

ATMOSPHERIC OXYGENATION AND BIOLOGICAL
DEOXYGENATION IN AN IDEALIZED
STREAMFLOW MODEL

By

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Submitted to the
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Oklahoma State University in partial
fulfillment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
May, 1967

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ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation to Dr. A. F. Gaudy, Jr., for his invaluable advice and constant encouragement, without which the completion of this work would not have been possible.

The author also wishes to express his sincere gratitude to Dr. E. T. Gaudy, who carefully read the manuscript of the dissertation and also imparted many suggestions used in the completed work.

The author wishes to acknowledge his indebtedness to Dr. J. L. Chao, Professor Q. B. Graves, and Dr. R. A. Mill, of the Civil Engineering Department, who carefully read through the manuscript of the dissertation and offered valuable suggestions.

The author wishes to express his sincere appreciation to Mrs. Grayce Wynd for her careful and accurate typing of the dissertation.

Lastly, the author wishes to express his most sincere appreciation to his dear wife, Pauline, and his children, who sacrificed so much yet always endured with extended love and patience.

The author wishes to acknowledge financial support in the form of a Bioengineering Fellowship provided by a grant (5T-1-WP-19), and financial support for equipment by Research Grant WP-00325 from the Water Pollution Control Administration.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
A. General	1
B. Justification for this Research	2
C. Objectives	4
D. Organization of Research Report	5
II. LITERATURE REVIEW	6
A. Solubility of Atmospheric Oxygen in Water	6
B. Atmospheric Oxygenation of Water	11
C. Deoxygenation Responses	23
III. THEORETICAL CONSIDERATIONS	32
A. Dissolved Oxygen Solubility	32
1. Experimental Determination of the Dissolved Oxygen Saturation Value	32
2. The Effects of C_S on the Reaer- ation Constant, k_2	40
B. Reaeration Rates	44
1. General	44
2. Dimensional Analysis	46
C. Deoxygenation Responses	49
IV. LABORATORY EQUIPMENT, PROCEDURES, AND MATERIALS	51
A. Experimental Equipment	51
1. General Description of the Turbu- lent Simulated River Apparatus	51
2. Depth and Velocity Monitoring	54
B. Experimental Procedures	57
1. General Dissolved Oxygen Monitoring	57
2. General Procedure for Reaeration Experiments	57
3. Experimental Procedure for Determin- ation of DO Saturation Value	59
4. Experimental Procedures for Deoxy- genation Response Studies	60

Chapter	Page
C. Analytical Procedures	61
1. BOD Determination	61
2. Biological Solids Determination	62
3. Carbohydrate Determination	62
V. RESULTS	63
A. Dissolved Oxygen Solubility	63
1. Results of Primary Reaeration Study	63
2. Results of Small Scale Experiments	74
B. Results of Mean Velocity Determinations	75
C. Reaeration Studies	82
1. Laboratory Results	82
2. Vibrational Effects in the Experimental System	89
3. Natural Stream Data of Churchill, et al.	97
4. Laboratory Data of Krenkel and Orlob	100
5. Summary of Results of Reaeration Studies	102
D. Deoxygenation Responses	103
1. Experiments using Glucose and Glutamic Acid	107
2. Experiments using Domestic Sewage	118
3. Experiment using Glucose	121
4. Study on the Effects of Seeding in the BOD Bottle	122
5. Summary of Results for Deoxygenation Responses	126
VI. DISCUSSION	136
A. DO Saturation Values	136
B. Reaeration	138
1. General	138
2. Summary	149
C. Deoxygenation Responses	152
1. First Stage of Oxygen Utilization	152
2. Second Stage of Oxygen Utilization	155
3. Third Stage of Oxygen Exertion	164
4. Effects of Seed and Substrate Concentration	165
5. Summary on Deoxygenation Responses	167

Chapter	Page
VII. SUMMARY AND CONCLUSIONS	171
VIII. SUGGESTIONS FOR FUTURE WORK	176
SELECTED BIBLIOGRAPHY	179
APPENDIX	186

LIST OF TABLES

Table	Page
I. Comparison of DO Saturation Values . . .	75
II. Composite Data of Reaeration Experiments	83
III. Observed First and Second Stage Oxygen Exertions	157

LIST OF FIGURES

Figure	Page
1. Effects of Estimated DO Saturation Values on Reaeration Curves	34
2. Definition Curve for Obtaining Error in Estimated Value of DO Saturation	37
3. Comparison of Atmospheric Reaeration Curves Based upon Two Different Values of DO Saturation	41
4. Photographs of Experimental Apparatus	52
5. Layout of Channel Cross-section used for Velocity Monitoring	56
6. Reaeration Experiments, Numbers 1, 2, 3, 4, and 5 from Table II	65
7. Reaeration Experiments, Numbers 21, 22, 23, 24, and 25 from Table II (Duplicates of Experiments shown in Figure 6)	66
8. Reaeration Experiments, Numbers 6, 7, 8, 9, and 10 from Table II	67
9. Reaeration Experiments, Numbers 26, 27, 28, 29, and 30 from Table II (Duplicates of Experiments shown in Figure 8)	68
10. Reaeration Experiments, Numbers 11, 12, 13, 14, and 15 from Table II	69
11. Reaeration Experiments, Numbers 31, 32, 33, 34, and 35 from Table II (Duplicates of Experiments shown in Figure 10)	70
12. Reaeration Experiments, Numbers 16, 17, 18, 19, and 20 from Table II	71
13. Reaeration Experiments, Numbers 36, 37, 38, 39, and 40 from Table II (Duplicates of Experiments shown in Figure 12)	72

Figure	Page
14. Comparison of Observed and Corrected DO Saturation Values	73
15. Velocity Distribution Measured in Experiment Number 4, Table II	76
16. Velocity Distribution Measured in Experiment Number 9, Table II	77
17. Velocity Distribution Measured in Experiment Number 14, Table II	78
18. Velocity Distribution Measured in Experiment Number 19, Table II	79
19. Comparison of Rim Velocities versus Average Streamflow Velocities Observed at Different Depths of Flow	81
20. Observed Effects of Vibration on the Reaeration Rate Constant	93
21. The Effects of Vibration on the Reaeration Rate Constant at Different Depths of Flow	95
22. Diurnal Variation in Reaeration Rate, taken from Churchill, et al. (6), Experiment Number 28	101
23. Comparison of Observed Reaeration Rates versus Computed Reaeration Rates Based on Author's Model and Data	104
24. Comparison of Observed Reaeration Rates versus Computed Reaeration Rates Based on Author's Model and Data from Churchill, et al. (6)	105
25. Comparison of Observed Reaeration Rates versus Computed Reaeration Rates Based on Author's Model and Data from Krenkel (55)	106
26. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 1 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid)	108

Figure	Page
27. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 2 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid) . . .	109
28. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 3 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid) . . .	112
29. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 4 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid)	115
30. Measurements of Oxygen Uptake in a Simulated Stream, Experiments 1 through 4 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid)	116
31. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 5 (Substrate: 1:10 Dilution of Settled Domestic Sewage) . . .	119
32. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 6 (Substrate: 1:5 Dilution of Settled Domestic Sewage . . .	120
33. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 7 (Substrate: 44 mg/l Glucose	123
34. Biochemical Oxygen Demand Curve Using Same Initial Seed Concentration as in the Simulated Stream (5 ml Sewage/l)	125
35. Comparison of BOD Exertion in the Simulated Stream and in BOD Bottles Using Same Seed Concentration (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid)	127
36. Comparison of Observed and Computed Sag Curves (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid)	129

Figure	Page
37. Comparison of Observed and Computed Sag Curves Using BOD Bottle Data of Figure 34 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid)	133
38. Comparison of Oxygen Uptake and Observed Sag Curves, Author's Experiment Number 7 versus Curves from Mancy, et al. (49)	160

CHAPTER I

INTRODUCTION

A. General

In the natural stream there are many innate stream factors which affect the dissolved oxygen concentration. Atmospheric oxygenation, biological deoxygenation, algal respiration and photosynthesis, and benthic life oxygen requirements are examples of oxygen exchange processes which may occur either independently or concurrently in a natural stream. The in vivo occurrences of all of these oxygen exchange mechanisms make separation of each of the individual contributing effects almost impossible under natural conditions.

The problem of accurately evaluating atmospheric oxygenation rates in turbulent flow systems, where only this one mechanism is present, has challenged investigators for decades. Still, they have been unable to define adequately this purely physical process to an extent such that one can make direct or independent measurements in the field, which can be used with a high degree of confidence to estimate atmospheric oxygenation rates.

Bacterial deoxygenation rates determined in quiescent standard BOD bottle tests have been used traditionally to estimate the effects of this process in natural streams. Indeed, there is still serious question as to whether the rate of BOD exertion in a turbulent system is the same as in the standard BOD bottle test. In addition, it is not known how to obtain accurate independent measurements of oxygen exchange due to algal respiration and photosynthesis, nor oxygen exchange due to benthic life demands.

The failure to define accurately any single one of these oxygen exchange processes has forced acceptance of gross oxygen exchange measurements and the hopeful view that they reflect what may be occurring in the natural streams.

B. Justification for this Research

Development of a dependable theory for predicting the individual effect of atmospheric oxygenation would enable stream pollution control engineers to gain much needed insight into some of the other biologically controlled mechanisms. Ultimate knowledge of all of the exchange mechanisms is required for the evaluation of the biological assimilative capacity of the natural stream. A dependable theory for predicting the purely physical atmospheric oxygenation process would enable researchers to approach the complex biological problems in a more rational manner, because it would aid in attempts to isolate and study each

contributing effect. Furthermore, as the water resources problem becomes more critical with expanding industrial activity and increased population, the necessity for understanding the natural stream purification process becomes extremely important. More accurate evaluation of the organic pollution loads that can be assimilated in a natural stream would be greatly enhanced by development of a theory describing the atmospheric oxygenation process. It would provide a valuable tool for study of the biological deoxygenation process in the natural environment. Ultimately, a stream's capability to abstract oxygen from the atmosphere and its biological population's capability to use this oxygen determines the stream's capacity to purify itself under desirable aerobic stream conditions.

It is the opinion of this author that to the present date the main reasons why an acceptable theory of atmospheric oxygenation has not been developed are that previous attempts have employed inadequate methods of separating the physical effect from the biological effects, and that most of the physical models previously investigated in the laboratories have been so remotely related to natural streams that correlation with the natural streams has been impossible. Examples of these types of studies are batch experiments with propeller-type mixing and oscillators placed below the surface of a fixed body of water.

The physical model, i.e., experimental apparatus, used in this research investigation is a somewhat differ-

ent and unique model. It is described in detail in Chapter IV. This experimental apparatus can be operated in such a manner as to produce conditions that are very close to those occurring in a stream of uniform cross-section flowing under steady uniform flow conditions.

C. Objectives

The primary objective of this study is to develop rationally an acceptable prediction equation which can be used to estimate atmospheric oxygenation as it occurs in natural streams. A further objective is to check the developed theory, using data gathered in the laboratory under controlled conditions, and to test its applicability to previously published field data taken on natural streams using statistical correlation analyses.

The secondary objective of this study is to utilize a controlled atmospheric oxygenation rate and to impose known pollution loads on the turbulent system in order to gain insight into the resulting biological deoxygenation responses by comparing observed responses of the turbulent system to the deoxygenation rate which occurs in concurrently conducted quiescent standard BOD bottle tests.

As a consequence of meeting the primary objective, a third objective is to gain some insight into the importance of knowing the precise value of dissolved oxygen saturation before any consistent measurements can be made of atmospheric oxygenation rates.

D. Organization of Research Report

In the course of conducting this investigation, three very important aspects of the overall stream purification process were studied: (a) dissolved oxygen saturation, (b) atmospheric oxygenation rates, and (c) biological deoxygenation responses. In most of the succeeding chapters of this report each of these aspects is presented separately.

CHAPTER II

LITERATURE REVIEW

A. Solubility of Atmospheric Oxygen in Water

In the following review concerning the solubility of atmospheric oxygen in water, there is no intention to refute or to belittle the generally accepted standard values of oxygen solubility in distilled water which are presently recommended for use and are currently published in "Standard Methods." It is intended to give some history of the origin and general acceptance of these published values, and to present some of the more recent research findings and ensuing discussions concerning these accepted values.

In 1909, C. J. J. Fox published his findings on oxygen solubility in distilled water (1). Immediate general acceptance of his work ensued. In fact, in 1910, G. C. Whipple and M. C. Whipple were actively undertaking the task of determining the solubility of oxygen in distilled water when they received a copy of the work of Fox. After reviewing this work, they decided that continuation of their work seemed unnecessary, since the work of Fox was so complete and his results agreed so very closely to theirs, so far as their work had been carried out.

G. C. Whipple and M. C. Whipple (2) took the experimental data of Fox, applied corrections for saturation pressure, and converted the results into parts per million. Their results are the widely used "Standard Methods" values of today. In the Tenth Edition of Standard Methods (3) these results were published with the following footnote:

"The second decimal in the above table is not accurately known. The average difference from the mean of five different investigators represents 0.07 ppm. Until further data are obtained, however, the second decimal place has been retained in the table."

In 1955 a group of researchers from England, Truesdale, et al. (4), completed and reported on its research work on oxygen solubility. Their findings indicated significant differences from the previously accepted saturation concentrations. This work cast serious doubt on the validity of the "Standard Methods" values. These researchers found dissolved oxygen saturation values to be 0.46 mg/l lower than the accepted values at 0°C., and observed decreasingly smaller differences at higher temperatures with a difference of 0.10 mg/l at 30°C.

As a consequence of the discussion and controversy brought about by the published results of Truesdale, et al., Morris (5) at Harvard University, undertook an experimental program to provide data which would either corroborate or refute the work of Truesdale, et al., or Fox. He conducted two groups of experiments under con-

ditions almost identical to those used by Truesdale and Fox. His results were reasonably close to those of Fox over the temperature range 5°C. to 30°C. The solubility values which he obtained were in all cases larger than those observed by Truesdale, et al.

During the period 1957-1959, Churchill and a group of researchers (6) were engaged in an extensive field study of streams in the Tennessee Valley Authority area. They were seeking to determine a method for predicting stream reaeration rates. Due to the need for obtaining very accurate dissolved oxygen saturation values and because of the ongoing controversy over the validity of the accepted values published in "Standard Methods," this group conducted an extensive experimental program aimed at determining the true saturation values of oxygen in distilled water throughout the normal range of natural stream water temperatures.

In July, 1960, the Twenty-ninth Progress Report (7) of the Committee on Sanitary Engineering Research of the Sanitary Engineering Division, A.S.C.E., was published under the title of "Solubility of Atmospheric Oxygen in Water." This committee, after reviewing the work of Fox, Truesdale, et al., Morris, and Churchill, et al., endorsed the oxygen saturation values determined by Churchill, et al. In the conclusion of their report the S.E.R. Committee stated that "the 'Standard Methods' values are sub-

stantially correct in the 0°C. to 5°C. range, but tend to be slightly high for temperatures between 10°C. and 30°C." The committee further stated that, in view of the consistency obtained in the large number of repetitive experiments completed in the work of Churchill's group and the substantiating evidence provided by results obtained by several other workers in the field, the dissolved oxygen saturation values of the Churchill group, which are tabulated in its report, are the most satisfactory of those presently available for application to natural stream conditions.

In the Eleventh and Twelfth Editions of "Standard Methods" (8, 9), the second decimal place of the previously accepted values of dissolved oxygen saturation was dropped and is no longer published.

References to the use of dissolved oxygen saturation values obtained and published by "Standard Methods," Truesdale, et al., and Churchill, et al., can be found in the literature on this subject. P. A. Krenkel and G. T. Orlob (10) make the following statements: "After accounting for the necessary volumetric corrections due to reagent additions, the resulting dissolved oxygen concentrations were subtracted from the saturation value as determined from the existing barometric pressure and water temperature." (The use of "Standard Methods" values are implied here.) Owens, Edwards, and Gibbs (11) indicate in

the methods section of their publication that "...saturation values were taken from Truesdale, et al. (1955)." Thackston and Krenkel (12) cite the use of the values of Churchill, et al. as the best available saturation values. One can see from these cited references that various workers have, during the last decade, accepted use of saturation values taken from all three of these published values.

Whether or not one set of these saturation values represents the true values for distilled water appears to be very important; however, attention to monitoring for saturation values and assessment of the effects of water quality on dissolved oxygen solubility may be two experimental criteria which have not received sufficient attention in determining the dissolved oxygen saturation values to be used in a particular investigation. The use of distilled water saturation values does not seem ideal when considering reaeration of natural waters.

In a recent report by Tsivoglou, et al. (13) of a reaeration study, using both distilled water and well water, the dissolved oxygen data for each experimental test was analyzed by several means to assure obtaining best values of reaeration rate constant, k_2 , and dissolved oxygen saturation value, C_s . Their analysis included use of a graphical method of plotting the observed changes in dissolved oxygen for equal time intervals on

semilog paper, the trial and error graphical method of selecting the C_s value that gave a straight line on semilog paper for a plot of dissolved oxygen deficit vs. time, and the Thomas slope method of calculating the desired constants (14). They reported that the results from the several methods were in good agreement. It was further reported that for the majority of tests the calculated C_s value was 95 per cent or more of the "Standard Methods" value, but that a result higher than 98 per cent usually was not obtained. Occasionally a result between 90 and 95 per cent was observed and, in one case, a result as low as 84 per cent was derived. These investigators cited use of a standard mercury barometer for measurement of atmospheric pressure changes.

If observed saturation values determined by assuming validity of first order kinetic behavior between dissolved oxygen deficit and time show such large differences from standard values, as reported by Tsivoglou, et al. after corrections for temperature and barometric pressure have been made, then it would seem that water quality must be affecting dissolved oxygen solubility to a greater extent than has been realized in the published literature.

B. Atmospheric Oxygenation of Water

Adeney and Becker (15) in 1919 showed that the absorption of oxygen into water is a first order kinetic process, and therefore the rate of absorption is propor-

tional to the oxygen deficit as follows:

$$\frac{dD}{dt} = -K_2 D$$

where D is the dissolved oxygen deficit and is equal to the difference between the dissolved oxygen saturation value, C_s , and the dissolved oxygen concentration value, C_t , at any time, t . The parameter, K_2 is the reaeration rate constant.

Much of the research reported in the literature has been aimed at development of a theoretical explanation of the reaeration rate constant, K_2 , as a function of turbulence in a dynamic fluid system. Various physical models have been proposed for explanation of this gross mass transfer process which occurs between the atmosphere and open bodies of water.

W. G. Whitman and W. K. Lewis in 1923 and 1924 (16, 17) presented what is probably the most generally used and most argumentative explanation of this absorption phenomenon, i.e., the so-called two film theory. These investigators proposed the existence of laminar layers of gas and liquid at the interface between the two phases. Both layers were assumed to offer resistance to the passage of gas molecules into the liquid. For slightly soluble gases such as oxygen, it was assumed that the resistance through the gas film was small compared to the resistance through the liquid film. Based upon the assumptions made by Whitman and Lewis, the reaeration rate

constant, K_2 can be expressed as follows:

$$K_2 = \frac{A}{V} \frac{D_m}{X}$$

where A is the exposed surface area of the film, V is the volume of liquid, D_m is the molecular diffusivity coefficient, and X is the thickness of the laminar liquid film. The validity of this expression has been quite controversial and very difficult to prove, since the existence of the liquid film has never been confirmed by physical measurement at the boundary of a gas-liquid interface.

R. Higbie (18) proposed a model for gas transfer known as the penetration theory model. Higbie deemed the two-film theory unacceptable because he could not believe the concept of a thin stagnant film. He proposed that the first stage in the absorption process must be penetration of the liquid film by the dissolved gas molecule and that, if the penetration process was not interrupted, the Whitman-Lewis theory would be operative. However, if the contact period of the dissolved gas molecule was not much longer than the penetration period, then the film theory with its steady flow would not be valid. According to the penetration theory, the reaeration rate is proportional to the square root of the diffusivity and may be given by the expression:

$$K_2 = 2 \frac{A}{V} \sqrt{\frac{D_m}{\pi t_s}}$$

where t_s is the average contact time of a turbulent eddy at the interface, and the other parameters are as previously defined. The parameter, t_s , presents an impossible physical measurement task.

In 1951, P. V. Danckwerts (19) presented what is known as the surface renewal theory. Concerning the laminar liquid film, he stated: "The conditions required to maintain a stagnant film at the free surface of an agitated liquid appear to be lacking, and it seems more probable that turbulence extends to the surface and no laminar boundary layer exists." His proposed theory is based on a system of turbulent eddies which are continuously exposing new surfaces to the atmosphere and are continuously removing layers of the surface that have been exposed for varying periods of time and returning them to the body of the liquid. According to the assumptions made in the theory, the reaeration rate constant can be expressed as:

$$K_2 = \frac{A}{V} \sqrt{D_m r}$$

where "r" is defined as the fractional rate of surface renewal. This parameter is physically impossible to measure.

O'Connor and Dobbins (20), working toward a dependable theory more applicable to natural stream reaeration conditions assumed Danckwerts' theory to be valid, and

extended it with some simplifying assumptions concerning the fluid flow characteristics of a stream. They proposed the following relations for the isotropic and non-isotropic flow conditions. (Isotropic turbulence was assumed to exist for Chezy coefficients greater than 17, and non-isotropic turbulence for values less than 17.)

$$k_2 = \frac{\left[D_m \bar{U} \right]^{1/2}}{2.31 H^{3/2}} \quad \text{Isotropic Flow}$$

$$k_2 = \frac{480 D_m^{1/2} S^{1/4}}{H^{5/4}} \quad \text{Non-isotropic Flow}$$

In these equations \bar{U} is defined as the mean stream velocity, H is defined as the average depth of flow, and S is taken as the bed slope of the channel. The validity of these proposed formulations has been doubted, partly due to the assumptions made in their development, and partly due to their inconsistency when compared with actual observations.

Churchill, et al. (6) reported on an extensive field study of selected stream reaches in the Tennessee Valley Authority area, where great care could be exercised over the control of stream flow conditions in stream reaches situated below dam sites. This is probably the best effort made toward gathering field data on stream reaeration rates, and is reasonably free of effects due to other natural stream oxygen transfer processes.

Based upon the data gathered in their study, this group performed extensive correlation analyses in an effort to define the reaeration rate constant in terms of measured stream variables. Although this group reported nineteen different relations giving approximately the same values of correlation coefficients, they recommended the following expression:

$$k_2 = \frac{5V}{H^{5/3}} (1.0241)^{T-20}$$

where V is the mean stream velocity, H is the average depth of flow, and T is the water temperature in degrees centigrade. The greatest objection voiced to this expression in the literature was that it was developed empirically and is not dimensionally homogeneous. However, another objection is that its predicted values of k_2 do not always agree with actual field observations on rivers taken in other areas.

Krenkel and Orlob (10) approached the problem of reaeration in a somewhat different manner than previous researchers. They reported on a laboratory investigation performed in a recirculating flume. They related a measured longitudinal mixing coefficient, D_L , in the flume to measured reaeration rates and average depth of flow in the channel. They also applied the Van't Hoff-Arrhenius theory to account for the effects of temperature on molecular processes. They proposed the equation:

$$k_2 = C e^{-E_A/RT} D_L H^{-2}$$

where E_A is the activation energy of the gas molecule required for transfer into a turbulent fluid, R is the universal gas constant, and T is the absolute temperature.

For a constant temperature-pressure condition, the group $C e^{-E_A/RT}$ would reduce to a constant, C' . No experimental data is presently available which permits accurate determination of E_A ; however, these researchers did receive a reasonably good correlation coefficient for the model,

$$k_2 = C' D_L H^{-2}$$

in an analysis of their experimental data.

Dobbins (21) proposed that the most acceptable model of the reaeration process is one based on an interfacial liquid film that maintains its existence in the statistical sense. The film is pictured as being ever present; however, the liquid content of the film is continuously being replaced in a random manner by the liquid from the main body of fluid. This model led Dobbins to propose the following equation for the reaeration rate constant:

$$K_2 = \frac{A}{V} \sqrt{D_m r} \operatorname{Coth} \sqrt{\frac{r x^2}{D_m}}$$

where r is defined as the average frequency of film replacement, and x is the film thickness. This model combines the film concept of Whitman and Lewis and the random mixing concept of Danckwerts. The group $K_2 \frac{V}{A}$ approaches

D_m/r as r approaches zero, indicating that the Whitman-Lewis theory is operative, and it approaches $\sqrt{D_m r}$ as r approaches infinity, indicating the Danckwerts theory is operative. Dobbins further stated that in actuality, K_2 varies with D_m raised to an exponent n . This exponent can have any value between 0.5 and unity.

The objections to Dobbins' model do not lie in its theoretical concept, but in his recommended empirical solutions for evaluating r and x . These objections are discussed very thoroughly in the literature (22, 23).

Thackston and Krenkel (12) reported on a laboratory investigation utilizing a recirculating flume. Their investigation included a study of reaeration and longitudinal mixing. Their efforts were aimed toward defining reaeration rate constant in terms of channel and flow characteristics observed in the flume. They were seeking to define reaeration in this manner, and then hoping to apply longitudinal mixing data taken on the same streams studied by Churchill, et al. in an effort to provide more definitive analysis of the data of Churchill's group. From the results of their flume study, they proposed the following equation to define the reaeration rate constant:

$$k_2 = 0.000125 \left[1 + \frac{(\bar{U})^2}{gH} \right] \left[\frac{S_e g}{H} \right]^{1/2}$$

where \bar{U} is defined as average channel velocity, S_e is the slope of the channel bed, H is the average stream depth of flow, and g is the gravitational constant. The group

$1 + \frac{(\bar{U})^2}{gH}$ was included in their equation to represent changes in surface area with flow conditions.

In this review of research work seeking to define the reaeration rate constant, the preceding discussions have dealt with attempts to give some theoretical basis for explanation of the oxygen transfer process. Without a doubt, the classical theory of Streeter and Phelps (24), who proposed the "sag equation," provided the stimulus to sanitary engineering researchers to engage in this area of study. The Streeter and Phelps theory is based upon the assumption that the BOD in a stream is exerted according to first order reaction kinetics along with simultaneous oxygen replenishment of the stream, which obeys the Adeney-Becker relation for reaeration. This equation can be shown to take the following integrated form:

$$D_t = \frac{K_1 L_o}{K_2 - K_1} \left[e^{-K_1 t} - e^{-K_2 t} \right] + D_o e^{-K_2 t}$$

where L_o denotes the ultimate first stage BOD at the upstream end of the river reach, K_1 is equal to the first order BOD reaction rate constant, D_t represents the dissolved oxygen deficit at a downstream point at time, t , and D_o represents the initial dissolved oxygen deficit at the upstream end of the stream reach at zero time.

The literature is replete with field applications of this equation, and investigations attempting to define reaeration in terms of stream parameters determined and

based on its validity. In these attempts to use this equation, it has been assumed that the BOD reaction obeys first order kinetics and that the BOD exerted in a standard bottle determination is equal to that occurring in the stream.

Using this sag equation, Streeter (25) was able to obtain a series of values for the reaeration rate constant for various reaches of the Ohio River. These values were calculated using observed changes in dissolved oxygen concentration in the river and data from bottle BOD determinations carried out on the polluted river samples. He then presented an equation of the form:

$$k_2 = a \frac{v^n}{H^2}$$

which could be used to calculate values of k_2 for a given stream reach based upon the hydraulic properties of the reach. Because of the dependence of the values of the constants "a" and "n" upon the turbulence characteristics of each stream reach, this equation has never found general application. The nature of "a" and "n" and the factors controlling them have never been defined in general terms of measurable hydraulic properties of stream reaches.

More recently, Owens, Edwards, and Gibbs (11) developed an empirical equation to predict reaeration rates based upon data taken from several reaches of streams in

England and the United States. They proposed the following equation:

$$k_{2-20}^0 = 9.4 U^{0.67} H^{-1.85}$$

These authors obtained a correlation coefficient value of 0.95 when a regression analysis was made on the combined data of Gameson, et al. (26), Churchill, et al. (6), and their own data.

The correlation coefficient value reported for this analysis is excellent. However, in this regression analysis the correlation coefficient may be reflecting false confidence, since the data contain two distinct ranges of k_{2-20} values separated by a large interval of no significant definition. These authors combined sixty-eight pieces of data. Forty-five of these observations have a k_{2-20} range of 0.31 to 6.18 (days^{-1}) of which twenty-two of these values have a k_{2-20} value less than unity. Twenty-three of the sixty-eight values fall within the k_{2-20} range of 12.04 to 57.7 (days^{-1}) of which seventeen k_{2-20} values are greater than 20.0 (days^{-1}). If a correlation analysis is made on these data, the twenty-three observations greater than 12.04 contribute almost all of the "total sum of squares" for the analysis. Since the number of smaller values (forty-five observations) is almost twice the number of larger values (twenty-three observations), the "mean sum of squares" is cushioned or made too small by this imbalance. Most of the "error sum of squares" is con-

tributed by the twenty-three large values. If three groups of data from different sources cannot be shown to have approximately the same equation independently, i.e.,

$$k_{2-20} = C V^a H^b$$

where the values of C, a, and b are reasonably constant for all three groups, then these groups should never be composited in a correlation analysis. One must first prove that each group belongs to the same statistical population before a composite analysis can be made. The best equation for the reported data of Churchill's group is:

$$k_{2-20} = 6.070 \frac{V^{0.9075}}{H^{1.761}}$$

These authors report the best equation for their data to be:

$$k_{2-20} = 10.09 \frac{V^{0.75}}{H^{1.75}}$$

When one compares the values of the constant C, 6.070 for Churchill's group, 10.09 for Owens, et al., and 9.4 for the composite, it is evident that the data of Owens, et al. are contributing the major influence to this constant. The constant "C" is the regression parameter measuring the net effect of the "mean sum of squares" which was previously suggested as being biased. The same predominating influence can be seen in comparison of the exponent "a" on velocity. For Churchill's group, "a" has a value of 0.9075; for Owens, et al., a value of 0.73, and for the composite, a value of 0.67. The variable, depth, appears to have a consistent effect.

Tsivoglou, et al. (13) attacked the reaeration problem, using a completely different approach. This group conducted laboratory and field investigations in which they monitored the relative rates of oxygen transfer and two inert tracer gases, Kr^{85} and Rn^{222} . Their laboratory investigations showed excellent results in that they found constant but different ratios for $K_{2\text{-oxygen}}/K_{2\text{-Kr}^{85}}$ and $K_{2\text{-oxygen}}/K_{2\text{-Rn}^{222}}$ over a wide range of turbulent conditions. They proposed to monitor these tracer gases in the field in lieu of monitoring oxygen. However, they were not able to develop monitoring control of the inert gases in their field study. This proposed method appears to have good potential if the field monitoring problems can be worked out.

C. Deoxygenation Responses

In January, 1962, O'Brien and Clark (27) published a compilation of 816 references in an extensive review of the historical development of the present day biochemical oxygen demand test. Hence, only a brief review of the theoretical concepts of this test and its past applications to the natural stream purification process will be presented in this report.

That microorganisms have the ability to consume oxygen dissolved in water for their metabolic processes was first proposed by Dupre' (28) in 1884; however, Theriault (29) credits Frankland (30) with first using the BOD test in 1870. Frankland incubated a series of river water

samples containing a high oxygen concentration in completely filled and tightly stoppered bottles. The DO remaining in the samples which were removed at 24-hour intervals was determined by boiling off the dissolved gases under vacuum and performing a gas analysis on the gases recovered. He obtained a seven-day curve which resembles present-day BOD curves.

Winkler (31) proposed his classic method for the dissolved oxygen determination in 1888. This method with its modifications [Rideal and Stewart (32) published in 1901; Alsterberg's azide modification (33) adopted in 1938] has become the basic chemical analysis used for oxygen monitoring in streams and in the present BOD test.

The modern biochemical oxygen demand test was developed by researchers in the field who continuously worked toward development of standard techniques aimed at obtaining reproducible results, and at augmenting the understanding of the biological kinetics involved in the BOD reaction. Today one is able to measure very precisely the oxygen changes that take place; however, the kinetics of the biochemical deoxygenation responses that occur in turbulent aqueous systems polluted with organic matter are just beginning to be partially explained.

Phelps (34) in 1909 established a mathematical relation describing the observed rate of deoxygenation of sewage in deriving his expression for relative stability. His expression was based upon observations which appeared

to obey monomolecular kinetics. Theriault (35), however, is credited with the development of the monomolecular BOD formula in its present-day form. Since Theriault's presentation, various modifications aimed at the solution of the monomolecular kinetic equation for the reaction rate constant, K_1 , and the ultimate oxygen demand, L_0 , have been developed. Gaudy, et al. (36) have recently compiled a manual which includes sixteen computational methods.

Streeter and Phelps (24) presented the classical "sag equation" which has been previously discussed in this review. This equation, so very appealing in its mathematical exactness, has probably contributed more toward acceptance of the monomolecular concept of BOD exertion than any other treatise of this subject. This is especially true in applications dealing with BOD exertion in the natural stream.

Multiphase carbonaceous BOD exertion has been observed by many researchers working with the BOD test. Bhatla, in a study on the kinetics and mechanism of phasic oxygen uptake, included an extensive examination of the literature on this subject in his doctoral thesis (37).

In 1911, Müller (38) correlated bacterial growth and oxygen uptake. He observed that maximum oxygen depletion per hour coincided with maximum bacterial numbers. Purdy and Butterfield (39) stated, concerning their BOD bottle studies using a synthetic waste seeded with pure cultures of sewage origin, that oxygen uptake occurred only while

the bacteria were multiplying. Oxygen absorption ceased after a limiting number of bacteria had been reached. An additional thirty to forty days of incubation caused no significant oxygen uptake.

Hoover, Jasewicz, and Porges (40) found BOD exertion on a milk waste to occur in two distinct phases. The first phase showed a rapid oxygen uptake coinciding with cell multiplication. This was followed by a slower endogenous oxygen uptake. They described these two stages as two successive first order decreasing rates. The first phase was completed within twenty-four hours, and the second phase continued throughout incubation. Buswell, Mueller, and Van Meter (41) observed a two-stage oxygen uptake during carbonaceous BOD progression. The first stage was associated with cell multiplication, and the second was related to a resting or dying bacterial population.

In 1958, Busch (42) reported a two-stage carbonaceous BOD curve with the two phases of oxygen uptake separated by a plateau. He suggested that the first phase of oxygen uptake was associated with conversion of substrate into cell material which included new cell synthesis and storage products. The second phase of oxygen demand was attributed to oxidative endogenous metabolism by the bacteria. He further suggested that oxygen usage during the second phase in excess of the respiratory activity was attributable to the action of predators.

Butterfield, Purdy, and Theriault (43) had previously observed that, upon addition of the protozoan Colipidium to a pure culture of Bacterium aerogenes, active oxygen uptake continued beyond the peak attributed to a bacterial population alone. They observed in this test almost twice as much oxygen depletion as in the bacterial control. After reaching a peak value, the bacterial count in the control did not decline significantly. However, the system containing the protozoa showed a rapid decline in bacterial count after one day followed by an increase in protozoan count reaching a peak after four days. From their investigation the group advanced a theory suggesting that the primary role of certain plankton in the biochemical oxidation process is to keep populations reduced below a saturation value. This would then provide conditions suitable for continuous bacterial multiplication, and result in a more complete oxidation.

Javornicky and Prokesova (44) more recently studied the role of protozoa on the BOD process. From their observation of high reduction in bacterial numbers during development of protozoa in the BOD bottle test, they concurred with the theory previously advanced by Butterfield, et al.

Recent research in the bioengineering laboratories at Oklahoma State University has contributed considerable insight into the occurrence and causation of diphasic oxygen uptake during BOD exertion. Gaudy, Bhatla, and

Abu-Niaaj (45), Gaudy and Bhatla (46), and Follett and Gaudy (47) have studied and authenticated the general occurrence of diphasic oxygen uptake, with the associated "plateau" occurring between phases. These investigators have demonstrated the general occurrence of the plateau under a variety of seeding and substrate conditions. In all of the studies reported, the first phase of oxygen uptake was accompanied by an increasing bacterial count. The plateau occurred in the range of steady bacterial numbers, and the second phase of oxygen uptake occurred with a marked decrease in viable bacterial count.

Gaudy and Bhatla (46) proposed four related theories to explain the causation of the plateau. The following theories were proposed:

(a) The release of intracellular components, from cell dieoff after maximum population has been attained can provide food for other organisms. The latter organisms are not the predominating ones, and time is required before they are present in sufficient numbers to express a measurable oxygen uptake. The second species may consist of bacterial predators.

(b) The second theory is similar to the first theory, except that no change in predominating species occurs, but an acclimation period is required before the predominating species can utilize the released intracellular components.

(c) After attainment of maximum population, cells do not die off but may lose ability to replicate. An accli-

mation period may be required before the cells can metabolize stored cellular components which were synthesized during the replicating process.

(d) During the first stage of rapid metabolism, the cells may release intermediates into the medium. An acclimation period may then be required before the new exogenous substrate(s) can be metabolized.

The general occurrence of diphasic and even multiphase oxygen uptake has been demonstrated and observed in BOD progressions. This is evidenced by the literature cited. Most of the observed systems have been studied either in BOD bottles, for low energy systems, or respirometer-type apparatus (Warburg) for high energy systems.

Some work has been conducted on the effects that turbulence or stirring might have on either the rate of BOD exertion or the ultimate value of BOD. Prokesova (48) reported on the effects that turbulence and aeration have on the BOD test results. She conducted two types of experiments: (a) In the first type, BOD determinations were made on bottles incubated under standard quiescent conditions vs. BOD determinations made on bottles which were rotated at 15.5 rpm on a specially designed piece of equipment. The latter was termed a "turbulent" system. (b) In the second type, BOD determinations were made as in procedure (a) except that an air bubble was left in the stirred bottles. This provided turbulence and aeration. After examining the resulting BOD determinations of waters from

different sources, it was concluded that turbulence alone did not cause an appreciable difference from standard BOD determinations. However, with turbulence and aeration present, the aerated system yielded significantly lower BOD velocity constants and ultimate BOD values. Based upon the results of her experimentation, she concluded that turbulence with aeration seemed to modify the entire process of purification.

