AN EXAMINATION OF THE HYDRODYNAMICS GOVERNING A LIQUID-PHASE RATE CONTROLLED GAS/LIQUID MASS TRANSPORT PROCESS AT CLEAN AND FILM-COVERED LIQUID SURFACES

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A dissertation submitted to the faculty of the Oregon Graduate Center in partial fulfillment of the requirements for the degree Doctor of Philosophy in Environmental Science and Engineering The dissertation "An Examination of the Hydrodynamics Governing a Liquid-Phase Rate-Controlled Gas/Liquid Mass Transport Process at Clean and Film-Covered Liquid Surfaces" by William E. Asher has been examined and approved by the following examination committee:

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# <u>Nomenclature</u>

a <sub>n</sub>	Regression constants used in Eq. 67 (cm <sup>'n</sup> )
A	Constant used in Eq. 13 (dimensionless)
Ae	Equal to the ratio $k'_0/k'_e$ (dimensionless)
An	pH vs. fluorescence intensity calibration coefficients (pH
	units ADC-counts <sup>n</sup> )
As	Equal to the ratio $k'_0/k'_s$ (dimensionless)
А	Wave amplitude (cm)
Ъ	Straight line regression y-intercept (application dependent)
b	Defined by Eq. 53 to be 2.303ec (cm <sup>-1</sup> )
с	Concentration of Orange-G in aqueous solution (mol $cm^{-3}$ )
С	Constant used in Eq. 20 to define $u^\prime$ and $v^\prime$ (dimensionless)
$C_{n}(z)$	$[CO_2]$ profile in the aqueous microlayer (mol cm <sup>-4</sup> )
C <sub>A</sub>	Mineral acidity of aqueous solution (mol $cm^{\cdot 3}$ )
С <sub>В</sub>	Mineral basicity of aqueous solution (mol $cm^{-3}$ )
С <sub>ь</sub>	Concentration of gas in the bulk liquid phase (mol $cm^{-3}$ )
C <sub>b</sub> (t)	Time varying concentration of gas in bulk liquid phase (mol $\rm cm^{-3}$ )
CD	Analytic concentration of DCFS in solution (mol cm $^3$ )
C <sub>H</sub>	Analytic concentration of HOPSA in solution (mol $cm^{-3}$ )
C <sub>s</sub>	Saturation $[CO_2]$ (mol cm <sup>-3</sup> )
C <sup>1</sup>	Total concentration of aqueous phase $CO_2$ species (mol cm <sup>-3</sup> )
d	Grid bar diameter (cm)
D	Molecular diffusion coefficient $(cm^2 s^{\cdot 1})$
ê	Molar absorptivity of Orange-G in aqueous solution $(cm^2 mol^{-1})$
erfc(x)	Complimentary error function of x (dimensionless)
exp[x]	Exponential function of x (dimensionless)
$f_h(h)$	Theoretical eddy approach distance density function $(cm^{-1})$
$f_{T}(T)$	Fluorescence fluctuation peak width density function $(s^{-1})$
$f_z(z_e)$	Empirical eddy approach distance density function (cm <sup>-1</sup> )
f <sub>T</sub> (T)	Eddy residence time density function (s <sup>1</sup> )

 $f_{z,T}(z_e,T)$  Joint density function for  $z_e$  and T (cm<sup>-1</sup> s<sup>-1</sup>) Flux of material across gas/liquid interface (mol  $cm^{2} s^{1}$ ) F Surface age distribution function (dimensionless)  $F_{r}(t)$ F(z)Fluorescence observed from depth z (ADC-counts  $cm^{-1}$ ) Fluorescence observed from depth z = 0 (ADC-counts)  $F_0$  $F_{T}$ Observed fluorescence intensity (ADC-counts) Maximum observed fluorescence intensity (ADC-counts) *F*T.0 FT Normalized fluorescence intensity (dimensionless) Theoretical eddy approach distance (cm) h Н Height of water in experimental apparatus (cm) i Data point index (dimensionless) i, Peak slope threshold count parameter (dimensionless) i, Peak slope regression width (dimensionless) Ionic strength (mol  $cm^{-3}$ ) Ι Depth-dependent incident excitation intensity (watts  $cm^{-1}$ ) I(z)Incident laser intensity at z = 0 (watts) In Aqueous phase mass transfer coefficient (cm  $s^{-1}$ ) k,  $H_2CO_3$  acidity constant (mol cm<sup>-3</sup>) k,  $HCO_3$  acidity constant (mol cm<sup>-3</sup>) k, DCFS acidity constant (mol  $cm^{3}$ ) k<sub>d1</sub> DCFS mono-anion acidity constant (mol  $\rm cm^{-3}$ ) k<sub>d2</sub> HOPSA acidity constant (mol cm<sup>-3</sup>) k<sub>h1</sub> k(pH(z)) Fluorescence intensity coupling constant for pH(z) (ADCcounts watts<sup>1</sup>) k'(pH(z)) Power normalized fluorescence coupling constant (defined as I<sub>0</sub>k(ph(z))) (ADC-Counts) k' Power normalized fluorescence intensity coupling constant for  $pH = pH_{b}$  (ADC-counts) k' Power normalized fluorescence intensity coupling constant for  $pH = pH_{c}$  (ADC-counts) Power normalized fluorescence intensity coupling constant for k'  $pH = pH_0$  (ADC-counts)

k <sub>12</sub>	Net hydration rate of $CO_2$ (s <sup>-1</sup> )
k <sub>21</sub>	Net dehydration rate of $HCO_3^{-1}$ (cm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
K <sub>1</sub>	Empirical constant from the Fortescue and Pearson (1967)
	model (dimensionless)
K2	Empirical constant from the Lamont and Scott (1970) model
	(dimensionless)
L	Integral length scale of turbulence (cm)
m	Linear regression slope (application dependent)
М	Grid mesh width (cm)
N	Normalization constant for $\phi_t(t)$ (s)
P <sub>n</sub>	Polynomial regression coefficients for $f_T(T)$ (s <sup>'n</sup> )
Pn	Laser power intensity (watts)
pH(z)	Aqueous phase pH gradient (pH units cm <sup>-1</sup> )
рН <sub>ь</sub>	pH of bulk solution (pH units)
рН <sub>s</sub>	pH of solution saturated with CO <sub>2</sub> (pH units)
рН <sub>0</sub>	Initial pH of bulk solution (pH units)
Q	Turbulence intensity (cm s <sup>-1</sup> )
Qn	Mass flux into an eddy (Harriott, 1962) (mol cm <sup>-2</sup> )
Ret	Turbulence Reynolds number (dimensionless)
5	Surface renewal rate (Danckwerts, 1951) (s <sup>-1</sup> )
s'	Grid stroke length (cm)
S <sub>c</sub>	Schmidt number (dimensionless)
S <sub>m</sub>	Threshold slope for peak detection in PWIDTH.FOR (s <sup>`1</sup> )
t	Time (s)
t	Surface element age (s)
t <sub>m</sub>	Maximum empirical surface lifetime defined by $T_m$ (s)
t <sub>i</sub>	Experímental time at data point í (s)
t <sub>s</sub>	Sampling time constant (s)
Τ	Temperature (°C)
Т	Fluorescence fluctuation peak width (s)
T <sub>A</sub>	Average T observed from individual experiment (s)
T <sub>m</sub>	Maximum observed T (s)
Т <sub>м</sub>	Mode of the distribution $f_{T}(T)$ (s)
T <sub>min</sub>	Minimum observed T (s) xí

u', v'	Turbulence velocity components in interfacial plane (cm s <sup>-1</sup> )
U <sup>*</sup>	Air side friction velocity (cm s <sup>-1</sup> )
υ <b>ູ້</b>	Water side friction velocity (cm $s^{-1}$ )
wʻ	Turbulence velocity component normal to interface (cm s <sup>1</sup> )
z	Distance normal to the $CO_2/H_2O$ interface (cm)
<sup>z</sup> c	Fluorescence cutoff depth (cm)
<sup>z</sup> e	Empirical eddy approach distance (cm)
$\hat{z}_{e}$	Mean empirical eddy approach distance (cm)
2 max	Maximum observed $z_e$ (cm)
z <sub>min</sub>	Minimum observed $z_e$ (cm)
Z	Grid depth (cm)
°1	Distribution coefficient for $HCO_3^{\cdot}$ (dimensionless)
az	Distribution coefficient for $CO_3$ (dimensionless)
β	Proportionality constant for L (dimensionless)
δ	Whitman (1923) stagnant film depth (cm)
٥ <sub>k</sub>	Kitaigorodskii (1984) diffusive layer psuedothickness (cm)
3	Turbulence dissipation rate $(cm^2 s^{-3})$
ъd	Dissipation rate due to wind-induced drift current $(cm^2 s^{\cdot 3})$
ε <sub>s</sub>	Dissipation rate due to mechanical generation $(cm^2 s^{\cdot 3})$
ε <sup>w</sup>	Dissipation rate due to wave motion $(cm^2 s^{\cdot 3})$
Θ	Radian wave frequency (rad s <sup>-1</sup> )
k	Radian wave number (cm <sup>-1</sup> )
λ	Turbulence dissipation length scale (cm)
v	Kinematic viscosity $(cm^2 s^{-1})$
٥	Density of air (g cm <sup>-3</sup> )
۶ <sub>w</sub>	Density of water (g cm <sup>-3</sup> )
σ <sup>2</sup>	Variance of regression (dimensionless)
$\sigma_m^2$	Variance of linear regression slope (s <sup>-2</sup> )
σ	Standard deviation of data point slopes (s <sup>`1</sup> )
т	Eddy residence time (s)
л т m	Turbulence macro timescale (s)
Ťυ	Turbulence dissipation timescale (s)
$\phi_t(t)$	Surface element age density function (s <sup>-1</sup> )
ω	Grid oscillation frequency (Hz)

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[CO <sub>2</sub> ]	Total concentration of $CO_2$ species = $C_T$ (mol cm <sup>-3</sup> )
[CO2]a9	Concentration of unhydrated $CO_2$ in aqueous phase (mol cm <sup>-3</sup> )
[H <sub>2</sub> CO <sub>3</sub> ]	Concentration of $H_2CO_3$ present in aqueous phase (mol cm <sup>-3</sup> )
[H <sub>2</sub> CO <sub>3</sub> *]	Equal to the quantity: $[CO_2]_{aq} + [H_2CO_3]$ (mol cm <sup>3</sup> )
[HCO <sub>3</sub> ]	Concentration of $HCO_3^{-}$ present in aqueous phase (mol cm <sup>-3</sup> )
[CO <sub>3</sub> <sup>2</sup> .}	Concentration of carbonate present in aqueous phase (mol $\mbox{cm}^{\cdot3})$
[H <sup>+</sup> ]	Concentration of $H^*$ (mol cm <sup>-3</sup> )
[OH ]	Concentration of OH (mol cm <sup>-3</sup> )
[HOPSA]	Concentration of neutral HOPSA present (mol cm <sup>-3</sup> )
[HOPSA]	Concentration of HOPSA mono-anion present (mol cm <sup>-3</sup> )
[DCFS]	Concentration of neutral DCFS present (mol $cm^{-3}$ )
[DCFS]	Concentration of DCFS mono-anion present (mol $cm^{-3}$ )
[DCFS <sup>2-</sup> ]	Concentration of DCFS di-anion present (mol $cm^{-3}$ )
[Na <sup>+</sup> ]	Concentration of Na <sup><math>+</math></sup> present (mol cm <sup>-3</sup> )

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#### Abstract

An Examination of the Hydrodynamics Governing a Liquid-Phase Rate Controlled Gas/Liquid Mass Transport Process at Clean and Film-Covered Liquid Surfaces

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The transport of a gas across a gas/liquid interface is of fundamental importance in environmental and geophysical sciences. In many cases of interest, it is desired to predict the flux of a particular gas into or out of a body of water. Modeling of this process requires knowledge of how changes in fluid mechanical and chemical parameters will affect the gas exchange rate. In many instances, the rate may be determined to a large extent by the intensity of turbulence in the liquid phase in addition to the cleanliness of the liquid surface. Therefore, understanding how variations in turbulence intensity, length scale, and interfacial cleanliness can affect the gas/liquid transport process is central to modeling fluxes.

The liquid phase rate controlled transport of  $CO_2$  across a gas/liquid interface into water was studied using a non-invasive laser-induced fluorescence technique. Turbulence in the liquid layer was generated by a vertically-oscillating grid. This allowed the transport process to be studied as a function of known levels of aqueous phase turbulence. The liquid phase mass transfer coefficient  $k_L$  and surface  $[CO_2]$  fluctuation timescales were measured under conditions of varying turbulence intensity and length scale for cleaned,

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uncleaned and organic monolayer-covered water surfaces. In addition, eddy approach distances were calculated from the surface [CO<sub>2</sub>] fluctuation data.

The cleaned-interface results show that surface renewal is an accurate physical description of the hydrodynamics associated with gas/liquid mass transport at film-free liquid interfaces. The monolayer-covered data show that surface renewal is not an appropriate hydrodynamical description of the transport process at film-covered interfaces. The results also show that surface penetration models are able to describe gas/liquid transport at both clean and film-covered liquid surfaces.

The present cleaned-interface k<sub>L</sub> results were also compared to k<sub>L</sub> values measured in wind tunnels by use of an aerodynamic surface renewal model. This comparison suggests that in the case of a clean liquid surface, the hydrodynamical dependence of wind-driven gas exchange is the same as found for transport governed by mechanically generated turbulence.

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### 1, Background Material

## 1.A. Motivation

Gas/liquid transport is an important and complex geophysical process. The aeration of surface waters, the uptake and release of many trace atmospheric gases, and the interaction of increasing levels of atmospheric carbon dioxide with the oceans are all examples of this phenomenon. The interaction of the atmosphere and ocean means that the air/sea exchange of gases is an important factor in global tropospheric chemistry. This chemistry is now thought to play a vital role in determining weather patterns regionally in addition to parameters such as total albedo, irradiance, and possibly precipitation (Charlson et al., 1987). Therefore, the study of gas/liquid transport processes is of fundamental importance in the environmental and geophysical sciences.

