceous biochemical oxygen demand.
C	concentration of dissolved oxygen.
C_s	concentration of dissolved oxygen at saturation.
C_A	defined by: $C_A = A_s/A_o$.
$C', C_1, C_2, C_3, C_4, C_5$	proportionality constants.
D	defined by: $D = C_s - C$, dissolved oxygen deficit.
D_E	eddy diffusivity of the gas through the body of the liquid.
D_G	molecular diffusivity of the gas through the gas film.
D_M	molecular diffusivity of the gas through the liquid film.
D_i	an effective diffusivity.
E	rate of energy dissipation per unit mass of water.
E_s	rate of energy dissipation per unit mass of water near the water surface.
f	friction factor.

g	gravitational constant.
h	is the mean depth of the stream above extreme low water level in feet.
H	mean depth of the stream.
K_1	first order BOD reaction rate constant.
k'	von Karman's constant.
k_L, K_L	mass transfer coefficient for oxygen into water to the base 10 and base e, respectively.
k_2, K_2	overall mass transfer coefficient for oxygen into water to the base 10 and base e, respectively. Defined by:
$K_2 = K_L A_s / V.$	
K'_L	apparent mass transfer coefficient for oxygen into water calculated on the assumption that: $A_s = A_o$.
$1/K_{LC}, 1/K_{LS}, 1/K_{LT}$	resistance to oxygen transfer due to the surface film of clean water, due to the surfactant layer and the total resistance, respectively.
L, L'	effective liquid film thickness, and the apparent effective liquid film thickness, respectively.
ℓ	Prandtl's mixing length near the surface.
m	mass.
M_s	surface compressional modulus, defined by: $\rho v^2 = \frac{M_s}{x}$.
n	a constant exponent.
N	Manning's coefficient for open channel flow.
p	surface pressure, defined by $p = \sigma_o - \sigma'$.
R	the total resistance to oxygen transfer, equivalent to $1/K_{LT}$.
R'	hydraulic radius: ratio of cross-sectional area to wetted perimeter.

Re	open channel Reynolds' number based on hydraulic radius.
r, r'	rate of surface renewal, and apparent rates of surface renewal, respectively.
S	open channel friction slope.
t	time.
T	temperature in degrees Centigrade.
u	velocity in the direction of bulk flow.
U	average velocity in the direction of bulk flow.
v	vertical component of eddy velocity.
$\sqrt{\bar{v}^2}$	root mean square of the vertical velocity fluctuations.
y	distance in the vertical direction.
x	"depth of surface region" -- where resistance to surface overturn exists.

Greek Symbols

$\beta_0, \beta_1, \beta_2$	coefficients used in multiple regression analyses.
ϕ_s, ϕ_v	shape, and velocity profile factors, respectively.
ρ	density of water.
σ	surface tension.
σ, σ_0	surface tensions of contaminated and clean portions of the liquid surface, respectively.
θ	temperature coefficient, defined by $K_{LT} = K_{L20} \theta^{T-20}$
ν	kinematic viscosity.