Mancy, Gates, and Shafie (49) conducted a study in which a small batch reactor was stirred by a propeller-type mixing apparatus. They first studied reaeration effects determined for different constant stirring speeds, and then polluted the system with known concentrations of substrate in order to compare the total oxygen response of this system to that predicted by the "sag equation." These investigators ran experiments using both sewage and specific substrates. In some cases they used pure cultures of Escherichia coli as seed. Their results did not agree with the "sag equation" theory. Some results of their work are discussed and interpreted in Chapter VI of this report. The conclusions drawn by this group were as follows:

- (a) The physical model utilized does not permit the evaluation of deoxygenation and reoxygenation processes when they are proceeding under identical conditions;
- (b) For the situations considered, the monomolecular expression for oxygen uptake by the biosphere is invalid. The assimilative capacity of the systems studied cannot

be analyzed on the basis of substrate concentration alone;

(c) Although the results can be considered only in very general terms with respect to other systems, they should be considered as indicative of probable inadequacies in present techniques of assimilative capacity evaluation.

CHAPTER III

THEORETICAL CONSIDERATIONS

A. Dissolved Oxygen Solubility

1. Experimental Determination of the Dissolved Oxygen Saturation Value

In the literature review concerning dissolved oxygen solubility, the controversy over various proposed values for DO saturation in distilled water was discussed. In the present work it is held that DO saturation values determined for highly purified distilled waters cannot be used indiscriminately for naturally occurring waters. However, it must be recalled that, for the most part, past workers have used values for distilled water when dealing with natural waters. In some cases corrections for barometric pressure, in addition to normal temperature corrections, have been used; however, it is a rarity to find investigators determining the DO saturation value of the actual water being investigated. The previously cited work of Tsivoglou, et al. (13) is one of these rare occurrences.

That the transfer of oxygen from the atmosphere into a turbulent water system truly obeys first order rate

kinetics, as advanced by Adeney and Becker, is a well-proven and accepted law. Since this is true, the task of determining the DO saturation value, C_s , for any water is basically a simple experimental problem.

There have been many methods proposed (36) for determining the reaction constants, k_1 and L_0 , in the familiar monomolecular model for BOD exertion,

$$\log \left[\frac{L_0}{L_t} \right] = k_1 t \quad (\text{III-1})$$

The Adeney-Becker equation for reaeration can be written in the same form:

$$\log \left[\frac{D_0}{D_t} \right] = k_2 t \quad (\text{III-2a})$$

In the reaeration equation, D_t is defined as the difference between the DO saturation value, C_s , and the DO concentration observed, C_t , at any time, t . If the true value of C_s is known, a plot of D_t vs. time on semilog paper results in a straight line which has a slope equal to the reaction rate constant, k_2 . However, if the true value of C_s is not known and one assumes some value, C'_s , the semilog plot of D'_t vs. time yields the following three possibilities which are illustrated in Figure 1:

(a) If C'_s is an overestimate of C_s , the curve will be concave upward and displaced along the ordinate by the amount of the overestimate, α . The curve must be concave upward because C'_s is greater than the true C_s value, hence the curve does not approach zero, but approaches a value

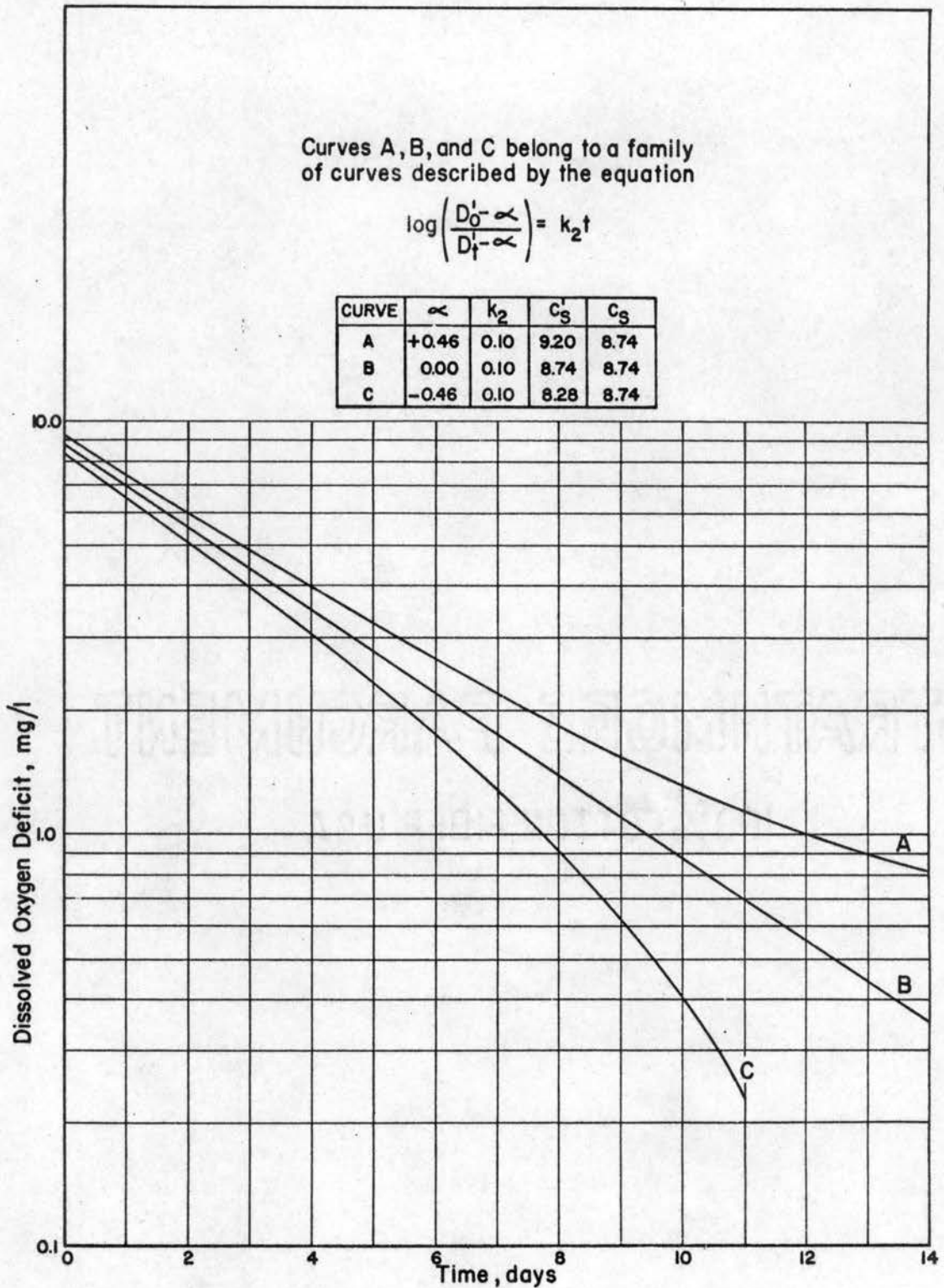


Figure 1. Effects of Estimated DO Saturation Values on Reaeration Curves.

which is greater than zero in this case.

(b) If C'_S is an underestimate of C_S , the resulting curve will be concave downward and displaced along the ordinate by the amount of the underestimate, α . In this case C'_S is less than C_S , hence the curve approaches some negative constant α , and will be concave downward.

(c) If C'_S is equal to C_S , or if no error is made in the estimated value, the plot yields the desired straight line curve.

Davis (50) gives a mathematical treatment for the semilogarithmic form

$$y = 10^{a+bx} + \alpha$$

He makes the following statement: "Many data that do not show linearity on semilogarithmic paper can be plotted as a straight line by adding to or subtracting from the dependent variable some quantity, α , so that the form of the equation is

$$y = e^{a+bx} + \alpha$$

or, more conveniently,

$$y = 10^{a+bx} + \alpha$$

In transposing the α term and taking logarithms,

$$\log(y - \alpha) = a + bx$$

an indication that plotting $(y - \alpha)$ against x on semilogarithmic paper $\left[\log(y - \alpha) \text{ vs. } x \right]$ leads to a straight line."

Equation (III-2a) can be transformed to yield:

$$\log D_t = \log D_o - k_2 t \quad (\text{III-2b})$$

The term α in Davis's development was introduced to correct a known measured dependent variable. However, if DO saturation value is not measured in situ, and is assumed to be the "Standard Methods" value of distilled water for all natural waters, then there could possibly be some error made in this assumption. Letting this possible error be equal to α , Equation III-2b can be rewritten as

$$\log (D'_t - \alpha) = \log (D'_o - \alpha) - k_2 t \quad (\text{III-2c})$$

where D'_o and D'_t are not necessarily the true values of DO deficit. They are the apparent deficits based on an assumed saturation value C'_s , which may or may not be equal to the true saturation value C_s .

The value of α may be determined from experimental data as follows: A smooth curve is drawn through coordinates defining an arithmetic plot of C_t vs. time as shown in Figure 2. The arithmetic mean of the time interval bounded by times, t_1 and t_2 is

$$t_3 = \frac{t_1 + t_2}{2} \quad (\text{III-3})$$

The value of t_3 is computed and the corresponding coordinate value D'_3 or $(C'_s - C_3)$ is read from the curve. All three points defined by coordinates (D'_1, t_1) , (D'_2, t_2) , and (D'_3, t_3) lie on the curve of the experimental data, hence

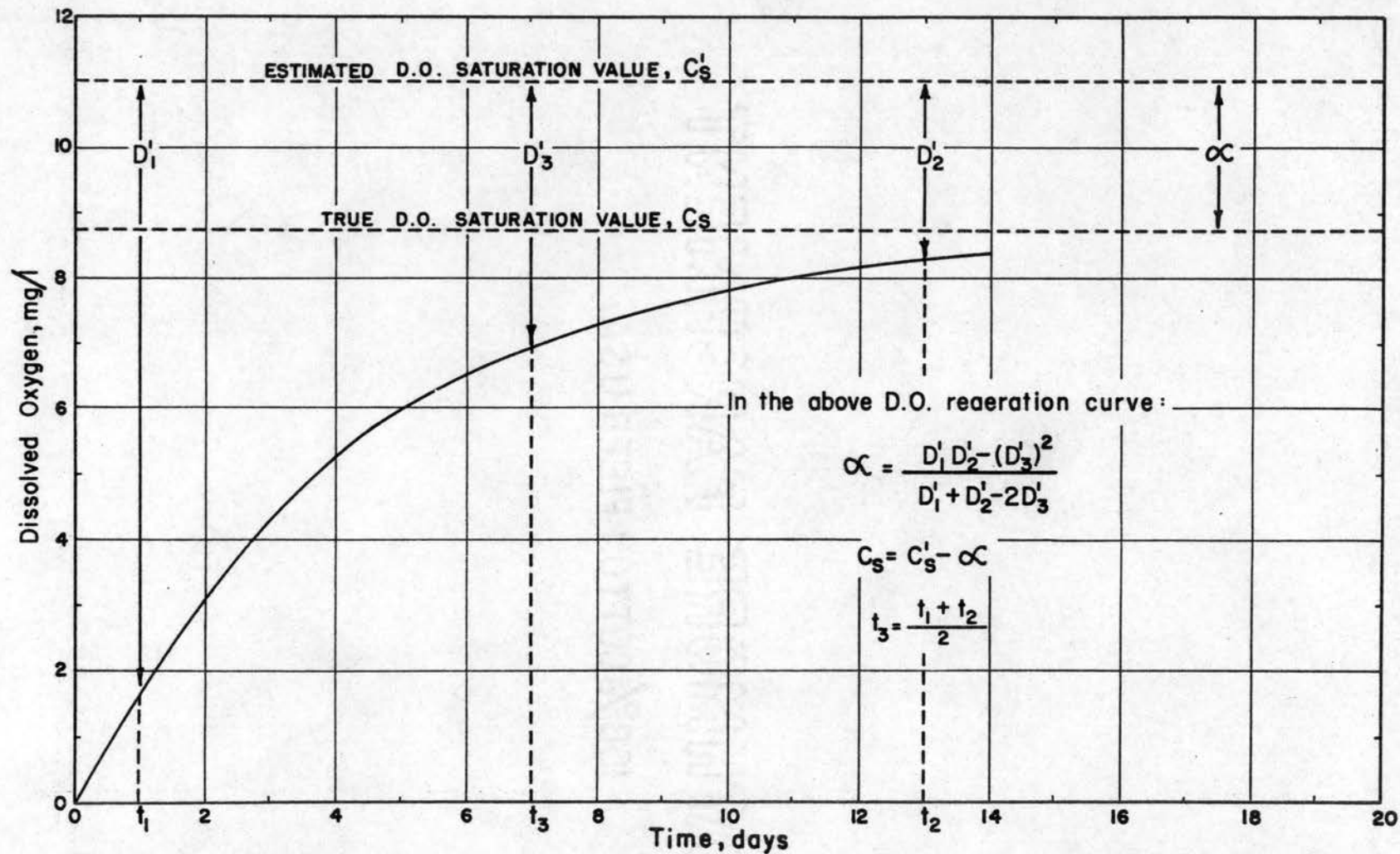


Figure 2. Definition Curve for Obtaining Error in Estimated Value of DO Saturation.

$$\log (D_1' - \alpha) = -k_2 t_1 + C \quad (\text{III-4a})$$

$$\log (D_2' - \alpha) = -k_2 t_2 + C \quad (\text{III-4b})$$

$$\log (D_3' - \alpha) = -k_3 t_3 + C \quad (\text{III-4c})$$

where C is a constant and equal to $\log (D_0' - \alpha)$. These logarithmic equations are solved for t_1 , t_2 , and t_3 :

$$t_1 = \frac{-\log (D_1' - \alpha) + C}{k_2}$$

$$t_2 = \frac{-\log (D_2' - \alpha) + C}{k_2}$$

$$t_3 = \frac{-\log (D_3' - \alpha) + C}{k_3}$$

The values so found are substituted into:

$$t_3 = \frac{t_2 + t_1}{2} \quad (\text{III-3})$$

and the following expression results:

$$\frac{-\log (D_3' - \alpha) + C}{k_2} = 1/2 \left[\frac{-\log (D_1' - \alpha) + C}{k_2} + \frac{-\log (D_2' - \alpha) + C}{k_2} \right].$$

Expansion leads to

$$\log (D_3' - \alpha) = 1/2 \left[\log (D_1' - \alpha) + \log (D_2' - \alpha) \right]$$

or

$$(D_3' - \alpha) = \sqrt{(D_1' - \alpha)(D_2' - \alpha)} \quad (\text{III-5})$$

Squaring both sides of Equation (III-5) and solving for α yields

$$\alpha = \frac{(D_1' D_2' - (D_3')^2)}{D_1' + D_2' - 2(D_3')} \quad (\text{III-6})$$

Thus Equation III-6 gives a mathematical definition of the error α , in terms of experimentally measured values. The true value of DO saturation, C_s , can be determined by subtracting the computed value of α from the assumed DO saturation value, C_s' .

The method described for determination of the DO saturation value, C_s , may be in slight error, due to the requirement of determining the values of D_1' , D_2' , and D_3' from the assumed "best fit" arithmetic plot of C_t vs. time. However, it is easier than a trial and error solution, and since the data are taken from an arithmetic plot, the ability to estimate D_1' , D_2' , and D_3' with the same degree of accuracy is ensured. The ability to estimate with the same degree of accuracy is not ensured on a semilog plot of the data, since D_t' values occur on a logarithmic scale for this type plot.

Equation (III-6) was developed for determining the value of the error, α , made in estimating C_s ; however, this form of equation is applicable for determination of the error made in estimating any unknown limiting concentration value where first order kinetics are applicable. As an example, this expression can be easily transformed

and used for determination of ultimate BOD value, L_0 , if BOD is assumed to be exerted in accordance with the first order kinetics. One can make an estimate of the ultimate BOD value, L_0' , and plot the $\left[L_0' - (O_2 \text{ uptake})_t \right]$ vs. time on arithmetic paper. Applying the following equation

$$\alpha = \frac{(L_1' L_2') - (L_3')^2}{L_1' + L_2' - 2L_3'} \quad (\text{III-6a})$$

where $L_t' = \left[L_0' - (O_2 \text{ uptake})_t \right]$, the error α made in estimating L_0 can be computed and subtracted from the estimated value L_0' to give the true value of L_0 .

2. The Effects of C_s on the Reaeration Constant, k_2

The need for knowing the nearly exact value of DO saturation, C_s , before determination of the reaeration constant, k_2 , is illustrated in the following hypothetical example:

Let it be known that a natural stream water at 20°C. and standard atmospheric pressure conditions has a true value of C_s equal to 8.74 ppm, or 95 per cent of the C_s value of 9.2 ppm reported in "Standard Methods." This water is known to be aerated at a k_{2-20} value of 0.1 days⁻¹ starting at an initial value of C_0 equal to 0.0 and reaerating for a period of fourteen days. Figure 3 contains a tabulation which displays the levels of D_t and C_t computed for the known true conditions (columns 4 and 5).

Now let it be assumed that the true value of C_s was not initially known, but that the value of C_s' of 9.2 as

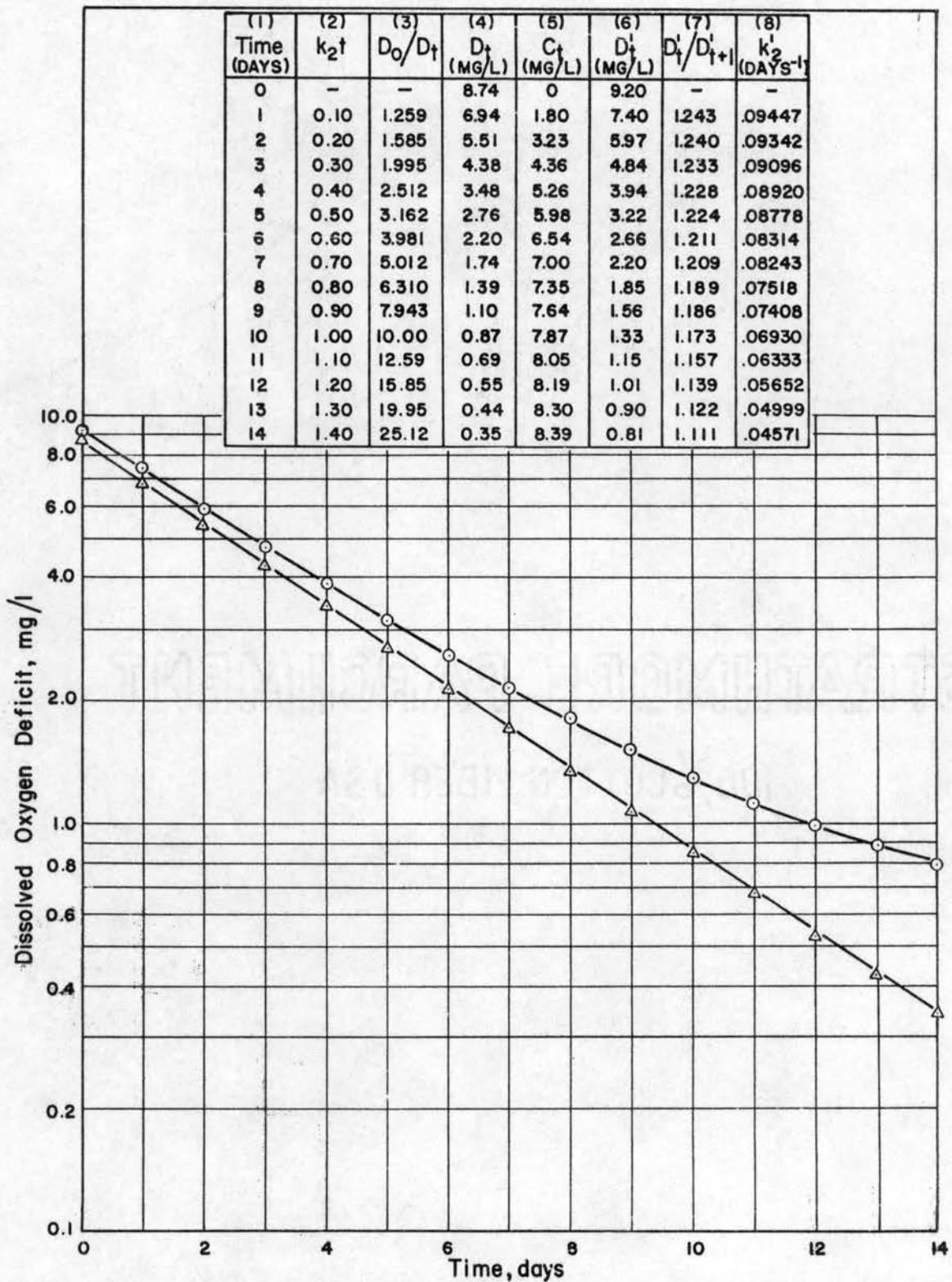


Figure 3. Comparison of Atmospheric Reaeration Curves Based upon Two Different Values of DO Saturation.

reported in "Standard Methods" was used for computation of the reaeration rate constant, k_2 . It is emphasized that the tabulated values of C_t (column 5) occurring at the end of each time period are truly the DO concentration values that would be observed under the ideal conditions and plotted values for D_t would yield the straight line shown in Figure 3. However, the new dissolved oxygen deficit values, D_t' , are based upon the overestimated C_s' value of 9.2 ppm. These are shown in column 6 of Figure 3, and the plotted values for D_t' would yield the upper curve on the figure. If each unit time period is treated as a separate computation for the apparent reaeration rate constant, k_2' , the values obtained continuously decrease, as shown in column 8, Figure 3.

It is common practice in stream survey work to base computations of k_2 on only two observations of C_t , i.e., at the upper and lower ends of the reach. When one observes the k_2 rate prevailing between two stations which have different oxygen tension levels from one independent stream sampling period to the next sampling period, computed values of the k_2 rate will vary regardless of whether the stream's hydraulic conditions are remaining constant, i.e., the values of observed k_2 rates computed in this manner will not remain constant unless the value of C_s' is not in error. Furthermore, one might even observe constant dissolved oxygen levels at the upper and lower reaches on different sampling days, thus yielding appar-

ently constant k_2 values for the reach, but this value would still be in error if C'_s is not the true C_s value. A true k_2 rate is obtained only when the true saturation value is known.

The example shown illustrates the effect of dissolved oxygen saturation value on computations made for the reaeration rate constant, k_2 . This type of error has most probably occurred to some degree in all of the field data previously collected. Furthermore, it has most likely caused consistently low value determinations of reaeration rates occurring in the natural streams, since in most cases natural stream waters have a lower value of C_s than the values reported for distilled water. Unless oxygen saturation values are determined for the actual water being investigated, this type of error is always present. Figure 3 indicates the type of curve yielded in the assumed hypothetical case, and k_2' values in column 8 can be multiplied by 1000 to yield the percent of the theoretical k_2 value of 0.1, i.e., the true value computed for each time period. The indicated magnitude of error dictates that such inconsistencies in the estimation of this parameter should be ensured against in the future in order to achieve good definition of the reaeration rate constant, k_2 . The errors will be particularly large at high O_2 concentration.

B. Reaeration Rates

1. General

In the literature review on reaeration, it was indicated that each of the theoretical models advanced to explain this transfer process, involved one or more variable which has been physically impossible to measure. Furthermore, it has been emphasized that in some cases estimation of DO saturation value, C_s , may have led investigators to inconsistent evaluations of the reaeration rate constant, k_2 . The common acceptance of the idea that BOD exertion obeys first order kinetics in streams and that the kinetic constant can be obtained in BOD bottle determinations has undoubtedly led to errors in reported values of stream reaeration rates. As a review and study of the previous work on reaeration was made, many pitfalls became apparent.

In order to approach the problem of defining the reaeration rate constant in terms of easily measured parameters which can be evaluated in a natural stream, a critical review of the physical models that have been used in experimentation by foregoing researchers was made.

Some investigations have been conducted using the natural stream. This is truly the perfect geometric model; however, the natural stream contains many as yet unpredictable oxygen transfer processes which have not been adequately defined, such as biological deoxygenation responses, algal respiration and photosynthesis, and benthic oxygen demands.

Furthermore, work under natural stream conditions presents many disadvantages relative to experimental control, such as flow regulation and irregular channel geometry. The natural streams are subject to various changes in climatic parameters and it is also quite expensive to conduct good stream surveys.

Recirculating laboratory channels have been used in efforts aimed toward defining reaeration rates in terms of flow conditions. This physical model has proven to be invaluable in simulation of other open channel fluid flow phenomena occurring in the natural streams. However, in studying oxygen transfer it has three distinct disadvantages: (a) It contains undefinable turbulence due to pumping and return of the water which undoubtedly sweeps oxygen into the system. (b) It continuously renews the water surface with every pass through the system. This completely negates any possible stability of a liquid film, if such a film truly controls the process. (c) Such an experimental apparatus possesses a "dead volume" in the return piping system which may influence the overall k_2 rate of the entire "system," i.e., the channel, the inlet and outlet, the transition zones, and the return piping system. The effect of "dead volume" will be discussed in Chapter VI.

Other methods used in efforts made toward defining reaeration rates, such as small batch reactors, agitated by propellers, oscillators, or diffused aeration may have

led to good interpretive experimental results for each specific device; however, these models were so remotely related to the natural stream model that correlation and/or extrapolation to stream variables has been essentially unsuccessful.

After reviewing the various types of experimental apparatus used by previous researchers, a new experimental apparatus was conceived and developed. This new apparatus, developed at Oklahoma State University, is a unique aeration device. It simulates very closely the fluid flow as it occurs in a natural stream. The experimental apparatus is described and discussed in detail in Chapter IV.

2. Dimensional Analysis

The primary objective of this research investigation was to determine, by controlled experimental measurement and associated correlation studies, a relationship describing the reaeration rate constant, k_2 , in terms of easily obtained fluid flow parameters. Before taking the problem into the laboratory, the suspected controlling variables were treated analytically by dimensional analysis. This was done in order to develop some guidelines for conducting the experimental measurements.

The following tabulated variables were selected for the analysis:

<u>No.</u>	<u>Variable</u>	<u>Symbol</u>	<u>Dimensions</u>
1	reaeration rate constant	k_2	T^{-1}
2	mean channel velocity	V	LT^{-1}
3	average depth of flow	H	L
4	molecular diffusivity	D_m	L^2T^{-1}
5	kinematic viscosity of water	ν	L^2T^{-1}
6	gravitational constant	g	LT^{-2}

Since six variables are considered and these variables are represented by only two dimensions, length and time, application of the Buckingham Π -Theorem (the number of dimensionless parameters equals the number of selected variables less the number of dimensions represented in the selected variables), predicts that four Π -terms are required to represent the selected variables for this analysis. The following Π -terms were formulated:

$$\Pi_1 = \frac{k_2 H^2}{D_m}$$

$$\Pi_2 = \frac{HV}{\nu} \quad \text{-- Reynolds Number, } N_R$$

$$\Pi_3 = \frac{V^2}{gH} \quad \text{-- Froude Number, } N_F$$

$$\Pi_4 = \frac{\nu}{D_m} \quad \text{-- Schmidt Number, } N_S$$

The general equation relating these dimensionless parameters can be written as follows:

$$\Pi_1 = \phi(\Pi_2, \Pi_3, \Pi_4)$$

or

$$\frac{k_2 H^2}{D_m} = \phi \left[\frac{HV}{\nu}, \frac{v^2}{gH}, \frac{\nu}{D_m} \right].$$

It was then assumed that Π_2 , Π_3 , and Π_4 might be a completely multiplicative function such that

$$\frac{k_2 H^2}{D_m} = C \left[\frac{HV}{\nu} \right]^a \left[\frac{v^2}{gH} \right]^b \left[\frac{\nu}{D_m} \right]^d \quad (\text{III-7})$$

where "C" is a constant of proportionality and "a", "b" and "d" are the exponents required on Π_2 , Π_3 , and Π_4 , respectively.

Equation (III-7) can be rewritten as

$$k_2 = C \left[\frac{D_m^{(1-d)}}{\nu^{(a-d)}} \frac{1}{g^b} \right] v^{(a+2b)} H^{(a-b-2)}. \quad (\text{III-7a})$$

If experimental conditions of temperature and pressure are kept reasonably constant, the group

$$C \left[\frac{D_m^{(1-d)}}{\nu^{(a-d)}} \frac{1}{g^b} \right]$$

would approach a constant, C' , and Equation (III-7a) can be expressed as:

$$k_2 = C' v^m H^p \quad (\text{III-7b})$$

where m equals (a+2b) and p equals (a-b-2)

Equation (III-7b) was used for a correlation analysis of the variables k_2 , v , and H . The experimental data collected on k_2 , v , and H were subjected to a least squares analysis of these variables in order to determine the value of the constants C' , m , and p .

C. Deoxygenation Responses

The applicability of the "sag equation" as presented by Streeter and Phelps (24) has been previously questioned, and it is felt that the true relationship describing a turbulent water system, in which both atmospheric oxygenation and bacterial deoxygenation responses are occurring, awaits delineation. In order to gain some insight into the bacterial deoxygenation responses occurring in a turbulent simulated river, the following numerical analysis technique was utilized in this study.

Gross changes in dissolved oxygen concentrations can be monitored and for small increments of time, Δt , the incremental DO deficit changes can be obtained from the resulting DO response curve. The latter parameter is herein termed (ΔD) , total change. The small changes in DO deficit due to reaeration can be computed assuming the validity of first order kinetics for this process. Hence $(\Delta D)_R$, small change due to reaeration, is equal to $-2.303k_2 \times D_{AVE} \times \Delta t$. Therefore, the following relation can be formulated:

$$(\Delta D) = (\Delta D)_R + (\Delta D)_D \quad (\text{III-8})$$

where $(\Delta D)_D$ is equal to the small DO deficit change due to the biological deoxygenation response. Equation (III-8) can be rewritten in a more usable form, as

$$(\Delta D)_D = (\Delta D) + 2.303 k_2 D_{AVE} \Delta t \quad (\text{III-8a})$$

This equation can be numerically integrated for the total time period containing "n" number of increments of time, Δt .

$$\sum_{i=0}^n (\Delta D)_{D,i} = \sum_{i=0}^n (\Delta D)_i + \sum_{i=0}^n 2.303 k_2 D_{AVE, i} \Delta t_i$$

(III-8b)

The resulting plot of $\sum_{i=0}^n (\Delta D)_{D,i}$ vs. time yields the oxygen uptake curve which depicts the associated biological deoxygenation response in the turbulent system.

The method described above was used in comparing bacterial deoxygenation response in the turbulent system to that of concurrently conducted bottle BOD determinations.

CHAPTER IV

LABORATORY EQUIPMENT, PROCEDURES, AND MATERIALS

A. Experimental Equipment

1. General Description of the Turbulent Simulated River Apparatus

The experimental apparatus developed and utilized in this investigation was a unique piece of laboratory equipment which was conceived by the author and developed at Oklahoma State University. It will be shown later that the fluid flow conditions which were made to prevail in this equipment closely simulate the flow conditions which prevail in a uniform open stream channel. Photographs of the experimental apparatus are shown in Figure 4; the velocity measuring device is also shown.

The basic apparatus employed consists of a right circular cylindrical torus-shaped tank. Inside the tank proper there are two concentric cylindrical shell walls which can be driven by the variable speed motors at any desired constant velocity. This arrangement permitted attainment of a velocity profile representing a desired experimental stream condition.

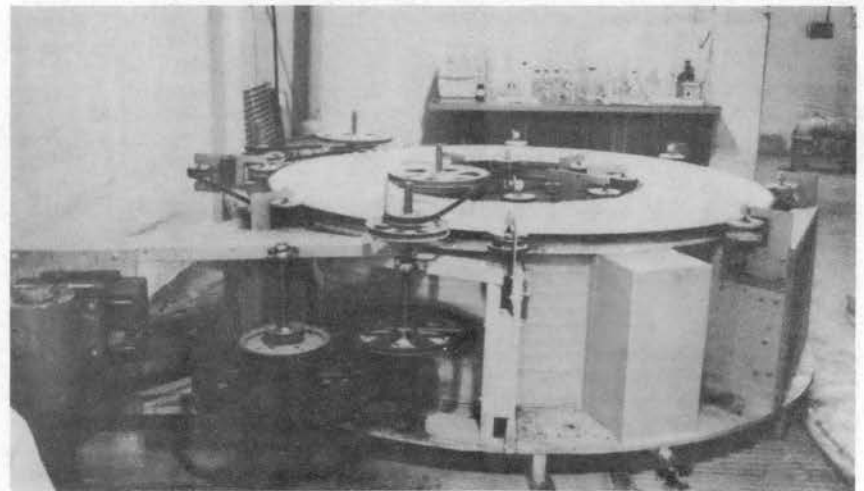
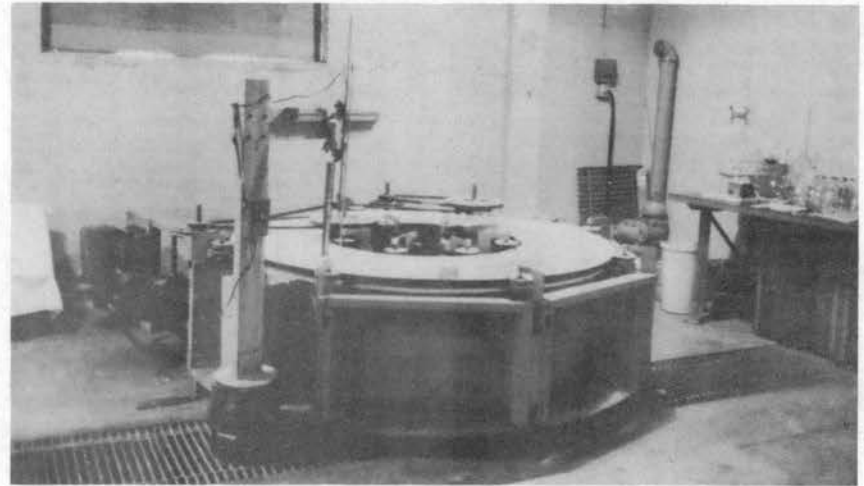
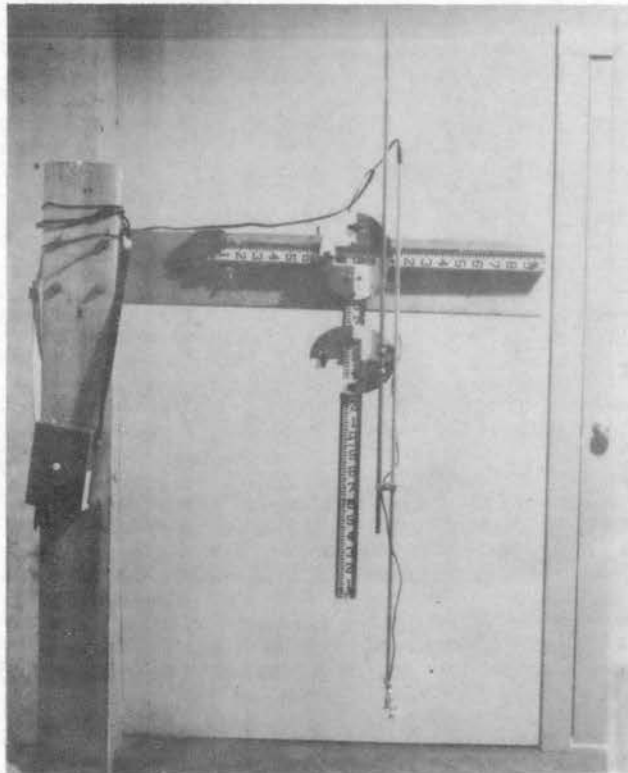


Figure 4. Photographs of Experimental Apparatus.

The mobile walls are analogous to continuously moving stream banks, providing a constant shear force on the relatively large prism of water contained between the walls. The constant shear force should cause the water between the walls to acquire a nearly uniform steady state flow condition over the tank bottom. The type of flow in this test facility is envisioned as being similar to that of a prism of water moving along in the central portion of a large natural flowing stream.

The influences of the channel bottom along with fluid viscosity as the major resistance mechanisms in the developed flow should be somewhat the same as they are in a regular stream. The difference in the flow conditions is that the impetus to flow in the experimental apparatus is the mechanical application of a constant shear force to the sides of the prism of water, while in a stream the impetus to flow is developed due to a constant gravitational influence. The resulting motion in either case is resisted by the viscous and frictional properties of the fluid and channel, respectively. It is emphasized that the primary difference between the experimental channel and a natural channel is the impetus to flow, not the general resistance to flow.

A very important feature of the experimental apparatus is that once a steady state condition is developed within the system, every longitudinal element of water along the path of motion should be undergoing a nearly uniform steady

flow condition barring slight variations caused by small geometric imperfections in the tank. The experimental system can be operated at any desired steady state condition for any length of time barring the possibility of mechanical failure.

The diameter of the inside rotating cylindrical shell is 4.0 feet, and the diameter of the outside rotating cylindrical shell is 6.0 feet. Maximum inside wall height of the tank is 22 inches, and the channel width is 12 inches. The movable walls are located 1/8th inch inside the walls of the tank proper. Each movable wall was independently driven by a variable speed 3-horse power motor. The volume of water in the system was approximately 23.6 cubic feet, or 668 liters at maximum operating depth.

2. Depth and Velocity Monitoring

The average depth of flow in the unit was fixed by varying the volume of tap water utilized in individual experiments. The apparatus was periodically checked for level with a Zeiss self-leveling level. The actual depth of water was measured at four points equally spaced around the tank. A steel gauge which could be read to the nearest 1/10th of an inch was used for this measurement. Five different depths of flow, 6", 9", 12", 15", and 18" were utilized in the reaeration study.