In most situations of interest, the relevant parameter is the flux F (mol cm<sup>-2</sup> s<sup>-1</sup>), of a gas into or out of a volume of water. In general, F depends on the concentration of the gas in both the aqueous and gaseous phases as well as the rate of transport across the gas/water interface. Reliable calculation of F requires knowledge of each of these parameters. This implies that for air/sea gas exchange, accurate prediction of globally averaged fluxes requires knowledge of the global variability of air/sea transport rates in addition to both the atmospheric and oceanic concentrations.

Of the parameters necessary in the calculation of F, gaseous and aqueous phase concentrations generally may be found by direct measurement. In contrast, air/sea transport rates are not easily determined experimentally in the open ocean. Therefore, it seems advantageous to predict transport rates from known physical conditions such as wind speed using models based on known hydrodynamic and/or aerodynamic relationships. Unfortunately this is not easily done since parameterization of the transport rate over the range of physical and chemical conditions found in the ocean in terms of these variables is quite complicated and not well understood. The problem is not the lack of a model for the air/sea exchange process, but rather which of the available models applies under a given set of conditions.

Prediction of transport rates requires knowledge of which physical and/or chemical parameters govern the gas exchange process. The rate at which a gas is absorbed by or desorbed from a liquid may be controlled in either or both of the two phases. In addition, it may show some interfacial or chemical control. When gas/liquid exchange processes are rate controlled in one of the two bulk phases and also are free of other effects such as bubbles, they are mainly dependent on the intensity of the turbulence present in the controlling phase. Thus, the understanding of the effect of turbulence on gas/liquid transport is of central importance if the detailed modeling of complex natural gas exchange processes is desired.

The presence of surface films composed of anthropogenic or natural organic material may affect the exchange process by alteration of

the hydrodynamics of the interaction of turbulence eddies with an air/water interface (Davies, 1972; Asher and Pankow, 1987A-C). These films may also directly affect transport by providing a chemical barrier (Springer and Pigford, 1970). Since many, if not all, environmental water systems have organic films at their surface (Liss, 1983), the effect of films on gas/liquid transport is also of great importance in the prediction of oceanic gas exchange rates.

While the effects of wind will generally dominate natural air/water gas exchange, the process may also be affected by waves, density stratifications, and bubbles. Because the relative importance of these phenomena in the generation of and interaction with turbulence is not clearly understood, their consideration in a comprehensive theory of gas/liquid transport has proven to be difficult. This makes the prediction of environmental gas transfer rates from physical data such as wind speed unreliable. It therefore seems potentially fruitful to study a system free from all effects save turbulence and films in the hope of fully understanding the roles of these two important phenomena in gas/liquid transport. Once this is accomplished, the results could be incorporated into a gas/liquid mass transfer model such as that derived by Kitaigorodskii (1984) for natural bodies of water which takes wind and other such effects into account.

While previous studies have examined the effect of turbulence on gas exchange rates (Dickey et al., 1984), no set of experiments has yet explored the effects of interfacial films under known turbulence conditions. Study of the transport process under these controlled

conditions also allows testing of gas/liquid transport models in a manner not previously possible. This is achieved by separation of interacting effects so that gas transport rate may be characterized in terms of known hydrodynamical parameters and interfacial cleanliness. Demonstration of which of the transport models studied are applicable under the range of conditions found in the ocean is of help in predicting air/sea exchange rates. It also allows measurements of transport rates made in different laboratories to be unambiguously compared based on known hydrodynamic and/or aerodynamic conditions.

This thesis provides an examination of the interaction of mechanically-generated liquid phase turbulence that has known length and velocity scales with a gas/liquid transport process that is rate controlled in the liquid phase. In addition, the effects of various liquid surface cleaning procedures and deliberately created organic monolayers on gas exchange rates was explored. Also studied were the effects of clean and organic film-covered interfaces on liquid phase turbulence eddies at the gas/liquid boundary.

A non-invasive laser-induced fluorescence (LIF) technique based on the pH-dependent fluorescence emissions of aqueous fluorescein dyes was used to study the process. The application of LIF to gas transport research allowed the gas exchange process to be sampled with no disruption of the liquid phase turbulence or the gas/liquid interface. Therefore, gas exchange rates and the interaction of liquid phase turbulence with a free gas/liquid interface could be measured as a function solely of the liquid or aqueous-phase turbulence.

### 1.B. Gas/Liquid Transport Theory and Models

## 1.B.1. Overview and the Effects of Turbulence

In a gas/liquid exchange process that shows liquid phase control and is characterized by well mixed and homogeneous bulk phases, F is generally described by the empirical equation (Danckwerts, 1970)

$$\mathbf{F} = \mathbf{k}_{\mathbf{L}} \left( \mathbf{C}_{\mathbf{s}} - \mathbf{C}_{\mathbf{b}} \right) \tag{1}$$

where  $C_s$  (mol cm<sup>-3</sup>) is the liquid phase saturation concentration as determined by Henry's Law,  $C_b$  (mol cm<sup>-3</sup>) is the concentration in the bulk phase of the liquid and  $k_L$  (cm s<sup>-1</sup>) is the liquid phase mass transfer coefficient or transport rate.  $C_s$  depends upon the chemical identity and the partial pressure of the gas involved, and also upon the temperature.  $C_b$  is a function of time inasmuch as it is a measure of how far the bulk system is from equilibrium. The hydrodynamical dependence of the process resides in  $k_L$ . Therefore  $k_L$  is of primary importance in this research.

The explicit hydrodynamical dependence of k<sub>l</sub> depends on the cleanliness of the gas/liquid interface. Turbulent eddies near a film-covered gas/liquid interface are damped differently than eddies close to a film-free surface (Davies, 1972). Since it is the eddies which come closest to the interface which have the greatest influence on gas exchange, this change in damping may have a profound effect on gas/liquid transport. Also, certain kinds of films have been shown to create a chemical barrier to transport (Springer and Pigford, 1970).

Each of these properties of surface films may affect the transport process. Therefore, the film-free and film-covered interfaces must be treated separately since they are hydrodynamically different and may be chemically distinct as well.

Clean versus film-covered interfaces provide the limiting behavior of gas/liquid transport systems. However, many interfaces may be only partially covered by insoluble organic material or may be covered by a a weakly surface active film. For these situations it is not expected that either clean or film-covered surface gas/liquid transport models will apply. Therefore a different model must be used for these situations which takes this intermediate behavior into account.

The three major gas/liquid transport models available include the stagnant film model (Whitman, 1923), surface renewal theory (Higbie, 1935) and surface penetration theory (Toor and Marchello, 1958). Each of these models will be discussed in terms of the interfacial cleanliness and hydrodynamic applicability in the following sections.

## 1.B.2. Film-Free Gas/Liquid Interfaces

Liquid phase turbulence velocity fluctuations parallel to the interfacial plane do not create large horizontal shear stresses at a film-free gas/liquid interface. The mobility of the liquid at the interface permits these fluctuations to persist up to the actual liquid surface. However, in the direction normal to the interface, the liquid damps velocity fluctuations through surface tension and

gravity. Therefore, the vertical velocity component at the interface must go to zero provided that the turbulence eddies do not grossly distort or penetrate the interfacial plane. Visualization of turbulence at an air/water interface has shown this is an accurate description of eddy motion at a clean surface (Davies, 1972). Therefore, models which describe gas/liquid transport at a clean interface should take this behavior into account.

Surface renewal theory describes the gas/liquid transport process in a manner that is phenomenologically consistent with the observed behavior of the turbulence. As proposed by Higbie (1935) and extended by Danckwerts (1951), surface renewal theory models the transfer process by assuming that patches of the surface are periodically replaced by fluid elements from the well-mixed bulk phase below. Gas is transferred into or out of these elements by molecular diffusion while they are at the interface. Higbie's original theory makes the assumption that all fluid elements have equal residence time at the interface. If this residence time is T (s), then  $k_L$  may be written as (Higbie, 1935)

 $k_{1} = 2(D/\pi \tau)^{1/2}$ (2)

where D  $(cm^2 s^{-1})$  is the diffusion coefficient of the gas in the liquid.

The assumption made by Higble (1935) of a constant T in the original derivation of surface renewal theory was physically unrealistic. Therefore, Danckwerts (1951) assumed that T could be defined as a random variable. This definition of T seemed more realistic in light

of the stochastic nature of the turbulence eddies, whose dynamical characteristics were assumed to govern T. Since T was defined as a stochastic variable, it was assumed that there was a stationary probability density of surface element lifetimes,  $f_{\tau}(\tau)$  (Danckwerts, 1951; Perlmutter, 1961).  $f_{\tau}(\tau)$  was then used to calculate a surface age distribution function  $F_{\tau}(t)$  which had the form

$$F_{t}(t) = \int_{0}^{t} f_{\tau}(\tau) d\tau$$
(3)

where it is assumed that  $f_{T}(\tau)$  is normalized. This normalization leads to  $F_{t}(0) = 0$  and  $F_{t}(\infty) = 1$ . F(t) was then used to calculate the surface lifetime probability density function  $\phi_{t}(t)$ 

$$\phi_{t}(t) = N^{-1} (1 - F_{t}(t))$$
(4)

where  $\tau$  was age of the surface element and N was the normalization constant for  $\phi_{\tau}(\tau)$  defined by

$$N = \int_{0}^{\infty} (1 - F_{t}(t)) dt$$
(5)

where, in general, N will not be unity. It also should be emphasized that the distribution  $\phi_t(t)$  is different from  $f_T(\tau)$ . The latter is a measure of how often eddies with a specified lifetime  $\tau$  reside at the interface. In contrast, the physical interpretation of  $\phi_t(t)$  is that it is the probability that any one patch of surface will remain unrenewed by bulk phase fluid for a time t. It follows from this definition that  $\phi_t(0) = 1$  and  $\phi_t(\infty) = 0$ . The calculation of  $k_{L}$  is done by integration of the mass flux into a patch of surface with lifetime t over  $\phi_{t}(t)$  (Danckwerts, 1951). This takes the explicit form

. . . . . . . . .

$$k_{L} = (D/\pi)^{1/2} \int_{0}^{\infty} t^{-1/2} \phi_{t}(t) dt$$
(6)

Danckwerts (1951) original derivation assumed that  $f_{\intercal}(\tau)$  could be defined as

$$f_{T}(I) = s\{\exp[-Is]\}$$
 (7)

where s (s<sup>-1</sup>) is defined to be the fraction of interface replaced in unit time. For  $f_T(T)$  defined as in Eq. 7,  $k_L$  is given by

$$k_{L} = (Ds)^{1/2}$$
 (8)

The assumption of a decaying exponential form for  $f_T(T)$  is not very realistic as it assumes that the most probable eddy found at the interface is one with T = 0. Mathematically, defining  $f_T(T)$  with a simple function as in Eq. 7 is attractive since it allows analytic integration of Eq. 6. However, experimentally determined  $f_T(T)$  may not necessarily be of the form given in Eq. 7 and analysis of  $k_L$  could be more complex.

In Eqs. 2, 6, and 8, the dependence of  $k_{\rm L}$  on the turbulence is present implicitly in T, t, and s respectively. Models based on surface renewal theory which deal with the explicit character of this dependence have been developed by Fortescue and Pearson (1967) with the large-eddy model and Lamont and Scott (1970) with the dissipation model. Fortescue and Pearson (1967) argued that for turbulence composed of large regular eddies,

$$k_{1} = K_{1} (DQ/L)^{1/2}$$
(9)

where  $K_1$  is an empirical constant determined by Fortescue and Pearson (1967) to be 1.46, L (cm) is the integral turbulence length scale (Tennekes and Lumley, 1972), and Q (cm s<sup>-1</sup>) is defined as the square root of twice the average turbulent kinetic energy, i. e.,

$$O = (u'^{2} + v'^{2} + w'^{2})^{1/2}$$
(10)

where u', v', and w' (cm  $s^{-1}$ ) are the mean turbulent velocity fluctuations in the x, y, and z directions, respectively.

Lamont and Scott (1970) used a model based on the small scale motions present in an eddy cell. With this model and the Kovasznay turbulent energy spectrum (Hinze, 1975), they arrived at the following expression for  $k_i$ 

$$k_{1} = K_{2} (\varepsilon v)^{1/4} S_{2}^{-1/2}$$
(11)

where  $K_2$  is an empirical constant which was found to be 0.4 (Lamont and Scott, 1970), v (cm<sup>2</sup> s<sup>-1</sup>) is the kinematic viscosity,  $S_c$  is the dimensionless Schmidt number of the fluid defined by

$$S_{c} = v/D \tag{12}$$

and  $\varepsilon$  is the turbulent energy dissipation rate which is defined in terms of the power dissipated per unit mass of fluid (cm<sup>2</sup> s<sup>-3</sup>). Dimensional analysis shows that  $\varepsilon$  may be estimated in terms of Q and L as (Tennekes and Lumley, 1972)

$$\varepsilon = AQ^3 / L \tag{13}$$

where A is a constant which Mellor (1973) found to be equal to 1/15.5.

Since Lamont and Scott (1970) used the Kovaszney turbulent energy spectrum, caution must be exercised in applying Eq. 11 to low turbulence intensities (Monín and Yaglom, 1975).

Both the Fortescue and Pearson (1967) model and the Lamont and Scott (1970) model provide a method of relating gas transport coefficients to turbulence parameters which may be measured in the laboratory. In this respect they provide a means to test surface renewal gas/liquid transport models. However, surface renewal models are not necessarily valid for film-covered gas/liquid interfaces.

## 1.B.3. Film-Covered Interfaces

Organic films on gas/liquid interfaces resist deformation and spreading. Therefore, their presence causes greater tangential stresses than found at a clean interface. This increase in stress leads to an increase in the damping of the turbulence motions at the surface. In fact, interfaces completely covered by hard or condensed monolayers will not allow velocity fluctuations in the interfacial plane (Gaines, 1966). This behavior precludes surface renewal since the entire volume of fluid in the interfacial layer cannot be replaced by liquid from the bulk phase. Therefore, gas transport at a filmcovered interface must be described by an alternative model.