Velocity measurements were made by fixing an Ott meter (propeller-type velocity meter-30 mm diameter) to a

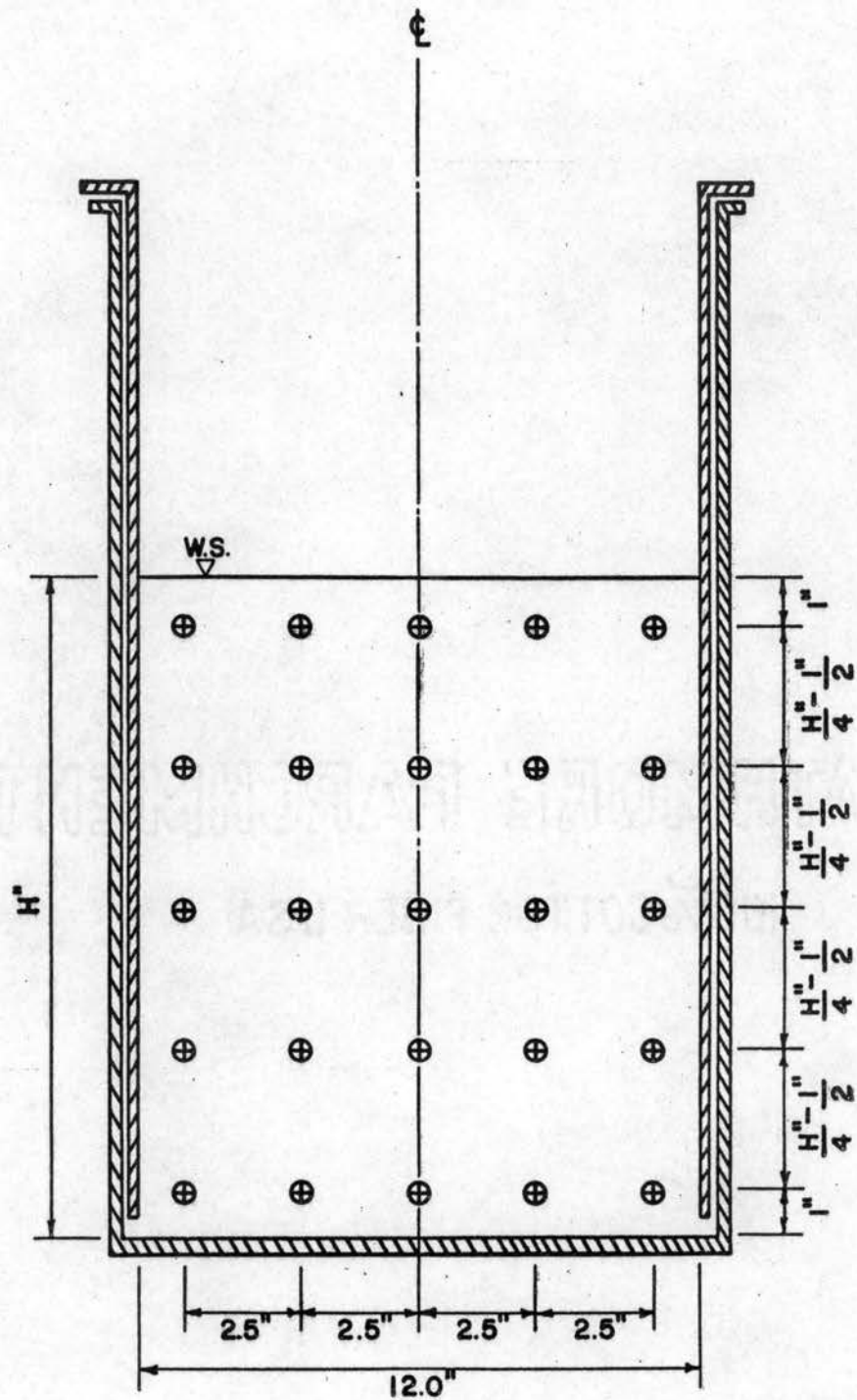
dual motion traversing device which could be located to the nearest 1/100th of a foot in both the horizontal and vertical directions. The device was also equipped with a bubble sight level.

Twenty-five field velocity measurements were made in a given channel cross-section in order to ascertain the average velocity of flow through the cross-section. The twenty-five point profile was used regardless of the depth of water in the tank. The general layout of the monitored cross-section is given in Figure 5.

Each point monitored was assumed to represent equal area velocity fields. This assumption was made for two reasons: (a) to facilitate ease in velocity computation; (b) since velocity is changing fastest at the walls, outer surface, and channel bottom, point velocities representing a velocity field adjacent to these boundaries were treated identical to interior velocity fields, although they usually contained a slightly smaller area than an interior field.

Average velocity in the cross-section was determined by computing the arithmetic mean of the twenty-five field velocity observations. This method is somewhat analogous to the midsection method for computing average velocity through a channel cross-section (51).

The velocity range covered in the reaeration experiments was 0.55 fps to 1.63 fps, i.e., approximately a three-fold change in velocity.



⊕ = POSITION OF POINT VELOCITY MEASUREMENTS

Figure 5. Layout of Channel Cross-section used for Velocity Monitoring.

B. Experimental Procedures

1. General Dissolved Oxygen Monitoring

Dissolved oxygen monitoring in a typical reaeration experiment was conducted in the following manner: Duplicate water samples were taken directly from the tank by siphoning through a rubber hose directly into a standard 300 ml BOD bottle. Each bottle was allowed to overflow for a period of fifteen seconds, which allowed approximately 200 ml to overrun the sample bottle. Each set of duplicate samples was immediately analyzed for DO by the standard Alsterberg azide modification of the Winkler Method as described in Standard Methods (9). The sodium thiosulfite solution was standardized daily, using biniodate.

2. General Procedure for Reaeration Experiments

Each reaeration experiment was conducted on a fixed volume of tap water. The volume used depended upon the mean depth of flow desired for the experiment. The system was set up so that the temperature of the water was very close to the ambient atmosphere's temperature. (Temperature remained nearly constant throughout the experiment, $\pm 1^{\circ}\text{C}.$) This was accomplished by blending hot and cold tap water in the experimental apparatus. The system was brought to desired volume, and allowed to sit overnight in a quiescent condition. The water was treated, after equilibrating overnight, with a fixed dose of sodium sul-

fite (10). The fixed dose provided quantitative removal of 8.0 ppm DO regardless of initial DO conditions of the water. This was done in order to maintain a fixed salt concentration throughout every experiment, except for variation in the salts of tap water. A fixed dose, 0.02 ppm, of cobalt chloride was used to catalyze the reaction between oxygen and sodium sulfite (10). The experimental apparatus was started and allowed to stir for fifteen minutes; then the initial duplicate DO samples were taken. The unit was then allowed to mix for an additional fifteen minutes, and a second pair of DO samples were taken. If the second set of samples showed a significant increase in DO over the first set, the second set was used to establish zero time for the reaeration run. If the second set of samples did not show a significant increase in DO, the procedure was repeated at fifteen-minute intervals until zero time was established.

Each reaeration run was monitored from an initial low DO value of 0.1 ppm to 2.0 ppm until it was either saturated or very close to saturation. A sufficient number of samples was taken to define both the reaeration rate constant, k_2 , and DO saturation value, C_s .

The following general procedure was employed in conducting all reaeration experiments:

(a) Fill experimental tank to desired test volume with tap water at temperature very close to ambient atmospheric temperature. Allow to stand quiescent overnight.

(b) Monitor depth at four points equally spaced around the tank in order to check correct test depth.

(c) Start up experimental apparatus and set system to desired rim velocities. Check the rim velocities for constancy and allow system to equilibrate for approximately thirty minutes.

(d) Determine twenty-five point cross-section velocity profile required to define average flow velocity.

(e) Dose equilibrated system with required amount of sodium sulfite and cobalt chloride.

(f) Establish zero time for the experiment.

(g) Monitor rim velocity, temperature, and DO at desired time intervals until system is at or near DO saturation value.

3. Experimental Procedure for Determination of DO Saturation Value

Each reaeration experiment was conducted for a sufficient period of time and monitored for an adequate number of DO samples to determine the DO saturation value. The apparent prevailing DO saturation value was determined by the method described in the Theoretical Considerations section (see pages 32 through 40).

In addition to the in situ measurement of DO saturation values, a number of small volume experiments were set up in a battery jar apparatus. Twelve-liter samples of (a) distilled water, (b) distilled water passed over

a deionizing column, and (c) tap water were stirred slowly, using a propeller-type mixer. These samples were monitored only for the apparent final DO value. This was assumed to be the prevailing DO saturation value. The length of these experiments ranged from one day to eight days. These experiments were conducted at a constant temperature ($\pm 0.2^{\circ}\text{C}$). Barometric pressure corrections were made utilizing the prevailing barometric pressure at the end of each experiment. Samples for dissolved oxygen determination were taken at approximately one-half day intervals until no apparent change in DO was observed.

4. Experimental Procedures for Deoxygenation Response

Studies

The following general procedure was used in conducting all of the experiments on deoxygenation responses:

(a) Conduct a reaeration experiment according to the procedure described previously in this chapter, section B-2. Omit determination of average flow velocity.

(b) Upon completion of reaeration experiment, add tap water back to system to adjust for the small volume removed during aeration experiment.

(c) Add standard mineral nutrients and phosphate buffer at a dosage of 1 mg/l as dictated for BOD dilution water in "Standard Methods."

(d) Add measured amount of substrate (food source) to the system.

(e) Add settled sewage seed, 24 hours to 48 hours old, at a dosage of 5 ml/l.

(f) Start up system and allow to equilibrate for thirty minutes.

(g) Measure DO concentration after equilibration period in order to establish DO level at this assumed zero time.

(h) Immediately remove sufficient sample from system and set up a series of BOD bottle determinations for the polluted system.

(i) Monitor DO and other desired parameters for period of test time desired. Also determine the course of BOD exertion in the BOD bottle.

C. Analytical Procedures

The following analytical procedures were utilized:

1. BOD Determination

The BOD tests were run in accordance with Standard Methods for the Examination of Water and Wastewater (9). Tap water was used for dilution water. The dilution water was prepared by addition of reagents prescribed in Standard Methods. The prepared dilution water was slowly stirred overnight in order to saturate it with oxygen. Dissolved oxygen was determined by the Alsterberg azide modification of the Winkler method. Bottles were incubated in the dark at 23°C. since this temperature was the average prevailing temperature for the turbulent system.

2. Biological Solids Determination

The membrane filter technique (Millipore Filter Corporation, Bedford, Mass., HA, 0.45 μ) was used for biological solids determination. The filters were dried for two hours at 103°C. and allowed to equilibrate overnight in a desiccator prior to determining the tare weight. The same procedure was used for final weight determination. The size of samples passed through the filter varied from 250 ml to 1000 ml, depending upon the amount of solids required to obtain accurate measurement of weight.

3. Carbohydrate Determination

The anthrone test, which is specific for carbohydrate, was used for determining the course of glucose removal in the polluted systems conducted in the large experimental apparatus. The test was performed using the technique described by Gaudy (52).

CHAPTER V

RESULTS

A. Dissolved Oxygen Solubility

1. Results of Primary Reaeration Study

Due to the controversy concerning DO saturation values, the necessity for making in situ determinations of this parameter for each reaeration experiment appeared to be the paramount prerequisite for attaining consistent results. The primary objective of this study was the ultimate development of a prediction equation for defining the reaeration rate constant, k_2 . The importance of knowing the best value of the prevailing dissolved oxygen saturation for each experiment was discussed in Chapter III.

For each of the fifty-nine reaeration experiments reported, the in situ dissolved oxygen saturation value, C_s , was determined by the graphical-computational method described in Chapter III. The two general equations used for this analysis were:

$$\log \frac{D_o' - \alpha}{D_t' - \alpha} = k_2 t \quad (\text{III-2c})$$

$$\alpha = \frac{D_1' D_2' - (D_3')^2}{D_1' + D_2' - 2D_3'} \quad (\text{III-6})$$

where

$$\alpha = C'_S - C_S.$$

Figures 6 through 13 depict the experimental observations of forty typical reaeration experiments. These figures show the observed DO concentration for the system vs. time. Also shown on each figure is an accompanying tabulation defining the experimental conditions. Average depth of flow, average velocity of flow, reaeration rate constant, computed C_S value, observed C_S value for the experiments continued to saturation, and the reported "Standard Methods" value of C_S for the prevailing average experimental temperature are given in the tabulations.

Figure 14 shows the differences between the "Standard Methods" values of C_S corrected for prevailing average barometric pressure and the computed value of the prevailing C_S for the forty reaeration experiments shown in Figures 6 through 13.

During these experiments the average correction for barometric pressure was 3.04 per cent of the C_S value reported by "Standard Methods." The average difference between the computed C_S value and the "Standard Methods" values was 7.94 per cent. Comparing these two average differences, the computed values for true in situ saturation were on the average 4.90 per cent less than "Standard Methods" values after correction for temperature and barometric pressure effects. It is apparent

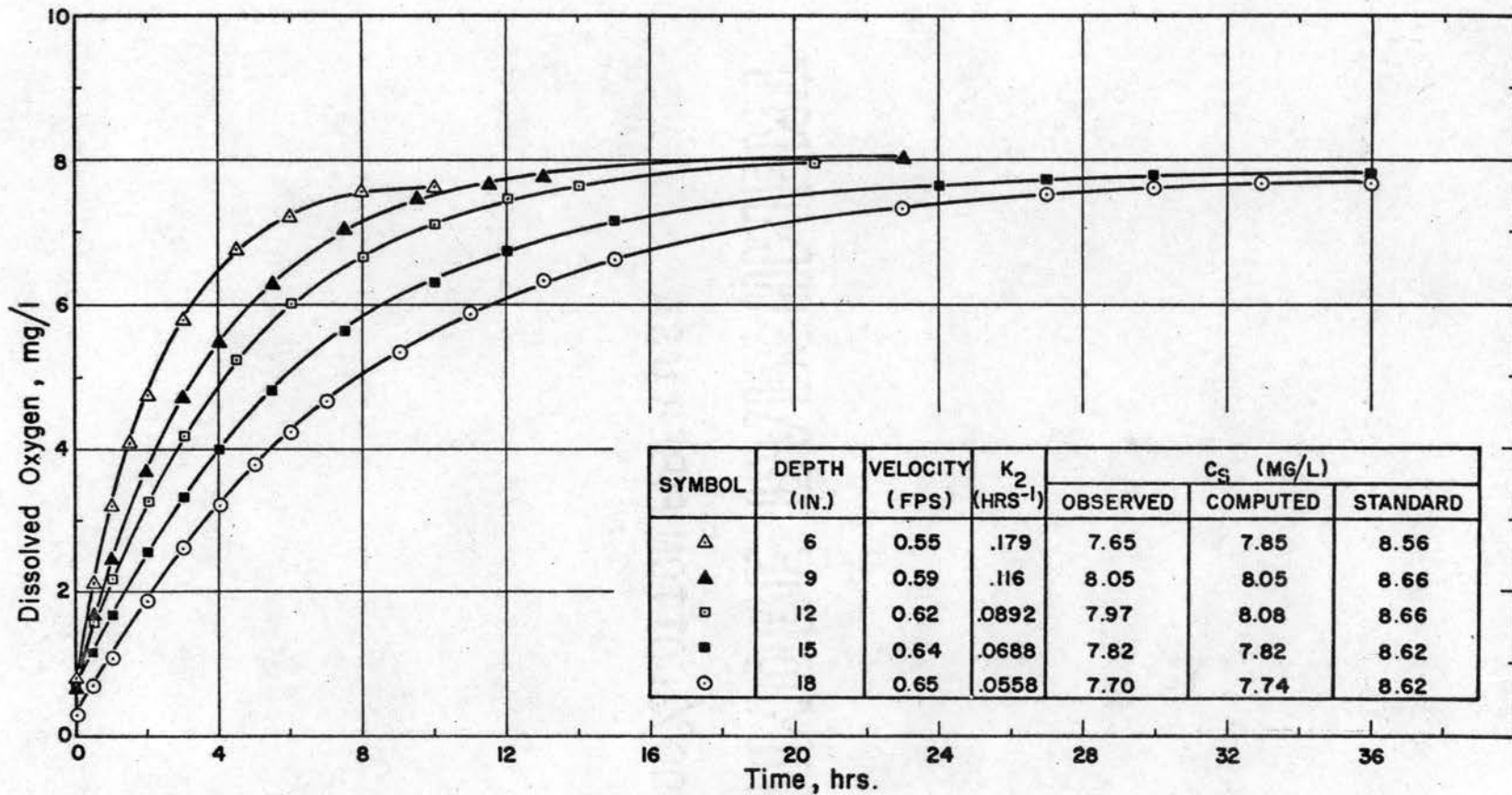


Figure 6. Reaeration Experiments, Numbers 1, 2, 3, 4, and 5 from Table II.

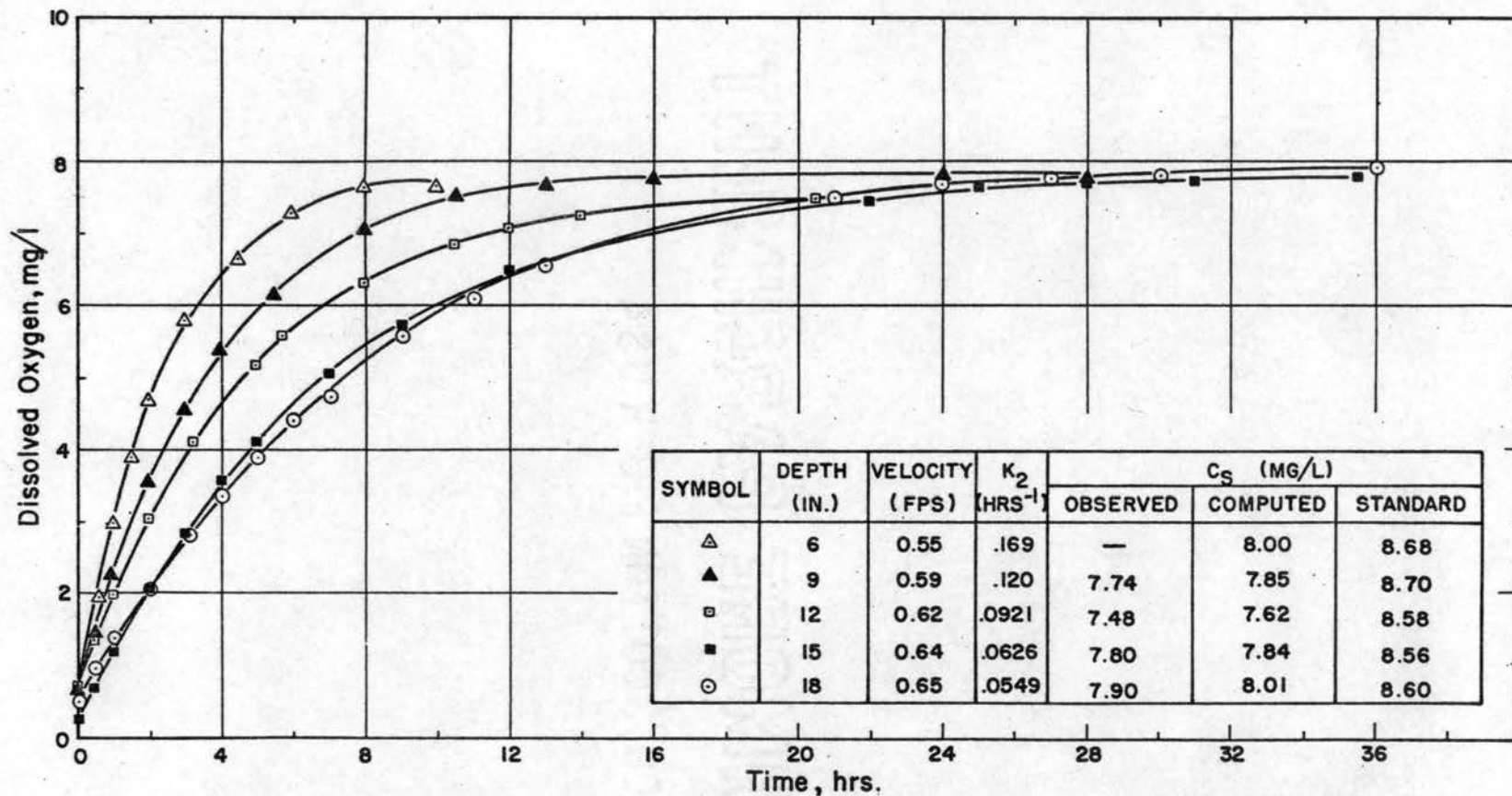


Figure 7. Reaeration Experiments, Numbers 21, 22, 23, 24, and 25 from Table II (Duplicates of Experiments shown in Figure 6).

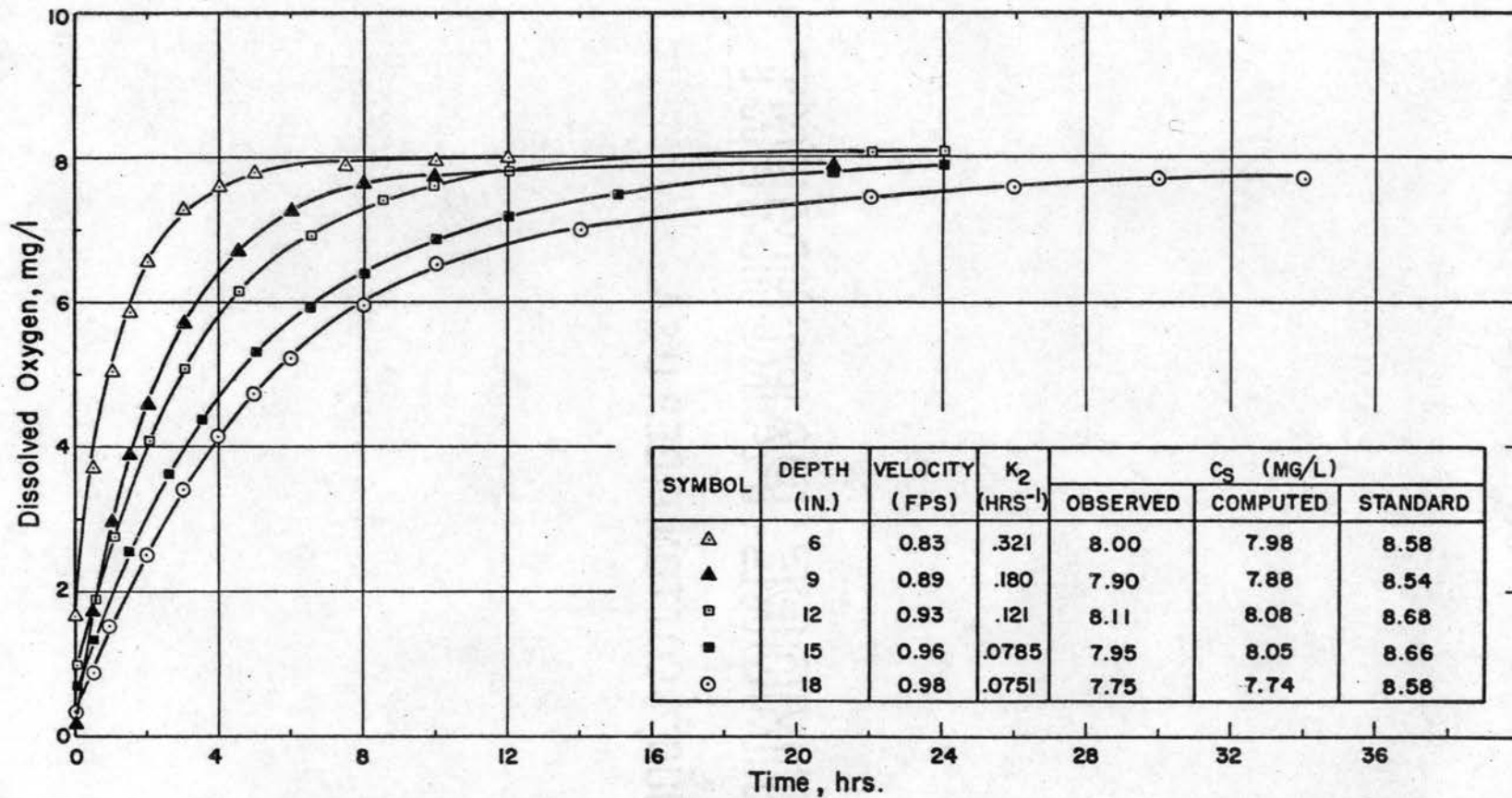


Figure 8. Reaeration Experiments, Numbers 6, 7, 8, 9, and 10 from Table II.

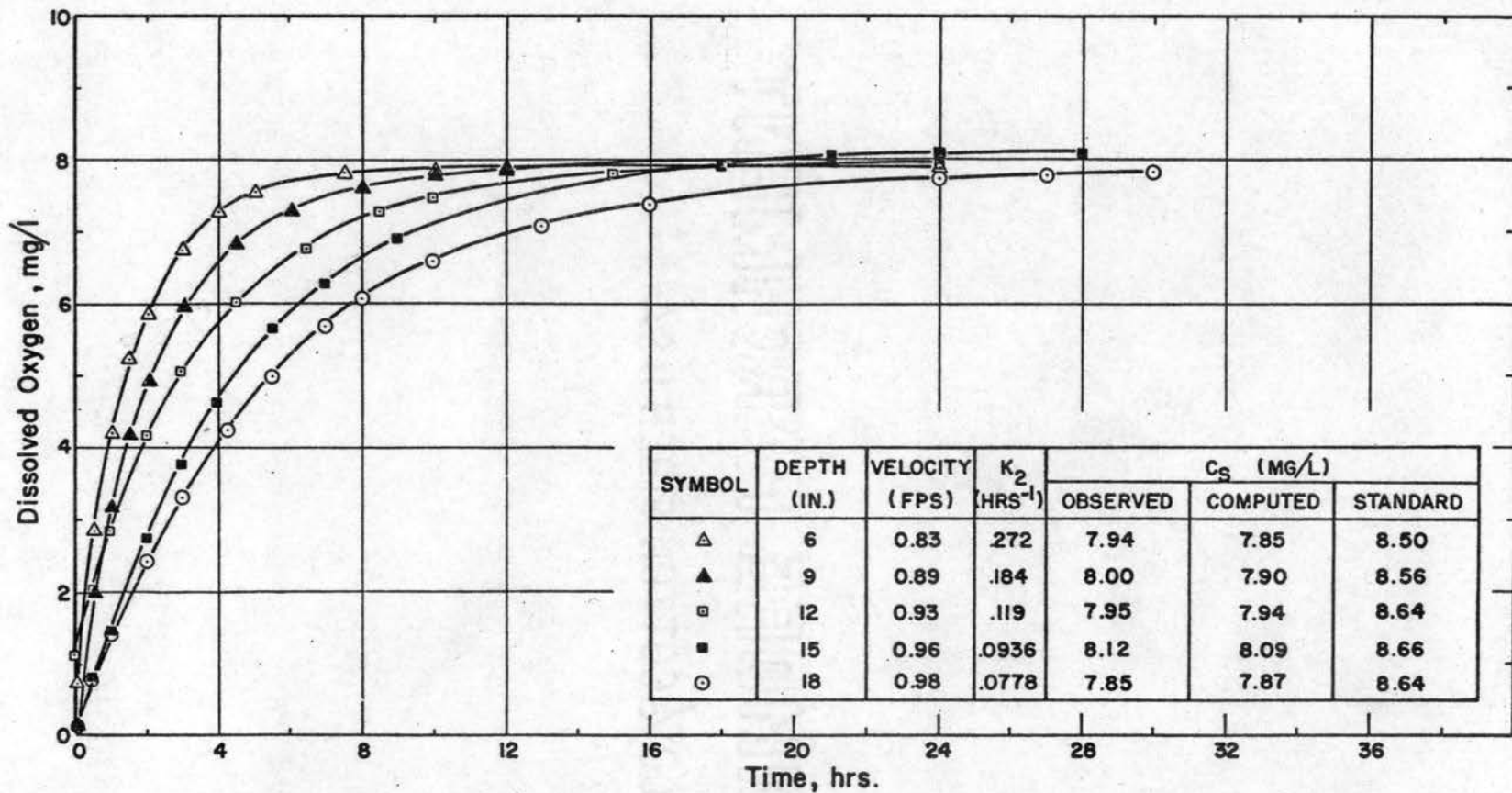


Figure 9. Reaeration Experiments, Numbers 26, 27, 28, 29, and 30 from Table II (Duplicates of Experiments shown in Figure 8).

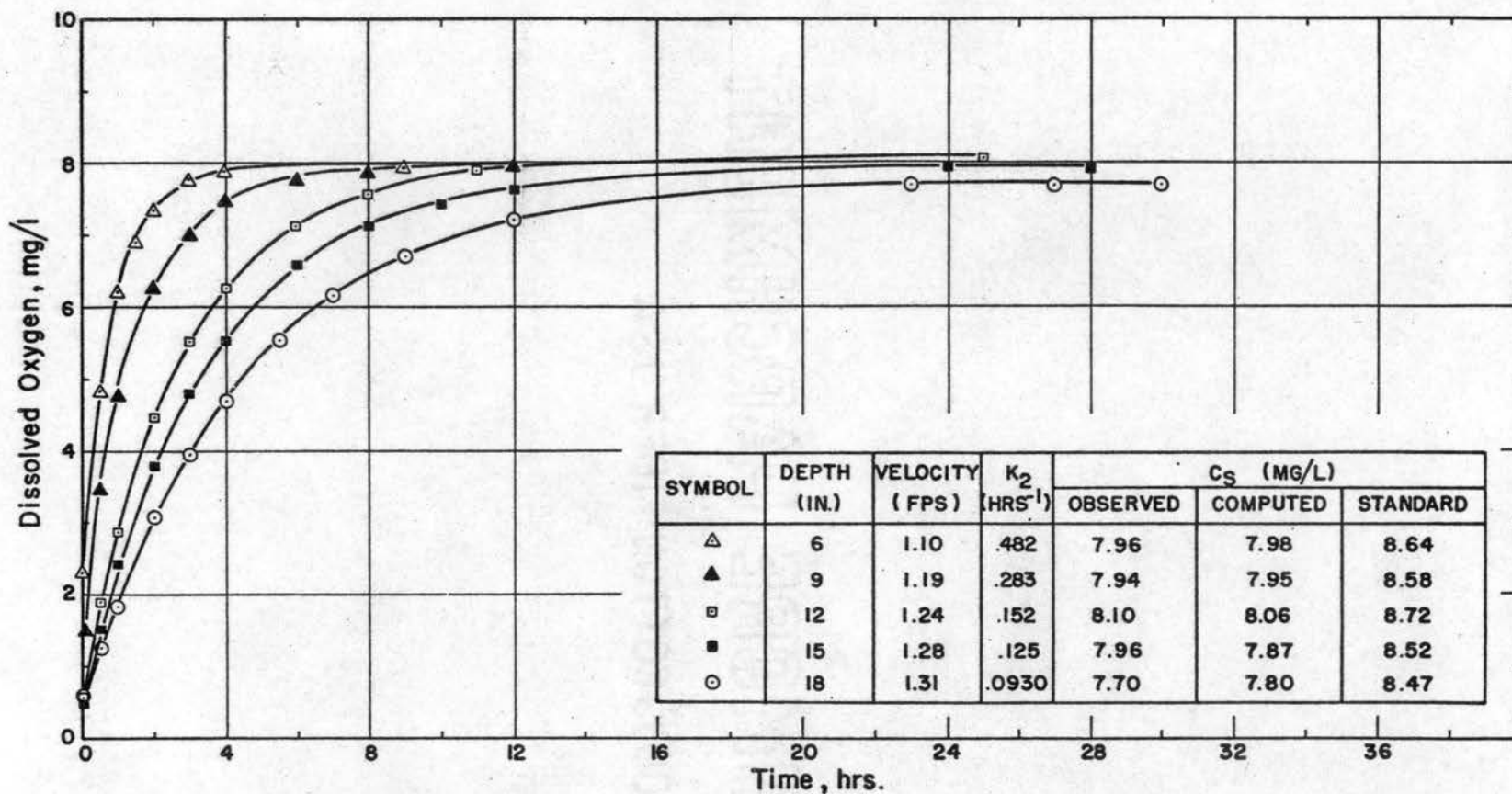


Figure 10. Reaeration Experiments, Numbers 11, 12, 13, 14, and 15 from Table II.

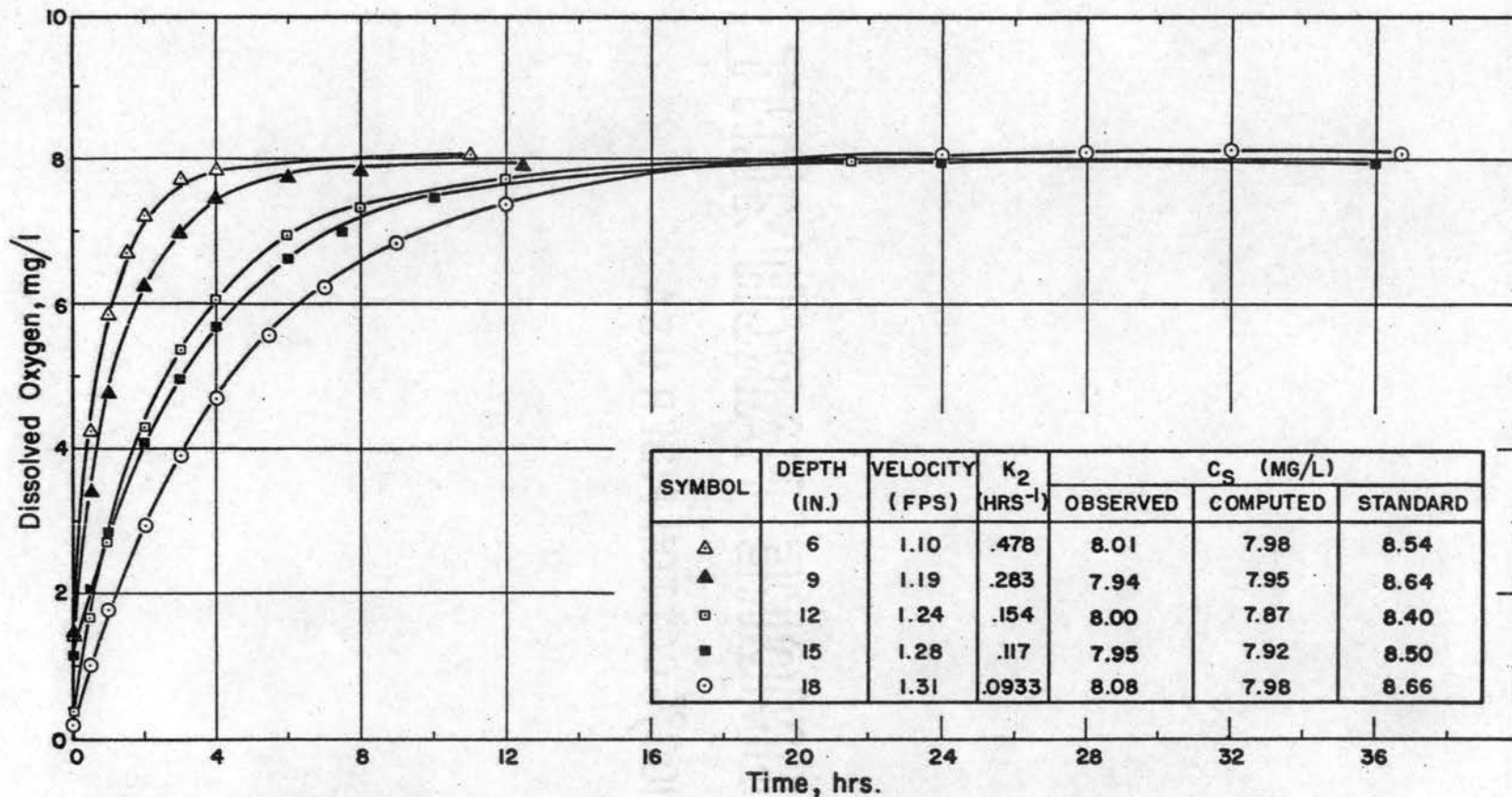


Figure 11. Reaeration Experiments, Numbers 31, 32, 33, 34, and 35 from Table II (Duplicates of Experiments shown in Figure 10).

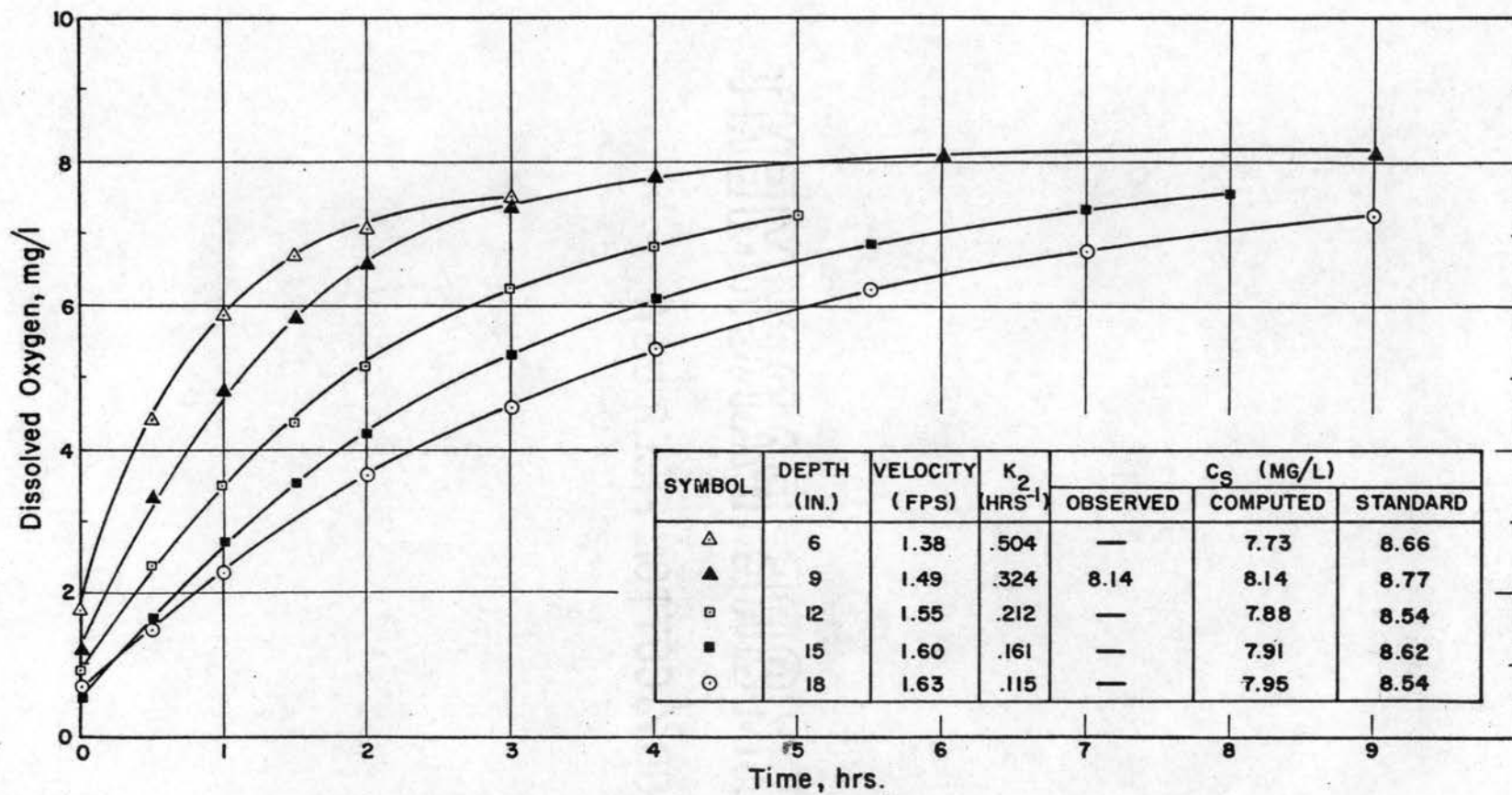


Figure 12. Reaeration Experiments, Numbers 16, 17, 18, 19, and 20 from Table II.