The behavior of turbulence at an organic film-covered interface is hydrodynamically analogous to that at a solid/liquid interface. It may be expected then, that transport at a film-covered gas/liquid interface is described by hydrodynamical relations similar to those for solid/liquid interfacial transport (Davies, 1972). At these types of interfaces, the transport process is postulated to be controlled by a diffusive sublayer in the laminar layer of the solid/liquid boundary. The transport rate is determined by the rate at which material diffuses through the laminar sublayer into the well-mixed bulk phase. This is analogous to the stagnant film model of Whitman (1923) which was applied to air/sea gas exchange by Liss and Slater (1974). The stagnant film wodel defines  $k_L$  in terms of D and the diffusive sublayer depth  $\delta$  (cm). This relation was given by Whitman (1923) for a solid/liquid interface as

$$k_{l} = D/\delta \tag{14}$$

Explicit hydrodynamical relations for  $\delta$  are discussed by Davies (1972). Empirical correlations based on the film model have shown that (Davies, 1972)

$$k_{1} = 0.13(\varepsilon v)^{1/4} S_{c}^{-2/3}$$
(15)

While comparison of Eq. 11 to Eq. 15 appears to show that the clean and film-covered interface transport regimes are hydrodynamically equivalent (i.e. same functional dependence on  $\varepsilon$ ), this is not the case. The difference in proportionality constants and dependence on  $S_c$  in Eq. 11 and Eq. 15 leads to a fundamentally different fluid mechanical interpretation of each. Note also that Eq. 15 represents an empirical correlation whereas Eq. 11 is derived.

A stagnant film model derived ab-initio from basic fluid mechanical variables is that of Kitaigorodskii (1984). This model, while originally proposed to describe gas transport at a clean gas/liquid interface in the presence of turbulence generated by breaking wind waves, is seen to be a form of stagnant film model. Kitaigorodskii (1984) defines  $k_{\rm L}$  in terms of a molecular diffusion sublayer pseudothickness  $\delta_{\rm F}$  given by

$$\delta_{L} = 1.58 S_{2}^{-1/2} (v^{3}/\epsilon)^{1/4}$$
(16)

Substitution of Eq. 16 into Eq. 14 yields an expression for  $k_L$  that is identical in functional form to the Lamont and Scott (1970) model. The difference between the Kitaigorodskii (1984) and Lamont and Scott (1970 model is in the constant  $K_2$ .

While being mathematically simple in their formalism, film models suffer from an unrealistic description of the behavior of eddies near a gas/liquid interface. The physical interpretation of  $\delta$  is that it represents the distance of closest approach to the interface of each turbulence eddy. However, it cannot be assumed that each eddy will penetrate to the same depth in the interfacial layer. In addition, film models were originally proposed to describe transport at clean gas/liquid interfaces. This application of film models seems even less realistic due to the shear-free behavior of clean interfaces described in the previous section.

If the surface is partially contaminated or the organic material comprising the film is weakly surface active, it is expected that the hydrodynamical dependence will fall somewhere between the clean gas/liquid and solid/liquid cases (Davies, 1972). Therefore, the clean surface models embodied by Eqs. 9 and 11 or the film model realized in Eqs. 14 and 15 are not expected to fully describe the transport process for an interface with a partial or weak surface film. These models provide the limiting behavior of a gas/liquid transport system. Their mathematical form is relatively simple mainly because  $k_{\rm L}$  in each model depends on only one hydrodynamical variable (r for surface renewal models and  $\delta$  for film models). An accurate description of the dependence of  $k_{\rm L}$  on the turbulence for partially covered interfaces is expected to require a more complex model.

#### 1.B.4. Interfaces Partially Covered by Films

At an interface that is partially covered by an organic film, turbulence eddies may or may not completely renew the gas/liquid interface. Therefore,  $k_1$  will depend on both I and the distance that the eddy approaches the gas/liquid interface h (cm). Models that describe the gas exchange process in this manner are termed surface penetration models and have been developed by Toor and Marchello (1958) and Harriott (1962). These models sacrifice mathematical simplicity for a realistic description of the transport process.

Surface penetration models assume the exchange process proceeds by molecular diffusion into the quiescent bulk phase of the fluid. As in surface renewal theory, the eddies are postulated to arrive periodically in the interfacial layer. However, the difference between surface renewal theory and surface penetration theory is that in the latter the eddy is not assumed to completely renew the interface. Fluid

renewal occurs in the interfacial layer up to the depth defined by *h*. Accumulated solute from the interfacial layer below this depth is swept into the well-mixed bulk phase below. The transport process then continues by molecular diffusion but at an increased rate due to the steeper concentration gradient (Figure 1).

Application of surface penetration theory is complex since there are now two independent fluid mechanical parameters (h and  $\tau$ ) involved. The procedure developed by Harriott (1962) assumes that h and  $\tau$  are each represented by an independent probability density function,  $f_h(h)$  and  $f_{\tau}(\tau)$  respectively. Pairs of  $h_n$  and  $\tau_n$  are then drawn from the distributions. The individual mass flux  $Q_n$  (mol cm<sup>-2</sup>) into each eddy is then calculated by assuming the process proceeds via molecular diffusion between subsequent eddy arrivals at the gas/liquid interface.  $Q_n$  is then calculated for each eddy by

$$Q_{n} = C_{s} (4Dt_{n}/\pi)^{1/2} - \int_{0}^{h_{(n-1)}} C_{(n-1)}(\xi) \operatorname{erfc}(\xi^{2}/4Dt_{n})^{1/2} d\xi$$
(17)

where  $C_{(n-1)}(z)$  is the initial concentration profile left by the (n-1)'th eddy and is given by

$$C_{n}(z) = C_{s} \operatorname{erfc}(z^{2}/4Dt_{n})^{1/2} + (1/(4\pi Dt_{n})^{1/2}) \int_{0}^{h_{(n-1)}} C_{(n-1)}(\xi) x$$

$$\{\exp[-(\xi-z)^2/4Dt_n] - \exp[-(\xi+z)^2/4Dt_n]\}d\xi; z < h_n$$
 (18)

$$C_{n}(z) = 0;$$
  $z > h_{n}$  (19)

where z is the depth or normal distance from the interfacial plane.



Figure 1. Schematic diagram of C(z) for surface penetration theory.

The individual  $k_{L,n}$  for each step are then calculated from

$$k_{L,n} = Q_n / C_s T_n \tag{20}$$

where it is assumed that since the transport is into an infinite resevoir, the solute concentration in the arriving n'th eddy is 0. The individual  $k_{L,n}$  are summed and then averaged over n. The procedure continues until the average converges.

Other procedures for applying surface penetration theory have been given by Bullin and Dukler (1972) and Thomas et al. (1975). These methods are less complicated computationally but suffer from difficulty in incorporating empirical results for  $f_h(h)$  and  $f_T(T)$  or individual measurements of h and T. This will be discussed in detail in Chapter 5.

The major shortcoming of surface penetration models is that there is as yet no a-prior method of determining  $f_h(h)$  or  $f_T(T)$  from the underlying fluid mechanical parameters. This means that the models can only be tested by direct measurement of these two parameters. Until now, surface penetration models have not been verified by comparison of  $k_L$  values calculated using empirical h and T with experimental  $k_L$  data. This is unfortunate since they seem to provide a very realistic description of the transport process. Additionally, it may be shown that for h=0, surface penetration theory is mathematically equivalent to surface renewal theory. Dimensional arguments show that  $k_L$  calculated using surface penetration theory with constant h>>0 has the same functional dependence on D as the stagnant film model.

### 1.C. Available Experimental Techniques

Most laboratory work in this area has been carried out using wind tunnels, stirred cells, and/or moving bands or films. The majority of the recent work has been performed with wind tunnels and stirred cells. In wind tunnel studies, gas is blown over a layer of liquid. Both linear and circular wind tunnels have been used. The measured value of  $k_{\rm L}$  is then related to such parameters as the friction velocity or wind speed. While fairly common, such studies are often complicated by the presence of waves and bubbles. In circular wind tunnels, there are also complicating effects due to the circular motion of the air and water. This motion with its accompanying constant centripetal acceleration creates cyclical roll cells across the liquid layer which may enhance the transfer rate (Jähne et al., 1979). These roll cells will also cause problems in turbulence characterization.

A stirred cell apparatus consists of a tank of water with a headspace in which the transferring gas(es) is (are) introduced. Either invasion or evasion may be studied. The mixing in the liquid phase is generally varied to produce changes in  $k_L$ . This stirring is usually intense enough to ensure that the bulk fluid is well mixed. Commonly used stirrers are rotating impellers (Davies and Lozano, 1979), recirculation pumps (Balls and Liss, 1983) and verticallyoscillating grids (Dickey et al., 1984).

The main drawback to rotary-stirred and pump-mixed experiments is that the turbulence generated is non-homogeneous. This means that the

turbulent length and velocity scales present at the fluid interface are not spatially uniform. This is a serious deficiency if surface renewal models are to be tested. It is also difficult to relate different experiments to each other since the turbulence generated by rotating stirrers and jets is highly dependent on the tank geometry, stirrer dimension, jet orifice size, and jet or stirrer velocity.

In contrast, a vertically-oscillating grid may be used to produce homogeneous turbulence at a gas/liquid interface. Experimental evidence exists to show that the turbulence so generated is nearly isotropic in the interfacial plane and may be related between different experiments and laboratories (Thompson and Turner, 1975; Hopfinger and Toly, 1976; Brumley, 1984; Dickey et al., 1984). Grids also have been shown to generate turbulence whose length and velocity scales may be related to easily measured parameters such as oscillation frequency  $\omega$ (Hz), stroke length s' (cm), and depth (Thompson and Turner, 1975; Hopfinger and Toly, 1976; Brumley, 1984; Dickey et al., 1984).

Hopfinger and Toly (1976) studied the turbulence generated by a grid of bars with square cross section. They found that for a flat grid of square bars with a ratio of bar cross section d (cm) to grid mesh spacing M (cm) of 1 to 5, u', v', w', and L could be related to  $\omega$ , s', M, and the distance from the virtual origin 2 by

$$u' = v' - CM^{1/2} s'^{3/2} w Z^{1}$$
(21)

$$w' = 1.25 u'$$
 (22)

$$L = \beta Z \tag{23}$$

where  ${\cal C}$  and  $\beta$  are known dimensionless functions of M and s' and Z

lies 0.5 cm below the mid-stroke grid position for a grid with M = 5 cm and d = 1 cm. This type of grid seems well suited to gas transfer research since it allows the generation of turbulence with known, reproducible scales.

Eqs. 21, 22, and 23 should not be seen as exact descriptions of the turbulence scales present in all grid-stirred tanks. The work of McDougall (1979) suggests that there are deviations from isotropy and secondary motions which may be present in some experiments. However, the scale relations of Hopfinger and Toly (1976) do provide useful approximations of the true scales u', v', w', and L present.

Knowledge of Q and L allows calculation of  $\varepsilon$  by use of Eq. 13. This allows calculation of the turbulence macro-timescale,  $\tau_m$ , and the micro-timescale  $\tau_u$  which are defined by

$$T_{m} = L/Q \tag{24}$$

$$T_{\mu} = (v/\varepsilon)^{1/2}$$
<sup>(25)</sup>

 $T_m$  may be thought of as the timescale of the large scale turbulence velocity fluctuations and  $T_u$  is the timescale at which the dissipation scale velocity fluctuations occur (Tennekes and Lumley, 1972). Substitution of Eq. 13 in Eq. 25 shows that

$$T_{u} \propto T_{m} \operatorname{Re}_{t}^{1/2}$$
(26)

where Re, is the turbulence Reynolds number defined by

$$\operatorname{Re}_{t} = \operatorname{QL}/v \tag{27}$$

This shows that for realistic turbulence intensities,  $\tau_u$  will be less than  $\tau_m$ . This is an important result since it shows that the fastest timescales present in the turbulence are defined by  $\tau_u$ . The major drawback to this turbulence generation system is that the water surface in a grid-stirred tank is prone to form adventitious surface films. These films are composed of organic matter which was 1) originally dissolved in the bulk liquid phase 2) on or in the tank walls and/or 3) deposited from the gas phase in the form of organic aerosols or vapors. Therefore, extreme care must be taken in the preparation of the tank water so that these effects will be minimized. Precautions may include scrupulous cleaning of the tank and grid, purification of the bulk aqueous phase, and cleaning of the water surface prior to an experiment.

Scott (1975) suggests that surface active contaminants may be removed from aqueous solutions by purging with He bubbles. The He bubbles will concentrate these compounds at the interface. The interface must then be cleaned by removal of the surface water. This technique, along with scrupulous cleaning of the actual grid and tank should allow the effects of surface films to be minimized. The measurement of gas transfer rates and surface concentration fluctuations after the deliberate creation of a controlled monolayer on the interface can provide a reference for determining when adventitious films are present. These measurements also provide information on the effect of surface films on the transport process.

Sampling should be done in a manner which does not generate or disrupt turbulence in the liquid, or disturb the gas/liquid interface. The development of a non-invasive method for studying the gas/liquid transport process requires that the system react to produce an easily-
measured product. Such a system is provided by carbon dioxide and water. The hydration of  $CO_2$  to the weak acid  $H_2CO_3$  allows pH to be used as a mass transfer indicator. It has simple aqueous phase rate control for pH < 5 (above pH = 5 the transport of bicarbonate ( $HCO_3^{-}$ ) and carbonate ( $CO_3^{2^{-}}$ ) ions becomes increasingly important). The only limitation is that the hydration rate is relatively slow (rate constant = 3.8 x  $10^{-2}$  s<sup>-1</sup>, Gibbons and Edsall, 1963). Since the attainment of the equilibrium pH requires the presence of hydration equilibrium, care must be taken so that the formation of  $H_2CO_3$  is not rate limited.

The non-invasive pH measurement technique developed by Pankow et al. (1984) to avoid the problems associated with pH electrode use relies on the pH-dependent fluorescence emissions of fluorescein dyes. This approach was first used by Ohkuma and Poole (1978) to study the pH of living cells. It utilizes the acid-base chemistry of the fluorescein structure in aqueous solution. Fluorescein may exist predominately as a cation, a neutral quinoid, a mono-anion, or a dianion, depending on the solution pH (Lindqvist, 1960). Since the mono-anion and dianion exhibit the most intense fluorescence and predominate at higher pH values, increasing the pH permits increasing fluorescence emissions.

The preferred light source for fluorescence excitation is the laser. It provides intense, monochromatic light and its coherent beam gives excellent spatial resolution. These features allow the fluorescence measurements to be made by simple optical filtering procedures.

An additional advantage is that the detection limits for fluorescein and its derivatives by LIF are extremely low. Lytle (1982) reported a detection limit of  $10^{-13}$  mol cm<sup>-3</sup> for fluorescein in basic aqueous solution. High sensitivity is important for this application since the concentration of the indicator dye must be low enough that  $CO_2$ species dominate the acid/base chemistry.

#### 1.D. Research Goals

Experiments were designed to allow each of the major models discussed in the previous sections to be tested by comparison of predicted  $k_{\rm L}$  values with experimental measurements of  $k_{\rm L}$ . The first set of experiments measured  $k_{\rm L}$  for  ${\rm CO}_2/{\rm H}_20$  transport as a function of Q and L, or  $\epsilon$ . The effects of organic monolayers and several aqueous surface cleaning procedures on  $k_{\rm L}$  were also examined. These measurements provided the experimental  $k_{\rm L}$  data used to test the predictive abilities of the various models. The bulk  $k_{\rm L}$  data also was used to study the Fortescue and Pearson (1967) and Lamont and Scott (1970) surface renewal models embodied by Eqs. 9 and 11 respectively, and the Davies (1972) empirical film model which is given in Eq. 15.

In addition to measurement of  $CO_2/H_2O$  exchange rates, the LIF technique was used to study  $CO_2$  concentration fluctuations in the interfacial layer caused by  $CO_2/H_2O$  mass transport. The timescales of these fluctuations were used to test surface renewal models. This could be done because the concentration fluctuations are directly

relatable to the timescales of the turbulence eddies. These measurements were also made for clean and organic monolayer covered fluid interfaces and were studied as a function of depth, Q, L, and c. These measurements allowed the first direct observation of individual surface renewal events and subsequent calculation of k<sub>L</sub> from their timescales.

The final set of experiments measured  $f_h(h)$  and  $f_T(T)$  as a function of turbulence parameters and aqueous surface state. It was possible to calculate these distributions from the CO<sub>2</sub> concentration fluctuation data using a procedure detailed in Chapter 5. The calculated  $f_h(h)$  and  $f_T(T)$  were then used to predict  $k_L$  by use of the surface penetration model of Harriott (1962).

The range of physical and interfacial conditions under which each model is applicable was found by testing the model's predictive ability with respect to experimentally determined transport rates based on known levels of aqueous-phase turbulence. These results could make prediction of air/sea and other important gas exchange rates more accurate by showing over what range of conditions the different gas/liquid transport models might be expected to apply in the field. As an initial step in this direction, a model for wind-driven gas/liquid transport developed by Cohen (1983) was used with good success to relate the present k<sub>1</sub> data to wind tunnel and field results.

This research provides a comprehensive examination of the role of turbulence and surface films in gas/líquid transport process. While the process is still not fully understood, these results provide answers to several important questions concerning the behavior of gas/liquid transport rates, the applicability of several common transport models, and the behavior of turbulence near clean and filmcovered gas/liquid interfaces. Answers such as these help in the understanding and accurate modeling of the complex natural exchange process. These data allow the first test of surface renewal and surface penetration gas/liquid mass transport models by direct experimental measurement of the relevant parameters.

Unfortunately, this research is not able to provide any new information concerning the functional dependence of  $k_{\rm L}$  on D. Inspection of the models discussed shows that  $k_{\rm L}$  scales with  $D^{1/2}$  for the surface renewal and Kitaigorodskii (1984) models, with  $D^{2/3}$  for the Davies (1972) empirical stagnant film model, and with D for the Whitman (1923) stagnant film model. Therefore, knowledge of how  $k_{\rm L}$  varies with change in D will provide additional evidence for the applicability of a specified gas/liquid transport model. However, since only  $CO_2$ could be studied by this LIF technique it was not practical to study variations in  $k_{\rm L}$  caused by changes in D.

#### 2. Experimental Methods

### 2.A. Introduction

The experimental work was divided into a study of bulk  $k_{\rm L}$  values as a function of turbulence and surface cleanliness and a study of the behavior of  $[CO_2]$  fluctuations and aqueous turbulence at the  $CO_2/H_2O$ interface. Each of the two sets of experiments were performed using the LIF pH measurement method described above. This technique was used since it provided non-invasive sampling with very fine spatial and temporal resolution. The aqueous phase turbulence was generated by a vertically-oscillating grid. This method was chosen since it was necessary to create known, reproducible levels of aqueous phase turbulence in the tank.

# 2.B. Bulk k Measurement Techniques

The apparatus used is shown schematically in Figure 2. It consisted of a square horizontal cross-section tank of water with a headspace for the transporting gas, a rack made from 0.3 cm thick, 2.5 cm square steel tubing, and a vertically-oscillating grid. The dimensions of the tank and grid, as well as the construction materials were the same as those used by Thompson and Turner (1975). To minimize mechanically-generated ripples on the  $CO_2$ /water interface, the rack was constructed so that the tank lid, grid, and grid drive



Figure 2. Diagram of the experimental apparatus showing tank, grid and grid drive train. LIF optics not shown.

train did not touch the walls of the tank. The grid support shafts were isolated from the gas/water interface by stainless steel sleeves. Careful construction and alignment of the system prevented lateral movement or twisting of the grid during operation.

The range for  $\omega$  was 2 to 6 Hz, and the range for Z was 7.5 to 18 cm. The value of s' was either 1.5 or 2.5 cm. The grid had the same d and M as that used by Hopfinger and Toly (1976) who found that C = 0.2 and that  $\beta$  varied from 0.13 to 0.18 for s' varying from 1.5 cm to 2.5 cm. Therefore, Q and L could be calculated in the tank by applying Eqs. 21, 22, and 23. This showed that the turbulence conditions gave Re, from 40 to 400.

Scale relations for Q and L similar to Eqs. 21, 22, and 23 for turbulence generated by a vertically-oscillating grid were also derived by Thompson and Turner (1975). However, these formulas were not used in this study since they allowed no method to separate Q into the individual velocity components u', v', and w'. This is an important feature of the Hopfinger and Toly (1976) relations as will be discussed later. In addition, the Thompson and Turner scale relations represent the best fit for several different types of oscillating grids (i.e. square and round bars, perforated plates) whereas the Hopfinger and Toly (1975) equations were found for grids composed of square bars.

The excitation light was provided by the 488 nm line of a Coherent Radiation Laboratory (Palo Alto, CA) CR-3 argon ion laser. A schematic diagram of the optical alignment is shown in Figure 3.



Figure 3. Schematic diagram of the bulk  ${\bf k}_{\rm L}$  measurement optical alignment. For clarity the second sampling laser beam has been omitted.

Prior to entering the tank, the incoming laser beam was split into two beams using a plate beamsplitter. The positions of the two beams were adjusted using mirrors so that they entered the tank perpendicularly to the incident face, and propagated through the tank at horizontal depths of 5 and 25 cm. The two beams were sampled concurrently at their mid-tank positions. Dual sampling was carried out to monitor the bulk liquid homogeneity. Each beam's fluorescence emission was monitored perpendicularly to the incident laser light to minimize noise from scattered laser radiation. A bandpass optical filter with a half-bandwidth of 8 nm centered on the fluorescence maximum at 525 nm was used to separate fluorescence radiation from scattered 488 nm laser light. The fluorescence emissions were measured using a Hammamatsu (San Jose, CA) S1223-BR photodiode and a Burr-Brown (Tucson, AZ) OP121A operational amplifier. The response time of the photodiodeamplifier combination was approximately 0.01 s.

A portion of the incoming laser beam was monitored by a separate photodiode/amplifier combination to track fluctuations in intensity in the 488 nm excitation light. This is also shown in Figure 3.

The output voltages from the photodiodes monitoring both the DCFS fluorescence and the laser power were sampled by a computer data acquisition system. This system consisted of a DEC micro-PDP-11 (Digital Equipment Corp., Maynard, MA) minicomputer using an ADAC 1023AD, 1023EX and 1620DMA (ADAC Corp., Natick, MA) direct memory access analog-to-digital (ADC) converter. The ADC was controlled by the set of FORTRAN IV-RT (Digital Equipment Corp., Maynard, MA)

subroutines ADLIB.RT (ADAC Corp., Natick, MA).

The pH range where the maximum fluorescence intensity change occurs can be controlled somewhat by the substitution of chlorines for hydrogens on fluorescein's aromatic rings. Due to the electrophilic character of chlorine, this tends to lower the pH transition range. Since the pH must be kept relatively low to keep CO<sub>2</sub> mass transfer simple, the fluorescein derivative chosen for this particular study was 2',7'-dichlorofluorescein (DCFS). Its maximum change in fluorescence occurs in the pH range 3.5 to 6.0 which corresponded extremely well to the expected pH range for these experiments.

Deionized water, which had its pH set at 5.0 by addition of small amounts of dilute HCl or  $CO_2$ -free NaOH, was first added to the dissolution cell. The value of the ionic strength I (mol cm<sup>-3</sup>) was adjusted to 1 x 10<sup>-5</sup> mol cm<sup>-3</sup> using reagent grade NaCl which had been heated to 500 °C to remove adsorbed organic material. This greatly simplified data analysis since the flux of  $CO_2$  into the water lead to increasing [H<sup>+</sup>] and [HCO<sub>3</sub>] during an experiment. The change in these two ionic species caused I to change over the course of an experiment. The presence of the NaCl at this relatively low concentration provided what was an effectively constant I.

The DCFS concentration in all runs was 6 x  $10^{-10}$  mol cm<sup>-3</sup>. Experiments and calculations showed that this concentration was a good balance between signal detection and chemical interference. The temperature of the water was allowed to equilibrate with the room temperature which was, between 20 and 23 °C. (Once stabilized, it

remained constant during the course of an experiment.) The bulk liquid and headspace were then purged of  $O_2$  and  $CO_2$  by bubbling filtered He (0.4 um HEPA, Gelman Sciences, Ann Arbor, MI) through the water column. This procedure also removed surface active contaminants from the bulk aqueous phase and concentrated them at the water surface (Scott, 1975).

This concentration of surface active contaminants at the aqueous interface necessitated cleaning of the water surface. Therefore, prior to the start of an experiment, a presumably clean surface was created by removal of the contaminated surface water with one of two procedures. The first employed sheets of additive-free lens paper (Fisher Scientific, Springfield, NJ) and the second used 100% rayon cloth (Fisher Scientific, Springfield, NJ) followed by surface "vacuuming" with a glass pasteur pipette connected to a peristaltic pump. After cleaning, an aliquot of the water was tested for surface active compounds by use of the Crits ring test (Crits, 1961). This test is a very general test for surface active material and is sensitive at the part-per-million level. In no case did this test show significant levels of such material.

As a further check on surface contamination, several experiments were performed with either no cleaning, or with a 1-octadecanol (1-OD, 95% grade, Aldrich Chemical Co., Milwaukee, WI) monolayer on the water surface. The monolayer was formed by pipetting 0.07 cm<sup>3</sup> of an 8 x 10<sup>-6</sup> mol cm<sup>-3</sup> solution of 1-OD in n-pentane onto the water surface and evaporating the pentane using dry N<sub>2</sub> gas. This amount of 1-OD was

calculated to be enough material to form a monolayer over the entire interface with respect to the small but finite aqueous solubility of 1-OD. After these experiments were completed, the tank, grid, and grid drive train were thoroughly washed to prevent 1-OD from being present during subsequent experiments.

During calibration only, a pH electrode was inserted into the tank via a port in the cover. pH was measured with an Orion Research (Cambridge, MA) 701A Digital Ionalyzer calibrated with NBS buffers at pH 4, 5, and 6. The fluorescence emissions were calibrated as a function of pH and incident laser power.

The incident power calibration allowed fluorescence measurements made at different incident laser intensities to be related to each other. A typical incident laser power vs. fluorescence intensity calibration is shown in Figure 4. For this particular experiment, the solution pH was 4.70 and a linear regression gave a slope of 0.81, yintercept of -1.42 and a correlation coefficient of 0.9999. The correlations corresponding to other pH values over the experimental range were also highly linear. This linearity allowed fluorescence measurements made at different incident power levels to be related to each other by simple ratio of the power levels. This took the explicit form

$$F_{1,2} = F_{1,1}(P_2/P_1)$$
(28)

where  $F_{I,n}$  represents fluorescence intensity and  $P_n$  is the incident laser power level. Both of these parameters were recorded in units of ADC-counts.



Figure 4. Plot of typical bulk phase fluorescence intensity vs. incident laser power calibration where both signals were measured in ADC counts. The bulk pH was 4.70.  $\Box$  - calibration data points, solid line is linear regression with m = 0.81 with y-intercept = -1.42 and a correlation coefficient of 0.9999. Experimental code IX-69.

Each pH vs. fluorescence calibration curve was fit to a third order polynomial of the form

$$pH = A_0 + A_1F_T + A_2F_T^2 + A_3F_T^3$$
(29)

where  $F_{\tau}$  represents the fluorescence signal in ADC-counts and the  $A_n$ are the polynomial coefficients as determined by a least squares polynomial regression (Bevington, 1969). A correlation coefficient of 0.999 for the power-corrected fluorescence intensities was typically obtained. The standard error of the regression was typically 0.01 pH units. As will be discussed below however, this was not an estimate of the precision of the LIF-DCFS pH measurement method. A typical pH vs. fluorescence calibration is presented in Figure 5.