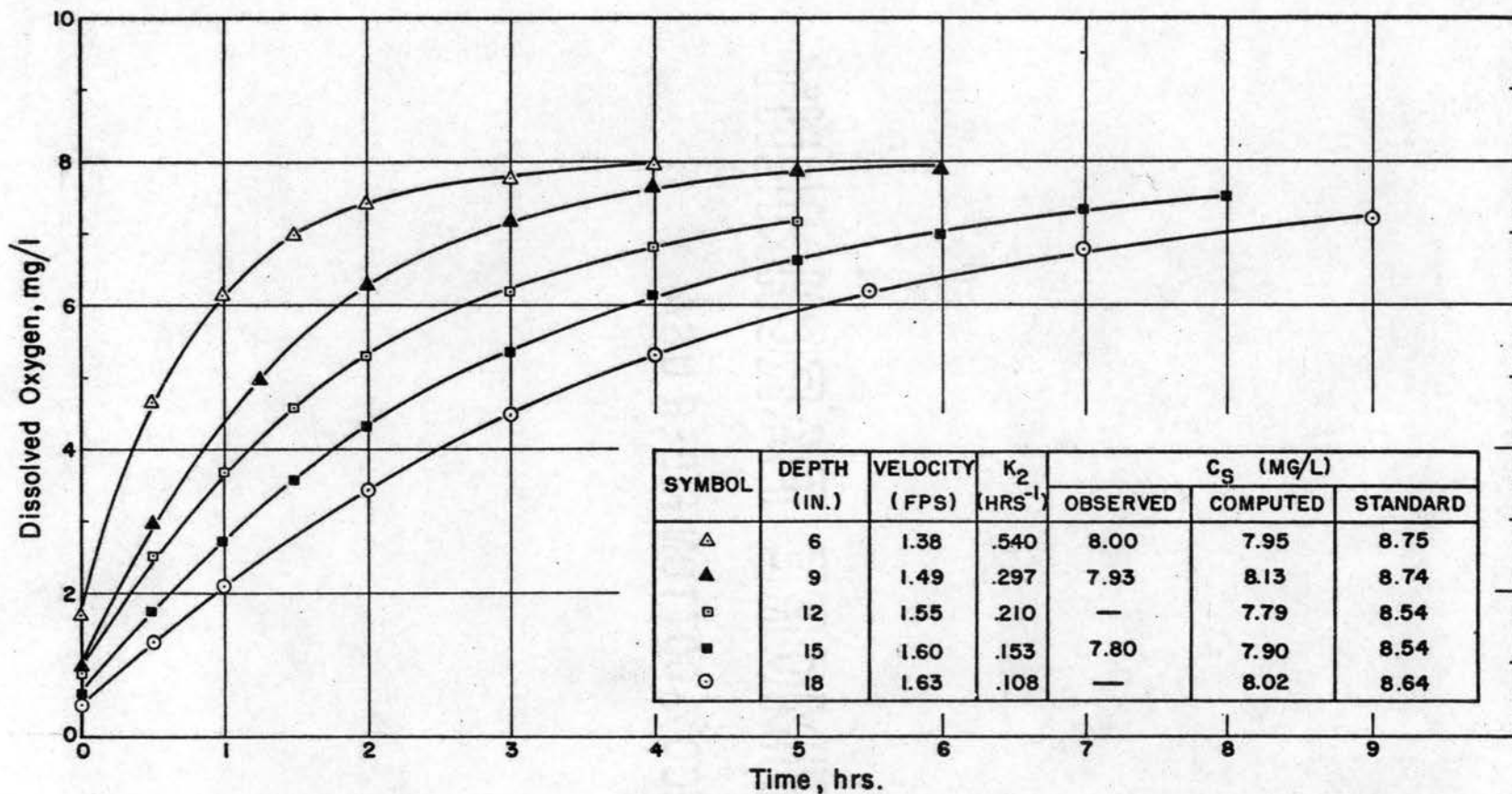


Figure 13. Reaeration Experiments, Numbers 36, 37, 38, 39, and 40 from Table II. (Duplicates of Experiments shown in Figure 12).

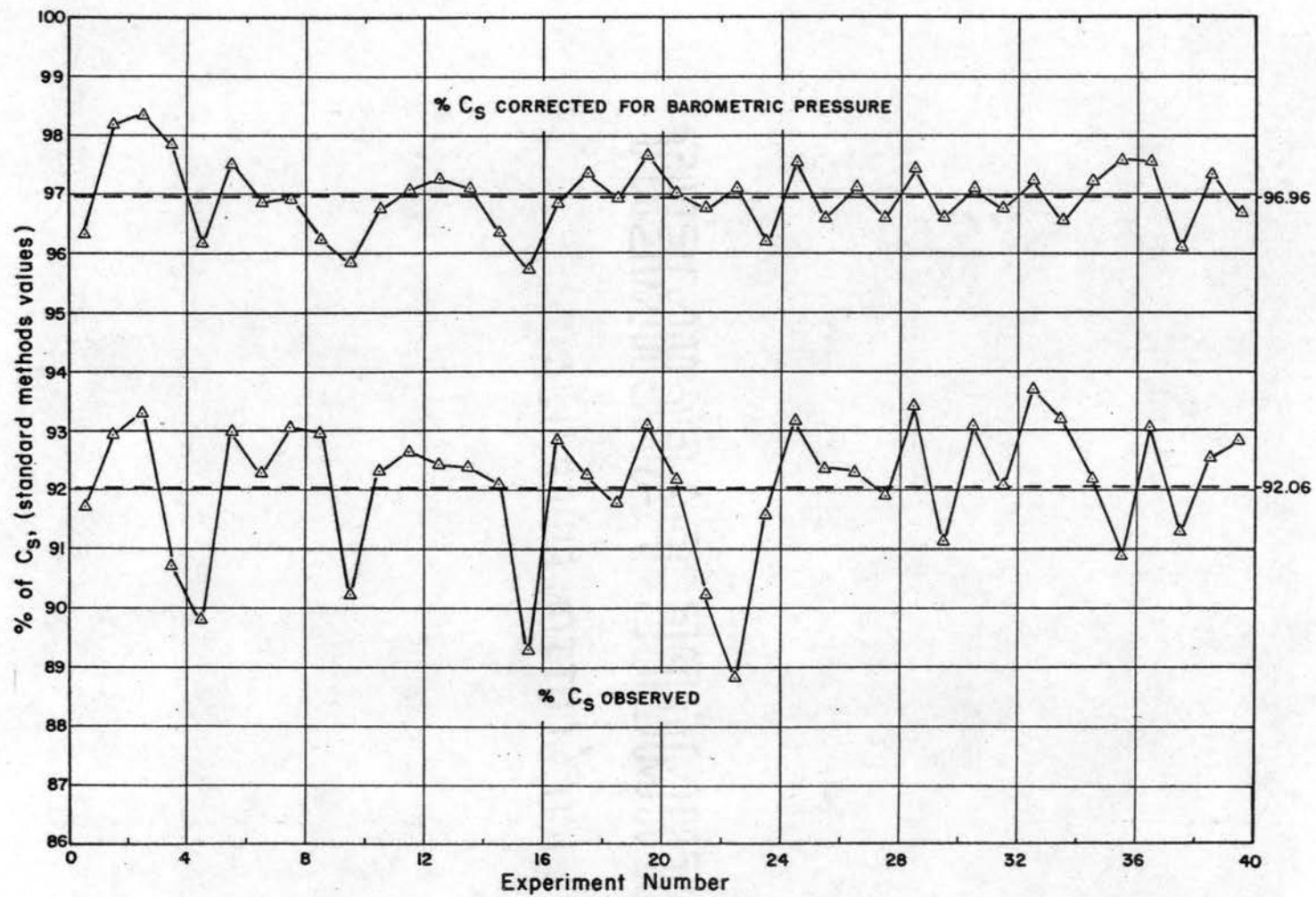


Figure 14. Comparison of Observed and Corrected DO Saturation Values.

that there were large differences between the computed saturation values and those given in "Standard Methods."

In comparing the computed C_s values to those actually observed for experiments continued to saturation (see tabulations shown in Figures 6 through 13), it can be seen here that these two values are essentially the same. The observed differences between these two values were never greater than 0.20 mg/l of DO, and these differences were usually less than 0.10 mg/l of DO. Dissolved oxygen determinations were accurate to the nearest 0.10 mg/l DO with the chemical assay procedures used throughout this investigation.

2. Results of Small Scale Experiments

Six experiments were conducted in a small battery jar apparatus under controlled temperature conditions. Two twelve-liter samples were monitored concurrently in a constant temperature bath. In two of the experiments a comparison of a sample of distilled water vs. a sample of distilled water passed over a deionizing column was made. In the other four experiments a comparison of distilled water vs. tap water was made. Table I shows the results of the six experiments.

It can be seen from Table I that the DO saturation values obtained for distilled water and deionized distilled water were identical, although these values were observed to be from 0.30 to 0.42 mg/l less than the reported stand-

ard values corrected for barometric pressure effect. It can also be seen from this table that DO saturation values of tap water compared to distilled water were observed to be consistently 0.15 mg/l less than the observed values for distilled water.

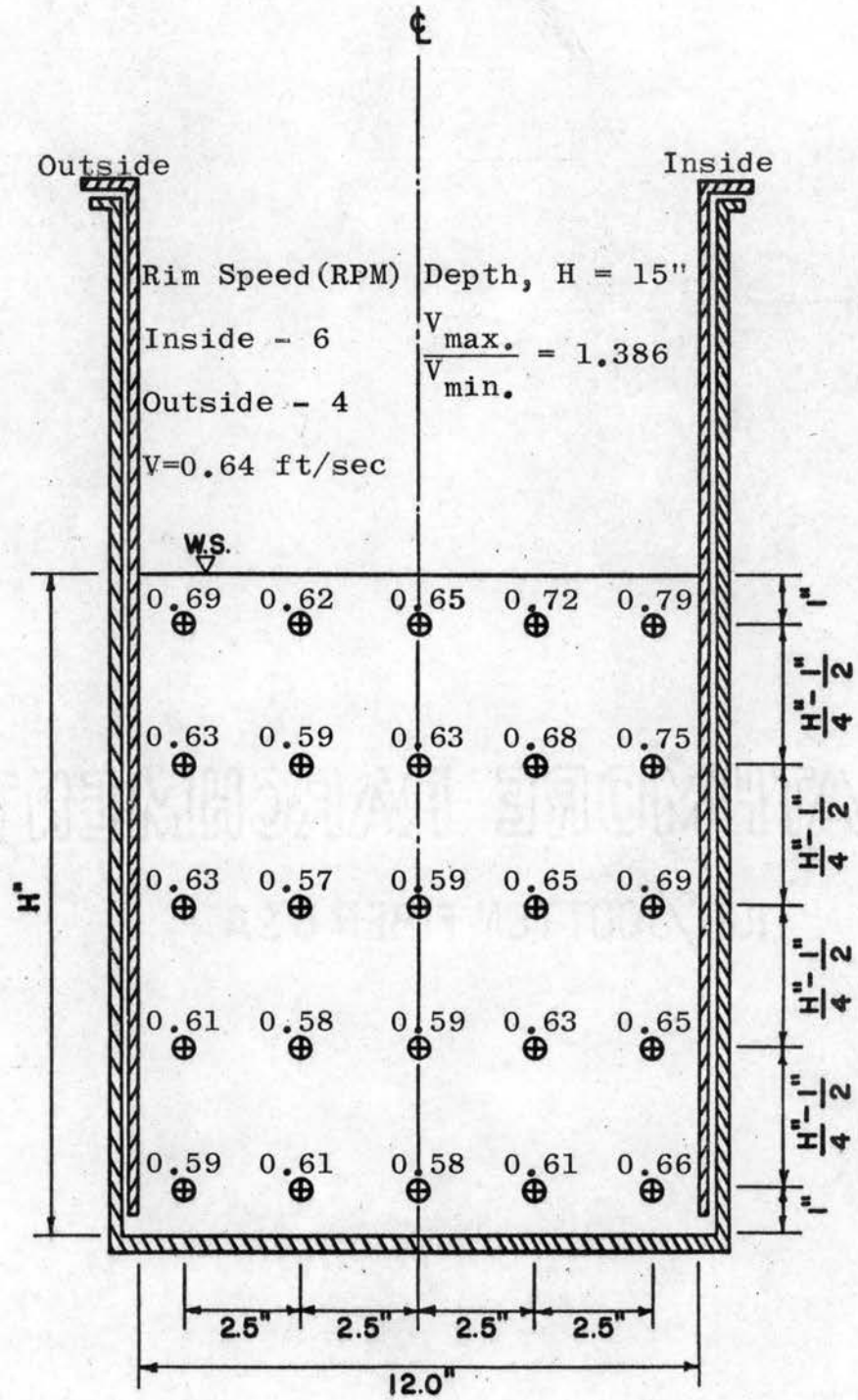
TABLE I
COMPARISON OF DO SATURATION VALUES

Exp. #	Temp. °C.	Sample	Barometric Pressure (In. in Hg.)	C _s Obs. (mg/l)	C _s * (mg/l)
1	22.4	DW	28.85	8.15	8.45
		DW (Deionized)		8.15	
2	23.3	DW	29.20	8.10	8.43
		DW (Deionized)		8.10	
3	22.7	DW	29.35	8.15	8.56
		TW		8.00	
4	22.8	DW	29.00	8.10	8.45
		TW		7.95	
5	23.1	DW	29.20	8.10	8.47
		TW		7.95	
6	22.5	DW	29.30	8.15	8.57
		TW		8.00	

* Standard Methods values for DO saturation corrected for prevailing barometric pressure

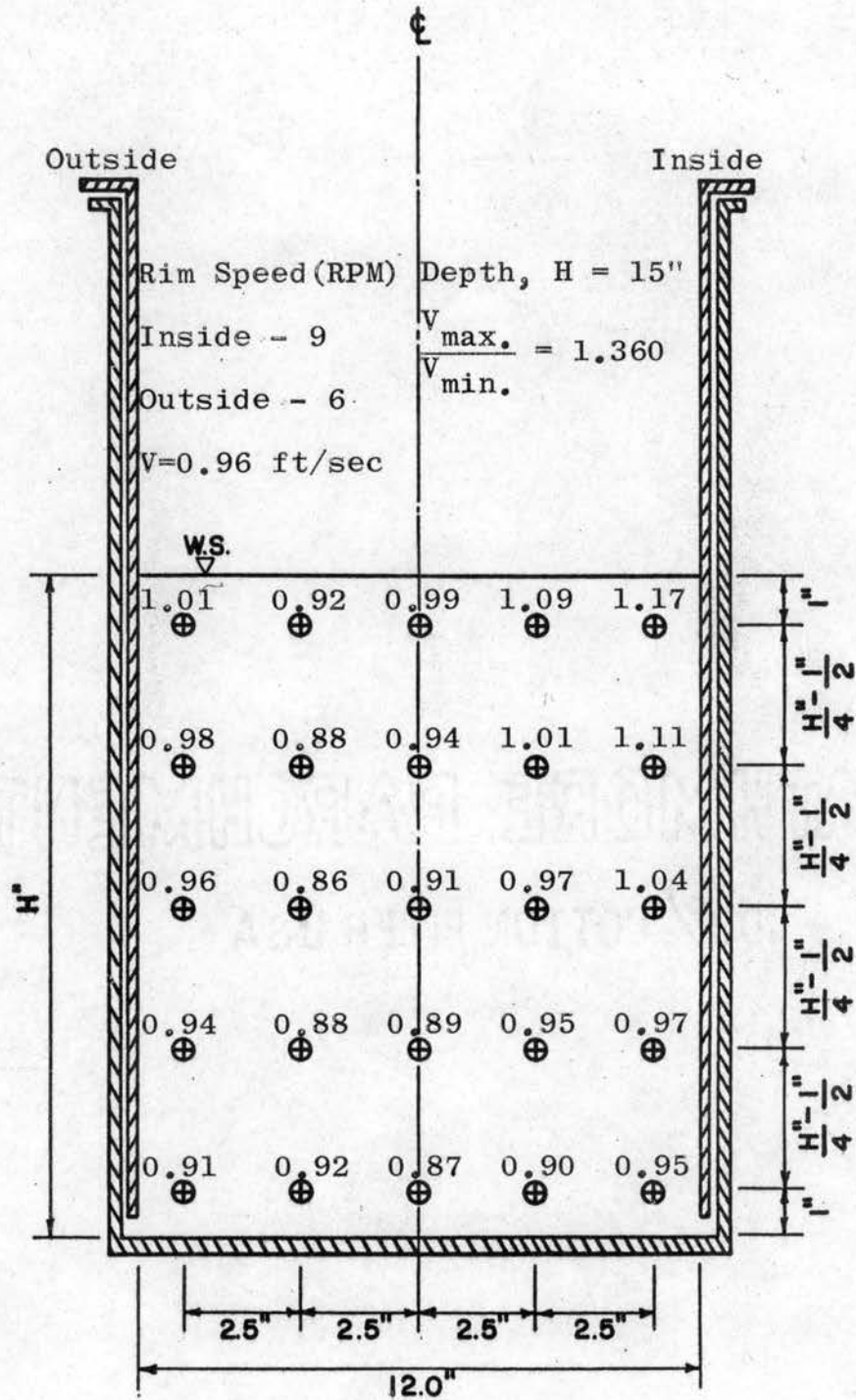
B. Results of Mean Velocity Determinations

Figures 15 through 18 show the results of four typical twenty-five point velocity profiles. In all cases velocity is expressed in feet per second. It can be determined from a comparative study of these profiles that the velocity



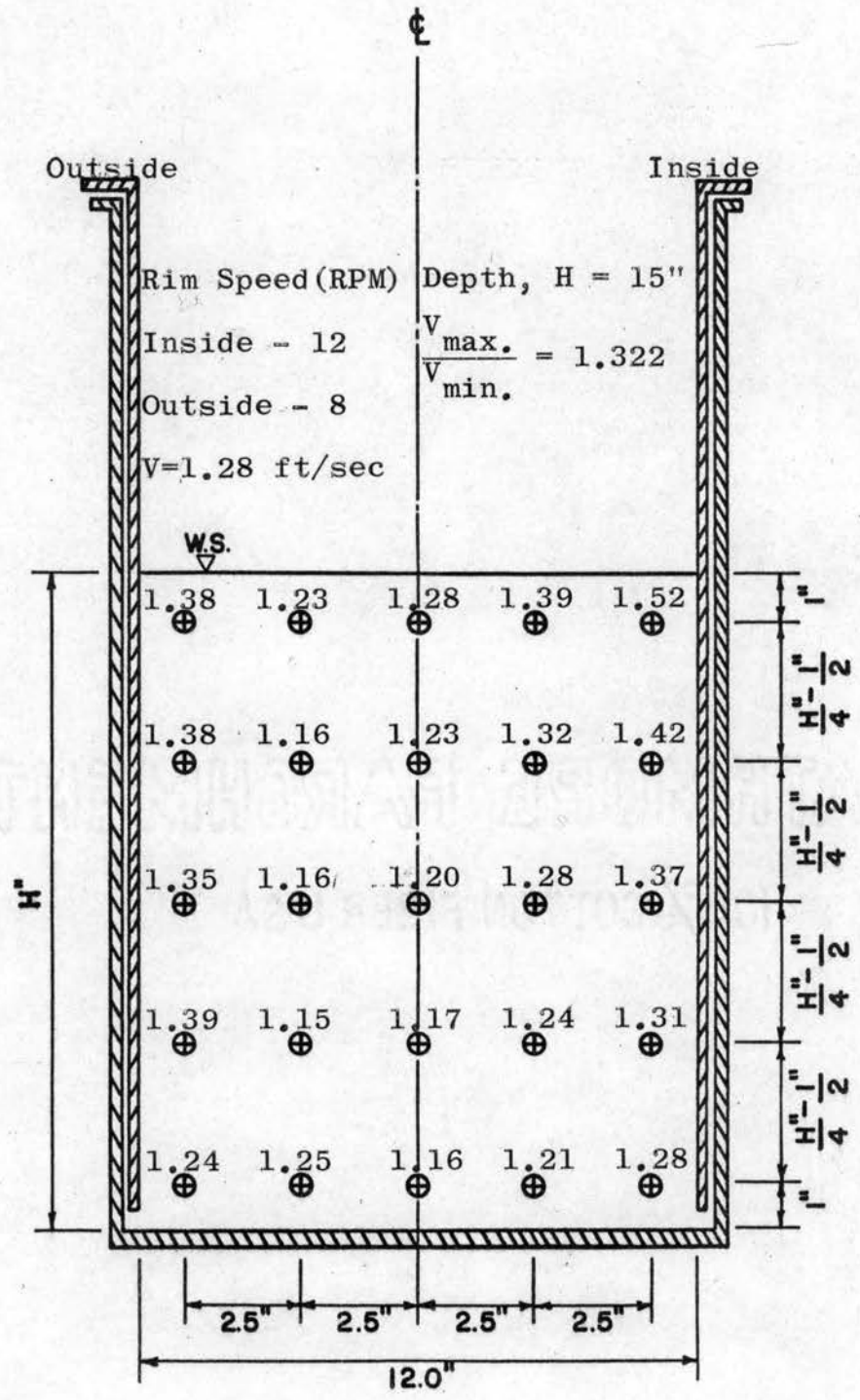
⊕ = POSITION OF POINT VELOCITY MEASUREMENTS

Figure 15. Velocity Distribution Measured in Experiment Number 4, Table II.



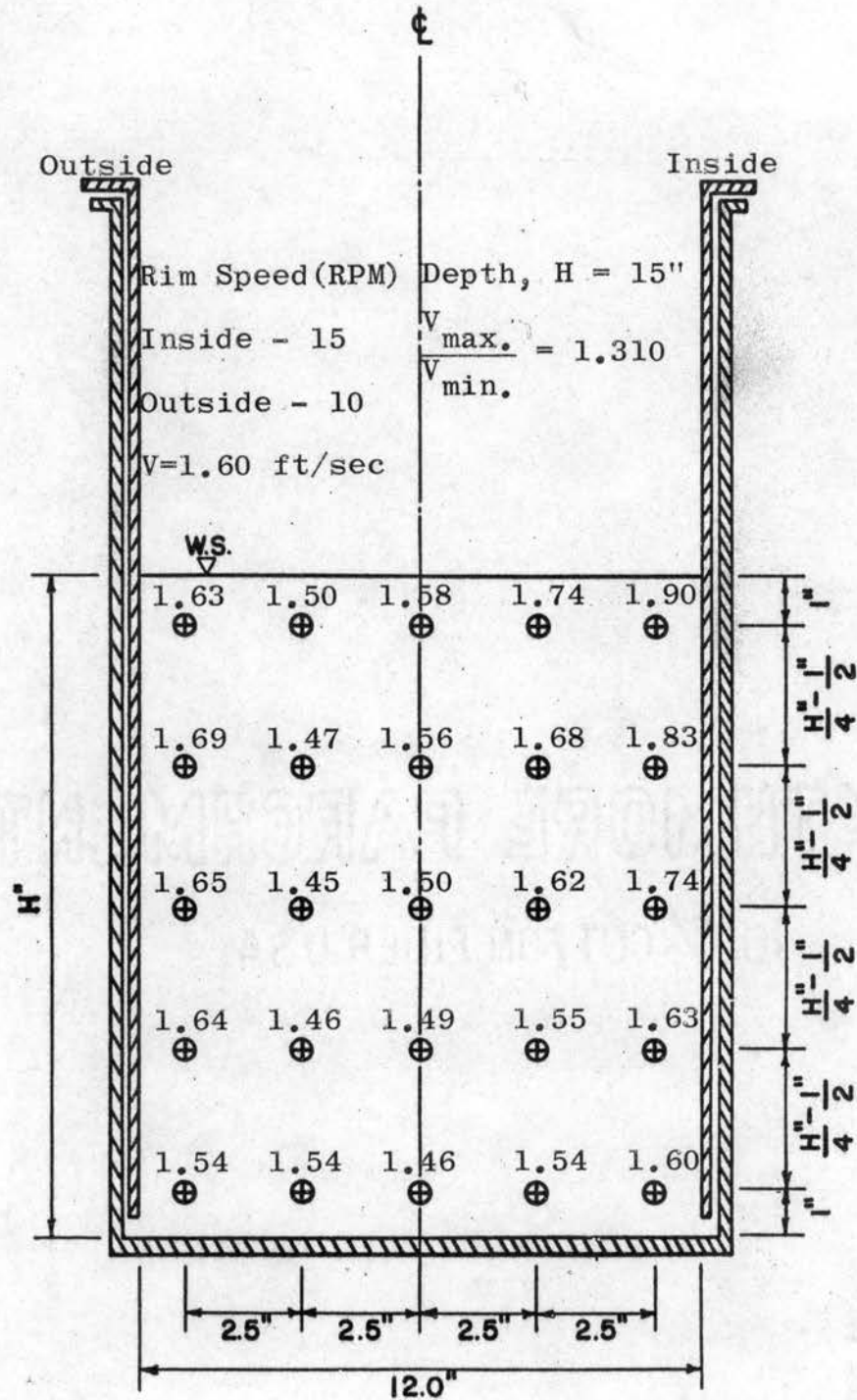
⊕ = POSITION OF POINT VELOCITY MEASUREMENTS

Figure 16. Velocity Distribution Measured in Experiment Number 9, Table II.



⊕ = POSITION OF POINT VELOCITY MEASUREMENTS

Figure 17. Velocity Distribution Measured in Experiment Number 14, Table II.



⊕ = POSITION OF POINT VELOCITY MEASUREMENTS

Figure 18. Velocity Distribution Measured in Experiment Number 19, Table II.

pattern developed in this experimental unit was very consistent over the full range of rim velocities utilized. The highest velocity always occurred along the inside rotating cylindrical shell regardless of the depth, and the lowest velocity usually occurred at approximately $3\frac{1}{2}$ inches from the outside cylindrical shell regardless of depth. The velocity for a given depth gradually decreased from a maximum at the moving walls to a minimum toward the center as it should, since the movable walls were operated at the same linear velocity, and retardation of velocity was expected as a fluid element became farther removed from the constant tangential driving force. Velocities generally decrease from a maximum value at the water surface to a minimum along the channel bottom. This trend is also consistent with the theory of fluids, since the major resistance to the flow is the roughness of the channel bottom. It was found that the most uniform velocity profile was obtained when the inside and outside rims were maintained at the same linear velocity.

The reproducibility of the average velocity in the channel is illustrated in Figure 19. It can be seen from this figure that average velocity varied linearly with rim speed and for the given rim speed combination the velocity decreased as depth decreased. This implies that the roughness of the channel bottom is very significant at low depths of flow, as would be expected.

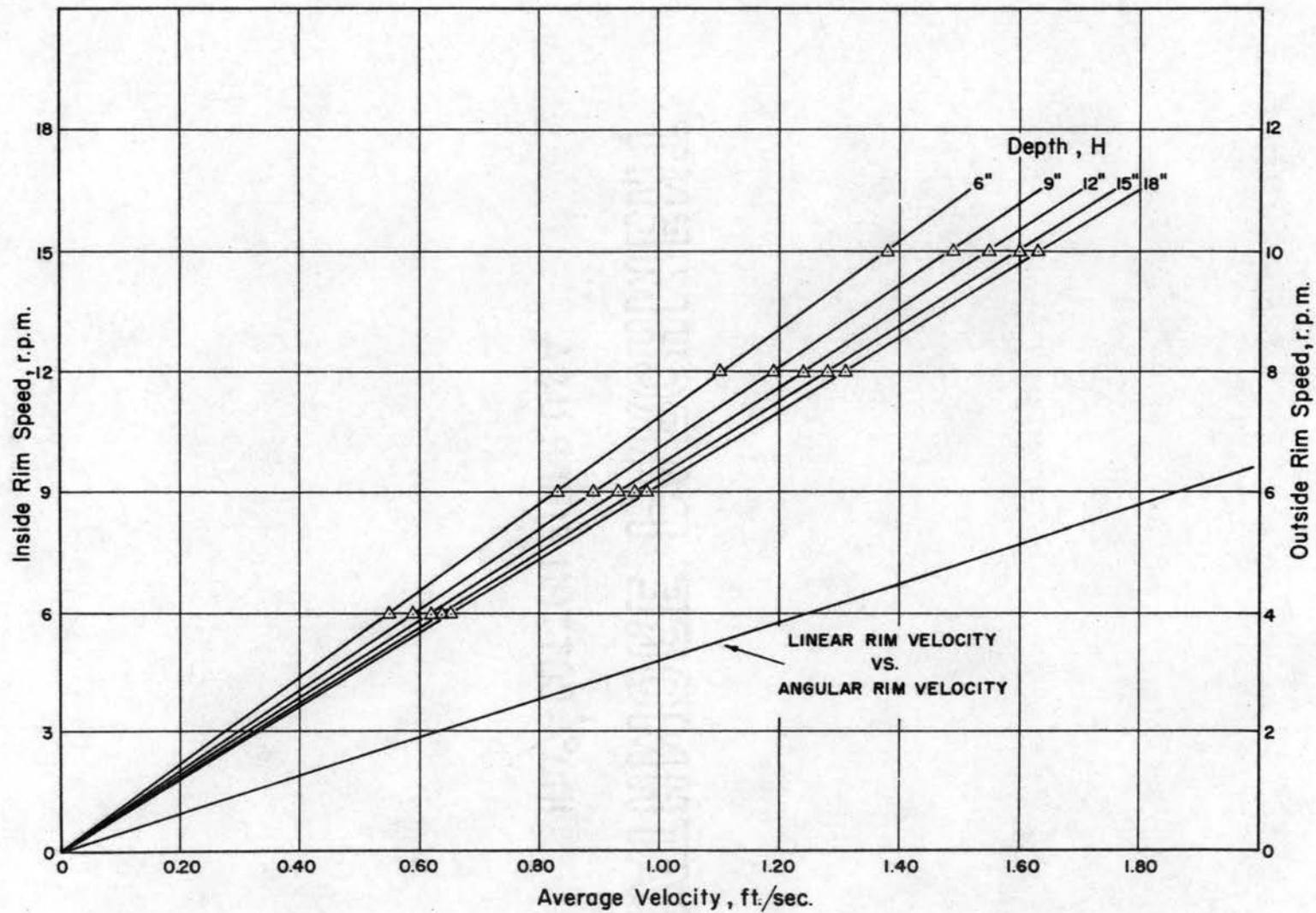


Figure 19. Comparison of Rim Velocities versus Average Stream Flow Velocities Observed at Different Depths of Flow.

That this system is truly a turbulent system is readily seen by the velocity profile. The velocity is for all practical purposes uniform throughout the cross-section; however, shown on Figure 19 is a curve showing the relation between linear rim velocity and angular rim velocity. At the six-inch depth the average velocity of flow is approximately forty-four per cent of the rim velocity, and at the eighteen-inch depth it is approximately fifty-two percent of the rim velocity, hence rapid retardation of velocity occurs within one inch of each wall, since approximately fifty per cent velocity loss occurs between the rim and the sampling points located one inch from each rim.

For a given depth and rim speed combination, the average velocity in this apparatus was always reproducible to the nearest one-hundredth of a foot per second. This can be discerned from Table II, page 83.

C. Reaeration Studies

1. Laboratory Results

The observed results of the fifty-two reaeration experiments conducted for this study are given in Table II. Forty of these experiments were previously shown in Figures 6 through 13. A multiple correlation analysis was performed on these tabulated experimental observations in order to determine a prediction equation defining the

TABLE II
COMPOSITE DATA OF REAERATION EXPERIMENTS

1	2	3	4	5	6	7	8	9	10
Exp. #	k_2-T (Hr ⁻¹)	Mean Depth H (ft)	Avg. Veloc. V (ft/sec)	Inside Rim Speed (RPM)	Outside Rim Speed (RPM)	Avg. Temp. °C.	Observed DO Saturation C _s (mg/l)	Computed DO Saturation C _s (mg/l)	Corrected Barometric Pressure (In. of Hg)
1	0.179	0.50	0.55	6	4	23.7	7.65	7.85	28.83
2	0.116	0.75	0.59	6	4	23.2	8.05	8.05	29.38
3	0.0892	1.00	0.62	6	4	23.2	7.97	8.08	29.43
4	0.0688	1.25	0.64	6	4	23.4	7.82	7.82	29.28
5	0.0558	1.50	0.65	6	4	23.4	7.70	7.74	28.78
6	0.321	0.50	0.83	9	6	23.6	8.00	7.98	29.18
7	0.180	0.75	0.89	9	6	23.8	7.90	7.88	28.98
8	0.121	1.00	0.93	9	6	23.1	8.11	8.08	29.00
9	0.0785	1.25	0.96	9	6	23.2	7.95	8.05	28.80
10	0.0751	1.50	0.98	9	6	23.6	7.75	7.74	28.68
11	0.482	0.50	1.10	12	8	23.3	7.96	7.98	28.95
12	0.2825	0.75	1.19	12	8	23.6	7.94	7.95	29.05
13	0.1524	1.00	1.24	12	8	22.8	8.10	8.06	29.10
14	0.1254	1.25	1.28	12	8	23.9	7.96	7.87	29.05
15	0.0930	1.50	1.31	12	8	24.3	7.70	7.80	28.83
16	0.504	0.50	1.38	15	10	23.2	-	7.73	28.65
17	0.324	0.75	1.49	15	10	22.3	8.14	8.14	28.98
18	0.212	1.00	1.55	15	10	23.8	-	7.88	29.13
19	0.161	1.25	1.60	15	10	23.4	-	7.91	29.00
20	0.115	1.50	1.63	15	10	23.8	-	7.95	29.23
21	0.169	0.50	0.55	6	4	23.1	-	8.00	29.03
22	0.120	0.75	0.59	6	4	23.0	7.74	7.85	28.95
23	0.0921	1.00	0.62	6	4	23.6	7.48	7.62	29.05
24	0.0626	1.25	0.64	6	4	23.7	7.80	7.84	28.78
25	0.0549	1.50	0.65	6	4	23.5	7.90	8.01	29.18
26	0.272	0.50	0.83	9	6	24.0	7.94	7.85	28.90
27	0.184	0.75	0.89	9	6	23.7	8.00	7.90	29.05
28	0.119	1.00	0.93	9	6	23.3	7.95	7.94	28.90
29	0.0936	1.25	0.96	9	6	23.2	8.12	8.09	29.15
30	0.0778	1.50	0.98	9	6	23.3	7.85	7.87	28.90
31	0.478	0.50	1.10	12	8	23.8	8.01	7.95	29.05
32	0.2833	0.75	1.19	12	8	23.3	7.94	7.95	28.95
33	0.1544	1.00	1.24	12	8	25.0	8.00	7.87	29.10
34	0.1167	1.25	1.28	12	8	24.0	7.95	7.92	28.88
35	0.0933	1.50	1.31	12	8	23.2	8.08	7.98	29.08
36	0.540	0.50	1.38	15	10	22.5	8.00	7.95	29.20
37	0.297	0.75	1.49	15	10	22.6	7.93	8.13	29.18
38	0.210	1.00	1.55	15	10	23.8	-	7.79	28.75
39	0.153	1.25	1.60	15	10	23.8	7.80	7.90	29.13
40	0.108	1.50	1.63	15	10	23.3	-	8.02	28.93
41	0.185	1.25	1.60	15	10	24.2	-	7.95	29.30
42	0.156	1.25	1.60	15	10	23.6	7.93	8.06	29.25
43	0.167	1.25	1.60	15	10	23.7	7.78	7.89	29.08
44	0.358	0.75	1.49	15	10	23.0	8.06	8.07	29.08
45	0.327	0.75	1.49	15	10	22.8	7.92	7.97	29.10
46	0.311	0.75	1.49	15	10	23.0	8.08	8.08	29.30
47	0.517	0.50	1.38	15	10	22.3	8.19	8.25	29.65
48	0.0860	1.00	0.62	6	4	22.8	-	8.00	29.05
49	0.195	0.75	0.89	9	6	23.3	-	7.97	29.10
50	0.153	1.00	1.24	12	8	20.0	-	8.07	29.30
51	0.127	1.00	0.93	9	6	19.0	-	7.85	28.85
52	0.557	0.50	1.38	15	10	22.7	8.00	7.96	29.18

reaeration rate constant, k_2 . Equation (III-7b) was the form of the general equation analyzed in the correlation analysis.

$$k_2 = C' V^m H^p \quad (\text{III-7b})$$

This equation was previously developed by dimensional analysis techniques.

For the correlation analysis, Equation (III-7b) was transformed to its equivalent logarithmic form in order to simplify numerical computations.

$$\log k_2 = \log C' + m \log V + p \log H \quad (\text{V-1})$$

A least squares analysis was performed on the fifty-two reaeration experiments in order to evaluate the constants C' , m , and p .

The preliminary analysis performed on the mean values of the twenty different experimental conditions represented in the fifty-two reaeration experiments yielded values of

$$m = 1.0027, \text{ and}$$

$$p = -1.4859$$

Since the value of m was found to be approximately unity, and the value of p was found to be approximately $-3/2$, the second analysis of the data was performed using the expression:

$$k_2 = C' \frac{V}{H^{3/2}} \quad (\text{V-2})$$

The least squares analysis performed to determine the applicability of the data to this expression yielded the

prediction equation

$$k_2 = 3.283 \frac{V}{H^{3/2}} \quad (V-3)$$

where k_2 has the dimensions of days⁻¹, V is measured in feet per second, and H is measured in feet.

The correlation coefficient determined by comparison of k_2 measured and k_2 predicted by Equation (V-3) was 0.989. It was decided after obtaining this excellent value of correlation coefficient that although refinement of the exponents m and p would yield slightly better definition of the data, it would be less acceptable from the computational point of view and probably from the standpoint of using the equation for possible theoretical explanation of the reaeration mechanism.