The precision of the LIF-DCFS pH measurement method pH was estimated by linear regression of pH values predicted by Eq. 29 versus pH measurements made with an electrode. Precision was estimated in this manner to arrive at an overall precision as opposed to the precision at any one specific pH. The plot of the standard residuals from the linear regression showed that there was no systematic trend in the uncertainties as a function of pH. The regression is shown in Figure 6. The slope of the line in Figure 6 is 1.02 with a yintercept of -0.0859 and a correlation coefficient of 0.999. Although the plot is not shown, there was no trend in the residuals of the linear regression (Ryan et al., 1976). Therefore, the precision of the LIF-DCFS method was estimated from the standard error of the linear regression shown in Figure 6 (Davies and Goldsmith, 1976). This showed that pH was predicted from fluorescence measurements with a



Figure 5. Plot of typical pH vs. bulk phase fluorescence intensity calibration where fluorescence intensity was measured in ADC counts. D - calibration data points, solid line - 3rd order polynomial regression of data. From Eq. 28 in text, pH =  $3.076 + 0.03964F_{\tau} - (3.860 \times 10^{-4})F_{\tau}^2 + (2.152 \times 10^{-6})F_{\tau}^3$ . The correlation coefficient was 0.9999 and the standard error of the fit was 0.005 pH units. Experimental code XIII - 71.



Figure 6. Plot of LIF predicted pH vs. electrode measurements of pH.  $\Box$  - experimental data points, solid line is linear regression with m = 1.02 with y-intercept = -0.0859 and a correlation coefficient of 0.999. Experimental code XI-39.

typical precision of  $\pm$  0.02 pH units ( $\pm$  1s).

During an experiment, dry filtered (0.4 um HEPA) CO<sub>2</sub> gas (Airco, Vancouver, WA, 2.8 grade) was admitted into the tank headspace and the resulting fluorescence changes were recorded by the computer data acquisition system. The bulk fluid pH was measured immediately before and after each experiment. This allowed corrections to be made for DCFS photodecomposition. A typical experimental data time series is shown in Figure 7.

The raw fluorescence data was corrected for laser power drift by use of Eq. 28 and a reference laser power level. The reference level used was the initial laser power. The pH was then calculated using Eq. 29. The total concentration of  $CO_2$  species in the bulk aqueous phase  $C_b$  (mol cm<sup>-3</sup>) at any time was determined from the pH by

 $C_{b} = \{(C_{B} - C_{A} + [H^{+}] - [OH^{+}])/(\alpha_{1} + 2\alpha_{2})\}$ (30) where  $C_{g}$  (mol cm<sup>-3</sup>) is the amount of mineral base present,  $C_{A}$  (mol cm<sup>-3</sup>) is the amount of mineral acid present, and  $\alpha_{1}$  and  $\alpha_{2}$  are known, dimensionless functions of the pH, temperature T (°C), acidity constants, and I (Stumm and Morgan, 1981).

Because  $C_A$  was known from the starting pH and  $C_B$  was 0 because the starting pH was always less than 7,  $C_b$  was calculated from Eq. 30. Use of Eq. 1 and making the assumption that the bulk aqueous phase was homogeneous allowed the concentration change with time t (s) to be written as

$$dC_{b}/dt = \{k_{L}/H\}(C_{s} - C_{b})$$
(31)

where H (cm) was the height of the water column. Integration of



Figure 7. Typical bulk  $k_{\rm L}$  experiment normalized fluorescence intensity time series. The solid line is the upper beam fluorescence signal and the dashed line is the fluorescence signal from the lower beam. Experimental code XVI-81.

Eq. 31 yields

$$\{k_{L}/H\}t = -\ln\{(C_{s} - C_{b})/C_{s}\}$$
(32)

where it is assumed that  $C_b = 0$  at t = 0. Therefore, since Eq. 1 described the mass transport process, plots of  $-\ln\{(C_s - C_b)/C_s\}$  vs. t gave a straight line where the slope, m, was  $k_L/H$ . This was determined by linear regression.

Application of Eq. 32 required that C<sub>s</sub> be calculated based on Henry's law and a measurement of the atmospheric pressure. The latter was determined with a NOVA (Princo, Southampton, PA) Hg barometer. This device was calibrated periodically to the barometric pressure recorded at Hillsboro International Airport which is situated approximately 8 km to the west of the Oregon Graduate Center.

All concentrations and acidity constants were corrected for ionic strength by calculation of activity coefficients using the extended Debye-Hückel model (Stumm and Morgan, 1981). The data was then plotted as discussed for Eq. 32 and a linear regression performed. Calculation of  $k_L$  was then trivial as H was easily measured and  $k_L/H$ was known from the linear regression. A typical plot of this type is shown in Figure 8. The data analysis was done on a DEC micro-PDP-11/23 minicomputer using the FORTRAN IV-RT program DCFS.FOR written for this research. This program and all internally declared function references are listed in Appendix A.

Application of the various gas exchange models required knowledge of the aqueous phase diffusion coefficient for  $CO_2$ . Literature values of D for  $CO_2$  in pure H<sub>2</sub>O were used. In the temperature range of these



Figure 8. Typical plot of  $-\ln\{(C_s - C_b)/C_s\}$  vs. t for  $CO_2$  invasion experiment with dual sampling at depths of 5 and 25 cm. + - upper beam data, solid line is linear regression with m = 7.3 x  $10^{-5}$  s<sup>-1</sup>, r = 0.997.  $\Box$  - lower beam data, solid line is linear regression with m = 7.0 x  $10^{-5}$  s<sup>-1</sup>, r = 0.996. Experimental code XIII - 75, DCFS #225.

experiments the value for D is  $1.76 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  (Ackgerman and Gainer, 1972).

It should be made clear that Eqs. 21, 22 and 23 describe the behavior of turbulence far from the interfacial boundary. The experiments of Brumley (1984) and Dickey et al. (1984) have shown that these equations do not fully describe the behavior of the turbulence scales close to a gas/liquid interface. Therefore, they were modified to describe Q and L in the interfacial region.

The Brumley (1984) data shows that w' goes to zero at the interface while u' is reasonably estimated there by Eq. 21. This result is to be expected if the turbulence causes no surface distortion (Hunt and Graham, 1978). This distortion may be defined in terms of L. Since the observed distortion in the present experiments was less than 0.01L, Q was calculated at the surface by assuming w' = 0 and u' = v' where u' was given by Eq. 21. Dickey et al. (1984) showed that the presence of a gas/liquid boundary affects the linear relation of Z with L and that the deviation from linearity at the interface is approximately 10%. This error was felt to be acceptable and Eq. 23 was used to calculate L using the constants of Hopfinger and Toly (1976).

A further caveat in the use of the scale relations of Hopfinger and Toly (1975) is that there is experimental evidence that Eqs. 21 and 23 may be inaccurate if applied to different grid-stirred tanks (McDougall, 1979). Ideally, the turbulence scales present should have been measured and calibrated in the apparatus used. However, this was not possible in the time frame of this thesis due to lack of necessary experimental apparatus and technique. Therefore it was assumed that Eqs. 21 and 23 accurately described u' and L. It was hoped that because the grid used in this study had the same M and d as that used by Hopfinger and Toly (1975), Eqs. 21 and 23 would be fairly accurate.

To further reduce the effects of any error caused by the use of Eqs. 21 and 23, great care was taken to ensure that the tank and grid were aligned in precisely the same manner for each experiment. The water was also allowed to reach a quiescent state before grid oscillation was initiated. Hopefully this minimized the effects of any secondary flows in the water column. In support of the use of the scale relations of Hopfinger and Toly (1975), evidence presented in Chapter 5 suggests that the calculated Q and L were not in serious error.

## 2.C. Interfacial (CO<sub>2</sub>) Fluctuation Experimental Technique

Turbulence was generated in the bulk aqueous phase by the same vertically oscillating grid and the aqueous solution preparation procedures were identical to those described in the previous section. Experiments were performed using either the rayon/vacuum surface cleaning technique or with a deliberately created 1-OD monolayer. The 1-OD monolayer was formed in a manner identical to that described previously.

The technique used to measure the depth-dependent  $[CO_2]$  fluctuations was based on the basic LIF-DCFS method with one modification. Measurement of  $[CO_2]$  fluctuations in the aqueous surface layer

required that DCFS fluorescence from the surface be decoupled from the bulk aqueous phase fluorescence. This was done by adding a non-fluorescent dye, Orange-G (OG, Aldrich Chemical Co., Milwaukee, WI) which strongly absorbs the 488 nm excitation light.

Since OG's absorption of 488 nm light follows Beer's law, the 488 nm light intensity I(z) (watts) at any depth z (cm) in the water column was calculated by

$$I(z) = I_0 10^{-ezc} \tag{33}$$

where  $I_0$  (watts) is the incident 488 nm intensity, e (cm<sup>2</sup> mol<sup>-1</sup>) is the molar absorptivity of OG, and c (mol cm<sup>-3</sup>) is the concentration of OG. Therefore, knowledge of c allowed calculation of z where I(z) = $I_0/100$ . Since the fluorescence intensity F(z) (ADC-counts) was proportional to I(z), at that same depth,  $F(z) = F_0/100$  where  $F_0$  (ADCcounts) is the fluorescence at z = 0 cm. The depth where I(z) = $I_0/100$  was defined as the fluorescence cutoff depth,  $z_c$  (cm).  $z_c$  is independent of  $I_0$  and easily varied by changing c. Calculations using Eq. 33 show that  $c = 7.2 \times 10^{-6}$  mol cm<sup>-3</sup> gives  $z_c = 150$  um. Figure 9 shows a plot of integrated F(z) versus z for  $c = 7.2 \times 10^{-6}$  mol cm<sup>-3</sup>.

The OG dye was not commercially available in reagent grade. Therefore, it was bought in the 90-95% pure form (Aldrich Chemical Co., Milwaukee, WI) and purified. This purification procedure was designed to remove any surface active contaminants present in the OG. Initially, 100 g of OG were dissolved in approximately 500 ml of deionized water. Insoluble material was then removed by filtration through Whatman pre-pleated paper filters. The aqueous OG solution



Figure 9. Plot of the function  $F_{T}(z) = \int_{0}^{z} F(\xi) d\xi$  vs. z where  $F_{T}(z)$  has been normalized to maximum value of one for  $z = \infty$ . This demonstrates that the total fluorescence observed is from the layer where  $z \ge z_{c}$ .

was then rinsed with three 500 ml aliquots of reagent grade dichloromethane (Omnisolve, Fisher Scientific, Springfield, NJ) in a clean 2000 ml separatory funnel. The resulting solution was then sparged with filtered He gas to remove any dissolved dichloro-methane. The concentration of OG in solution was determined by spectroscopic measurement of the optical density.

To observe the smallest spatial scale fluorescence fluctuations, the incoming laser beam was focussed onto the  $CO_2$ /water interface with a plano-convex lens. This prevented spatial averaging of the data by ensuring that the observation area was on the same order of scale as the smallest spatial scale of the turbulence. This spatial scale was defined by the dissipation length scale  $\lambda$  (cm) which was estimated by (Tennekes and Lumley, 1972)

$$\lambda = (v^3/\varepsilon)^{1/4} \tag{34}$$

Application of Eq. 34 showed that the minimum spatial scale of the turbulence in the tank was 0.07 cm. Therefore, the incoming laser beam was focussed to a spot size of 0.1 cm. This diameter, while not as small as the calculated minimum spatial scale, was the smallest beam diameter which could be used effectively. It was on the same order of magnitude as  $\lambda$  so spatial averaging was not felt to be a problem. As will be discussed later, analysis of the results have indicated that a spot size of 0.1 cm resolved all spatial scales present. It should also be noted that since  $\lambda$  is inversely related to  $\varepsilon$ , the minimum value of  $\lambda$  quoted above was for the most intense turbulence studied. For turbulence intensities below this maximum level, a

spot size of 0.1 cm was much smaller than  $\lambda$ .

Spot diameters smaller that 0.1 cm were not readily achievable due to heating of the aqueous surface by dissipation of the incident 488 nm laser radiation. If intense enough, this heating could cause convection in the water surface and so produce anomalous results. Assumption that all of the incident laser energy was converted to heat and dissipated in aqueous surface to a depth defined by  $z_c$  showed that if the incident power level = 40 mW,  $z_c$  = 450 um, and the spot size was 0.1 cm, the temperature rise was approximately 4 °C s<sup>-1</sup>. This was negligible due to the small spot size and relatively fast turnover time of the interface.

At the lowest turbulence intensities studied the surface layer was renewed with a timescale of approximately 2 s. This implies that the maximum temperature rise was on the order of 10 °C by use of the heating coefficient given above. The corresponding decrease in the density of water for  $T_1 = 20$  °C and  $T_2 = 30$  °C is calculated to be 0.003 g cm<sup>-3</sup>. Therefore, the timescale of the buoyancy-driven motions was negligible in relation to the maximum expected timescale of the turbulence. Smaller spot diameters were avoided due to the non-linear relation between spot diameter and dissipation volume in addition to the concomitant decrease in signal-to-noise ratio.

The "spot" of DCFS fluorescence observed at the interface was imaged by a second plano-convex lens onto a silicon PIN photodiode (S-1227BR, Hammamatsu, Palo Alto, CA) connected to an operational amplifier (OPA-121KP, Burr-Brown, Austin, TX). A schematic diagram of

the optical alignment is shown in Figure 10. The low fluorescence light intensities necessitated the use of a very high gain amplifier. The photodiode-amplifier circuit used is shown in Figure 11. It had a calculated current to voltage gain of  $10^{10}$  and time constant of 0.1 s. Tests with a digitally-pulsed flash lamp and oscilloscope showed that this response time was fast enough to resolve the fastest fluorescence fluctuations.

Concentration fluctuations were studied for  $z_c$  equal to 150 um, 300 um, and 450 um for a rayon/vacuum cleaned interface, and for  $z_c =$ 300 um for the 1-0D film-covered interface. A range of turbulence conditions was studied by varying  $\omega$  from 2.5 Hz to 6 Hz, setting s' equal to 1.5 cm or 2.5 cm, and varying Z from 7.5 cm to 12.5 cm. These parameters led to a calculated range for Re<sub>t</sub> of 100 to 400. The fluorescence fluctuation data was collected and stored by a computer data acquisition system with a sampling rate of 80 Hz and total sampling time of 375 s. The collection frequency was calculated to be fast enough to resolve the fastest temporal fluctuations of the turbulence which were defined by T<sub>u</sub>.

As a test that this sampling rate was resolving the fastest fluorescence fluctuations, several experiments were performed with a sampling rate of 180 Hz. Concentration fluctuation frequency power spectra for both data sets were then computed by use of a fast-fourier transform algorithm (Jenkins and Watt, 1968). Visual comparison showed that no higher concentration fluctuation frequencies were resolved at 180 Hz than were resolved at 80 Hz. A sampling rate of



Figure 10. Interfacial  $[CO_2]$  concentration fluctuation experimental optical alignment showing incoming laser beam and path of fluorescence emissions to monitoring photodiode. The PCX lens which focussed the incoming laser beam to a small spot has been omitted for clarity.





Figure 11. Photodiode amplifier circuit diagram for the fluorescence monitoring photodiode and the laser power reference photodiode.

180 Hz was not chosen for general use since total data acquisition time was constrained by available RAM in the computer used for the data acquisition. Therefore, use of the higher rate implied that the time available for continuous sampling of the transport process was less than 180 s.

Figure 12 is a plot of the normalized fluorescence intensity  $\hat{F}_{T}$ , vs. time for  $z_c = 300$  um,  $\omega = 5.8$  Hz, s' = 2.5 cm, Z = 7.5 cm, and a rayon/vacuum cleaned interface with no  $CO_2$  in the tank headspace and therefore no transport underway.  $\hat{F}_{T}$  is equal to  $F_{T}$  divided by the average signal observed at the maximum pH of the experiment,  $F_{T0}$ . Figure 13 shows a  $\hat{F}_{T}$  fluctuation time series for  $CO_2$  invasion with turbulence and  $CO_2/H_2O$  interface conditions identical to those for Figure 12. The aperiodic increases in  $\hat{F}_{T}$  correspond to parcels of water with higher pH being advected into the sampling region. The decreases were caused by these parcels absorbing  $CO_2$  and undergoing a reduction in pH. Each cycle of increase and decrease in  $\hat{F}_{T}$  was viewed as an individual surface renewal event.

Figure 14 is a background  $\hat{F}_{T}$  fluctuation time series for a 1-OD monolayer covered interface with turbulence conditions identical to those for Figure 12. Figure 15 is a  $\hat{F}_{T}$  fluctuation time series for CO<sub>2</sub> invasion through a 1-OD covered interface. The same type of aperiodic fluctuations of intensity are visible in Figure 15 as are seen in Figure 13.

If the acid-base chemistry of an event is fast in relation to the fluid mechanics, the duration of the fluorescence fluctuation can be



Figure 12. Fluorescence fluctuation time series under conditions of no net  $CO_2$  transport and a rayon/vacuum cleaned interface. The top time series was for bulk solution pH = 8.3, the bottom time series was for bulk pH = 4.0. The fluorescence intensities of both time series were normalized to the average intensity of the pH = 8.3 time series. Grid parameters were  $\omega = 5.8$  Hz, Z = 7.5 cm, and s' = 2.5 cm with  $z_c = 300$  um.



Figure 13. Fluorescence fluctuation time series for  $CO_2$  transport into an unbuffered aqueous phase through a rayon/vacuum cleaned interface. The fluorescence intensity was normalized to the mean intensity of the pH = 8.3 background trace of Figure 12. Grid parameters were  $\omega = 5.8$  Hz, Z = 7.5 cm, and s' = 2.5 cm with  $z_c = 300$  um.



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Figure 14. Fluorescence fluctuation time series under conditions of no net CO<sub>2</sub> transport and a 1-OD monolayer covered interface. The top time series was for bulk solution pH = 8.3, the bottom time series was for bulk pH = 4.0. The fluorescence intensities of both time series were normalized to the average intensity of the pH = 8.3 time series. Grid parameters were w = 5.8 Hz, Z = 7.5 cm, and s' = 2.5 cm with  $z_c = 300$  um.



Figure 15. Fluorescence fluctuation time series for  $CO_2$  transport into an unbuffered aqueous phase through a 1-OD monolayer covered interface. The fluorescence intensity was normalized to the mean intensity of the pH = 8.3 background trace of Figure 14. Grid parameters were  $\omega = 5.8$  Hz, Z = 7.5 cm, and s' = 2.5 cm with  $z_c = 300$  um.

used to provide an estimate of the timescale of the hydrodynamical fluctuation. This will be the case if the timescale of the hydration of  $\rm CO_2$  to  $\rm H_2\rm CO_3$ , which is the rate-limiting step in the aqueous phase chemistry, is faster than  $\tau_u$ . Since the net rate of hydration is pH dependent, modeling of the  $\rm CO_2$  hydration kinetics was performed to determine an optimum pH range for the experiments. This was done by numerically solving the differential rate equation describing the  $\rm CO_2$  hydration and then calculating the time evolution of the pH. The differential rate equation is (Gibbons and Edsall, 1963)

$$d[HCO_{3}]/dt = k_{12}'[CO_{2}]_{ac} - k_{21}'[H^{*}][HCO_{3}']$$
(35)

where  $[CO_2]_{aq}$  is the concentration of unhydrated aqueous phase  $CO_2$ present,  $k_{12}'$  is the net hydration rate of  $CO_{2aq}$ ,  $k_{21}'$  is the net dehydration rate of carbonic acid species ( $H_2CO_3$ ,  $HCO_3'$ ,  $CO_3^{-2}$ ), and  $[H^*]$  is defined by the aqueous ionic charge balance equation which takes into account all ionic species present (Stumm and Morgan, 1981). In Eq. 35 it was assumed that the deprotonation of  $H_2CO_3$  was very fast in comparison to the hydration of  $CO_{2aq}$ . The modeling was done using the FORTRAN IV-RT program CO2KIN.FOR which was written for this research and is listed in Appendix A. The differential equation was integrated by use of the Runge-Kutta-Merson algorithm (Hall and Watt, 1976). Calculation of  $\{H^*\}$  was performed by the FORTRAN IV-RT function CHHODC.FOR which iteratively solved the aqueous solution charge balance equation for  $[H^*]$ . A more detailed explanation of this procedure is listed in Appendix B. CHHODC.FOR is also listed in Appendix A. The results of this modeling showed that only over the pH range 5 to 9 was the hydration timescale at the interface at least three times faster than  $\tau_u$ . This pH range presented a problem in that the DCFS fluorescence response range was pH 3.5 to 6. Therefore, the pH response range was increased by the addition of a second dye, 1-hydroxy-pyrenetrisulfonic acid (HOPSA, Eastman Kodak, Rochester, N.Y.) which also exhibits pH-dependent fluorescence. The absorbance maximum of HOPSA in basic solution is 470 nm (Zhujun and Seitz, 1984) and its fluorescence maximum is 520 nm (Zhujun and Seitz, 1984). The concentration of HOPSA was 1 x 10<sup>-9</sup> mol cm<sup>-3</sup>. The combined DCFS-HOPSA fluorescence response range was pH 4 to 8.5.

Figure 16 shows the pH vs. time response for an unbuffered aqueous solution with initial pH = 8.0 that contained the experimental concentrations of DCFS and HOPSA. The pH response was calculated by use of Eq. 35 and CO2KIN.FOR. In this example, it is seen that the pH has fallen to approximately 4 in under 0.1 s. This is significantly faster than the minimum expected turbulence timescale.

Since the CO<sub>2</sub> chemistry was faster than the hydrodynamic fluctuations, [CO<sub>2</sub>] fluctuation timescales were directly relatable to the peak widths of the fluorescence fluctuation time series data. The peak widths were calculated by a procedure based on a gas chromatographic peak detection algorithm (Spectra-Physics, 1977). This algorithm required the slope of the time series data to be computed at each data point i. One of the simpler methods of approximating the slope at i was to perform a linear regression on a subset of points of


Figure 16. CO<sub>2</sub> hydration kinetics pH response. pH vs. t calculated by integration of Eq. 34 for a solution containing  $C_{\rm D} = 10^{-9}$  mol cm<sup>-3</sup> and  $C_{\rm H} = 10^{-9}$  mol cm<sup>-3</sup> with starting pH = 8.0. The rate constants used were  $k_{21} = 0.0375$  s<sup>-1</sup> and  $k_{21} = 5.5 \times 10^7$  cm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> (Gibbons and Edsall, 1963).

length  $i_r$  which was centered on i. A peak beginning was then detected once this slope rose above a certain predetermined threshold value  $S_m$ for a user determined number of data points  $i_c$ . The peak end was found when the slope rose above the negative of  $S_m$  for  $i_c$  points after going through a zero crossing followed by a local minimum. This situation is shown graphically in Figure 17. Actual implementation of this method required  $i_r$ ,  $i_c$ , and  $S_m$  to be calculated from the experimental data and  $T_m$ .

Since linear regression is mathematically equivalent to a lowpass filter (Bloomfield, 1975),  $i_r$  and  $i_c$  were determined with respect to the data sampling rate and  $T_u$ . This was done so that the fastest temporal fluctuations could be resolved into discrete peaks. Therefore,  $i_r$  was defined by

$$i_{r} = \tau_{u}/2t_{s} \tag{36}$$

where  $t_s$  was the data sampling time constant which for a sampling rate of 80 Hz was 0.0125 s.  $i_c$  was defined to be equal to  $i_r - 1$ . Defining  $i_r$  and  $i_c$  in this manner ensured that the peaks with the smallest width (fastest timescale) could be resolved discretely with minimal filtering.

 $S_m$  was calculated from fluorescence background fluctuation time series such as shown in Figure 12. This was done by computing the slope at each point in the background time series using  $i_r$  calculated from Eq. 36. These slopes were then averaged and a standard deviation



Figure 17. Schematic diagram of relation between  $F_{\tau}$  and data slope. This demonstrates how the peak detection algorithm determines peak beginnings and endings.

of the average computed.  ${\rm S}_{\rm m}$  was then defined to be

$$S_{m} = 2\sigma_{s}$$
(37)

where  $\sigma_s$  is the standard deviation of the average background slope. Calculations showed that if the slopes were distributed in a gaussian manner and the relative noise levels were similar in the experimental and background time series, defining  $S_m$  in this manner filtered out 90% of the noise peaks.

The peak width calculations were performed by the FORTRAN IV-RT program PWIDTH.FOR which is listed in Appendix A.  $S_m$  was calculated by the FORTRAN IV-RT subroutine SLOPE.FOR which called by PWIDTH.FOR. The flow chart for the peak detection section of the program is shown in Figure 18.

Fluorescence intensity was calibrated to pH in the same manner as described in the previous section. The larger pH range made it necessary to use a fifth order polynomial to accurately fit the calibration data. This took the explicit form

$$pH = A_0 + A_1F_T + A_2F_T^2 + A_3F_T^3 + A_4F_T^4 + A_5F_T^5$$
(38)

A typical plot of a surface pH calibration and associated regression parameters is shown in Figure 19.



Figure 18. Flowchart of peak detection logic for the FORTRAN IV-RT program PWIDTH.FOR listed in Appendix A. i - data point number,  $i_{B}$  - peak beginning marker,  $i_{c}$  - peak threshold slope count,  $i_{e}$  - peak end marker,  $i_{em}$  - peak slope ending count,  $i_{m}$  - peak maximum detection count, m - data slope at point i,  $S_{m}$  - threshold slope.



Figure 19. Plot of typical pH vs. surface microlayer fluorescence intensity calibration where fluorescence intensity was measured in ADC counts.  $\Box$  - calibration data points, solid line - 5th order polynomial regression of data. From Eq. 37 in text, pH = 1.927 +  $0.02539F_{\rm T}$  - (1.059 x 10<sup>-4</sup>) $F_{\rm T}^2$  + (2.193 x 10<sup>-7</sup>) $F_{\rm T}^3$  - (1.978 x 10<sup>-10</sup>) $F_{\rm T}^4$  + (6.485 x 10<sup>-14</sup>) $F_{\rm T}^5$ . The correlation coefficient was 0.9997. Experimental code XVII - 93.

# 3. Bulk k Measurements

### 3.A. Objectives of Experiments

The purpose of these experiments was to characterize  $k_{L}$  as a function of Q, L,  $\varepsilon$ , and interfacial cleanliness. The motivation in so doing was to show which, if any, of the mentioned gas/liquid transport models that incorporate these known fluid mechanical parameters (Eqs. 9, 11, and 15) were accurate in the prediction of  $k_{L}$  for a given set of turbulence and interfacial conditions. Knowledge of the chemical and physical conditions under which each transport model is applicable would provide information regarding the hydrodynamical mechanisms of gas exchange. In addition to this mechanistic information, the bulk  $k_{L}$  results also "calibrated"  $k_{L}$  in the tank as a function of turbulence and interfacial cleanliness. This is an important asset of these experiments as will become obvious in later chapters.

# 3.B. Bulk k, Results and Discussion

The precision of  $k_{L}$  is found by using a standard propagation of errors starting with a relative uncertainty in  $[H^{+}]$  of  $\pm 4$ % ( $\pm$  1s) and assuming that all other uncertainties are negligible. This assumption leads to a constant uncertainty in the regression parameter  $-\ln((C_{s} - C_{b})/C_{s})$ . Therefore, the standard formulas for the uncertainties in linear regression coefficients may be used (Bevington,

1969). Therefore, the standard deviation  $\sigma_m$  in  $k_L/H$  is defined in terms of the variance of  $k_L/H$ . Hence  $\sigma_m$  is determined from

$$\sigma_{m}^{2} = N \sigma^{2} / (N \Sigma t_{i}^{2} - (\Sigma t_{i})^{2})$$

$$i=1$$

$$i=1$$
(39)

where N is the number of data points,  $t_i$  is the time at the i'th point and  $\sigma$  is the variance of the regression defined by

$$= (N - 2)^{-1} \sum_{i=1}^{N} (-\ln((C_s - C_{b,i})/C_s) - b - k_L t_i/H)^2$$
(40)

where b is the y-intercept of the regression and  $C_{b,i}$  is the  $[CO_2]$  in the bulk aqueous phase at time  $t_i$ . Use of these equations shows that the values for  $k_L$  and their calculated uncertainties for the data shown in Figure 8 are 2.6 x  $10^{-3} \pm 0.4 \times 10^{-3}$  and 2.5 x  $10^{-3} \pm 0.4 \times 10^{-3}$  cm s<sup>-1</sup> for the upper and lower beams, respectively.