Equation (III-7b) is the simplified form of the more general Equation (III-7a):

$$k_2 = C' V^m H^p \quad (III-7b)$$

$$k_2 = C \left[\frac{D_m^{(1-d)}}{\nu^{(a-d)}} \right] \frac{1}{g^b} V^{(a+2b)} H^{(a-b-2)} \quad (III-7a)$$

where m is equal to $(a+2b)$ and p is equal to $(a-b-2)$. Solution of the equations defining m and p yields values of

$$a = 2/3, \text{ and}$$

$$b = 1/6$$

Referring to the original definition of the exponent, a , (given in Equation III-7), it can be seen that the reaera-

tion rate constant k_2 is directly proportional to the two-thirds power of the Reynold's Number, N_R :

$$k_2 \propto N_R^{2/3}$$

In reference to the original definition for the exponent, b , it can be seen that the reaeration rate constant, k_2 , is directly proportional to the one-sixth power of the Froude Number, N_F :

$$k_2 \propto N_F^{1/6}$$

Substitution of the values obtained for "a" and "b" into Equation (III-7a) yields the expression

$$k_2 = C \left[\frac{D_m^{(1-d)}}{\nu^{(2/3-d)}} \quad \frac{1}{g^b} \right] \frac{V}{H^{3/2}} \quad (V-4)$$

Any numerical value of the remaining unknown exponent, d , would yield a dimensionally homogeneous equation. In order to ascertain a numerical value for "d", it was assumed that the group $\left[\frac{D_m^{(1-d)}}{\nu^{(2/3-d)}} \right]$ would reflect all changes in k_2 response due to the effects of temperature on this parameter. Although there has been much controversy concerning the effect of temperature on the reaeration rate constant, k_2 , a review of the literature on this subject indicates that Churchill, et al. (53) conducted extensive tests to determine this effect and have, in the writer's view, accomplished the best effort to date to determine the effects of temperature on the reaeration rate constant, k_2 .

The Sanitary Engineering Research Committee (54) made the following conclusions in the report on their study of the literature pertaining to this subject:

"A substantial degree of confusion exists in the literature regarding the value of temperature coefficient θ of the reaeration coefficient k_2 . A series of carefully controlled experiments is reported here that indicates θ to be 1.0241. This coefficient remains substantially constant over a wide range of turbulence conditions. Thus the rate of reaeration has been shown to increase at the geometric rate of 2.41% per °C. throughout the temperature range found in natural streams."

The parameter θ is defined in the expression:

$$k_{2-T} / k_{2-20^\circ} = \theta^{(T-20)}$$

Utilizing the recommended equation for temperature variation of k_2 , one can formulate the expression

$$\left[\frac{D_m^{(1-d)}}{\nu^{(2/3-d)}} \right]_T / \left[\frac{D_m^{(1-d)}}{\nu^{(2/3-d)}} \right]_{20^\circ\text{C.}} = (1.0241)^{T-20} \quad (\text{V-5})$$

By substitution of known values of molecular diffusivity and kinematic viscosity at various temperatures, a "trial and error" type solution yields a value for "d" equal to 1/2. One can now make this substitution into Equation (V-4) to formulate the final form of the prediction equation as

$$k_2 = \left[\frac{C D_m^{1/2}}{\nu^{1/6} g^{1/6}} \right] \frac{v}{H^{3/2}} \quad (\text{V-6})$$

This equation is dimensionally homogeneous.

It can be seen in Equation III-7 that the exponent, d , was originally defined as the exponent associated with the Schmidt Number $\left[\frac{\nu}{D_m} = N_S \right]$. Therefore the reaeration rate constant, k_2 , is found to be directly proportional to the square root of the Schmidt Number:

$$k_2 \propto N_S^{1/2}$$

Equation (V-6) can be expressed as follows:

$$k_2 = C N_R^{2/3} N_F^{1/6} N_S^{1/2} \quad (V-7)$$

However, Equation (V-7) is somewhat cumbersome to use, therefore, for computational purposes Equation (V-8) is recommended:

$$k_{2-T} = C_{20} \frac{V}{H^{3/2}} (1.0241)^{T-20} \quad (V-8)$$

The author's data were analyzed by least squares theory using Equation (V-8) and measured temperature data. This analysis yielded the following:

$$k_{2-T} = 3.053 \frac{V}{H^{3/2}} (1.0241)^{T-20} \quad (V-9)$$

The associated correlation coefficient for this analysis was found to be 0.989. Since this correlation coefficient value is identical to the one obtained without including temperature effects, it may be surmised that a temperature correction for the short range of temperatures covered in this investigation showed essentially no effect on the correlation coefficient value.

The numerical value of C_{20} is discussed in Chapter

VI as it has been found to be different for the various groups of reaeration data which were considered in this investigation.

2. Vibrational Effects in the Experimental System

The foregoing analysis, i.e., Chapter V, Section C-1, includes all of the experimental observations of k_2 except seven which were obtained at the end of the experimental program designed for the determination of factors affecting the reaeration rate, k_2 . During the latter stages of this study it was observed that although reasonably good reproducibility was obtained for most experimental conditions, occasionally a larger deviation than could be attributed to experimental error occurred.

If the experimental observations were made on successive days, reproducibility was usually good. However, if special care was not taken to ensure that the experimental apparatus was operating identically to the previous day, then reproducibility was somewhat erratic. The following discussion is based upon observations made during the experiments, and is presented as a probable explanation for deviations in observed k_2 values that were obtained under identical flow conditions.

Each of the moving cylindrical shell walls of the experimental apparatus is supported upon eight adjustable roller bearings equally spaced around the periphery of the non-moving side walls of the tank. Furthermore, each

moving wall is held in position by eight guide rollers equally spaced and attached to the periphery of the non-moving side walls. In operating a mechanical unit of this large size, these thirty-two adjustable roller bearings and guide rollers are very difficult to retain in exactly the same position from day to day unless special precautionary measures are taken. Any imperfections in the wall construction which cause them to deviate from a true circular shape create a tendency for binding at various positions around the periphery. Adjustments of the roller bearings and guide rollers were always made if frictional binding could be detected visually. However, this experimental apparatus is relatively large, and visual observation did not always detect these inconsistencies from uniform motion. In fact, measurement of velocity of the water in the experimental unit did not reveal any differences or inconsistencies in the uniform motion of the movable side walls.

The general tendency of a frictionally bound mechanical system is to free itself; i.e., to attain an unrestrained condition with continued operation. Toward the end of the experimental program, attention was given to studying the vibrational conditions which were observed during an experimental test in which the water level was at a six-inch depth. It was observed that the water surface during this particular experiment exhibited a small and noticeable transverse wave action. The apparatus was

vibrating noticeably and the k_2 value observed for this experiment was higher than expected for this experiment. Although there had been other k_2 values observed which deviated about the same magnitude from the general trend line, i.e., k_2 vs. $\frac{V}{H^{3/2}}$, it was at this time that visual observation of a transverse wave action was associated with a noticeably vibrating system. Three additional experiments were conducted in which special care was taken to maintain this highly vibrational situation. It was found that k_2 values for these last four experiments were on the high side of the general trend line.

The apparatus was then adjusted to give smooth running operation again. The next four experiments produced k_2 values which were smaller than the general trend of values. This suggested that the apparatus was running smoother than usual, although there were other k_2 values observed during the initial forty-eight experiments which deviated below the general trend line by about the same magnitude.

Three final experiments were conducted without any further adjustment of the apparatus, and the k_2 values obtained from these three experiments again fell into the general trend of values. There was no noticeable change in the running condition from that of the smooth condition; however, it is again emphasized that this experimental apparatus is large, and slight changes in vibrational behavior are not easily detected.

Prior to the detection of the vibrational effect of the system, routine periodic adjustments were made on the roller bearings and guide rollers in order to maintain a smoothly operating experimental system. This was accomplished by conducting maintenance on the experimental unit at an approximate bi-weekly time interval. This maintenance consisted of proper oiling and greasing of the movable parts and motors, along with a general check and adjustment of roller bearings and guide rollers. This general maintenance procedure was deemed a necessary precautionary measure from the start of the experimental program; however, it was during the latter stages of the experimental program when the vibrational effects were first observed and then investigated.

Figure 20 shows all fifty-nine experiments. Fifty-two of these experiments were included in the previous analysis of the data. The four experiments which are labeled as known high vibration experiments were also included in the original correlation analysis. Also shown on the figure are the four known smooth experimental runs. The last three experiments are also identified.

Although it is now evident that the experimental apparatus may have been operating with slightly varying degrees of vibration throughout the experimental period, this was not known conclusively until the last seven experiments were conducted. At this time an intentional effort was made to obtain a smoothly operating apparatus,

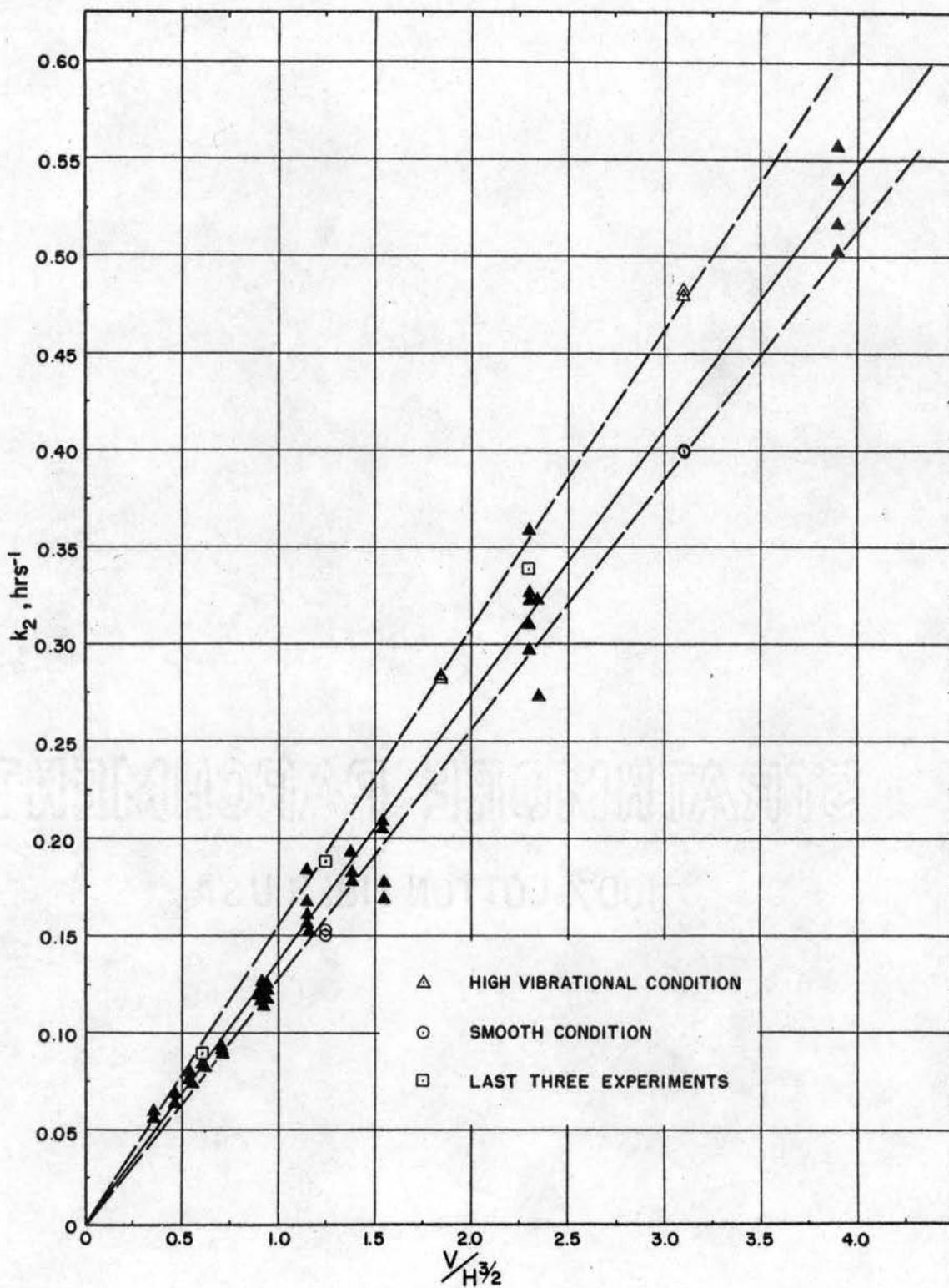


Figure 20. Observed Effects of Vibration on the Reaeration Rate Constant.

hence a known biased change in operation was made on the system; therefore the last seven experiments were not included in the original correlation analysis of the data. It can be seen from Figure 20 that only seven of the initial experiments lie outside the region enclosed by the lines defining the highly smooth operating system. Three of these values lie above the line defining the highly vibrational system and suggest that these values may have occurred in experimental tests where the vibration was greater than that observed for the known highly vibrational system. Also, four of the initial forty-eight values lie below the line defining the smooth condition, and suggest that the apparatus may have operated at a smoother condition than the known smooth condition. Since the dates for maintenance of the equipment were not recorded, any further interpretation of the initial data can be derived only from speculation. However, it is emphasized that the four experiments defining the known highly vibrational system were duplicate runs at two different experimental conditions, and these duplicate runs exhibited good reproducibility when the system was known to be operating under controlled vibrational conditions. Furthermore, the duplicate runs of the two different experimental conditions defining the known smooth operation show good reproducibility.

Figure 21 shows all fifty-nine of the reaeration experiments. The individual experiments shown on this fig-

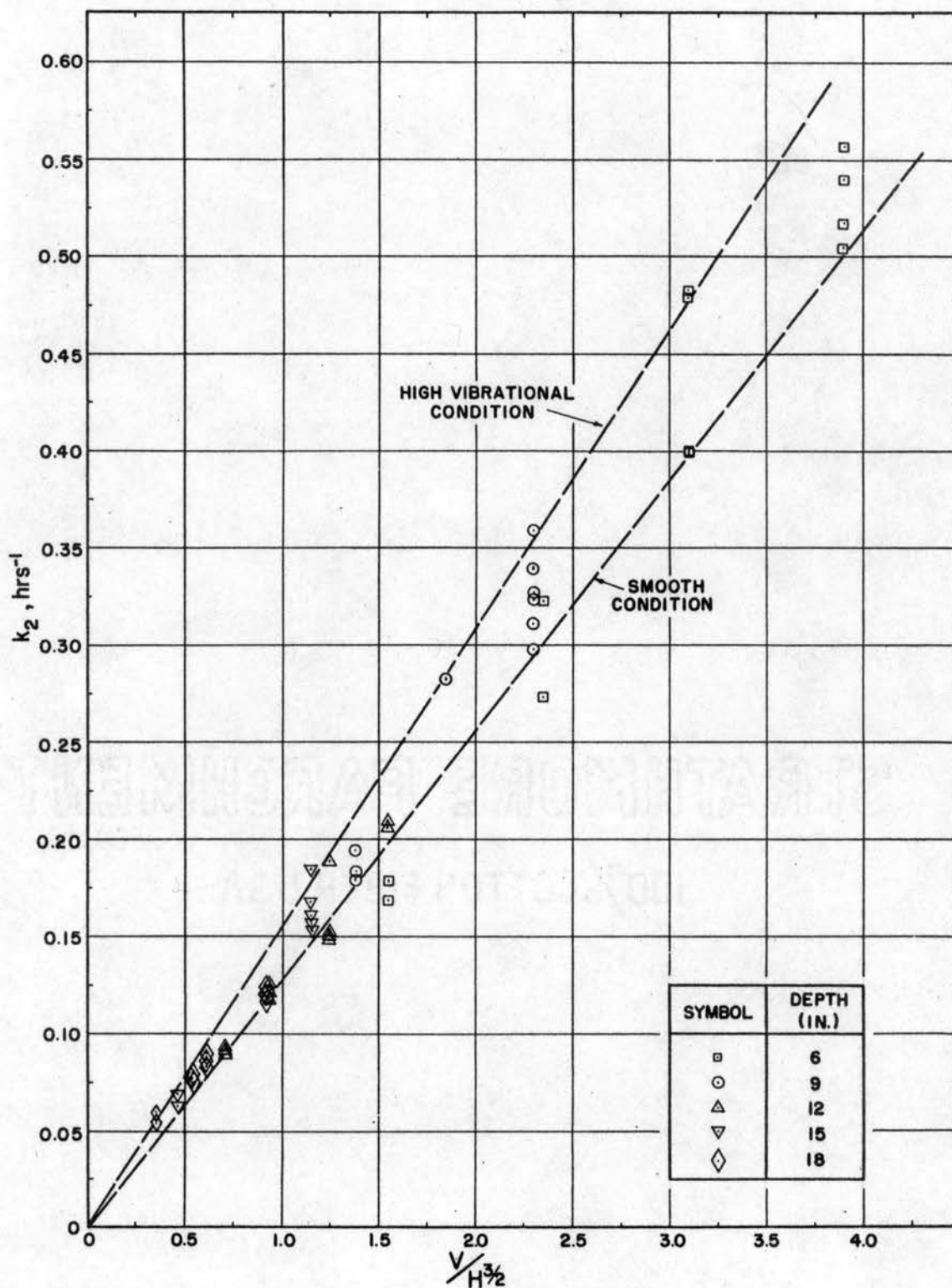


Figure 21. The Effects of Vibration on the Reaeration Rate Constant at Different Depths of Flow.

ure are identified according to depth of water carried in the experimental unit. It can be seen from this figure that experimental observations made at the six and nine-inch water depths show the largest deviations in k_2 values for a constant hydraulic condition defined by $\frac{V}{H^{3/2}}$. The vibration in the experimental apparatus emanates from the top of the side walls where the roller bearings and guide rollers are mounted. The amplitude of the vibratory motion is greatest at the bottom of the side walls. Hence, as depth decreased, the vibratory effect was more pronounced, or caused larger deviations in the reaeration rate, k_2 . As the depth of water was increased, the vibratory effect was cushioned by the larger depth of water, and also the amplitude of the wall vibration at the water surface was smaller. The writer believes that most of the experimental error observed in this investigation can be attributed to a varying vibrational effect which was observed in the latter stages of this experimental program, but could not be physically measured. During the study on vibrational effects, three attempts were made to obtain photographs of the wave surface in order to show the surface rippling at the highly vibrational condition and the smooth condition. However, the lighting and inaccessibility to the necessary camera position for photographing the surface did not allow any distinction to be made between the photographed surface of the two conditions. Although the vibrational effect observed in this investi-

gation caused the writer some difficulty, nevertheless it is an effect which may lead future researchers to a better understanding of the overall reaeration process. This aspect is discussed further in Chapter VI, pages 136 through 170.

3. Natural Stream Data of Churchill, et al. (6)

The ultimate acceptance of an equation to predict k_2 , which is developed utilizing multiple correlation techniques applied to experimental data obtained in the laboratory, will be dependent upon its applicability to natural stream conditions. A review of the literature indicated that, although numerous k_2 measurements have been made on natural streams, one must be hesitant in accepting the reported measurements, due to the manner and conditions under which they were made.

Reported measurements that were based on use of the "sag equation" must be questioned, since the assumption upon which this equation is based has never been proven to be correct under controlled conditions. The recent work of Mancy, et al. (49) casts serious doubt upon applicability of the "sag equation" in such a system. Experimental results are presented later in this thesis which compare well with those reported by Mancy, et al. If one considers all of the natural stream data pertaining to k_2 which have been obtained utilizing the theory of the "sag equation" to be of doubtful validity, then the work

of Churchill, et al. represents the only field data which was procured under controlled conditions reasonably free of natural oxygen exchange mechanisms other than atmospheric oxygenation, since the streams they studied were relatively unpolluted.

A correlation analysis was performed on the thirty field conditions reported by Churchill's group. The object of the analysis was to determine whether the previously developed general equation

$$k_{2-20^{\circ}} = C_{20^{\circ}} \frac{V}{H^{3/2}}$$

could be used to predict occurrences under these reported natural stream conditions.

The following two equations were determined by the correlation analyses utilizing least squares theory:

$$k_{2-20^{\circ}} = 4.020 \frac{V}{H^{3/2}} \quad (V-10)$$

and

$$k_{2-20^{\circ}} = 3.739 \frac{V}{H^{3/2}} \quad (V-11)$$

Equation (V-10) was based on all thirty field observations reported, and it has an associated correlation coefficient equal to 0.898*. Equation (V-11) was based upon twenty-

*One might wonder how a better correlation coefficient value was obtained in this analysis than was obtained by Churchill's group on the same type of analysis relating the identical variables. Churchill, et al. reported correlation coefficients determined on 516 separate obser-

nine of the field observations. Experiment number 28 was omitted in this analysis. Equation (V-11) had an associated correlation coefficient value of 0.948. The omission of experiment number 28 was made after a judicious consideration of the conditions under which the measurements were made. The stream reach of the Watauga River (experiment number 28) was 528 feet in length. Its average velocity was reported at 5.0 ft/sec. This condition allows for a time interval between sampling stations of 105.6 seconds. The measured average k_2 value for this stream reach was 4.464 at a mean water temperature of 10.8°C. The oxygen tension levels at the time of monitoring ranged from approximately 7.15 mg/l to 8.10 mg/l. The C_s value, reported by Churchill's group for this condition, was 11.06 mg/l. With these facts known, one can compute the expected maximum change in DO deficit between sampling stations to be 0.022 mg/l. The technique used for DO measurements was an amperometric titration. These DO determinations were reported to have a standard deviation of 0.007 mg/l DO.

variations of k_2 . They then compiled their data and reported the mean values of k_2 , V , and H , for the thirty stream reaches considered in their investigation. The equation they reported

$$k_{2-T} = 5.026 \frac{V^{0.969}}{H^{1.673}} (1.0241)^{T-20}$$

was based upon all 516 separate observations, not the thirty reported mean condition values. They obtained a correlation coefficient value of 0.822 for the reported equation.

For the previously mentioned amperometric titration technique, the standard deviation of 0.007 mg/l DO is 31.82 per cent of the expected change in DO deficit (0.022 mg/l). It appears that the stream conditions under which the measurements were made for experiment number 28 do not allow for a significant amount of oxygen to be measured accurately by the assay techniques employed. Furthermore, if one studies the diurnal fluctuations of k_2 observed for experiment number 28, reproduced here in Figure 22, it appears that the results reflect the presence of algal activity. One can see in Figure 22 that the diurnal k_2 curve shows the highest k_2 values at approximately 3:00 P. M. which is, in general, the time of day during which algal activity is at its highest. Churchill's group corrected for algal activity in some of their experiments; however, they did not report any correction to experiment number 28.

The large increase in correlation coefficient obtained by omitting experiment 28 (0.898 to 0.948) raises a serious doubt that experiment number 28 can be considered a member of the same statistical population of values as the other twenty-nine observations.

4. Laboratory Data of Krenkel and Orlob

The reaeration data (55) which were reported by Krenkel and Orlob (10) were obtained on a recirculating open channel flume. These data were subjected to a cor-

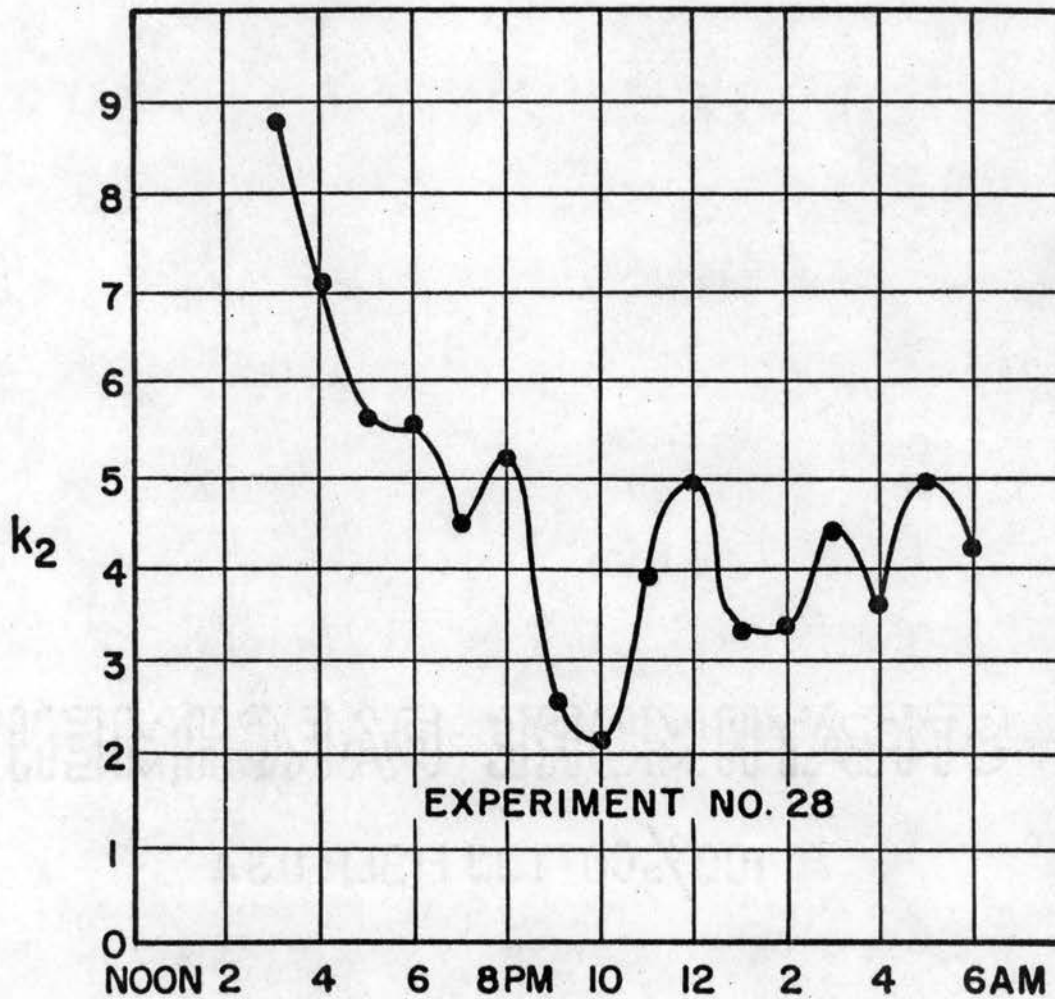


Figure 22. Diurnal Variation in Reaeration Rate taken from Churchill, et al. (6), Experiment Number 28.

relation analysis in order to determine the applicability of the proposed general prediction equation

$$k_2 = C \frac{V}{H^{3/2}}$$

The results of this analysis are defined by the equation

$$k_{2-20^\circ} = 2.440 \frac{V}{H^{3/2}} \quad (V-12)$$

The associated correlation coefficient was 0.950.

Krenkel and Orlob did not report on any attempt to correlate their results in terms of k_2 , V , and H . Their best reported correlation coefficient was 0.963 for the regression equation:

$$k_{2-20^\circ} = (1.138 \times 10^{-5}) D_L^{1.321} H^{-2.32}$$

where D_L is a longitudinal mixing coefficient determined by tracer dye dispersion studies in their recirculating open channel flume. These authors used a temperature coefficient, θ , equal to 1.016 rather than the 1.0241 which has been recommended by the SER Committee since their work was published.

5. Summary of Results of Reaeration Studies

From Equations (V-9), (V-11), and (V-12), which were obtained by correlation analysis of the author's data, the data of Churchill, et al., and Krenkel's data, respectively,

$$k_{2-20^\circ} = 3.053 \frac{V}{H^{3/2}}$$

$$k_{2-20^{\circ}} = 3.739 \frac{V}{H^{3/2}} \quad (V-11)$$

and

$$k_{2-20^{\circ}} = 2.440 \frac{V}{H^{3/2}} \quad (V-12)$$

it can be seen that the difference in these equations is simply that the constant, C, varies for each group of data analyzed. A correlation analysis could have been made by grouping all of the data; however, this would in no way help explain the differences. These differences are discussed in Chapter VI.

Figures 23, 24, and 25 show the three groups of data considered in this study. It can be seen in Figure 23 that although deviations in k_2 values due to vibrational effects are inherent in the data, the writer's data are more or less defined with an excellent correlation coefficient value.

D. Deoxygenation Responses

The second objective of this research investigation was to gain an insight into the kinetic responses (particularly rate of oxygen utilization) of a heterogeneous bacterial population subjected to known organic pollution loads in a turbulent system similar to a stream. The goal of this part of the investigation was to determine whether the BOD progression in a controlled turbulent system could be equated to that which occurs in a standard BOD bottle determination.

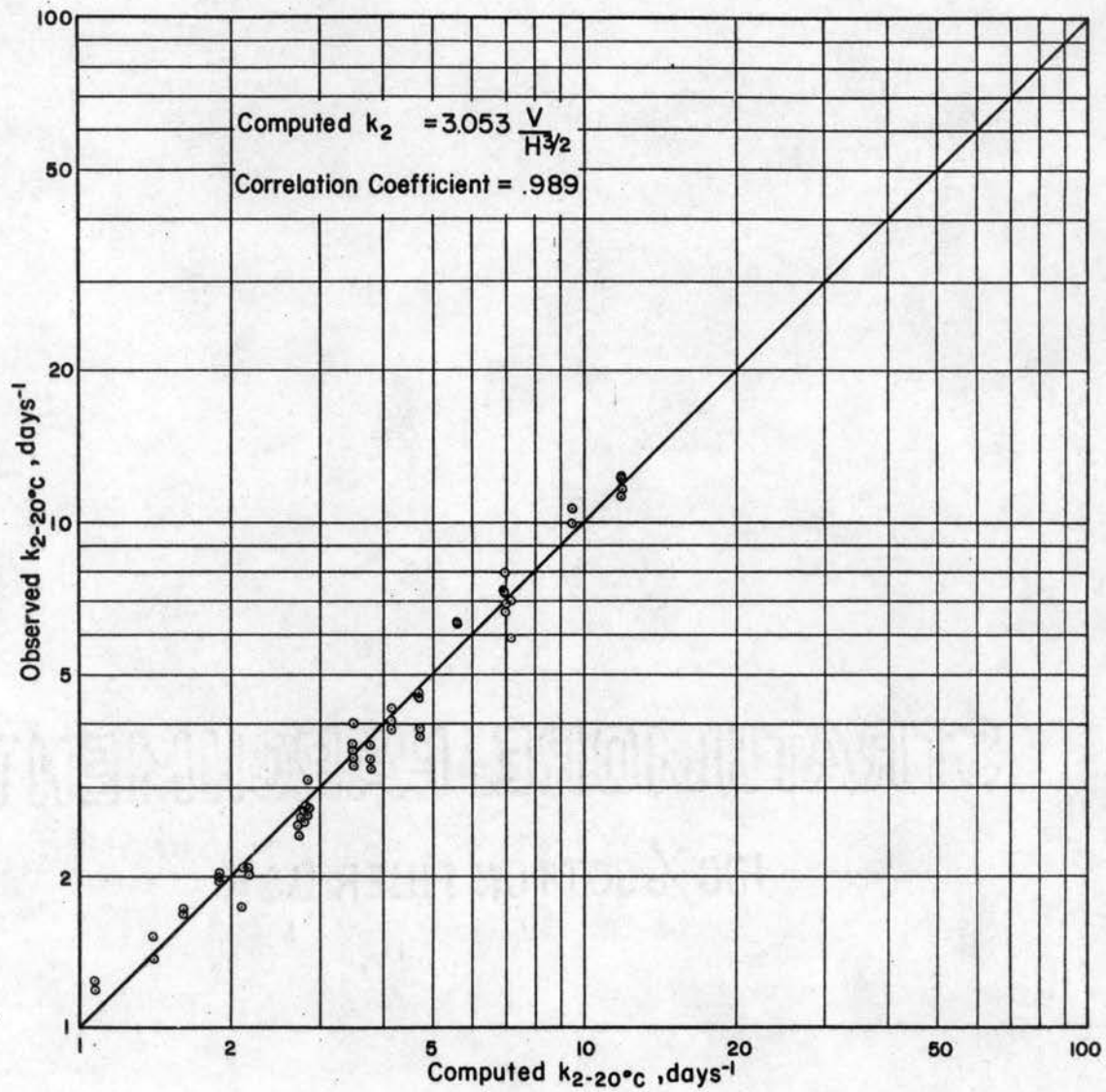


Figure 23. Comparison of Observed Reaeration Rates versus Computed Reaeration Rates Based on Author's Model and Data.

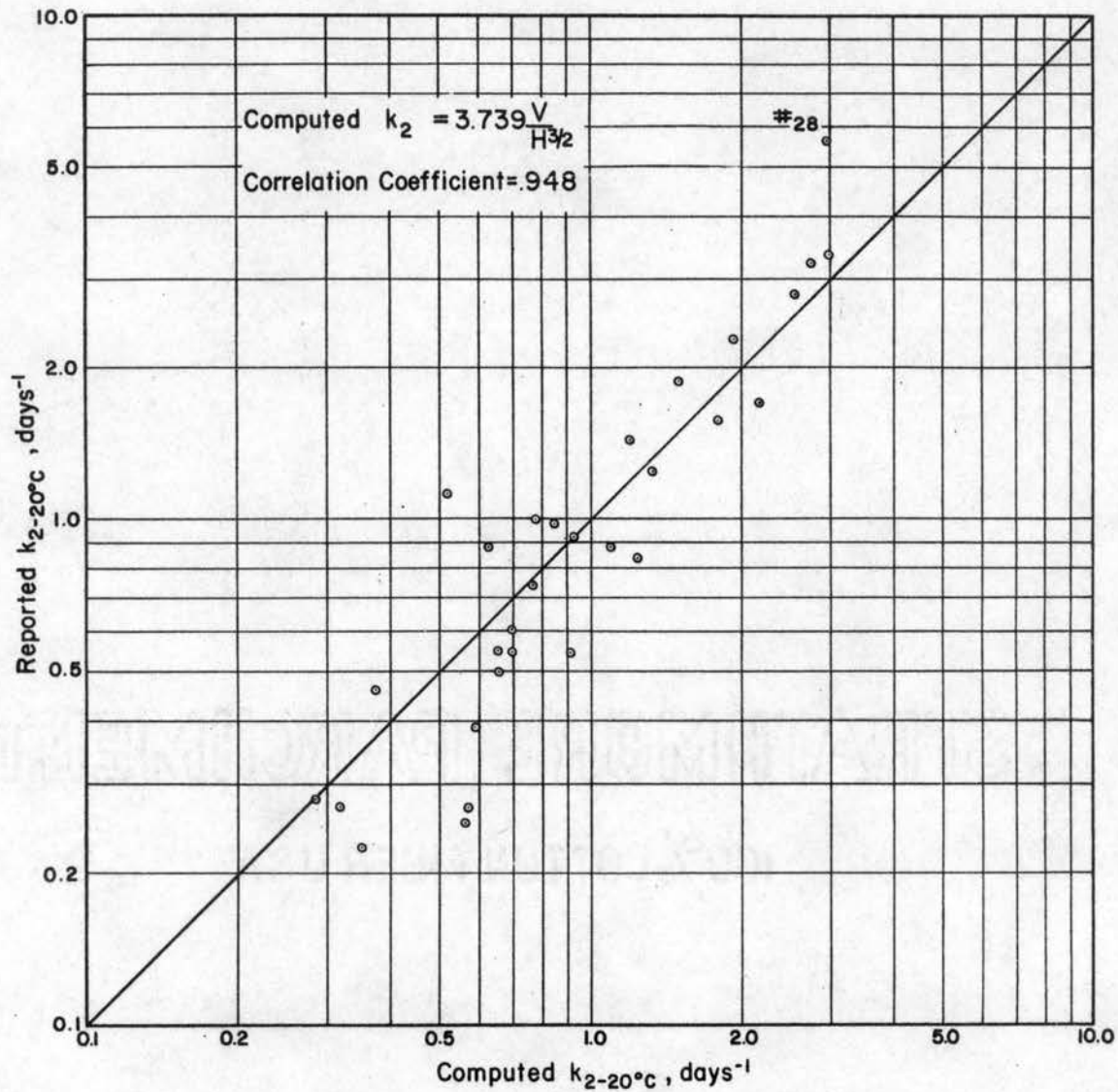


Figure 24. Comparison of Observed Reaeration Rates versus Computed Reaeration Rates Based on Author's Model and Data from Churchill, et al. (6).

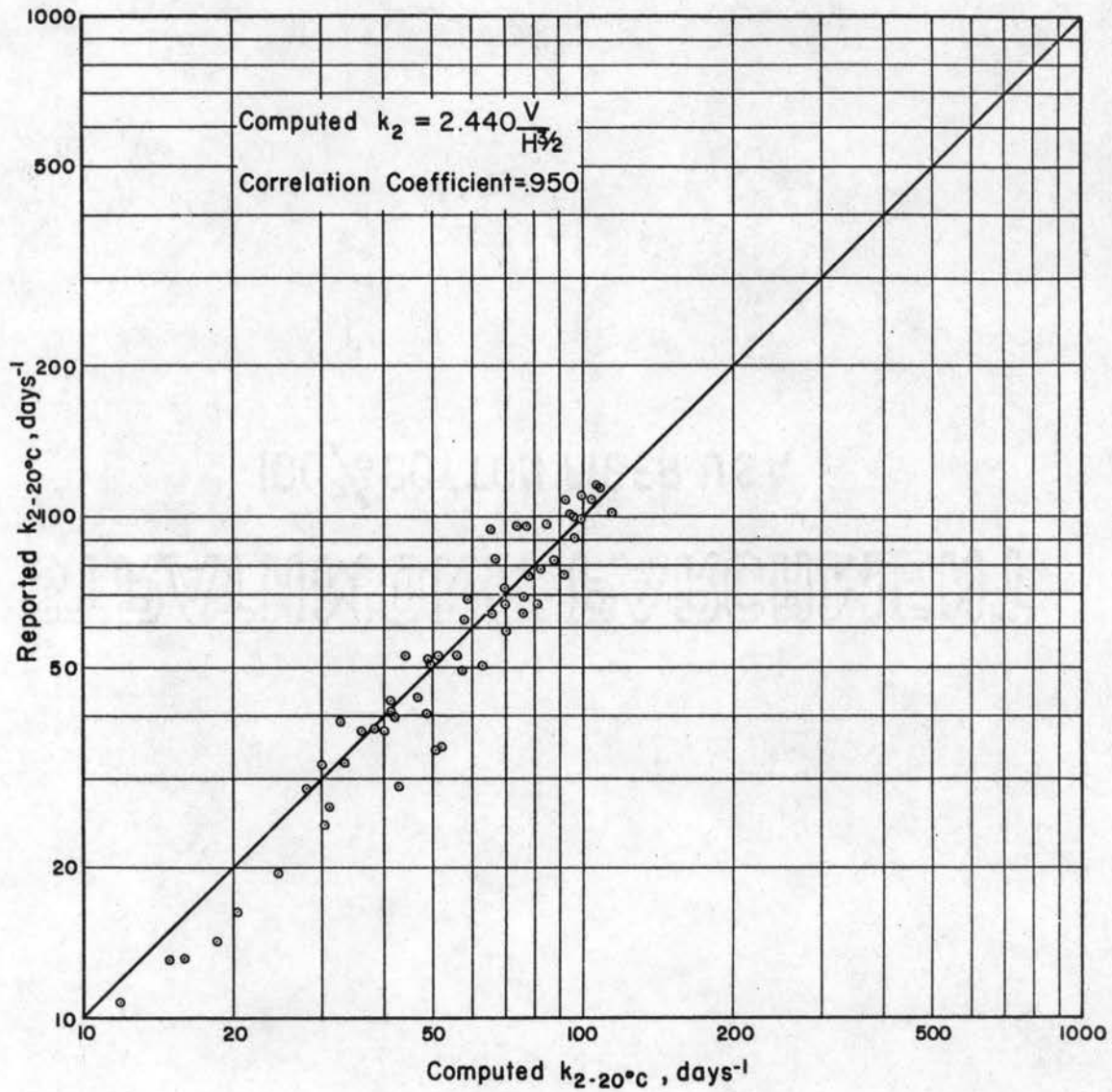


Figure 25. Comparison of Observed Reaeration Rates versus Computed Reaeration Rates Based on Author's Model and Data from Krenkel (55).