The experimentally determined  $k_{\rm L}$  values were grouped by similar turbulence parameters and aqueous surface preparation technique (i.e. no cleaning, lens paper cleaning, rayon/vacuum cleaning, and 1-OD monolayer covered). The  $k_{\rm L}$  values from experiments with similar conditions were then averaged. These average  $k_{\rm L}$  values were then plotted against  $(DQ/L)^{1/2}$  and  $(\varepsilon v)^{1/4}S_{\rm c}^{-1/2}$ . This tests the validity of the two clean-interface surface renewal models represented by Eqs. 9 and 11 by showing if the data correlated linearly as predicted by each model. Additionally, plotting the data in this manner enables a direct comparison of  $k_{\rm L}$  predicted by hydrodynamical variables with directly measured  $k_{L}$  data. These plots are shown in Figures 20 and 21. In both plots Q, L and  $\varepsilon$  were computed at the interface from Eqs. 13, 21, and 23.

Also shown in Figures 20 and 21 are the results from linear regression of the stirred-tank gas/liquid transport data of Dickey et al., (1984). This previous gas exchange study measured  $k_L$  for  $CH_4$ ,  $CO_2$ ,  $O_2$ ,  $N_2$ , and Rn as a function of Q and L for grid-generated turbulence. Therefore, it was possible to directly compare the data to the present results. Dickey et al., (1984) studied gas transport through uncleaned aqueous surfaces and comparison of their data with the uncleaned and 1-OD monolayer transport results from the present research shows excellent agreement. Because Dickey et al. (1984) directly measured Q and L in their apparatus this correlation suggests that the Hopfinger and Toly (1976) scale relations gave reasonable estimates of Q and L in the tank.

Use of Eq. 11 results in fair prediction of the measured  $k_{\rm L}$  for the rayon/vacuum cleaned data for low turbulence intensities with the prediction becoming quite good for higher levels of turbulence. Eq. 9 does not predict  $k_{\rm L}$  quite as well as Eq. 11 although the linear correlation is similar for each data set as is discussed below.

Both sets of experiments where the water surface was cleaned show little or no significant increase of  $k_L$  with increasing turbulence intensity until a threshold value of  $(DQ/L)^{1/2}$  or  $(\epsilon v)^{1/4}S_c^{-1/2}$  is reached. At higher turbulence levels, the correlation is linear as predicted by Eqs. 9 and 11. In the rayon/vacuum cleaned data set this



Figure 20. Application of the macro-scale hydrodynamic surface renewal model of Fortescue and Pearson (1967). Plot of experimentally determined k for rayon/vacuum cleaned, lens paper cleaned, uncleaned and 1-OD monolayer covered interfaces vs.  $(DQ/L)^{1/2}$  calculated by use of Eqs. 11, 20, and 22. Data key is:  $\diamond$  - represent average value of 4 independent determinations of k for a rayon/vacuum cleaned interface (Small dashed line is linear regression for  $(DQ/L)^{1/2} \times 10^4 > 22$ cm s<sup>-1</sup> with m = 3.20, r = 0.99),  $\Box$  - represent average value of at least 4 independent measurements of k for a lens paper cleaned interface (Solid line is linear regression for  $(DQ/L)^{1/2} \times 10^4 > 25$  cm s<sup>-1</sup> with m = 1.29, r = 0.97.),  $\triangle$  - represent averages of 4 independent determinations of k for an interface covered by a 1-OD monolayer (Large dashed line is linear regression with m = 0.45, r = 0.995), O - represent average of 4 independent determinations of k for an uncleaned interface. Medium dashed line is the linear regression of the transport data of Dickey et al., (1984).



Figure 21. Application of the dissipation scale hydrodynamic surface renewal model of Lamont and Scott (1970). Plot of experimentally determined k<sub>L</sub> for rayon/vacuum cleaned, lens paper cleaned, uncleaned and 1-OD monolayer covered interfaces vs.  $(\varepsilon v)^{1/4} S_c^{-1/2}$  calculated by use of Eqs. 12, 13, 20, and 22. Data key is:  $\diamond$  - rayon/vacuum cleaned interface plotted as in Figure 20 (Small dashed line is linear regression for  $(\varepsilon v)^{1/4} S_c^{-1/2} \times 10^4 > 30$  cm s<sup>-1</sup> with m = 1.37 and r = 0.98),  $\Box$  - lens paper cleaned interface plotted as in Figure 20 (solid line is linear regression for  $(\varepsilon v)^{1/4} S_c^{-1/2} \times 10^4 > 40$  cm s<sup>-1</sup> with m = 0.59, r = 0.96),  $\triangle - k_L$  data for 1-OD film covered interface plotted as in Figure 20 (Large dashed line is linear regression with m = 0.213, r = 0.97),  $\bigcirc - k_L$  data for uncleaned interface plotted as in Figure 20. Medium dashed line is linear regression of the transport data of Dickey et al. (1984).

transition occurs where  $(DQ/L)^{1/2} \simeq 1.9 \times 10^{-3}$  cm s<sup>-1</sup> and  $(\varepsilon v)^{1/4} S_c^{-1/2} \simeq 3.0 \times 10^{-3}$  cm s<sup>-1</sup>. The transition in the lens papercleaned results is found at  $(DQ/L)^{1/2} \simeq 2.5 \times 10^{-3}$  cm s<sup>-1</sup> and  $(\varepsilon v)^{1/4} S_c^{-1/2} \simeq 4.5 \times 10^{-3}$  cm s<sup>-1</sup>.

This transition may be explained if the scale relations given by Eqs. 21, 22 and 23 became inapplicable for low turbulence intensities. If the calculated turbulence scales were accurate however, this transition may imply that for weak turbulence the models represented by Eqs. 9 and 11 do not adequately describe the transport process. This may be due to eddies at the lower turbulence levels not having the dynamic thrust necessary to renew the gas/liquid interface. If this interpretation is correct it implies that transport at both lens paper cleaned and rayon/vacuum cleaned surfaces resembles gas exchange at film-covered interfaces at low turbulence intensities. However, it may not be concluded that the cleaned and monolayer covered interfaces behave in exactly the same manner. Any similarities that do exist are most likely due to the presence of small amounts of surface active contaminants in spite of the cleaning procedure.

A second conclusion that may be drawn from this hypothesis is that the transition observed in the stirred-tank data is analogous to that in plots of  $k_{\rm L}$  versus wind speed or friction velocity from wind tunnel data (Broecker et al., 1978; Liss et al., 1981). There the transition is thought to be due to the onset of capillary waves and concomitant change from a smooth to rough aerodynamic surface. This alters the functional dependence of  $k_{\rm L}$  on aerodynamic parameters in a manner analogous to differences observed between the clean interface case embodied in Eq. 11 and the film-covered theory embodied in Eq. 14. In other words, the transition in the present stirred-tank data might be due to a fundamental change in the fluid mechanical dependence of the transport process.

A third explanation is that the observed change in slope might have been caused by the presence of weak surface films. At higher levels of turbulence, the eddies were energetic enough to penetrate the film and cause renewal of the interface. This ambiguity in the interpretation of the cleaned-interface  $k_{\rm L}$  data cannot be resolved by study of the relation of  $k_{\rm L}$  with turbulence alone. What is needed is information concerning how the turbulence eddies were interacting with the  $CO_2/H_2O$  interface. Data of this type will be discussed in the following chapter.

The major difference between the two cleaned surface data sets is the slope of the high turbulence intensity data. The slope of the rayon/vacuum cleaned results is much greater than that of the lens paper cleaned data. Since surface films tend to decrease  $k_L$  for a given turbulence intensity (Davies, 1972), the difference in slopes suggests that the rayon/vacuum cleaned technique produces a cleaner aqueous surface. However, due to the presence of the transition in slope in the data set it cannot be concluded that the rayon/vacuum cleaned surfaces were entirely free of spontaneously generated interfacial films.

Although it cannot be definitely asserted that the rayon/vacuum

cleaned technique produced a  $CO_2/H_2O$  interface which was totally free of contaminants, making this assumption allows further interpretation of the bulk  $k_L$  results. This includes an interesting feature of the rayon/vacuum cleaned interface data sets seen in an examination of the slopes for the high turbulence intensity data.

If the relations given by Eqs. 24 and 25 for the turbulence timescales  $T_m$  and  $T_U$  respectively, are substituted for T in Eq. 2, the functional form of both the Fortescue and Pearson (1967) model (Eq. 9) and the Lamont and Scott (1970) model (Eq. 11) are obtained. The fluid mechanical interpretation of this is that either  $T_m$  or  $T_U$  may be thought of as T in the Higbie (1935) surface renewal model. It is not surprising that this substitution predicts different values for K<sub>1</sub> and K<sub>2</sub> than found by Fortescue and Pearson (1967) and Lamont and Scott (1970) respectively. In these earlier studies, both K<sub>1</sub> for the Fortescue and Pearson (1967) study and K<sub>2</sub> for the Lamont and Scott (1970) results were determined by fit of experimental transport data to the functional form of the respective model. In each case however, transport rates were measured without assurance that the liquid surface was free from contaminants. This could have led to an underestimation of K<sub>1</sub> and K<sub>2</sub> as seen from the present transport data.

If it may be assumed that  $\tau$  at a clean aqueous interface may be approximated by either  $\tau_m$  or  $\tau_u$ , it is not clear which is a better choice. However, if  $\tau_m$  is an appropriate choice for  $\tau$  then the theoretical slope of the clean-interface  $k_L$  data plotted using the Fortescue and Pearson (1967) model in Figure 20 should be 1.13.

Similarly, if  $\tau_u$  is the appropriate choice then the slope of cleaninterface  $k_L$  data plotted in Figure 21 should be 1.13. Since the rayon/vacuumed technique has already been reasoned to produce the cleanest interface among the present data sets, it is these results which will be of interest in comparison of the slopes.

Linear regression of the rayon/vacuum cleaned data in Figure 21 for which  $(\varepsilon v)^{1/4} S_c^{-1/2} > 3.0 \times 10^{-3}$  cm s<sup>-1</sup> shows that the slope is 1.37 with a correlation coefficient r = 0.98. Analysis of the rayon/vacuum cleaned data in Figure 20 for which  $(DQ/L)^{1/2} > 1.9 \times 10^{-3}$ cm s<sup>-1</sup> shows the slope is 3.20 with r = 0.99. Therefore, there is a large discrepancy in the empirical and theoretical slopes for the large eddy model of Fortescue and Pearson (1967). The data plotted by use of the dissipation scale eddy model of Lamont and Scott (1970) shows much better agreement between the empirical and theoretically predicted slopes. This suggests that it is the small scale eddies represented by  $\tau_u$  and not the large scale eddies represented by  $\tau_m$ which are important in the determination of  $k_L$ .

The quality of the linear fit for the high turbulence intensity rayon/vacuum cleaned data is similar for the large eddy and dissipation models. This is demonstrated by the fact that the correlation coefficients of the regressions were similar for both models. This is most likely due to the relatively weak functional dependence of  $k_l$  on the turbulence parameters Q and L in the large eddy model (Eq. 9) or  $\varepsilon$ in the dissipation model (Eq. 11). This may be seen by substitution

of Eq. 13 into Eq. 11 from which the following is derived

$$(\varepsilon v)^{1/4} S_c^{-1/2} = (DQ/L)^{1/2} Re_t^{1/4}$$
(41)

This shows that the dissipation model is functionally different from the large eddy model only by a weak dependence on  $\text{Re}_t$ . In the apparatus used, it is probable that the range of  $\text{Re}_t$  was not large enough to resolve this difference given the scatter in the  $k_t$  data.

The 1-OD film data have a much lower slope than either of the cleaned-surface data sets and no apparent transition in slope is observed. This lack of transition suggests that the hydrodynamical dependence of  $k_{\rm L}$  is constant over the range of turbulence intensities studied. If the break in the cleaned-interface data is caused by a fluid mechanical transition, it might be expected that an analogous break would be observed in the 1-OD data at some higher level of turbulence than used in this study. This change in slope would presumably occur where the turbulence eddies were energetic enough to break up the 1-OD monolayer. Therefore, it is unfortunate that higher turbulence intensities were not possible in the experimental apparatus. This might have shown that the 1-OD film data also show a break in the slope of  $k_{\rm L}$  versus turbulence intensity.

All of the data sets appear to be equivalent for low turbulence intensities. This supports the hypothesis that the cleaned interfaces are either contaminated by weak surface films or behaving in a hydrodynamic sense as if they are covered by a film. However, since the slopes of the cleaned and film-covered interface data sets are different for the high turbulence regime, it is assumed that in that region

the cleaned surfaces behavior is hydrodynamically different from the behavior of film-covered surfaces in relation to gas/liquid mass transport.

Experiments done with no surface cleaning at all resulted in measured  $k_{\rm L}$  values which are very similar to the 1-OD results. This shows the importance of removing adventitious surface films prior to the measuring of  $k_{\rm L}$ . It also demonstrates the sensitivity of a liquid-phase rate controlled gas/liquid transport process to the presence of interfacial films.

Use of the empirically derived film-covered gas/liquid transport model given by Eq. 15 results in poor prediction of the  $k_{\rm L}$  values for the 1-OD film data as well as the cleaned-surface results. This suggests that even a severely film-contaminated gas/liquid interface does not behave exactly like a solid/liquid interface with respect to gas/liquid mass transfer. As will be shown later however, direct application of Eq. 14 (the stagnant model) with an experimentally determined estimate of results in very good prediction of the 1-OD film results. The results from the application of Eq. 15 are shown in Figure 22.