1. Experiments using Glucose and Glutamic Acid

Figures 26 and 27 show the results observed in two controlled experiments using a mixture of 22.0 mg/l glucose plus 22.0 mg/l glutamic acid. Dissolved oxygen response, oxygen uptake occurring in the turbulent system and oxygen uptake occurring in a standard BOD bottle system were monitored or computed for each of these experiments. At the end of each monitoring period in the turbulent system, a sample was transferred to BOD bottles in order to extend the O_2 uptake curve to the same length of time as the BOD bottle determinations. It can be seen in this portion of the curves that the two systems behaved approximately the same during the period occurring after transfer from the turbulent system had been made. The theoretical reaeration curves based upon the reaeration rates determined for the system immediately prior to each experiment are also shown on Figures 26 and 27.

The dissolved oxygen responses observed for both of the turbulent systems indicate that after an initial lag period of approximately three-quarters of a day, a rapid rate of oxygen demand occurred until a minimum dissolved oxygen value was reached. Immediately following the minimum point on the DO response curve, this curve almost parallels the theoretical reaeration curve for approximately three-quarters of a day, indicating that there are no significant oxygen demands on the system during this period. This period corresponds, in general, to the

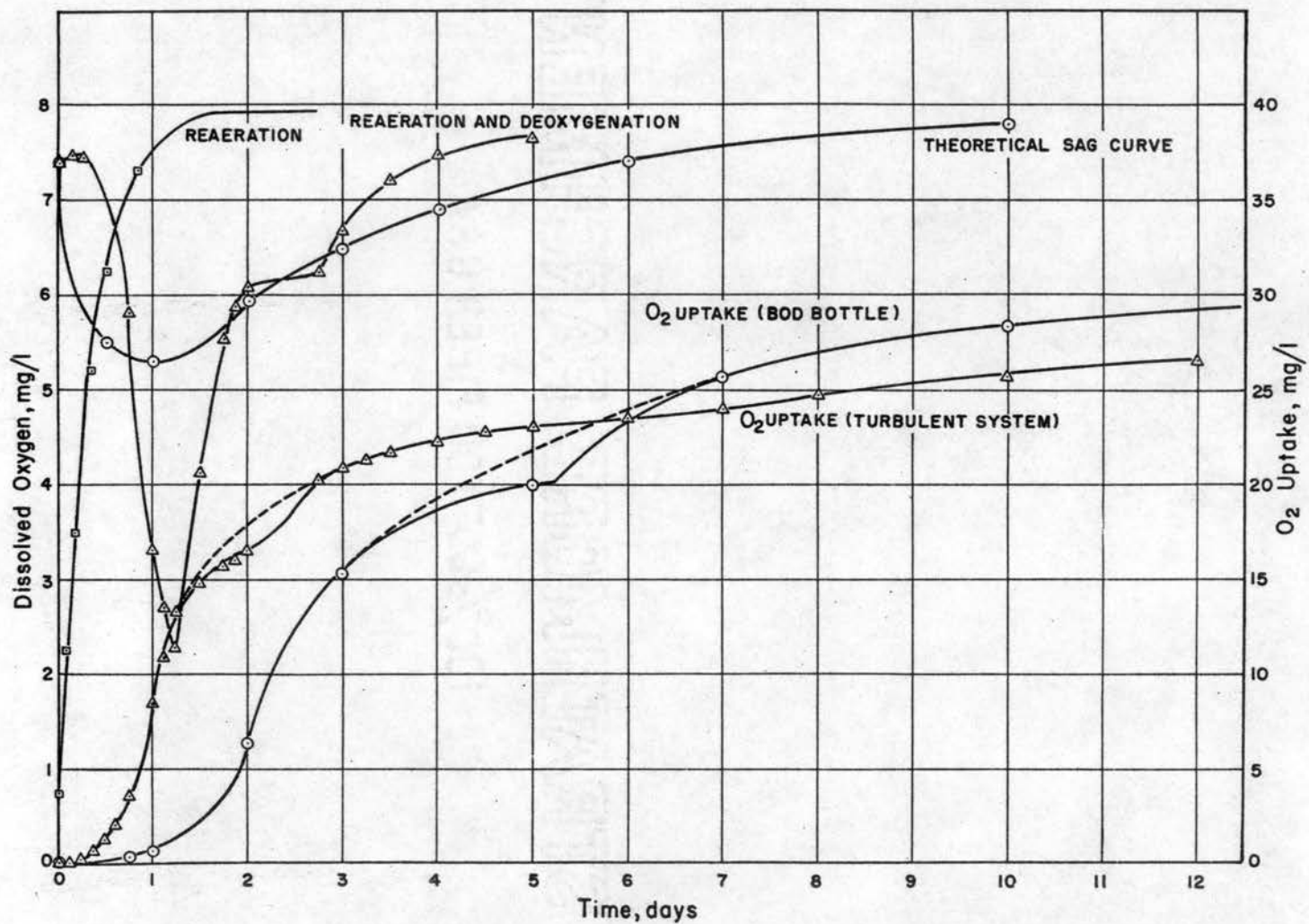


Figure 26. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 1 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

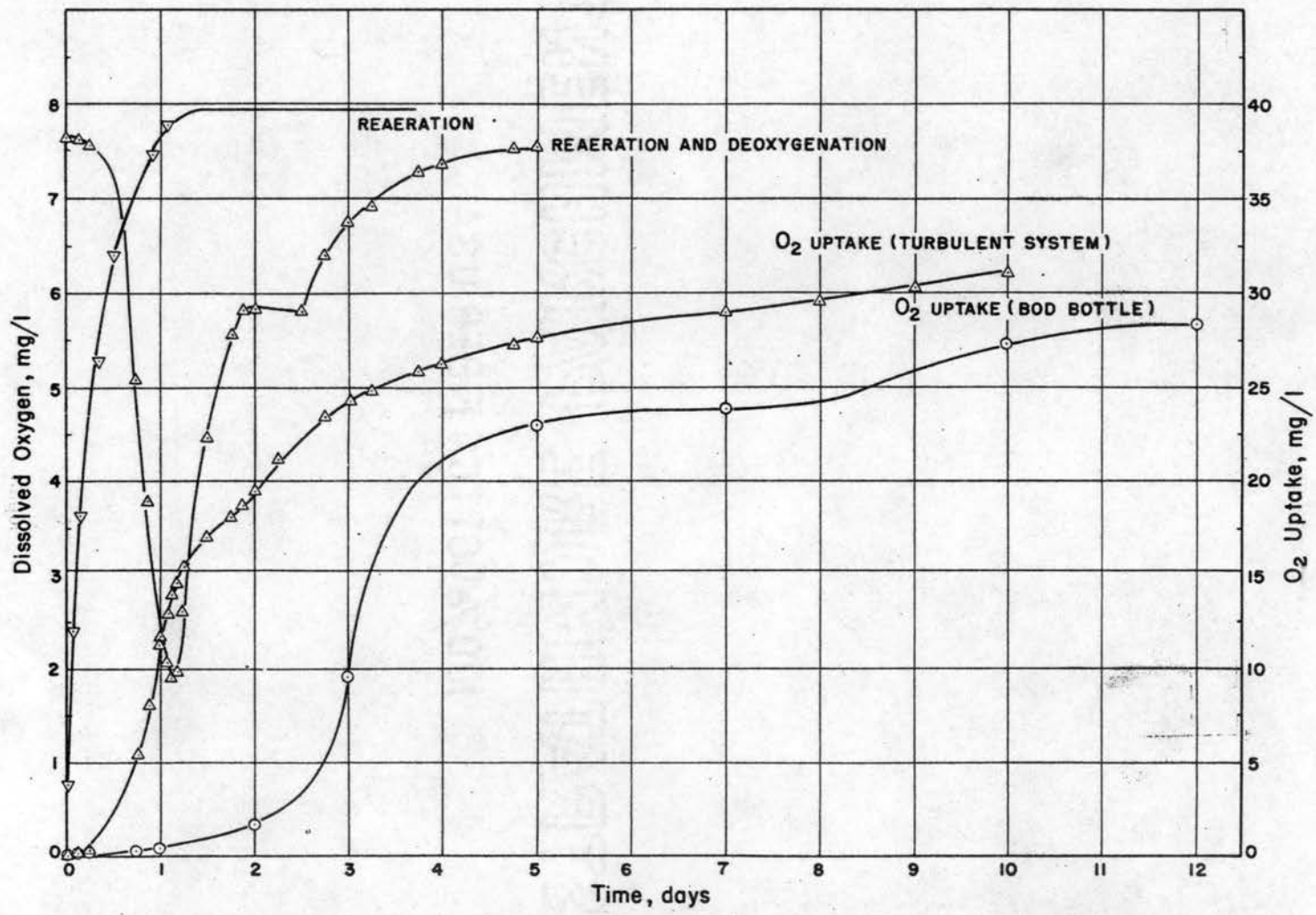


Figure 27. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 2 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

region of the plateau in the BOD exertion curve. Following the plateau in the BOD exertion curve there is a second stage demand of approximately 25 per cent of the magnitude of the first strong demand. The second demand appears to discontinue after about three-quarters of a day, and it then appears that the system continues to use oxygen at a slow, reasonably constant rate throughout the five-day test period.

Comparing the turbulent system oxygen uptake to the concurrently monitored BOD bottle oxygen uptake, one can see that the first strong demand was essentially complete in about two days in the turbulent system, while approximately five days were required in the quiescent bottle system. In both cases the total times required to exert the first demand, i.e., two days vs. five days, were significantly influenced by the initial lag periods for each system. Also, the magnitude of the first demand is about 3 mg/l less in the turbulent system than it is in the quiescent system. Although this difference may be considered to be small, it was apparent for most experiments.

Both the rate and amount of the second phase oxygen demand appear to be of the same order of magnitude for turbulent and the quiescent systems. The third phase oxygen demand, which may be termed as an endogenous stage, progressed at about the same rate in both the turbulent and the quiescent systems.

In order to gain additional insight into this apparent three-phase BOD exertion, a third experiment conducted

under the same conditions as the previous two experiments was set up. In the third system, the progression of carbohydrate removal was monitored by the anthrone method described by Gaudy (52). Also, biological solids were measured using the Millipore filter technique.

Figure 28 shows the results obtained for this experiment. The DO response curve along with the oxygen uptake curves for both the turbulent and quiescent systems are essentially identical to those obtained for the first two experiments conducted using the same substrates. It can be seen in Figure 28 that carbohydrate removal parallels the rapid first stage BOD exertion. This is discernible by comparison of the DO response curve and the carbohydrate removal curve along with the oxygen uptake curve for the turbulent system. The point of complete removal of carbohydrate occurs at the same time as the point of minimum dissolved oxygen. Furthermore, biological solids increased during the first stage of oxygen exertion, and peaked concurrently (approximately) with the minimum DO response and the point of complete removal of carbohydrate. Biological solids concentration held steady for approximately six hours; i.e., during the plateau period, and then dropped off rapidly during the second stage of oxygen demand. After a sharp drop in biological solids during the second stage demand, the solids concentration gradually decreased during the third stage of oxygen uptake.

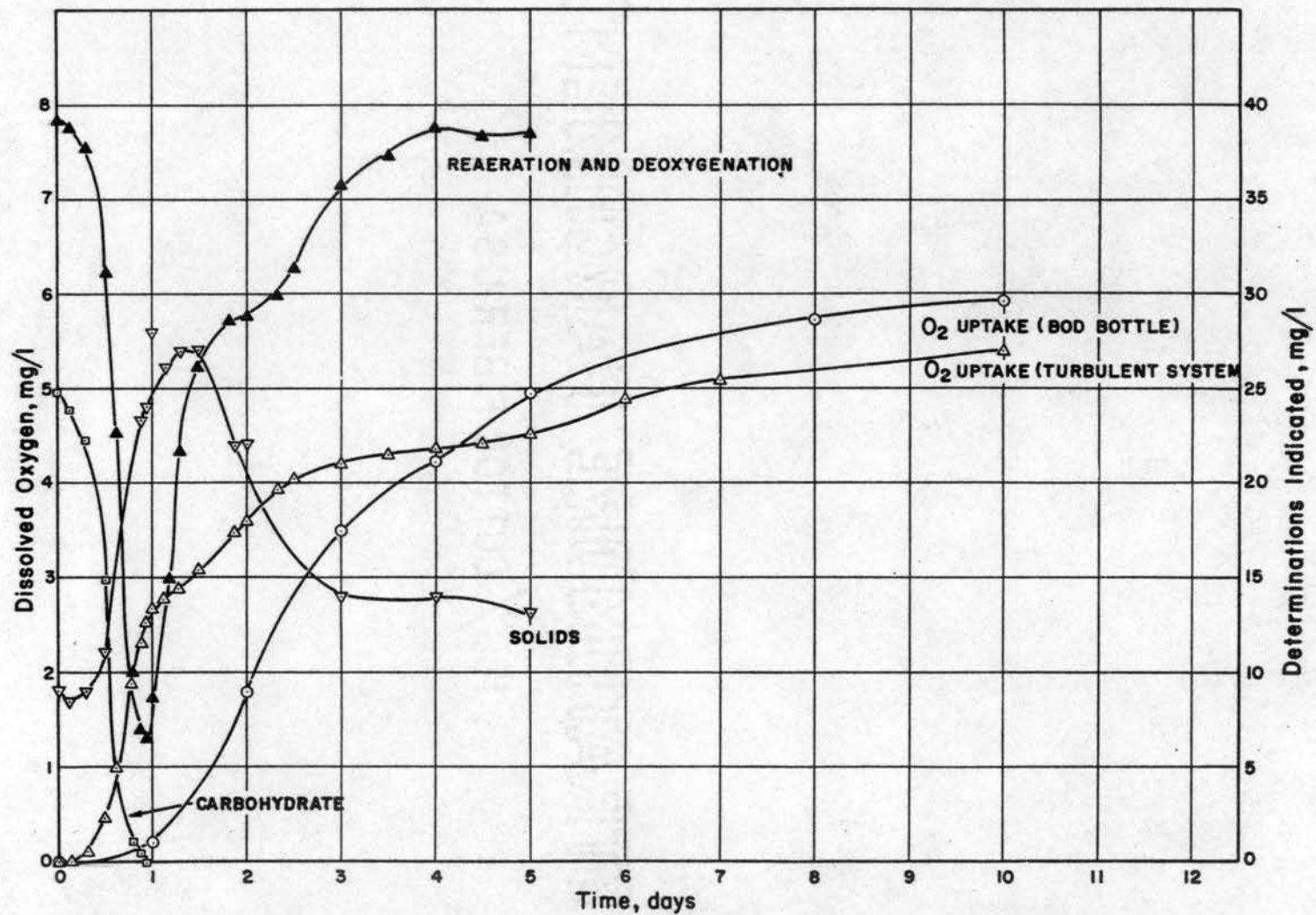


Figure 28. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 3 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

Although protozoan counts were not conducted during this experiment, microscopic examinations were made during the period of second stage oxygen exertion, and significant numbers of protozoa were present. Distinct clarification in the turbulent system was always observed concurrently with second stage oxygen uptake. Clarification is generally associated with high protozoan activity (56).

Referring to Figure 28, an oxygen balance can be made at the time of the peak in solids. From zero time to thirty-one hours the system showed a net gain in biological solids of approximately 18.0 mg/l. Gaudy, Bhatla and Gaudy (57) found that young cells grown on a nutritionally balanced glucose medium had an average COD of 1.52 times the cell weight. Using this value, the net gain in cells is equivalent to 27.4 mg/l of oxygen. The oxygen uptake at that time was 14.55 mg/l. The sum of these two components equals 41.95 mg/l of oxygen. The theoretical oxygen equivalent of 44.0 mg/l of the glucose-glutamic acid mixture is 44.88 mg/l. Thus, the oxygen balance yields a recovery of 93.5 per cent of the original substrate.

An important fact to be noted is that at the point of maximum solids, 61.1 per cent of the oxygen equivalent of the initial substrate had been converted to cells (synthesis), and 32.4 per cent was registered as respiration (O_2 uptake), representing a 1.89:1 cell synthesis to respiration ratio observed for the turbulent system during the period of first stage oxygen demand. At the end of the

first stage demand in the corresponding bottle system (4 days), 21.2 mg/l of oxygen uptake had occurred; therefore, respiration had accounted for 47.2 per cent of the original substrate, indicating that cell synthesis to respiration ratio for the control BOD bottle system is closer to 1:1 during the first stage exertion.

A fourth experiment was conducted using the same concentration of glucose-glutamic acid and initial seed; however, the velocity of the moving stream was increased to yield a reaeration rate approximately twice the previous rate. Figure 29 shows the results observed in this experiment. The same general trends were apparent in this experiment, except that the first stage oxygen demand was smaller than in the previous three systems. The oxygen uptake curves for all four experiments in the turbulent system are shown in Figure 30. The difference between the oxygen uptake exerted during the first stage demands for the turbulent and quiescent systems (this can be seen by comparing the O_2 uptake curves for turbulent and quiescent systems in Figures 26 through 29) indicates that the degree of turbulence may possibly play an important role in establishing the synthesis to respiration ratio during removal of the original substrate or during the period of first stage oxygen demand. Also, variations in seeding differences between turbulent and quiescent systems could be causing this observed effect.

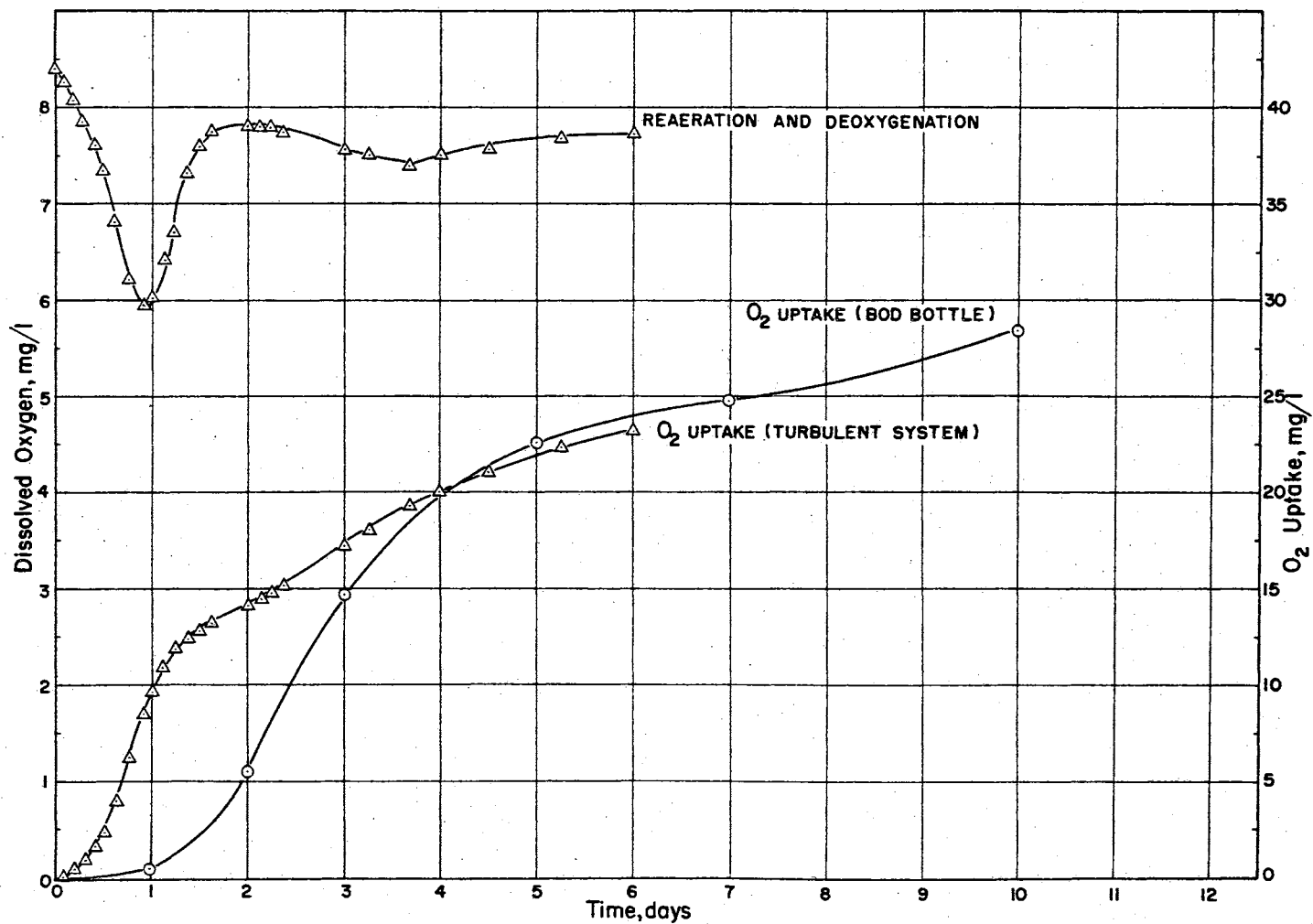


Figure 29. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 4 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

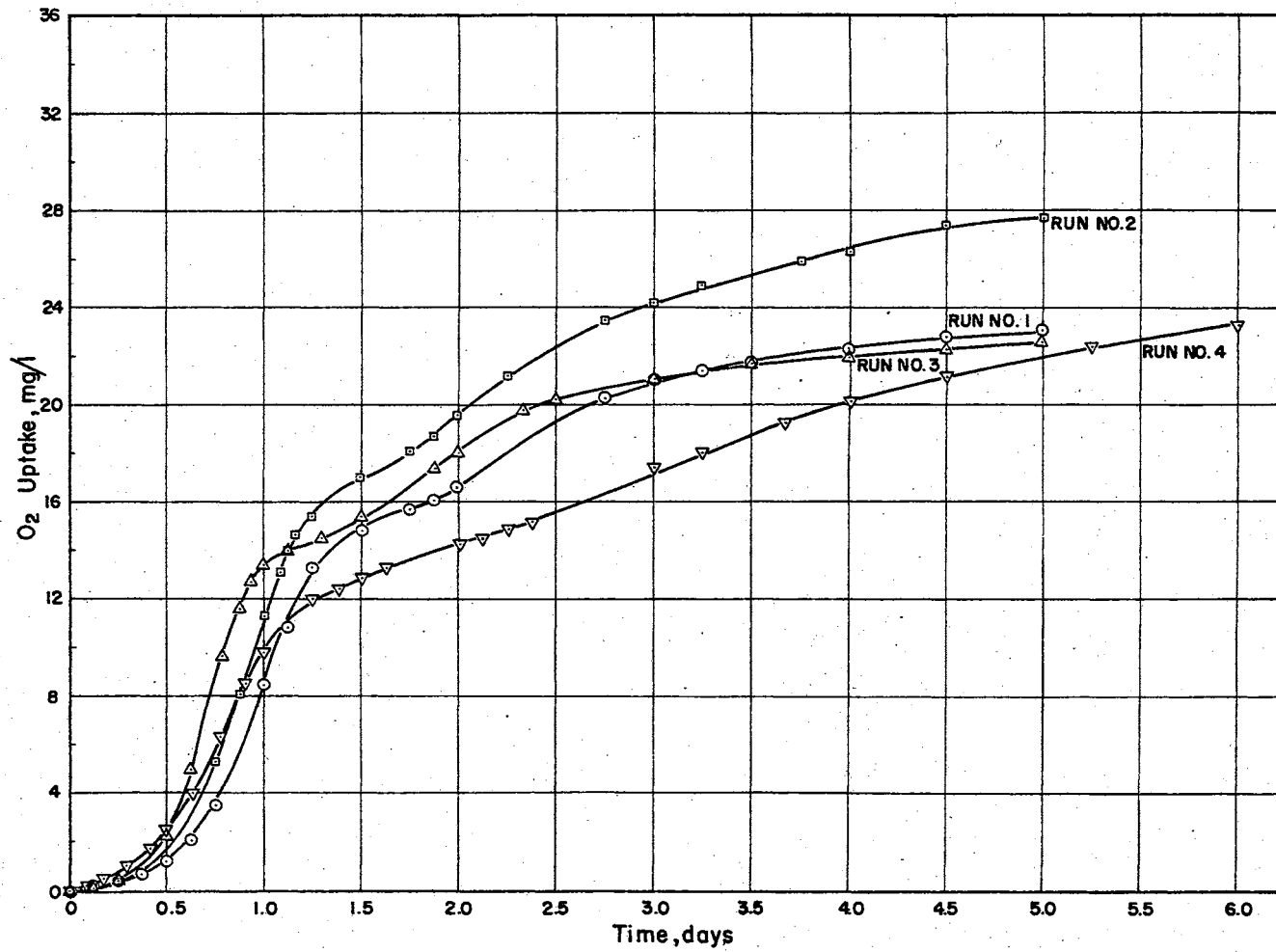


Figure 30. Measurements of Oxygen Uptake in a Simulated Stream, Experiments 1 through 4 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

Referring to Figure 30, the second stage demand for the more turbulent system (run number 4) occurred at a lower rate than the second phase rates of the other three experiments; however, the amount of second stage demand was larger for the more turbulent system than it was for the other experiments. The sum of the first stage demand plus second stage demand was approximately equal for all four of the experiments. The sum of these two components for run number 2 is approximately 3 mg/l higher than the others; however, it is believed that a pre-aeration of the settled sewage seed for approximately four hours prior to that experiment caused a higher initial seeding in this system. The seeding suspension for other systems (i.e., runs 1, 3, and 4) was not pre-aerated.

In the fourth experiment where the reaeration rate, k_2 , was approximately twice the value used in the first three experiments, a total first stage oxygen demand of 12.04 mg/l of oxygen was exerted in twenty-seven hours. This first stage is only 26.9 per cent of the theoretical COD of the original substrate. If it is assumed that all of the original substrate is removed at this time and the remaining 73.1 per cent has been channelled into cell synthesis, this can be interpreted to be a 2.72:1 cell synthesis to respiration ratio for the more turbulent system.

2. Experiments using Domestic Sewage

Figures 31 and 32 show the results of two experiments in which settled domestic sewage was used as the substrate in the system. A 1:10 dilution of settled domestic sewage taken from the effluent of the primary sedimentation tank of the municipal sewage treatment plant at Stillwater, Oklahoma, was used in the experiment shown in Figure 31.

The oxygen uptake response in the turbulent system was small; however, the same trend, i.e., three phases of oxygen uptake exertion were apparent. The third stage oxygen demand appears to have a somewhat higher rate than was observed in the glucose-glutamic acid systems.

The results shown in Figure 32 were obtained using a 1:5 dilution of settled domestic sewage (hence the BOD bottle system was a 1:25 dilution of settled domestic sewage). Again, the same basic trends were observed. The primary differences between the domestic sewage systems and the glucose-glutamic acid systems were:

(a) For domestic sewage the amount of the second stage demand was of about the same magnitude as the first stage demand, while in the glucose-glutamic acid systems (runs 1, 2, and 3) the second stage demand was only about twenty-five per cent of the first stage demand. It was approximately forty per cent for run 4 (the more turbulent system).

(b) The third stage demand for the domestic sewage systems appears to be large and to have a rate too rapid

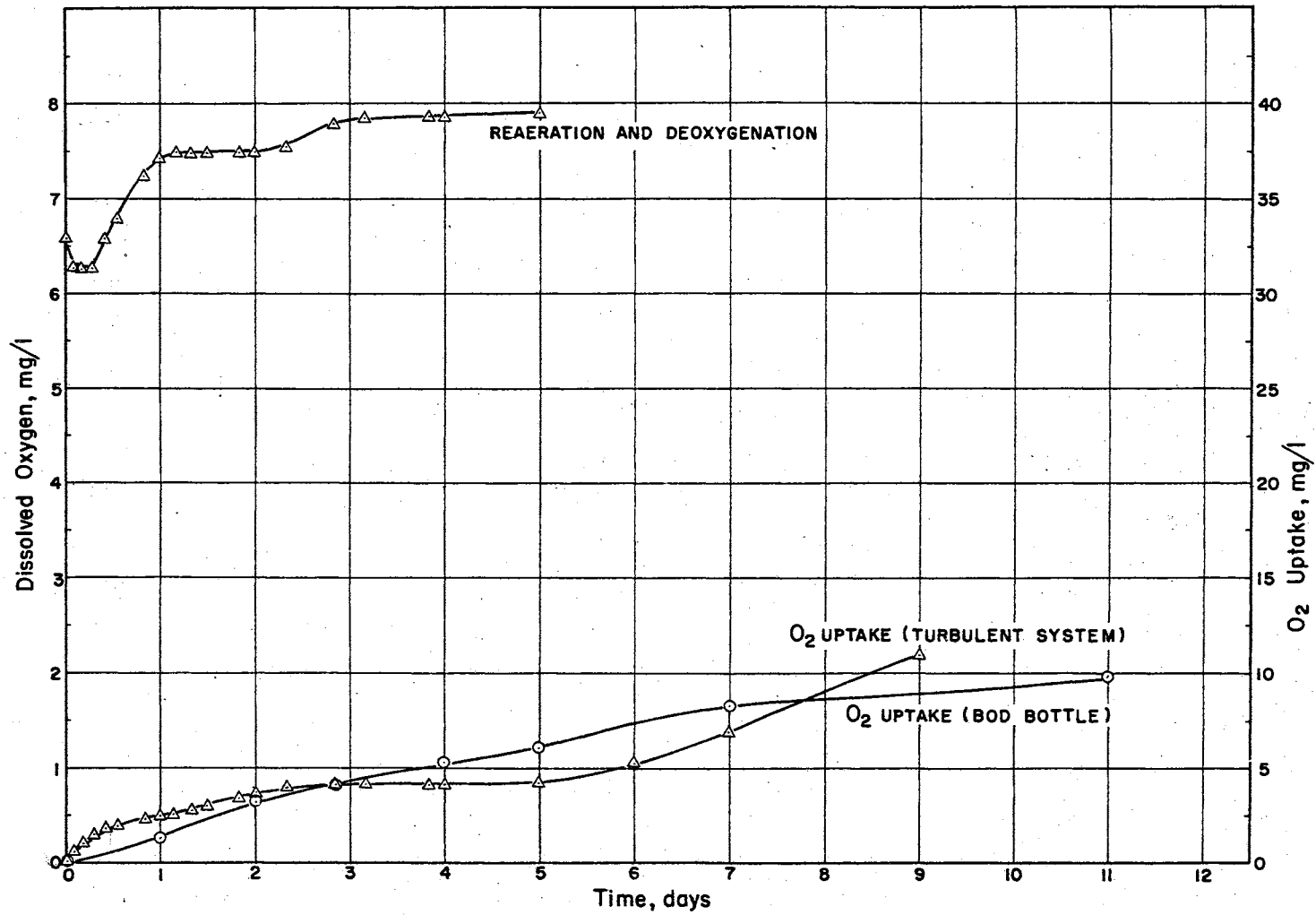


Figure 31. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 5 (Substrate: 1:10 Dilution of Settled Domestic Sewage).

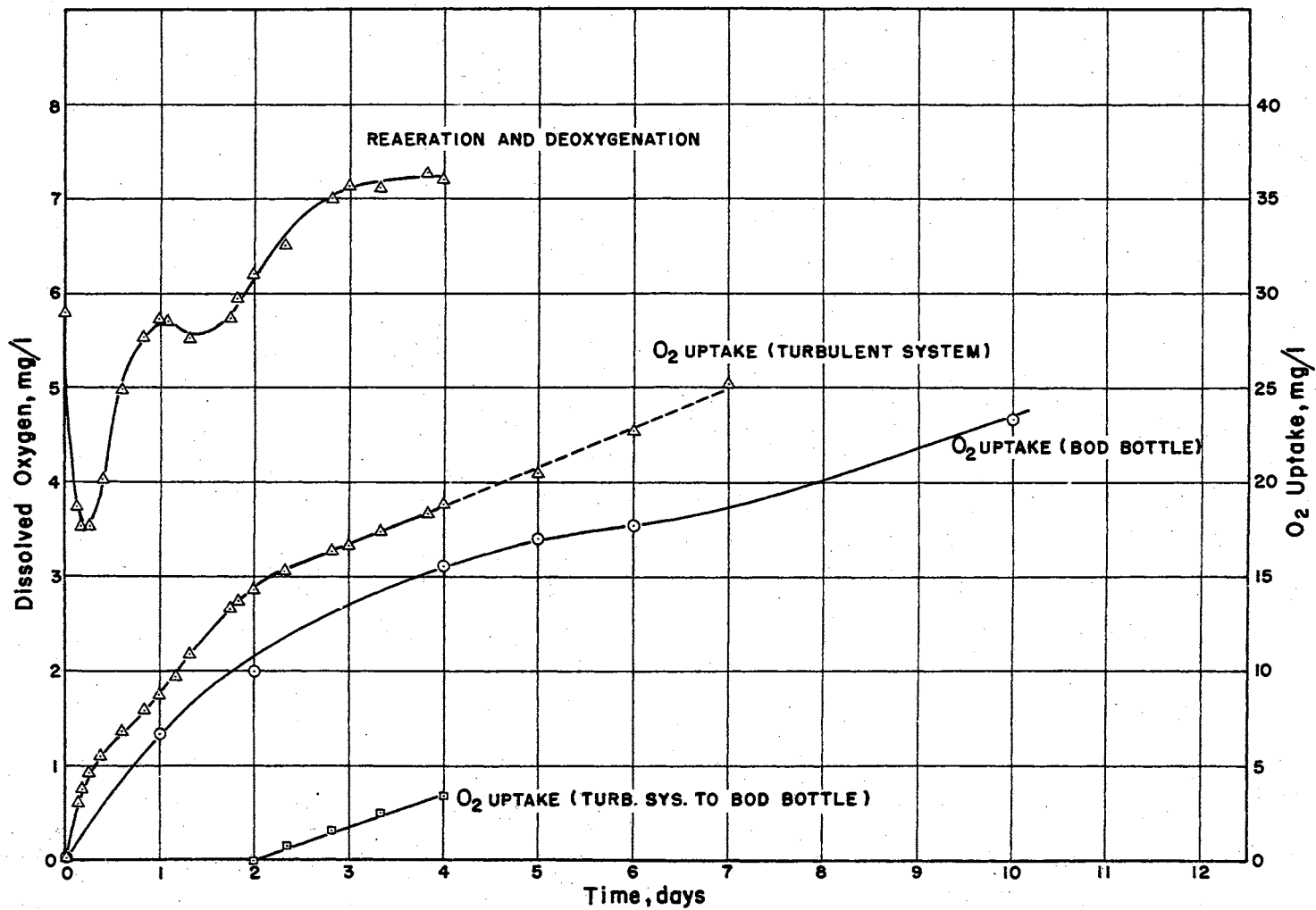


Figure 32. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 6 (Substrate: 1:5 Dilution of Settled Domestic Sewage).

to be considered endogenous respiration. The high rate of oxygen utilization observed in the region of third stage demands might possibly be due to the onset of nitrification. The abundance of available nitrogen sources in sewage and the increased volume of seed in the domestic sewage system (i.e., 200 mg/l of settled domestic sewage in a 1:5 dilution vs. 5 ml/l of seed placed in a glucose-glutamic acid system) might cause a quicker exertion of the nitrification stage in the domestic sewage systems than in the glucose-glutamic acid systems.

Figure 32 also shows a small curve at the bottom of the figure, which is labeled " O_2 Uptake Turbulent System to BOD Bottle." This curve is based upon a small series of BOD bottle determinations which were set up from samples taken from the turbulent system at the end of two days. The samples were transferred directly from the turbulent system to BOD bottles without any dilution. It can be seen from this curve along with the O_2 system curves that all of the oxygen uptake curves for this two-day observation period are essentially parallel. This observation suggests that there are essentially no differences between the turbulent and quiescent system after the first and second stages of oxygen demand have been satisfied.

3. Experiment using Glucose

Figure 33 shows the results of an experiment con-

ducted using 44.0 mg/l of glucose as substrate. The basic trend, i.e., three stages of oxygen exertion, is not as readily apparent as it was for the previously employed substrates. Although relatively few BOD determinations were made in the bottle system, the oxygen uptake curves for the turbulent and quiescent systems are somewhat the same except that the initial lag periods are significantly different. Also, the total oxygen demand of the quiescent system was about 3.0 mg/l greater than the turbulent system.

4. A Study on the Effects of Seeding in the BOD Bottle

In all of the BOD bottle determinations which were conducted concurrently with the turbulent systems, an initial seeding of 5 ml/l of settled sewage was placed into the turbulent system. One-fifth dilutions were made on a sample (substrate + seed) taken from the turbulent system by placing the one part into four parts of dilution water (mineral nutrients but not seeding material). This procedure reduced the amount of seed in the BOD bottle determinations to one-fifth of the amount contained in the turbulent system.

All BOD bottle determinations except those for the experiments using settled sewage as the substrate showed a large initial lag period. It has been previously pointed out that these sewage experiments contained from twenty to forty times more seed than the other systems after being placed in the BOD bottle. It was felt that

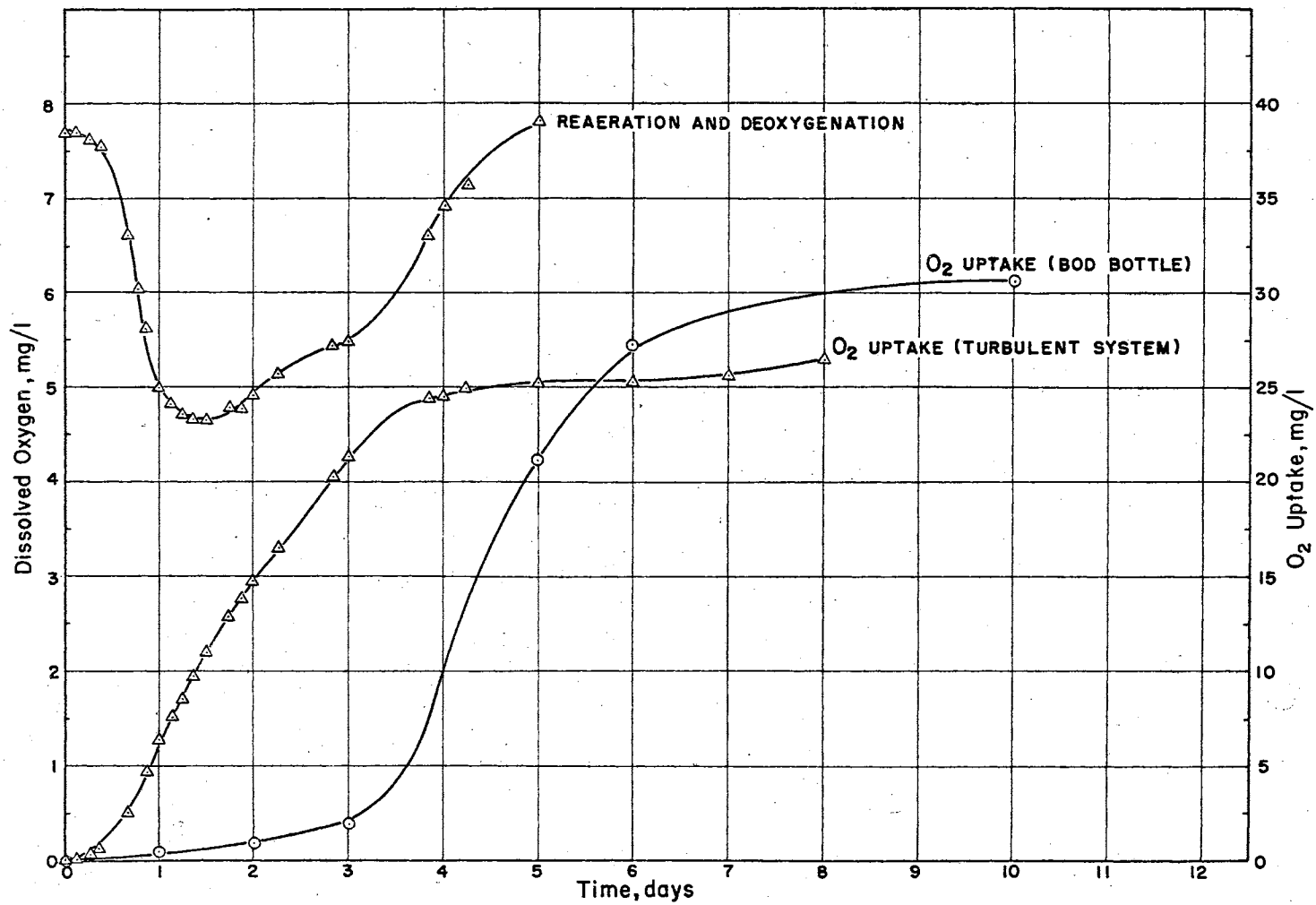


Figure 33. Comparison of Oxygen Uptake in a Simulated Stream and in BOD Bottles, Experiment Number 7 (Substrate: 44 mg/l Glucose).

the reduced amount of seed in the bottle systems may have been partially responsible for the large initial lag period. Furthermore, this reduced amount of seed may have been partially responsible for the differences observed in the ratio of synthesis to respiration during the first stage demand.

A BOD bottle experiment was conducted in which three dilutions of a 44.0 mg/l glucose-glutamic acid mixture were set up with all dilutions containing 5 ml/l of settled domestic sewage as seed (the same amount which was always placed in the turbulent system). Figure 34 shows the results of this experiment. No appreciable lag period was observed for the 1:5 and 1:2 dilutions; however, the 1:1 dilution showed a lower value of BOD exerted than the other dilutions for the first sample removed after one-half day. This dilution (1:1) showed a zero DO value when sampled again after one day of incubation; the available oxygen in the bottle had been completely removed. The lower BOD value for the one-half day sample of the 1:1 dilution was not expected. This observation may or may not be significant; however, the 1:2 dilution always gave BOD values slightly less than the 1:5 dilution.

The important fact to be noted about this experiment is that when the oxygen uptake for this system was compared to all of the turbulent systems in which the same concentrations of seeding was used, the oxygen uptake at all times was greater than that exerted in any of the tur-

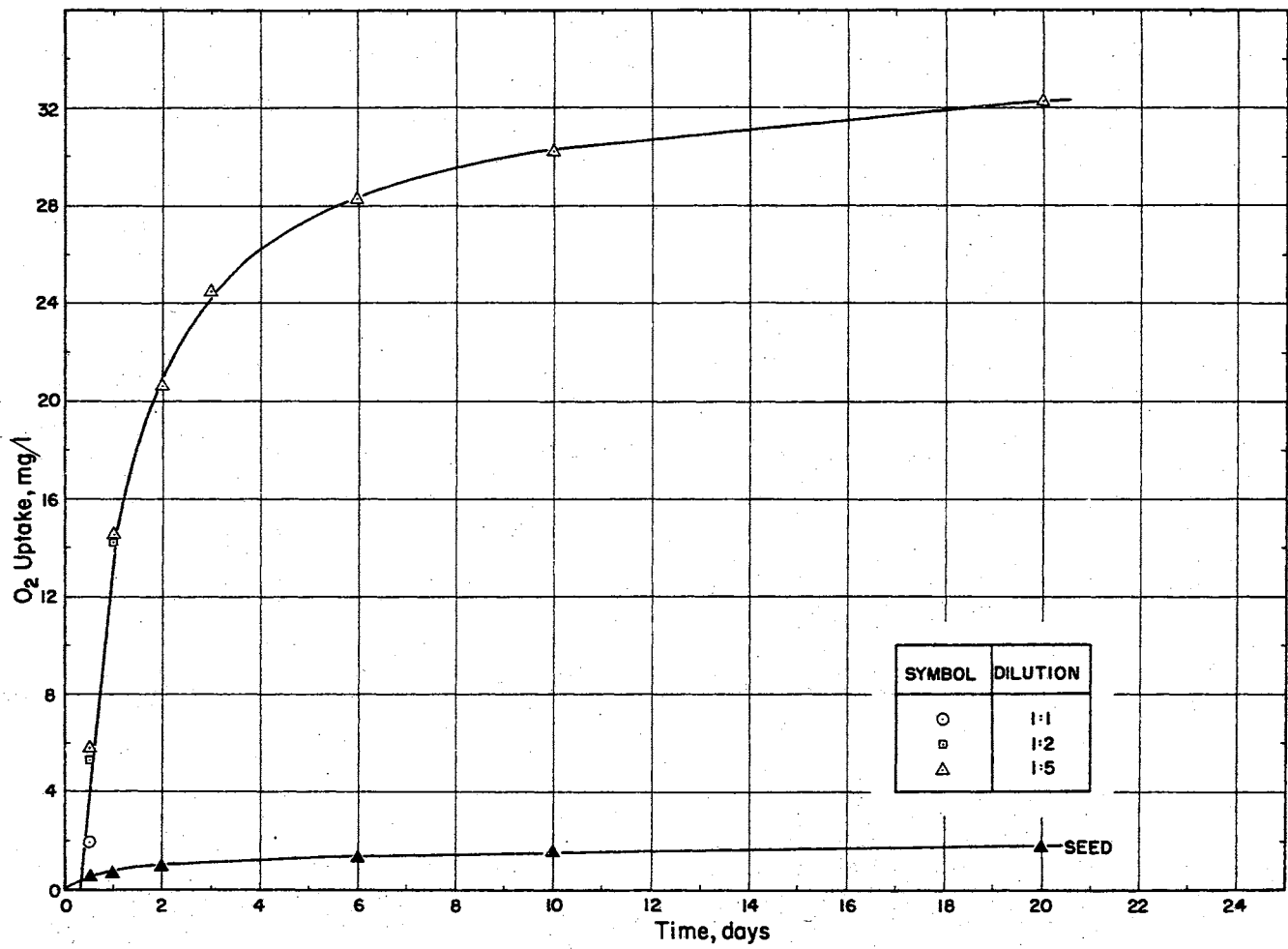


Figure 34. Biochemical Oxygen Demand Curve Using Same Initial Seed Concentration as in the Simulated Stream (5 ml Sewage/l).

bulent systems. This can be seen in Figure 35. Multiphase oxygen demands were not distinguishable for this experiment although the infrequency of sampling may not allow for this distinction between phases to be made in this case. Also, the greater seed concentration could have allowed the plateau to be masked in the BOD bottle. The higher respiration (O_2 uptake) throughout this curve does suggest that the synthesis to respiration ratio was lower for this bottle system than in the turbulent systems compared, hence this was consistent with the previous observation that quiescent systems appear to have a lower synthesis to respiration ratio than turbulent systems during the first stage of oxygen exertion.

5. Summary of Results for Deoxygenation Responses

In most of the experiments reported in this section of the results, there appeared to be a three-stage oxygen exertion. There appeared to be a rapid first stage exertion which could be approximated (for engineering computational purposes) by a first order rate equation of the type

$$\frac{dL_p}{dt} = -k_1' L_p \quad (V-13)$$

where L_p is denoted as the first stage BOD remaining at any time t , and k_1' is the associated first order rate constant. For some of the experiments an initial lag period prior to this assumed first order rate reaction

must be taken into account. There appeared to be a second stage oxygen uptake which could be approximated by a zero order rate reaction defined as follows:

$$\frac{dY_S}{dt} = C_S \quad (V-14)$$

where Y_S is the second stage oxygen uptake and C_S is the constant rate of O_2 uptake during this second stage. It is emphasized that the second stage of oxygen uptake appears in some cases to be somewhat autocatalytic in its early stages; however, this period appears to be of short duration, hence a constant rate of O_2 uptake appears to approximate, for computational purposes, the overall second stage O_2 demand. A third stage of O_2 uptake occurred which could be approximated by a zero order rate reaction as given by the following equation:

$$\frac{dY_E}{dt} = C_E \quad (V-15)$$

where Y_E is the third stage oxygen uptake and C_E is the zero order rate constant of the third stage oxygen uptake. Again, it is emphasized that the third stage has a slow decreasing rate; however, for engineering computational purposes it can be approximated by a zero order rate reaction.

Figure 36 shows the results of an attempt to reproduce theoretically the true oxygen response curve for the first glucose-glutamic acid system (Figure 26). For the first stage of oxygen demand the basic form of the classical sag equation

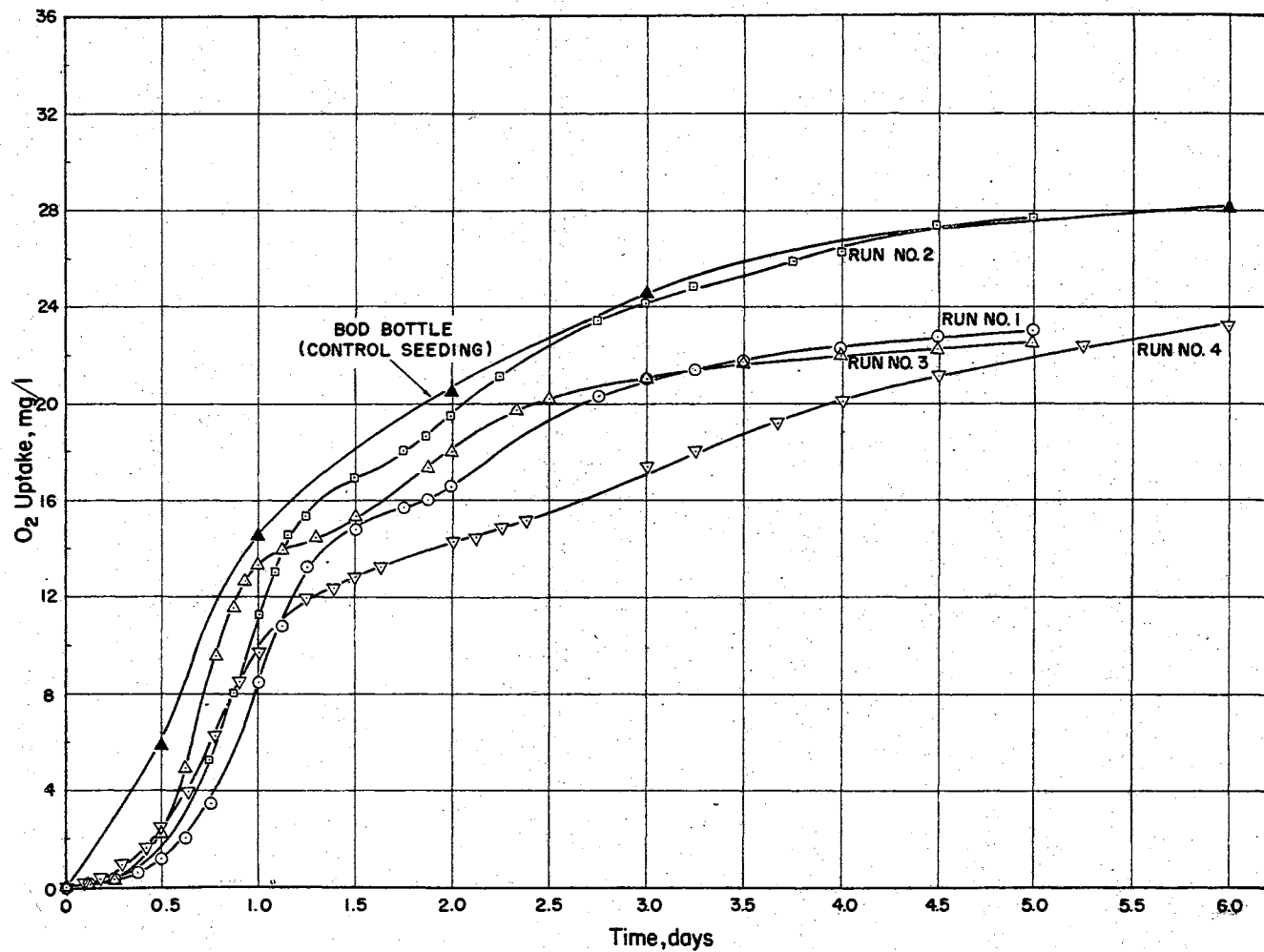


Figure 35. Comparison of BOD Exertion in the Simulated Stream and in BOD Bottles using Same Seed Concentration (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

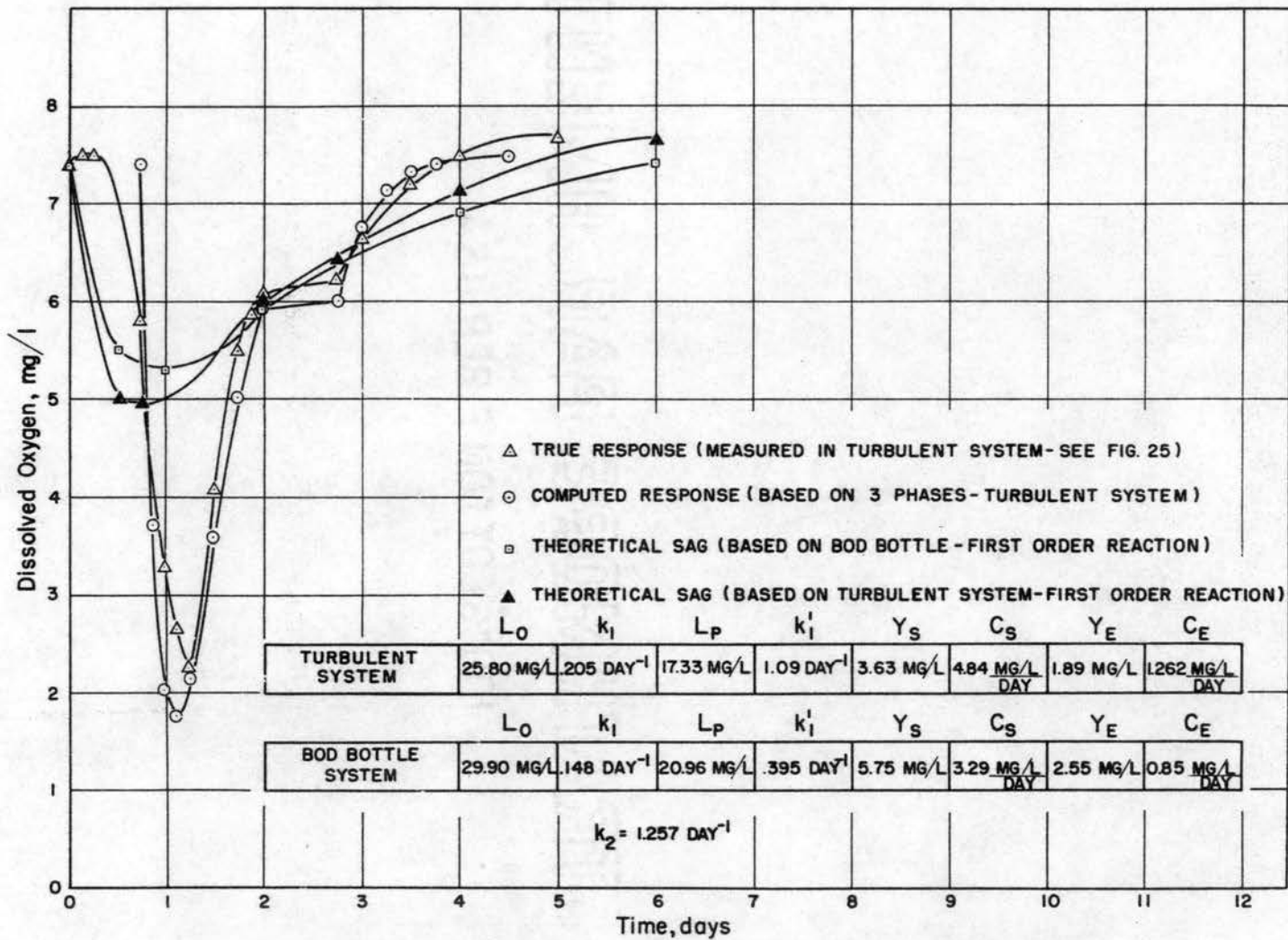


Figure 36. Comparison of Observed and Computed Sag Curves (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

$$D_t = \frac{L_{p-o} k_1'}{k_2 - k_1'} \left[10^{-k_1' t} - 10^{-k_2 t} \right] + D_o 10^{-k_2 t} \quad (V-16)$$

was used to predict the oxygen deficit at any time, t .

It should be noted that L_{p-o} (total first stage demand) replaces L_o (ultimate carbonaceous BOD), and k_1' , as defined in Equation (V-13) replaces k_1 . For the second stage of oxygen demand, solution of the following differential equation

$$\frac{dD}{dt} = C_S - K_2 D \quad (V-17)$$

yields the following expression for dissolved oxygen deficit at any time, t .

$$D_t = \frac{K_2 D_o - C_S}{K_2 e^{K_2 t}} + \frac{C_S}{K_2} \quad (V-18)$$

where D_o is taken as the dissolved oxygen deficit at the beginning of the second stage of oxygen exertion and zero time is also assumed at this point for computations of second stage changes in DO deficit.

Computations for DO deficits during the period of the third stage exertions were made by assuming a zero order rate reaction. The general form of Equation (V-18) is also used in this analysis.

$$D_t = \frac{K_2 D_o - C_E}{K_2 e^{K_2 t}} + \frac{C_E}{K_2} \quad (V-19)$$

where D_o is taken as the DO deficit at the end of second

stage exertion or at the beginning of third stage exertion (these two times are assumed to coincide) and zero time is adjusted to this point. Also given on Figure 36 is a tabulation showing the numerical value of the rate constants determined for this analysis. The deoxygenation rate constants were determined from the oxygen uptake curve for the turbulent system by considering each stage of oxygen uptake separately. An initial lag period of three-quarters of a day was assumed for this analysis in order to correct for the observed lag in the first stage exertion. Other than this initial lag period, there are no other breaks in time for the curve showing the computed oxygen response. The adjustment to zero time for each stage of oxygen exertion was made as described; however, the computed curve is continuous from 0.75 days to 5.0 days.

It is emphasized that in the region of the plateau in the BOD exertion curve small oxygen exertions were occurring. The first stage of oxygen exertion was approximately eighty per cent completed (see Figure 26) by the time that the DO response curve reached a minimum point; however, computations for the second stage demand were not started until this second stage occurred (at approximately two days).

It can be seen in Figure 36 that the computed curve based upon the three assumed models for the three phase oxygen exertion approximates very closely the true response curve. Of course, it should, since the O_2 uptake curve for the turbulent system, which was obtained indirectly

from the true oxygen response curve (sag curve) was the basis from which the reaction rate constants for the three assumed models were obtained. However, the point to be delineated here is that the sag curve can be reproduced with a fairly good degree of accuracy using first order BOD exertion in the first stage followed by two separate zero order exertions in the second and third stages. Also shown in Figure 36 are computed sag curves based upon the assumption that one first order kinetic reaction alone can be used to approximate the true oxygen response curve, and it is seen that neither the turbulent system nor the quiescent BOD bottle system yielded an overall first order reaction rate that could be used to approximate the true oxygen response curve very well. Indeed, they yielded very high estimates of the minimum DO in the simulated river.

Figure 37 shows the results of an attempt to reproduce the observed DO response curve for run 1 (same as that shown in Figure 36) utilizing the BOD bottle data obtained in the experiment where 5 mg/l of seed were used in the BOD bottle system (see prior discussion of this experiment on pages 122 through 126). This analysis was made because this BOD bottle experiment was the only BOD bottle experiment conducted using the same seed concentration as was used in all of the turbulent systems where glucose-glutamic acid was used as the substrate. It can be seen from Figure 37 that the computed response curve,

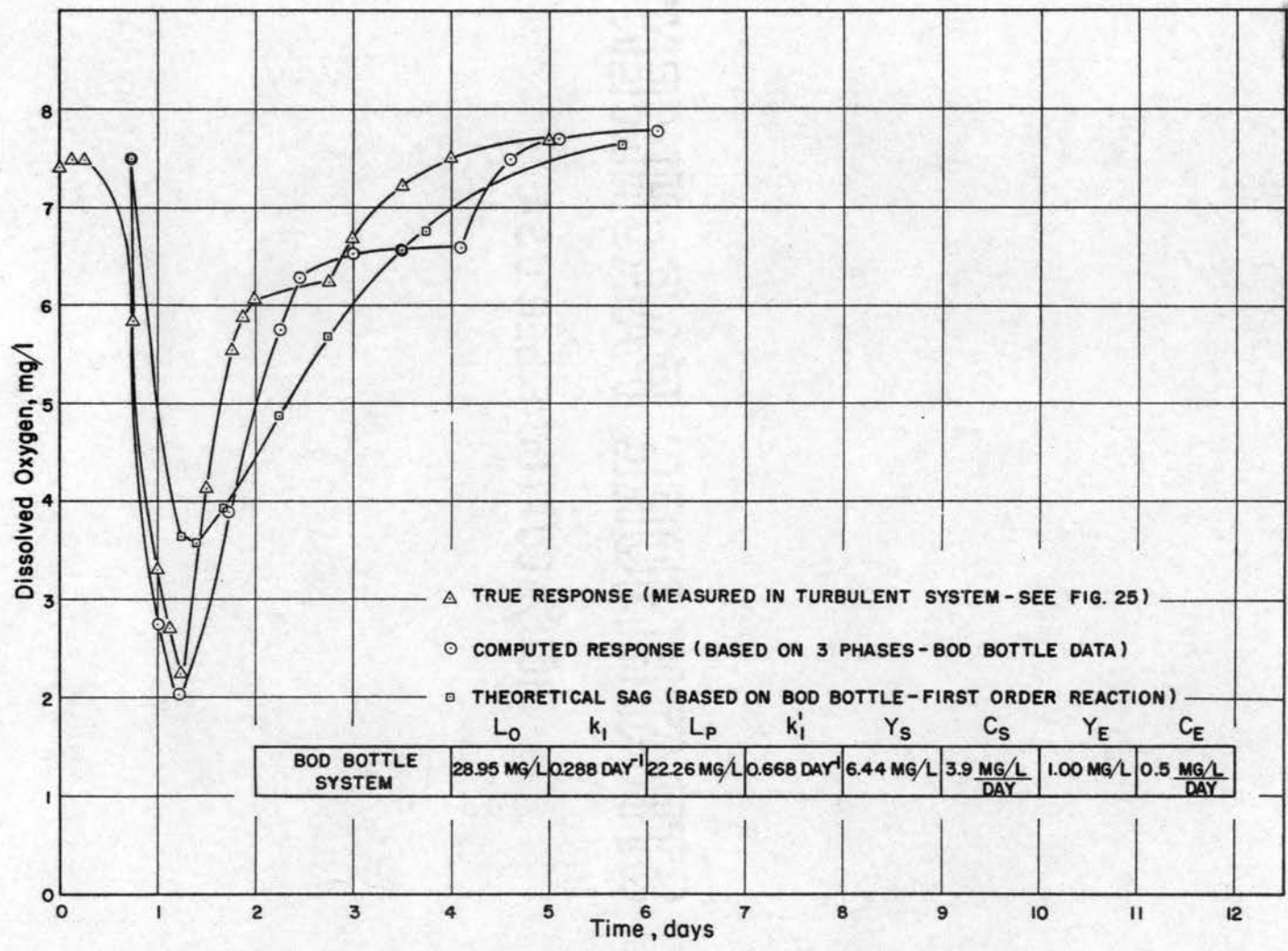


Figure 37. Comparison of Observed and Computed Sag Curves Using BOD Bottle Data of Figure 34 (Substrate: 22 mg/l Glucose + 22 mg/l Glutamic Acid).

which was based upon the proposed models for three stages of oxygen exertion and the assumption that this BOD bottle progression contained an oxygen exertion which could be broken into three stages, approximates fairly closely the minimum DO point obtained in the turbulent system. Actually, the entire first stage exertion is somewhat approximated. The second stage oxygen exertion for the computed curve estimates the rate of second stage demand fairly well; however, the total period of this second stage is much larger than that observed in the true response curve. The third stage of exertion occurs at a much smaller rate than in the true response curve, and due to the extended period of the second stage exertion, it is predicted to occur much later than it does in the true response curve. Also shown on Figure 37 is the theoretical sag curve based upon the assumption that one first order reaction rate, determined from this same BOD bottle progression, can be used to predict the actual DO response curve. It can be seen from this curve that the use of one first order reaction rate will not approximate very well the true oxygen response curve. It gives a high estimate of the DO concentration in the region of the minimum DO, which is the most critical region of the entire response curve.

As a result of the comparisons made and shown in Figure 37, one can conclude that it is necessary to analyze a BOD bottle progression for the first stage of oxygen

exertion regardless of whether it appears to be masked by the immediate onset of the second stage of oxygen exertion. Thus it is seen that phasic O_2 uptake as reported by Bhatla and Gaudy (58) must be taken into account in order to predict the course of BOD exertion. Furthermore, it is emphasized that although there were differences observed throughout this investigation between DO responses occurring in turbulent systems and DO responses occurring in quiescent systems, nevertheless, the BOD bottle progression, if interpreted as three stages of oxygen exertion, can be used to give a better estimate of the true DO response which occurs in a turbulent system during the first stage oxygen demand than can be obtained using one first order reaction rate to describe the complete BOD progression.

The number of experiments conducted during this portion of the research investigation does not permit conclusive theoretical postulations; however, it does seem apparent that computations dealing with assimilative capacity based upon the validity of the classical sag equation and applicability of BOD bottle determinations of k_1 and L_0 for representing occurrences in a turbulent system may be in gross error.

CHAPTER VI

DISCUSSION

A. DO Saturation Values

The dissolved oxygen saturation values for the tap waters used in this investigation were found to be significantly less than DO saturation values for distilled water. On the average they were 4.90 per cent less than the values reported in "Standard Methods" for distilled water after corrections for temperature and barometric pressure effects had been taken into account.

Explanation of the reasons or underlying causes of these differences was not considered as a goal in this experimental investigation. However, it is a well-established fact that the solubility of gases in water is usually decreased by the addition of other solutes, especially electrolytes. The extent of this effect varies considerably with different salts (59).

In this investigation the cause of the decrease in solubility was deemed less important than knowing the actual value of the solubility for a particular experimental investigation. Hence, the experimental data necessary to determine the in situ DO solubility was obtained and a theoretical equation defining first order

reaction kinetics was advanced and used to compute the apparent DO solubility for each reaeration experiment.

Equations (III-3) and (III-6), which are offered as a method for determining DO solubility for a system reaeration according to first order reaction kinetics, are presented. These equations are valid mathematical relationships which have been used for empirical definition of data in the past (50). A physical meaning has been given to the parameter α which defines the overestimates or underestimates made in assuming some value for the DO saturation.

The necessity of knowing the true DO saturation value before any determination of the true reaeration rate, k_2 , can be made was discussed in Chapter III. The magnitude of errors made in determination of k_2 rates was illustrated by an example where a five per cent error was made in overestimation of DO saturation value. This illustration was selected, since a 4.90 per cent average deviation was observed in this investigation. Thus the magnitude of the overestimate is very much within the limits that one can expect. To further emphasize the importance of this seemingly small overestimate of DO saturation, the errors made in k_2 prediction in the example ranged from slightly greater than five per cent to about fifty per cent.

There seems to be little doubt that future workers concerned with stream purification problems will have to make in situ determinations of DO saturation values for the actual waters they are testing. True values of the

reaeration rates cannot be determined unless the true value of DO saturation is known.

B. Reaeration

1. General

A rational model of the reaeration process has been presented and results obtained by controlled experimentation have been utilized to evaluate the constants associated with the model. The final model was presented as Equation (V-9):

$$k_{2-T} = 3.053 \frac{V}{H^{3/2}} (1.0241)^{T-20} \quad (V-9)$$

where 3.053 represents the group

$$\left[C D_m^{1/2} \left(\frac{1}{\nu^{1/6}} \right) \left(\frac{1}{g^{1/6}} \right) \right]_{20^\circ C.}$$

By substituting the known numerical values

$$D_{m-20^\circ} = 2.193 \times 10^{-8} \text{ ft}^2/\text{sec}$$

$$\nu_{20^\circ} = 1.091 \times 10^{-5} \text{ ft}^2/\text{sec}$$

and

$$g = 32.2 \text{ ft}/\text{sec}^2$$

the constant C is evaluated to be 0.06339. The equation for k_{2-T} can be expressed as

$$k_{2-T} = 0.06339 \left[\frac{D_{m-T}^{1/2}}{\nu_T^{1/6} g^{1/6}} \right] \frac{V}{H^{3/2}} \quad (VI-1)$$

However, Equation VI-1 is not as easy to use for computational purposes as Equation (V-9).

This model has been shown to correlate very well with both the natural stream data gathered by Churchill's group (6) and the laboratory data of Krenkel and Orlob (10).

In the correlation study using the natural stream data of Churchill's group, the following equation was obtained:

$$k_{2-20^{\circ}} = 3.739 \frac{V}{H^{3/2}} \quad (V-11)$$

This equation had an associated correlation coefficient value of 0.948. The major difference between Equation (V-9) and Equation (V-11) is the value of the constant C. The natural stream data predict k_2 values 1.225 times larger than the author's data. This difference was probably due to differences in channel geometry. A rectangular channel cross-section was employed in this investigation while the channel cross-sections of natural streams are of irregular shape. Generally, natural stream channel cross-sections are deep in the central portion of the channel and shallow at the stream banks. The depth H, used for natural stream channels, is based upon the mean depth defined by the mean width of the cross-section occurring in a stream reach.

Churchill's group observed higher DO concentrations near the stream banks than in the central portion of the stream. They attributed lateral variations in DO to the following: "(1) incomplete mixing into the flow of upstream tributary inflows, (2) increased reaeration near the banks because of longer time of water travel and

shallower depth, and (3) unequal effects across the stream of photosynthesis and respiration by attached aquatics." It was further indicated that no variation was found in the vertical direction from the surface to the stream bed. If lateral diffusion is much smaller than vertical diffusion, it is highly conceivable that a shallow portion of a stream cross-section could reaerate much faster than a deeper portion within the same cross-section. Whether or not the arithmetic mean depth, based upon mean channel width of a stream reach is the true measurement of depth in the reaeration equation for an irregular-shaped cross-section has not been established, since laboratory investigations have been conducted using rectangular cross-sections. Furthermore, the effect upon reaeration caused by increased surface area greater than the horizontal projected surface has not been established. Most attempts made thus far to evaluate this effect have been correlation studies of existing data (21, 12). These attempts have used the Froude Number in the following general form:

$$k_2 \text{ (observed)} = k_2 \text{ (predicted)} (1 + aN_F^b)$$

where k_2 (predicted) is given by a proposed mathematical relation defining the hydraulic variables in the stream, and a and b are constants. However, the writer does not believe that the Froude Number alone can be used to estimate area changes. The width-to-depth ratio of a stream channel plays an important role in determining the type

and size of stable surface wave patterns that can be established for a given flow condition. While the general surface flow variations are probably best characterized by the Froude Number, it is believed that a geometric scale factor will be of almost equal importance. Area changes which occur in a small-scale laboratory channel should be small compared to area changes which occur in a large-scale natural stream channel, i.e., a one-foot wide laboratory channel limits the scale of a steady surface wave compared to that which can occur in a five hundred-foot wide natural stream channel of the same depth.

It seems apparent to the writer that surface areas greater than that of the horizontal projected surface areas exist in natural streams, and this factor may play a significant role in determining k_2 . As the width-to-depth ratio of a stream is increased, the steadiness of a surface wave is increased. Any deviation of the surface from the horizontal position will increase the surface area. For a fixed volume of water, the mean depth of flow will not change so long as the horizontal projected area is used to determine this mean depth measurement. One only needs to view a natural stream surface to see that a highly complex rippled wave pattern exists on these surfaces to some degree at all times.

It was observed during the studies on the vibratory effect that surface wave patterns appeared to increase in size as the width-to-depth ratio was increased; i.e.,

as the depth was decreased for this channel with a fixed width.

The vibrational effect encountered in this investigation caused inability to reproduce reaeration measurements with exact precision; however, these vibrational differences may offer an avenue of investigational approach (under controlled vibrational conditions) which could lead to a more thorough understanding of the effects of changes in surface area upon the reaeration rate constant, k_2 .

Based upon the foregoing discussion concerning natural channels, it is felt that the difference between the values of the constant $C_{20^{\circ}}$, 3.053 for the author's data and 3.739 for the data of Churchill, et al., is not unreasonable. The important point to be delineated is that the proposed equation for prediction of k_2 derived from the laboratory data of the present investigation provided a relatively good correlation of the data obtained by Churchill, et al., under natural stream conditions. Future work on natural streams and in the laboratory should reveal the causes of the differences in the constant, $C_{20^{\circ}}$. As suggested earlier, the differences are probably associated with channel geometry.

When the proposed model was applied to the laboratory data of Krenkel and Orlob, the following equation was obtained:

$$k_{2-20^{\circ}} = 2.440 \frac{V}{H^{3/2}} \quad (V-12)$$

The associated correlation coefficient value was 0.950. Comparison of the value 2.440 to 3.053 indicates that the data obtained in a recirculating flume predict k_{2-20° values which were only 79.9 per cent of those predicted by the experimental results of this investigation.

Recently, Thackston and Krenkel (12) reported on an investigation carried out on a recirculating flume. They proposed the following equation:

$$k_2 = 0.000015 \frac{D_L}{H^2}$$

where D_L is a measured longitudinal mixing coefficient. However, using their proposed model and the data of Krenkel and Orlob, they obtained the equation:

$$k_2 = 0.000052 \frac{D_L}{H^2} .$$

They indicated that, in comparing these two equations, Krenkel and Orlob's was about 3.5 times that of their investigation. It was further stated that, after checking over both groups of work, no mistakes in procedures or mathematics were found, and that no explanation for the apparent difference could be found. It would seem that an "apparent" 3.5-fold difference is an extremely large difference, and it was deemed necessary by the author to examine it more closely than was done by Thackston and Krenkel. In the writer's review of the two investigations (Krenkel and Orlob's, and Thackston and Krenkel's), the major differences found between the two recirculating

flumes were channel width and volumes of water in the return piping systems. Channel width should not influence the reaeration rate at this small laboratory scale. However, the numerical values obtained using the indirect method which they employed for obtaining the channel reaeration rates between sampling stations may have been influenced significantly by the volumes of water contained in the return piping system. The theory underlying this indirect computation method is not being questioned; however it has never been proven conclusively to be valid; i.e., measurements are indirect and based upon the surmised validity of a presupposed theory. That theory is based upon the assumption that the dissolved oxygen deficit vs. time curve obtained for the upstream station reflects past history of the water passing that station; however, the position at any time of this upstream reaeration curve is influenced by the volume of water contained in the return system. Furthermore, the position of DO deficit for the downstream station is influenced by the volume of water in the return system.

It appears that return piping volume differences may be used to explain the approximate 3.5-fold difference between the two apparently identical channels. The channel used by Krenkel and Orlob contained a 6-inch diameter return pipe. The channel used by Thackston and Krenkel contained two return pipes (8-inch diameter and 10-inch diameter). The system used by Thackston and Krenkel

recirculated water through either or both of the return pipes. Scheduling of individual return system piping arrangements for their system was not published, therefore the volumetric data for comparison of similar conditions in both systems is not known by this investigator. However, these investigators relayed through personal communication (60) that series A of their experimental program was conducted almost entirely using both return pipes simultaneously. Their equation for series A experiments was

$$k_2 = 0.000014 \frac{D_L}{H^2}.$$

For the purpose of analyzing possible effects of the return pipeline on reaeration, it may be assumed that on the average the system used by Thackston and Krenkel can be treated as having a return volume equal to the volume of the combined 8-inch and 10-inch return piping system. It is further assumed that since each system, i.e., the system used by Krenkel and Orlob and the system used by Thackston and Krenkel, had a channel length of sixty feet, they both contained at least sixty feet of return piping. The volumes of water in the two assumed return systems would be approximately 53.66 cubic feet in the dual pipe system, and 11.78 cubic feet in the single pipe system.

For the purpose of this illustration, it is assumed that the true reaeration response, k_{2t} , might be determined by the following equation:

$$k_{2t} = k_2 \text{ (reported)} + CV_R$$

where V_R is the volume in the return system and C is a constant which corrects for any effect caused by the differences in the return system volumes. It is emphasized that this proposed equation for computing k_{2t} is not necessarily the ultimate form of the equation that should be used for investigating the possible effects of return system volumes. However, since the writer has very little information concerning the accurate volumes contained in the channel and return systems for each individual experiment, this equation is proposed for determining approximations of the effects of return system volumes on the indirectly measured k_2 -rate constants. Utilizing the two equations reported by Thackston and Krenkel, the following two equations are proposed:

$$k_{2t} = 0.000014 \frac{D_L}{H^2} + 53.66C \quad (\text{Equation for Thackston}$$

and Krenkel's data), and

$$k_{2t} = 0.000052 \frac{D_L}{H^2} + 11.78C \quad (\text{Equation for Krenkel}$$

and Orlob's data).

Since the two systems are now assumed to be identical, these two equations can be solved simultaneously in order to evaluate the constant, C . The simultaneous solution yields the following:

$$C = 0.0000009074 \frac{D_L}{H^2}.$$

Substitution of this value of C back into the equation defining the data of Krenkel and Orlob yields

$$k_{2t} = 0.000052 \frac{D_L}{H^2} + 0.0000107 \frac{D_L}{H^2} \quad (\text{VI-2})$$

or

$$k_{2t} = 0.0000627 \frac{D_L}{H^2} \quad (\text{VI-2a})$$

This, then, implies that the observed k_2 value is equal to only 82.9 per cent of the assumed true value, k_{2t} . Based upon this simple assumption having some validity, Equation (V-12) can be rewritten as:

$$k_{2-200} = \frac{2.440}{0.829} \frac{V}{H^{3/2}}$$

or

$$k_{2-200} = 2.943 \frac{V}{H^{3/2}} \quad (\text{VI-3})$$

If a comparison of the constant, C, equal to 3.053 which was obtained using the author's data is made with this adjusted value of the constant for the data of Krenkel and Orlob, the latter constant is 96.4 per cent of the value obtained using the author's data. Hence the data of Krenkel and Orlob when analyzed for possible effect of the value of the return flow, agrees very closely to the author's results.

Since the scheduling of return piping arrangements made during the individual experiments of Thackston and Krenkel was not known, their reaeration data were not con-

sidered for a separate correlation analysis in this investigation. However, based upon the arguments presented concerning return piping volumes, substitution of the value

$$C = 0.0000009074 \frac{D_L}{H^2}$$

back into the equation defining the series A experiments leads to the equation

$$k_{2t} = 0.000014 \frac{D_L}{H^2} + 0.0000487 \frac{D_L}{H^2} \quad (\text{VI-4})$$

or

$$k_{2t} = 0.0000627 \frac{D_L}{H^2} \quad (\text{VI-4a})$$

which is identical to the value of k_{2t} defining the data of Krenkel and Orlob. This implies that Thackston and Krenkel observed only 22.3 per cent of the assumed true k_{2t} values in their experimental investigation. However, their return piping system volume was 4.56 times the return piping system volume of Krenkel and Orlob.

The writer has made an assumption concerning two groups of data which were reported to have been conducted on two seemingly identical recirculating flumes. No explanation for the apparent difference between the two groups of data was found by the authors of the latter investigation. It is proposed that the suggested effect of the return piping volumes may have influenced the indirect measurements obtained for reaeration rate in the recirculating flume type systems.

In summary, the writer's analysis suggests an explanation for the large difference between the data reported by Krenkel and Orlob and those reported by Thackston and Krenkel. These two groups of data were obtained on two seemingly identical recirculating open channel flumes. It was surmised by the writer that the major difference between these two reported channels was that of the return system volumes. Based upon estimations made for the return systems, the data of Krenkel and Orlob were adjusted, and their data appeared to be well-defined by the prediction equation for k_2 which was derived in this thesis. An explanation by the original authors for the large differences between the data gathered on two seemingly equivalent open channel flumes will surely aid future investigators. Regardless of how these authors explain these differences, an experimentally substantiated explanation by them would certainly add insight to the knowledge concerning factors affecting reaeration of streams.

2. Summary

The writer's proposed model

$$k_{2-T} = 3.053 \frac{V}{H^{3/2}} (1.0241)^{T-20} \quad (V-9)$$

or

$$k_{2-T} = 0.06339 \left[\frac{D_m^{1/2}}{\nu^{1/6} g^{1/6}} \right] \frac{V}{H^{3/2}} \quad (VI-1)$$

has been shown to correlate well with most of the reaer-

ation data reported in the literature to this date. Reaeration data obtained on the assumption of validity of the classical "sag equation" were not considered in this report. Data of this type were considered in preliminary analysis; however, definition of a purely physical process, i.e., atmospheric reaeration in turbulent streams, was the primary objective of this investigation. Hence, only data considered to be reasonably free of the influences of other oxygen transfer processes were considered to be valid for these comparisons.

The effect of temperature on reaeration rates was not investigated experimentally; however, it was found that the proposed expression

$$\left[\frac{D_m^{1/2}}{\nu^{1/6}} \right]_{T^{\circ}\text{C}} / \left[\frac{D_m^{1/2}}{\nu^{1/6}} \right]_{20^{\circ}\text{C}} = (1.0241)^{T-20}$$

would satisfy the accepted experimental findings of Churchill, et al. (52) concerning these temperature effects.

It is recalled here that the Schmidt Number, N_S , equal to ν/D_m was considered as one of the dimensionless parameters in the original dimensional analysis treatment:

$$\frac{k_2 H^2}{D_m} = C N_R^a N_F^b N_S^d \quad (\text{III-7})$$

Bennett and Meyers (61) made the following statement concerning the role of the Schmidt Number on the mass transfer coefficient: "Most experimental work indicates a value of d closer to 0.5 than to zero, thus supporting

the belief that the penetration theory is a more accurate mechanism for representing interphase mass transfer than the stagnant film theory."

The fact that k_2 was found to be directly proportional to the square root of molecular diffusivity and that this result fits well with past findings of temperature effects, strengthens the model developed in this investigation of reaeration in a simulated stream channel.

The fact that this investigation was conducted in a simulated stream channel where direct accurate measurements of k_2 , V , and H could be made is a new development in reaeration research investigations. The reaeration rates measured are those of the overall experimental system; however, the entire system is a continuous channel where all of the water contained in the system is exposed to reaeration and undergoes a uniform steady state flow condition throughout the entire period of testing.

Based upon the findings in this investigation, the proposed equation for reaeration in a simulated stream channel is

$$k_{2-T} = 3.053 \frac{V}{H^{3/2}} (1.0241)^{T-20} \quad (V-9)$$

where k_{2-T} has the dimensional units of days^{-1} , velocity is expressed in feet per second, and depth is expressed in feet. This equation is believed to be an improvement over any of the equations developed to this date for determining the reaeration rate constant, k_2 in terms of

physical stream parameters which can be measured.

C. Deoxygenation Responses

In this study, experimentation under controlled conditions was conducted using three different substrates, and observations of oxygen utilization occurring in both turbulent and quiescent systems were made. In general, a three-phase oxygen exertion was observed in most systems. The rates of oxygen uptake for each phase and the total amount of oxygen utilized during a particular phase varied markedly when comparison of the turbulent and quiescent systems was made. The effect of seeding concentration on the oxygen uptake response appeared to be quite important in establishing the extent of an initial lag period in the overall oxygen uptake response and also important in the progression of the first stage of oxygen exertion.

1. First Stage of Oxygen Utilization

In every turbulent system monitored there was a first stage oxygen exertion which appeared to be associated with an increase in biological solids (see Figure 28). In 1958, Busch (62) reported a diphasic oxygen uptake curve with the two phases separated by a plateau. He attributed the first phase of oxygen uptake to the conversion of substrate into new cells and storage products (synthesis). Bhatla and Gaudy (58) in a report on kinetics and mechanisms of phasic oxygen uptake attributed the first phase of rapid oxygen uptake to bacterial metab-

olism of the extracellular carbon source and the readily-available intracellular substrates. Also, according to these authors, during the first phase the cells respire part of the substrate to provide energy for the associated anabolic processes and the bacterial population increases and reaches a limiting value which is dependent upon the environmental conditions and available substrate.

From the observations made during this experimental investigation and literature cited, it appears that the first stage of oxygen exertion is associated with removal of extracellular substrate from the medium with concurrent cell synthesis and the respiration required for anabolic processes. Furthermore, the differences between a turbulent system and a quiescent system during this period of rapid oxygen utilization appear to be controlled by the relative partitioning of the substrate for new cell synthesis and the respiration required for these anabolic processes. In the turbulent systems the synthesis to respiration ratio occurring during first stage utilization was observed to be higher than it was in the quiescent systems. Furthermore, as the turbulence in the system was increased, the synthesis to respiration ratio appeared to increase. However, the effect of dilution of the initial seeding material in the quiescent systems could be responsible for their lower synthesis to respiration. Rao and Gaudy (63) in a study of the effects of sludge concentration on various aspects of biological

activity in activated sludge, showed that the percent of theoretical oxygen demand exerted at the time of complete COD removal decreased as the concentration of initial biological solids increased. This suggests that the synthesis to respiration ratio increases with increasing levels of biological solids. Nevertheless the turbulent system with the higher stream velocity was observed to have the higher synthesis to respiration ratio (see Figure 30). The seeding concentration (volume basis) was the same in all of the turbulent systems conducted using the glucose-glutamic acid mixture as the substrate. This suggests that no matter what one does to make the seed concentration the same in the BOD bottle as in the river, complete equivalence may never be attained if exertions in a river system depend upon turbulence.

The limited number of experiments conducted in this investigation does not allow for delineation of the kinetics and mechanisms of the first stage of oxygen utilization; however, it does appear that the monitored exertions can be approximated by a first order rate reaction as given in Equation (V-13) if an initial lag period is taken into account.

At present, complete definition of the total first stage demand cannot be made because the relative amounts of the partitioning of substrate for cell synthesis and concurrent respiration have not been established. This partitioning effect appeared to be quite dependent upon

a measure of turbulence (reaeration rate constant, k_2) and initial solids concentration in the system; however, extensive experimentation will be required before these effects can be completely delineated.

If and when a definitive expression has been developed for establishing the relative synthesis to respiration ratios for varying degrees of turbulence and initial solids concentrations, then possibly an initial COD measurement can be made on biodegradable waste and its effect on a stream can be predicted. Of course, the expected exertion rates of oxygen uptake for specific wastes will also have to be defined in terms of turbulent system values. Ultimately, though, one may be able to define both the rate of this first stage oxygen utilization and the expected partitioning effect in a turbulent system with a known concentration of initial solids. If this situation does come to pass, initial COD measurements on a previously characterized waste could become a good partial criterion for predicting what will occur in a defined turbulent system.

2. Second Stage of Oxygen Utilization

The second stage of oxygen utilization, observed in the systems studied, appeared to be exerted at a reasonably constant rate. The cause of this second stage oxygen exertion was not definitely determined in this investigation. However, in all of the turbulent systems studied, definite clarification was observed to occur in

the systems during the period of second stage oxygen exertions. Bhatla (37) in his studies of phasic oxygen uptake made the following conclusions: "The diphasic oxygen uptake expression with two phases separated by a plateau, commonly observed in low (BOD bottle) and high energy (Warburg) systems, is primarily due to changes in predominance in population; i.e., protozoa over bacteria." He further states: "The role of protozoa in the total purification process is that of clarification; i.e., destruction of the bio-mass, and in the absence of predators little or no clarification is possible. In a system comparable to a BOD bottle, purification is achieved in two phases. Bacteria are mainly responsible for the first phase of chemical purification, followed by a second phase of destruction of bacterial cells by protozoa (visible purification)."

Bhatla and Gaudy (58) reported that the second phase of oxygen utilization which they interpreted to include all of the oxygen utilization occurring after the first stage exertion (i.e., everything beyond plateau) was approximately thirty per cent of the ultimate BOD. Gaudy, et al. (64) also reported that the first stage demand usually was from thirty to forty per cent of the theoretical COD of the pure compounds which they investigated; however, they found a total range of twenty-five to forty-three per cent. Table III gives a tabulation of the similarly computed percentages which were obtained in this

investigation for the systems where pure compounds or pure compound mixtures were used as substrate. These tabulated values agree very closely with the previously cited ranges of these two corresponding percentage values. It is readily seen that neither of these percentages is constant, hence the first and second stage oxygen exertions cannot be assumed to be a fixed percentage of the theoretical COD. Substrate alone cannot be used as a single criterion for such an assumption.

TABLE III
OBSERVED FIRST AND SECOND STAGE OXYGEN EXERTIONS

Experiment Number	Substrate	2nd Stage Exertion % Ultimate BOD	1st Stage Exertion % Theoretical COD
1	Glucose-Glutamic Acid	25	39
2	"	35	40
3	"	32	34
4	"	45	27
5	Glucose	31	38

Bhatla (37) also showed that only one of fifty-seven pure culture organisms which he investigated showed a diphasic oxygen uptake curve and that the second phase, in this case, was found to be due to utilization of volatile acids excreted into the medium during glucose metabolism. Second phase oxygen uptake was concluded to be a fairly rare occurrence for pure bacterial cultures.

Sequential substrate utilization may take place in low energy systems and cause a diphasic oxygen uptake curve. Bhatla and Gaudy (65) reported on sequential substrate removal in a dilute system by heterogeneous microbial populations. They showed that when glucose and sorbitol were placed in the BOD bottle with glucose-acclimated seed, substrate utilization in the first stage was sequential and oxygen utilization occurred in two phases. By using specific tests to assay for the substrates used, it was shown that 2 mg/l of O_2 uptake occurred in the removal of 5 mg/l of glucose followed by 2.1 mg/l of additional O_2 uptake, while 5 mg/l of sorbitol was being used. The sorbitol concentration remained at 5.0 mg/l until glucose was removed. The important fact to be noted about this reported experiment is that for sequential substrate removal the oxygen uptake for each component should be approximately proportional to the magnitude of each substrate which is present and is being removed sequentially. For the glucose-glutamic acid systems reported here, there was no evidence that the first stage oxygen utilization was a result of sequential substrate removal. Grady and Gaudy (66) reported that glucose and glutamic acid were removed concurrently in a batch activated sludge system where cells were acclimated to glutamic acid. Hence the two-phase oxygen exertions observed in this writer's experiments using glucose and glutamic acid are not believed to be a result of sequential substrate removal.

For the observations made during this investigation, the second stage of oxygen uptake was always associated with visible clarification of the turbulent system. It is believed that protozoa caused the second stage oxygen uptake. Referring to Figure 28, following the maximum steady level in biological solids, a sharp drop in biological solids level occurred concurrently with the exertion of the second stage in oxygen demand. The cessation of this rapid dropoff in solids occurred simultaneously with the change from a reasonably constant high rate of oxygen utilization to a reasonably constant low rate of oxygen utilization.

Figure 38 shows the comparison of two experiments in which glucose was used as the substrate. Curve A was taken from Mancy, et al. (49). Its associated oxygen uptake curve was computed by the author (by the method proposed in Chapter III, pages 49-50). Mancy, et al. did not attempt to separate or evaluate the actual O_2 uptake occurring in their experimental system. Curve A was obtained by using a turbulent system in which a pure culture of Escherichia coli was placed into a 50.0 mg/l balanced glucose medium. It can be seen in the associated oxygen uptake curve that only one phase of oxygen utilization occurred.

Curve B (Figure 38) is the oxygen response curve which the author obtained in the present study using 44.0 mg/l glucose and a settled domestic sewage seed (Fig-

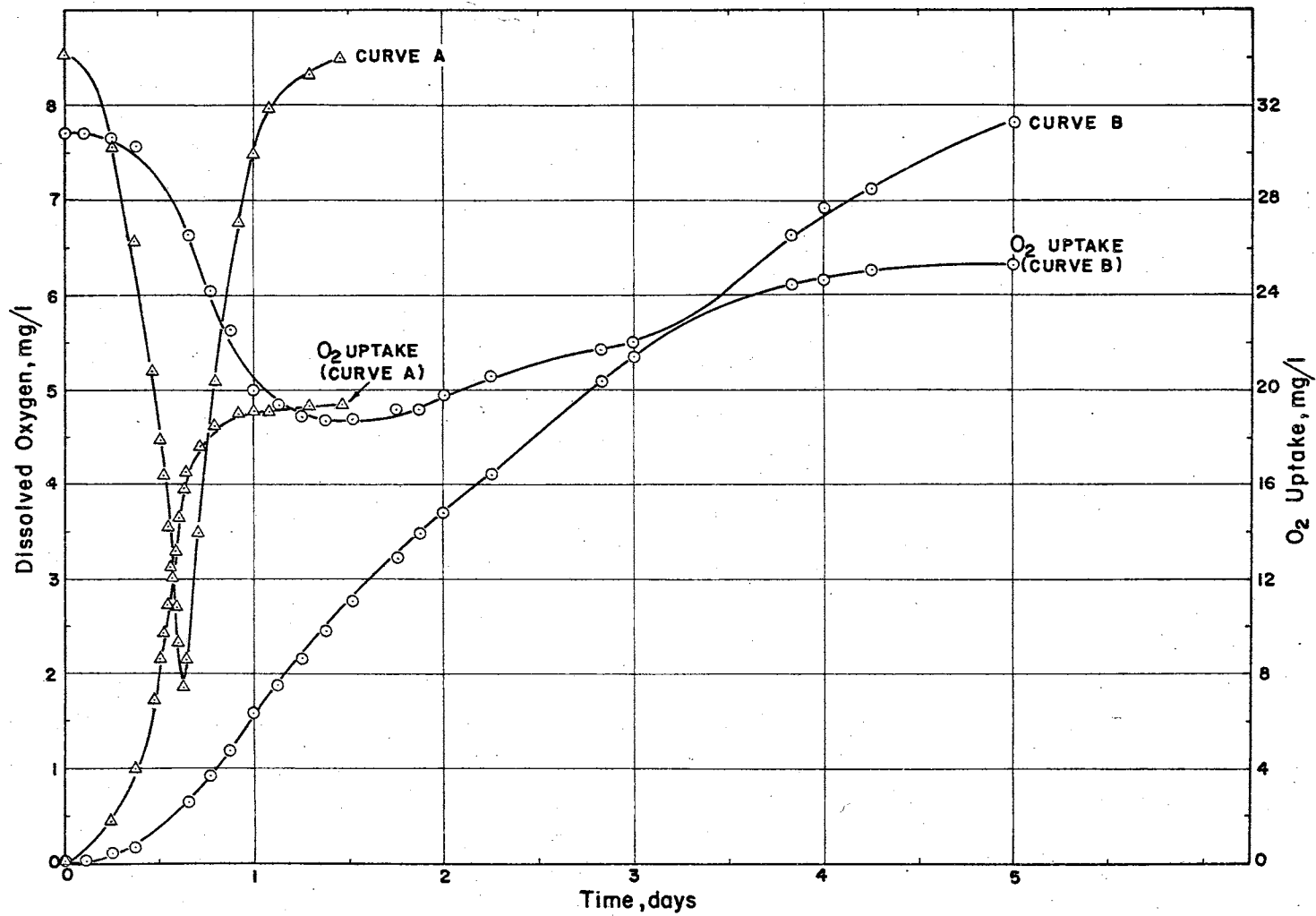


Figure 38. Comparison of Oxygen Uptake and Observed Sag Curves, Author's Experiment Number 7 versus Curves from Mancy, et al. (49).

ure 33). The reaeration rate for the system of Mancy, et al. was approximately 1.25 times the rate used in the author's experiment. The experiment of Mancy, et al. was probably run using a more turbulent system than the one used by the author, i.e., if reaeration rate can be used as a gross measure of turbulence. However, it is believed that part of the difference in relative rates of O_2 exertion between the two experiments is due to prior acclimation of a pure culture organism to glucose in the case of the experiment by Mancy, et al., compared to settled sewage seed placed in a glucose-BOD dilution water medium used in the author's experiment. Although these differences are important, the significant difference is that of single phase oxygen exertion vs. two-phase oxygen exertion. It can be seen by comparison of the two O_2 uptake curves that although the substrate concentration used by Mancy, et al. was 1.14 times the concentration used in the writer's experiment, the total oxygen uptake for the writer's system was about 1.31 times that for the system of Mancy, et al. Their system did not show a second stage oxygen exertion; however, this can be somewhat explained since Bhatla had observed that only one out of fifty-seven pure culture organisms which he studied showed two phases of oxygen exertion.

Although the second phase of oxygen exertion was not as apparent in the experiment shown in Figure 38 as it was for other systems reported, it appears that the second

stage of exertion is contained in this oxygen uptake curve but masked by an immediate onset of the second stage exertion which is exerted at a reasonably constant rate.

It is believed that the second phase of oxygen demand will occur in the majority of systems containing predators in the seed. Furthermore, both the rate of oxygen exertion and the amount of the oxygen demand is believed to be dependent upon the bacterial mass present at the end of first stage oxygen removal and upon the numbers and types of predators present at this time.

Bhatla (37) investigated the interaction of bacteria and protozoa with a pure culture of Serratia marcescens. An assessment of the amount of oxygen utilization in the second stage due to metabolism of bacteria by the protozoa was made. A series of Warburg flasks containing 249 mg/l, 592 mg/l, and 1185 mg/l of bacterial cells was inoculated with 2 ml of protozoa-rich seed per 100 ml of cell suspension. He found that the amount of oxygen consumption in the protozoa-inoculated flasks containing 249 mg/l and 592 mg/l of initial solids was proportional to the initial solids concentration, but the flask containing 1185 mg/l of initial solids showed a somewhat lower value than expected. In reviewing Bhatla's experiment, the writer noted that the ultimate rate of oxygen utilization was nearly the same for all three initial solids concentrations. Since the initial number of protozoa in each system was constant, these results may be interpreted as

suggesting that the rate of O_2 uptake in second stage was fixed by the initial number of predators present, i.e., the substrate concentration (the bacteria) was above that which would limit growth rate for all three systems. A crowding effect may have caused the system containing the higher concentration of solids to give a somewhat lower value of total oxygen demand than expected.

It appears from the observations made in this investigation and from the evidence presented in the literature cited that predators play an important role in the second stage oxygen exertions. It is believed that future work may establish a method for estimating both the rate of the oxygen exertion and the expected amount of exertion.

In every system studied in this investigation except the experiment conducted at the highest reaeration rate, the rates of second stage exertion were essentially equal. This was true for both bottle systems and turbulent systems. Whether the one highly turbulent system studied, which showed a difference in this rate of second stage exertion, is significant cannot be determined on the basis of this one experiment. The second stage of oxygen exertion appeared to be approximated (for engineering computational purposes) by a zero order rate reaction of the form given in Equation (V-14):

$$\frac{dY_S}{dt} = C_S \quad (V-14)$$

3. Third Stage of Oxygen Exertion

The third stage of oxygen exertion observed throughout this investigation was considered to be endogenous respiration. The rates of exertion were reasonably constant for the periods of time monitored, although they undoubtedly decrease at a very slow rate. The third stage oxygen demand is believed to be exerted by the residual biological mass remaining in the system after the first two stages of metabolic activity have occurred. This remaining biological mass is envisioned as being the residual mass living in an environment essentially free of required food material to such an extent that continued replication processes could not be supported except at the expense of other members of the population. The oxygen utilized during this period is believed to be that which is required to maintain life in a slowly but steadily declining population, i.e., an endogenous system. The rate of oxygen exertion should be dependent upon the amount of bio-mass present and dependent upon the ability of the bio-mass to use cellular components stored or released upon lysis.

For engineering computational purposes, the third stage of oxygen exertion appeared to be approximated by Equation (V-15):

$$\frac{dY_E}{dt} = C_E \quad (V-15)$$

4. Effects of Seed and Substrate Concentration

The procedures used throughout this investigation during the comparative study of turbulent and quiescent systems, i.e., dilution of the seed and substrate contained in the polluted system, in order to assay for BOD by the standard bottle determination method is the generally accepted procedure for conducting BOD determinations in natural streams. Dilution of the polluted natural stream such that the total demand can be measured in the BOD bottle is practiced because it is felt that the natural biota found in the stream serve as a better seeding material than domestic sewage seed. Thus, BOD determinations are viewed with assurance that the same species are present in the BOD bottle as in the stream; nevertheless, the population is lower in the BOD bottle because of dilution.

In every turbulent system studied in this investigation, except the study using sewage as the substrate, a significant lag period in O_2 uptake was observed in the concurrently conducted BOD bottle determinations. A 1:5 dilution of the seed and substrate contained in the turbulent system was always used in the BOD bottle system. When an experiment was set up using the same amount of seed (volume basis) in the BOD bottle as was used in the stream, no significant lag period was noted. The oxygen uptake occurring in this system was slightly greater at all times than the uptake of any of the similarly seeded turbulent systems (see Figure 35).

Although the results of this experiment were quite different in terms of initial lag occurring in the O_2 uptake curve, the ultimate BOD values for all the bottle systems were essentially equal. Dilution of seed appeared to separate the three stages of oxygen uptake in the quiescent bottle systems, while no separation of the three stages was discernible when the seeding in the bottle was equal to that in the turbulent system. This may have been due to a large initial protozoan population in the BOD bottle system which received the higher amount of seed, in accordance with the cited results of Bhatla and Gaudy (58). However, the use of the higher seed concentration did not prevent separation of the phases in the turbulent systems. It may be possible that turbulence (or velocity) may affect the rate of growth of bacteria more than it affects the rate of growth of protozoa, i.e., in the turbulent system the bacteria grew up rapidly enough so that the peak in bacterial population was separated far enough on the time scale from the peak in protozoan population to result in a discernible separation of phases or the so-called plateau. Bhatla and Gaudy have concluded from their work that the plateau, a visible separation of first and second stage O_2 uptake, will be observed only if the protozoan growth curve lags considerably the bacteria growth curve. Slightly increased values of O_2 uptake were observed at the more dilute substrate concentration. This similar effect has been previously reported by the Analyt-

ical Reference Service, in an article entitled "Reliability and Precision of BOD and COD Determination," (67)

5. Summary on Deoxygenation Responses

Based upon the observations made in this investigation, there appear to be large differences between BOD measured in a turbulent system and BOD measured in a quiescent system. These differences appear to be a result of the initial partitioning of substrate into cell synthesis and the associated respiration which occurs during the rapid removal of the substrate from the system. Turbulent systems were observed to have a higher synthesis to respiration ratio during removal of substrate than quiescent systems. This difference may be due to the fact that higher initial cell concentrations were used to seed the turbulent systems or it may be due to increased turbulence. Additional work on this problem will have to be conducted in order to differentiate these two possible causes. The oxygen uptake occurring during this rapid removal of substrate constituted the first stage of oxygen exertion in the system. This first stage of oxygen exertion appeared to obey first order kinetics if an initial lag period was taken into account.

A second stage of oxygen exertion was observed to occur after the initial substrate had been essentially removed from the system. This stage of oxygen exertion was shown to occur concurrently with a rapid dropoff in

biological solids. Distinct clarification of the turbulent systems occurred concurrently with the second stage exertion. This second stage of exertion is believed to be brought about by the metabolism of the bacterial mass by protozoa. If sufficient numbers of protozoa are present at the end of first stage exertion, the second stage exertion may be approximated for computational purposes by a zero order rate reaction. Actually, this exertion appears to be somewhat autocatalytic and a short lag period occurs before the zero order rate reaction predominates.

A third stage of oxygen exertion was observed which appeared to be typical endogenous respiration. For the period of time monitored in these experiments, this third stage exertion could be approximated for computational purposes by a zero order rate reaction; however, this stage of exertion undoubtedly must decrease in rate as stored cellular components become less available for oxidation by the residual bio-mass.

The concentration of seeding material and substrate concentration appeared to have some effect on the overall oxygen uptake curves. The concentration of seeding material appeared to be very important in establishing the length of initial lag and possibly in establishing the initial synthesis to respiration ratio during first stage O_2 exertions. As dilution of substrate concentration in the BOD bottle increased, the BOD expressed at any time also appeared to be slightly increased. The

kinetic models (equations for representing the three stages of oxygen exertion) proposed as a result of the investigation were shown to approximate quite closely the total response curve observed in a turbulent system. These equations and computational procedures appear to be quite useful for making engineering calculations; however, extensive experimentation will have to be conducted in order to establish a more complete definition of the overall biological deoxygenation process.

The observations made in this study indicate that the biological deoxygenation processes in receiving streams consist of a series of complex interdependent reactions, and that future investigations of these complex biological phenomena as they occur in and affect the prediction of the kinetic course of changes in receiving streams are warranted. It is evident from these investigations that the phasic phenomena in BOD exertion reported by Bhatla and Gaudy (58) for dilute systems (BOD bottle) and in high energy systems as well do occur to a discernible degree in receiving streams (in any event, in a simulated one). Furthermore, they do affect the predictive value and utility of sag curve analysis. It is seen that adequate prediction of minimum DO and the time or downstream distance in which it is attained could not be made without considering the phasic nature of O_2 uptake.

The common use of one first order reaction to describe the total biological deoxygenation response

will not enable engineers to make good estimates of the assimilative capacity of natural streams.

CHAPTER VII

SUMMARY AND CONCLUSIONS

A unique experimental apparatus was used to determine the effects of average stream velocity and channel depth upon the reaeration rate constant, k_2 , in a simulated turbulent stream. The determination of in situ dissolved oxygen saturation values was found to be the paramount prerequisite for consistent prediction of the true reaeration rate constant. A model defining the effect of temperature upon the reaeration rate constant was presented which agrees with the currently accepted empirical model defining this temperature variation, and a dimensionally homogeneous equation was proposed for definition of the reaeration rate constant as it occurs in a turbulent stream.

The biological deoxygenation responses occurring in a polluted turbulent stream system were monitored, and definite trends were manifested in these controlled systems. Bottle BOD determinations conducted concurrently with the stream study on the same polluted systems showed somewhat the same general trends. Although complete proof of the postulations advanced concerning the differ-

ences between the turbulent and quiescent systems cannot be made from this investigation, the observed differences indicate that the present concepts used for determination of stream assimilative capacities may be in gross error.

Based upon the results reported in this dissertation, the following conclusions may be drawn:

1. The reaeration rate constant, k_2 , was directly proportional to average stream velocity. It was also found to be inversely proportional to the average stream depth raised to the 3/2 power. The proposed model for the reaeration rate constant is defined by the following equation:

$$k_2 = C \left[\frac{D_m^{1/2}}{\nu^{1/6} g^{1/6}} \right] \frac{V}{H^{3/2}}$$

The best value of the constant C for a rectangular-shaped stream cross-section is 0.06339.

2. The accepted value of the temperature coefficient for the reaeration rate constant, i.e., θ equal to 1.0241, is satisfied by the following expression relating the fluid properties:

$$\left[\frac{D_m^{1/2}}{\nu^{1/6}} \right]_{T^{\circ}C} / \left[\frac{D_m^{1/2}}{\nu^{1/6}} \right]_{20^{\circ}C} = (1.0241)^{T-20}$$

where D_m is the molecular diffusivity of oxygen in water, and ν is the kinematic viscosity of water.

3. The DO saturation value, C_s , in the tap waters used in this investigation were found always to be less

than the reported standard values for distilled water even after corrections for temperature and barometric pressure effects had been taken into account.

4. Attention to measurement of the true in situ DO saturation values was found to be the paramount prerequisite for obtaining a constant value of the reaeration rate during specific reaeration experiments.

5. The general procedure given in Chapter III of this dissertation, which was used to determine in situ DO saturation values for each experiment, will yield an accurate value of dissolved oxygen saturation for a reaeration system which obeys first order reaction kinetics.

6. The BOD exerted in a polluted turbulent stream system and in a quiescent BOD bottle system appears to occur in three rather distinct phases:

(a) The first phase was shown to be associated with concurrent increase in biological solids and simultaneous removal of original substrate. This observation agrees with the previous findings of Bhatla and Gaudy (58).

(b) The second phase of O_2 uptake was always accompanied by distinct visible clarification and concurrent rapid decrease in biological solids. These observations are consistent with the theory concerning the role of protozoa in BOD exertion advanced by Bhatla and Gaudy (58).

(c) The third phase appears to be a typical endogenous respiration.

7. The phasic nature of BOD exertions observed in turbulent and quiescent systems in this investigation must be taken into account in making predictions of oxygen depletions occurring in streams where atmospheric reaeration and biological deoxygenation are occurring simultaneously. This observation should be taken as an indication that the present concept of using the classical "sag equation" for determining assimilative capacities of natural streams may be in gross error.

8. The phasic nature of BOD exertion observed in this investigation could be approximated for engineering computational purposes by the following models given for each phase of O_2 uptake:

(a) The first phase of oxygen exertion can be approximated by a first order kinetic reaction:

$$\frac{dL_P}{dt} = k_1' L_P$$

(b) The second phase of oxygen uptake can be approximated by a zero order kinetic reaction:

$$\frac{dY_S}{dt} = C_S$$

(c) The third phase of oxygen uptake can be approximated by a zero order kinetic reaction:

$$\frac{dY_E}{dt} = C_E$$

9. The role of turbulence and initial biological solids concentration in a polluted system was not fully delineated; however, these two variables appear to be associated to some degree with an initial partitioning effect of the original substrate into new cell synthesis and the associated respiration occurring during this anaerobic process which occurs during the first stage of oxygen uptake.

10. The use of bottle BOD values, initially inoculated with a seed concentration equivalent to that used in all turbulent systems, could be used to predict the time of critical DO occurrence in the stream reasonably well, if the bottle BOD system was interpreted as three distinct phases of O_2 uptake.

CHAPTER VIII

SUGGESTIONS FOR FUTURE WORK

Based upon the results of this investigation, the following suggestions are made for possible future research investigation in the area of stream pollution control:

1. A study on the effect that various naturally-occurring solutes have on the solubility of oxygen in water should be undertaken under controlled conditions in order to establish a more accurate set of standards for oxygen saturation values to be used in natural streams. The use of in situ measured values for the specific stream may prove to be the best possible standard; however, more basic data are needed to explain the causes of variations in dissolved oxygen solubility.

2. A study on the effect that various degrees of channel roughness have on the reaeration rate constant should be made to establish whether degree of turbulence can be completely defined in terms of average velocity of flow and average stream depth.

3. A study on the effect that changes in channel geometry have on the reaeration rate constant is needed in order to establish whether mean depth of flow is the

proper depth measurement required to define this physical process for all channel shapes as it was found to be for a rectangular stream cross-section.

4. A controlled study of the effects that surface waves have on the reaeration rate constant should provide valuable information. Such wave action obviously changes the surface area available for gas transfer, and it is important to determine the extent of the effect on k_2 for streams of various depths and geometric configuration.

5. Extensive field studies conducted on natural streams where atmospheric reaeration and biological deoxygenation are the predominant mechanisms causing oxygen exchange in the environment would be an ideal extension of the laboratory studies.

6. Studies using an apparatus similar to the one used in this investigation which include effects of algal activity during light and dark periods should be initiated.

7. Studies should be initiated on apparatus similar to the one used in this investigation, which would include the effect of benthic muds. These could be packed along the bottom of the channel and studied concurrently with atmospheric reaeration.

8. Laboratory studies in which algal activity, benthic demands, biological deoxygenation, and atmospheric reaeration are studied concurrently would complete the study of all major factors affecting the oxygen resource in a receiving stream.

9. Studies on the effects and feasibility of using point probes or surface disturbing devices to increase the reaeration rate in natural streams would provide valuable information.

10. Basic studies are needed on the effect of turbulence on the biological deoxygenation process.

11. Basic studies are needed on the effect of initial biological solids concentration on the biological deoxygenation process. These should be conducted in turbulent and quiescent systems.

12. Basic studies on the effect that turbulence and mixing have on the growth rate of protozoa are needed.

13. Basic studies are needed to determine the interrelations involved in growing bacteria and protozoa in the same growth medium. The relative growth rate of each type of biota at various concentration levels of each organism would possibly aid in making better predictions concerning the first and second stage of oxygen demand as observed in this investigation and others.

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APPENDIX

LIST OF SYMBOLS

a	- arbitrary constant
b	- arbitrary constant
c	- arbitrary constant
C	- arbitrary constant
C'	- arbitrary Constant
C _E	- zero order rate constant of third state O ₂ uptake
C _S	- dissolved oxygen saturation value
C' _S	- assumed value for dissolved oxygen saturation
C _S	- zero order rate constant of second state O ₂ uptake
C _t	- dissolved oxygen concentration at any time, t
C _T	- fixed constant at T ^o C
C _{20^o}	- Fixed constant at 20 ^o
d	- arbitrary constant
D	- dissolved oxygen deficit
D _L	- longitudinal mixing coefficient
D _m	- molecular diffusivity of oxygen in water
D _t	- dissolved oxygen deficit at time, t
D' _t	- dissolved oxygen deficit based upon assumed value of dissolved oxygen saturation, C' _S at time, t

- D_0 - dissolved oxygen deficit at zero time
 D'_0 - dissolved oxygen deficit based upon assumed value of dissolved oxygen saturation C'_s at zero time
 D_1, D_2, D_3 - dissolved oxygen deficit at time t_1, t_2, t_3
 D'_1, D'_2, D'_3 - dissolved oxygen deficit based upon assumed value of dissolved oxygen saturation C'_s at time t, t_2, t_3
 e - natural base logarithm
 g - gravitational constant, 32.2 ft/sec²
 H - average depth of flow
 k_1 - first order rate constant for carbonaceous BOD (\log_{10})
 k'_1 - first order rate constant for first stage of BOD (\log_{10})
 k_2 - reaeration rate constant (\log_{10})
 k'_2 - reaeration rate constant based upon C'_2 (\log_{10})
 k_{2-1} - reaeration rate constant at T °C (\log_{10})
 k_{2-20} - reaeration rate constant at 20°C (\log_{10})
 k_1 - first order rate constant for carbonaceous BOD (\log_e)
 k_2 - reaeration rate constant (\log_e)
 L_p - first stage of BOD remaining at any time, t
 L_{p-0} - ultimate first stage O_2 demand
 L_0 - ultimate carbonaceous BOD
 m - arbitrary constant
 n - arbitrary constant
 N_F - Froude Number, V^2/gH
 N_R - Reynolds Number, VH/ν
 N_S - Schmidt Number, ν/D_m

p	- arbitrary constant
t	- time
t_1	- time at an early occurring point on reaeration curve
t_2	- time at a late occurring point on reaeration curve
t_3	- mean time of interval bounded by t_1 and t_2 $(t_1+t_2)/2$
T	- temperature, °C
V	- average stream velocity
X	- general independent variable
y	- general dependent variable
Y_E	- third stage of O_2 uptake
Y_S	- second stage of O_2 uptake
α	- error made in estimating dissolved oxygen deficit, C_s'
ν	- kinematic viscosity of water
θ	- temperature coefficient of reaeration rate, k_2

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