# 3.C. Bulk k<sub>L</sub> Conclusions

Both the large eddy and the dissipation model correlate with the data equally well in the high turbulence regime for the rayon/vacuum cleaned results and no preferential choice can be made between them on



Figure 22. Application of the empirical film covered interface gas transport model of Davies (1972). Plot of experimentally determined  $k_{\rm L}$  for rayon/vacuum cleaned, lens paper cleaned, uncleaned and 1-OD monolayer covered interfaces vs.  $(\epsilon v)^{1/4} S_{\rm c}^{-2/3}$  calculated by use of Eqs. 12, 13, 20, and 22. Data key is:  $\bigcirc$  - rayon/vacuum cleaned interface plotted as in Figure 20,  $\square$  - lens paper cleaned interface plotted as in Figure 20,  $\square$  - lens paper cleaned interface plotted as in Figure 20,  $\square$  - k<sub>L</sub> data for 1-OD film covered interface plotted as in Figure 20,  $\blacksquare$  - k<sub>L</sub> data for uncleaned interface plotted as in Figure 20,  $\blacksquare$  - k<sub>L</sub> data for uncleaned interface plotted as in Figure 20. Solid line is slope of one with zero y-intercept.

this basis. However, an analysis of the magnitude of the slopes of the rayon/vacuum cleaned data for both models leads to the preliminary conclusion that the dissipation model provides a more appropriate description of the gas exchange process for a clean gas/liquid interface and intense turbulence. This could not be proven by use of the bulk  $k_{\rm L}$  data alone. However the surface concentration measurements provide further evidence for this conclusion. These experiments are discussed in the next chapter.

The transitions in  $k_{\rm L}$  observed in the cleaned-surface experiments might have been due to a change in the fluid mechanical dependence of  $k_{\rm L}$ . This change may have been caused by the presence of weak surface films or it may represent a fundamental property of gas/liquid interfaces. Unfortunately, this cannot be resolved at the present time due to lack of information on the actual surface conditions that were present in the tank. A third explanation is that the transition in slope for the cleaned-surface  $k_{\rm L}$  data may have been caused by Eqs. 21 and 23 inadequately describing the behavior of weak turbulence in the presence of a gas/liquid interface. While this last explanation could not be ruled out using the bulk  $k_{\rm L}$  results alone, examination of the behavior of the turbulence eddies near the gas/liquid interface suggested that Eqs. 21 and 23 were accurate over the range of turbulence conditions studied. This is discussed in the proceeding chapter.

Experiments done with no surface cleaning and an intentionallycreated organic monolayer, have shown that k<sub>L</sub> is very sensitive to the

presence of interfacial films. The presence of interfacial films not only affects the absolute magnitude of  $k_l$ , but the functional dependence of  $k_l$  on the turbulence parameters as well. This result is important because it shows the importance of careful surface preparation techniques. If it is not known that the gas/liquid interface is free from surface films the exchange rate could be in error by as much as a factor of 4 over the range of turbulence intensities studied.

The final result of these bulk phase measurements was that  $k_{\rm L}$  in the experimental apparatus was determined as a function of turbulence parameters for clean and film-covered interfaces. This allowed these results to be used to test the predictive ability of gas/liquid mass transport models which use parameters measured in the surface concentration fluctuation experiments discussed in the following chapter.

## 4. Interfacial [CO<sub>2</sub>] Fluctuation Experiments

#### 4.A. Introduction

While bulk studies have provided evidence in support of surface renewal models for gas transport at clean gas/liquid interfaces, quantitative measurement of surface element timescales or observation of individual surface renewal events has not been attempted. Surface renewal models could be tested further if such measurements could be made. Combined with the data presented in the previous chapter, this would allow comparison of  $k_{\rm L}$  values predicted by surface renewal models with experimental  $k_{\rm L}$  data. These measurements might also allow resolution as to which of the two hydrodynamically explicit surface renewal models embodied by Eqs. 9 and 11 provides a more accurate physical description of the gas/liquid transport process.

In this chapter, the results from the LIF-DCFS-HOPSA measurement of  $\{CO_2\}$  fluctuations in the aqueous surface microlayer as a function of depth in the microlayer, mechanically-generated aqueous phase Q, L, and c, and interfacial cleanliness are discussed. Since the timescales of the  $[CO_2]$  fluctuations are related to the surface element timescales of surface renewal theory, they may be used to predict  $k_L$ . This is done using both the Higbie (1935) and Danckwerts (1951) models. These predicted  $k_L$  values are compared to measurements of  $k_L$ described in the preceding chapter under identical turbulence conditions for both clean and 1-OD film-covered interfaces. This allows the first use of direct measurements of surface element timescales to test the Higbie (1935) and Danckwerts (1951) surface renewal models for applicability under a range of chemical and hydrodynamical conditions. The results provide additional evidence that prediction of  $k_{L}$ by Eq. 11 is to be preferred over Eq. 9.

4.B. Interfacial  $[CO_2]$  Fluctuations Results and Discussion

Peak widths of the fluorescence fluctuation peaks shown in Figures 13 and 15 were calculated using the procedure previously described for each value of Q, L, and  $z_{\rm c}$  studied for both the 1-OD filmcovered and rayon/vacuum cleaned interfaces. The average peak width,  $T_A$  (s) was calculated for each experiment. The data shown in Figure 13 is characterized by  $T_A = 0.44$  s and for the data shown in Figure 15,  $T_A = 0.66$  s. The peak widths also were grouped into bins to allow a peak width frequency distribution,  $f_{T}(T)$  to be estimated for each experiment. This was done by the FORTRAN IV-RT subroutine PWSORT.FOR which was called by PWIDTH.FOR. Both programs are listed in Appendix A. Since each  $f_T(T)$  was skewed, the mode of the distribution,  $T_M$  (s) was distinct from  $T_A$ .  $f_T(T)$  computed from the rayon/vacuumed cleaned data of Figure 13 is shown as the solid line in Figure 23.  $T_{\rm M}$  for the data shown in Figure 13 is 0.33 s.  $f_{\rm T}({\rm T})$  calculated from the 1-OD film-covered interface data shown in Figure 15 is shown as the dashed line in Figure 23.  $\mathrm{T}_{M}$  for the data in Figure 15 is 0.42 s. While there is no significant dependence of either  $T_A$  or  $T_M$  on  $z_c$  it is seen



Figure 23. Peak width distribution computed from the two fluorescence fluctuation time series shown in Figures 13 and 15. The solid line is the rayon/vacuum cleaned data shown in Figure 13 with  $T_A = 0.44$  s and  $T_H = 0.30$  s. The 1-OD monolayer covered interface data shown in Figure 13 is the dashed line with  $T_A = 0.66$  s and  $T_H = 0.42$  s.

in Figure 23 that the presence of the 1-OD monolayer alters the shape of  $f_T(T)$ . The qualitative effect of the 1-OD monolayer is to skew  $f_T(T)$  towards longer peak widths and decrease the number of peaks observed.

Quantitative analysis of the effect of the 1-OD monolayer on  ${\rm T}_{\rm A}$ and  $T_{N}$  is shown in Figure 24. This is a plot of  $T_{A}$  averaged over experiments which had similar turbulence conditions for the rayon/vacuum cleaned data ( $T_A(clean)$ ) plotted vs.  $T_A$  averaged over experiments with the same turbulence conditions as  $T_A(clean)$  for the 1-OD film results ( $T_A(film)$ ). Also shown is the averaged  $T_M$  data for the rayon/vacuumed data (T $_{\rm M}({\rm clean}))$  plotted vs. the averaged T $_{\rm M}$  1-OD film data  $(T_{\mu}(film))$ . If the presence of the 1-OD monolayer does not affect  $T_A(film)$  or  $T_M(film)$  then all the points would be expected to fall on or around the solid line which has slope equal to 1 and yintercept equal to 0. If it is assumed that each point has a probability of 0.50 of lying above the line, the data in Figure 24 may be modeled by the binomial distribution (Meyer, 1975). This procedure shows there is a probability of 0.03 of any seven points lying above the line. Therefore, the fact that all but one of the points lie above this line implies that  $T_A(film)$  and  $T_M(film)$  are larger than  $T_A(clean)$  and  $T_M(clean)$ , respectively.

Since each data point in Figure 24 represents a pair of averages (i.e.  $(T_A(clean), T_A(film)); (T_M(clean), T_M(film)))$  with an associated standard deviation, t-tests were performed on each to check if any have  $T_A(film)$  significantly different statistically from  $T_A(clean)$  or



Figure 24. The effect of the 1-OD monolayer on  $T_A$  and  $T_M$ . Data key is: O -  $T_A$ (film) vs.  $T_A$ (clean) with  $z_c = 300$  um, O -  $T_M$ (film) vs.  $T_M$ (clean) with  $z_c = 300$  um.

 $T_M$ (film) significantly different statistically from  $T_M$ (clean). Because the individual distribution modes or averages could be assumed to be normally distributed around their true values a t-test could be applied to pairs of averaged values of parameters derived from nonnormal distributions.

The result of this test is that no differences are found to be significant at the 0.05 level. This null result is most likely due to the small sample size for each average and the relatively small differences in the clean and film-covered timescales. The fact that there is a consistent trend among all timescales suggests that the presence on the 1-OD monolayer increased both  $T_A$  and  $T_M$  in the interfacial layer.

The hydrodynamical implication of this inference is that the presence of the monolayer slowed the eddies. This is to be expected due to the increased shear stress at a film-covered gas/liquid interface (Davies, 1972). The film's resistance to deformation and stretching causes this increase in shear stress. In turn, this leads to an increase in the rigidity of the gas/liquid interface.

Since it is known that the fluorescence fluctuations were faster than the hydrodynamical fluctuations,  $T_A$  and  $T_M$  from each rayon/vacuum cleaned experiment were compared to calculated values of the turbulence timescales,  $T_m$  and  $T_u$ . While there are four possible intercorrelations of these values, only the correlation of  $T_A$  with  $T_m$  and  $T_M$  with  $T_u$  will be discussed. Comparison of  $T_A$  with  $T_u$  and  $T_M$  with  $T_m$ results in large discrepancies between the measured and calculated timescales. In addition, the assumption that  $T_A$  is equal to  $T_U$  while  $T_M$  is equal to  $T_m$  makes no physical sense since in most cases  $T_A$  is greater than  $T_M$ . This implies that for the turbulence in the tank,  $T_U > T_m$  which is in contradiction of Eq. 25.

While there is no firm theoretical reason for assuming that  $T_A$  should be related to  $\tau_m$  and  $T_M$  to  $\tau_u$ , a heuristic argument may be made to show such relations are plausible.  $\tau_m$  represents the average time-scale of the turbulence and  $T_A$  represents the average timescale of the fluorescence fluctuations. Because the fluorescence fluctuations are caused by the aqueous-phase turbulence it is reasonable to assume that  $T_A$  will be equal to  $\tau_m$ . Therefore, it is expected that  $T_A$  and  $\tau_m$  will be highly correlated.

As mentioned previously,  $T_u$  represents the timescale of the eddies that are responsible for the viscous dissipation of the turbulent kinetic energy. Because the macro-scale eddies contain the majority of this kinetic energy at any one time, it may be reasoned that the dissipation scale eddies will predominate in terms of population number. In other words, it will take a large number of small eddies to dissipate the energy of one large eddy. Therefore, it might be expected that for reasonable turbulence intensities, the mode of the distribution of eddie timescales will be defined by  $T_u$ . If this is the case then it is expected that  $T_u$  will correlate with  $T_M$ .

Figure 25 shows a plot of  $T_A$  versus  $T_m$  and Figure 26 is  $T_H$  versus  $T_{_U}$ . Linear regression of the respective data sets in Figures 25 and 26 shows that each had a correlation coefficient r = 0.97. These



Figure 25. Plot of measured  $T_A$  vs.  $\tau_m$  calculated using Eq. 23. Key for rayon/vacuum cleaned interface data is:  $\Box - z_c = 150$  um,  $\triangle - z_c = 300$  um,  $\Diamond - z_c = 450$  um. Key for the 1-0D monolayer covered interface data is:  $\bigcirc - z_c = 300$  um. Solid line is slope of 1 with zero intercept.



Figure 26. Plot of measured  $T_{\rm M}$  vs.  $\tau_{\rm U}$  calculated using Eq. 24. Data key is identical to Fig. 25.

comparisons showed that  $T_A$  accurately predicted  $T_m$  while  $T_M$  consistently overestimated  $T_u$ . The overestimation of  $T_u$  by  $T_M$  may be explained by the relatively low  $Re_t$  causing the microscales of the turbulence to be underdeveloped. Therefore, Eq. 25 might not have been an accurate estimate of the true  $T_u$  present.

The results shown in Figures 25 and 26 should be interpreted with caution due to the fact that  $T_A$  and  $T_\mu$  are Eulerian measurements of anisotropic turbulence and  $T_m$  and  $T_u$  are derived as Langrangian quantities for isotropic turbulence (Tennekes and Lumley, 1972). The difference between Eulerian and Langrangian quantities in relation to turbulence timescales is discussed in detail by Tennekes (1975). In addition, the differences between the two types of timescales becomes smaller as Re<sub>t</sub> decreases. Therefore it is expected that these effects were small in the low turbulence regime present in the tank. The effect of the anisotropic nature of the turbulence near the  $CO_2/H_2O$  interface on the timescales is harder to quantify.

Independent measurement of Q and L in the tank could confirm or refute the observed relations between  $T_A$  and  $T_m$  and between  $T_H$  and  $T_U$ . Unfortunately, it was not possible to perform these turbulence measurements in the time frame of this thesis. However, making the assumption that the empirical turbulence relations of Hopfinger and Toly (1976) Eqs. 21, 22, and 23 accurately estimated  $T_m$  and  $T_u$  in the tank allows additional analysis of the results of prediction of  $k_L$  detailed in the next section.

4.C. Prediction of  $k_i$ , Results and Discussion

The fluorescence fluctuation timescales were used to predict  $k_{L}$  using both the Higbie (1935) and Danckwerts (1951) models for both the 1-OD film and rayon/vacuum cleaned data. In the case of the Higbie (1935) model, this was done by substitution of  $T_{A}$  or  $T_{M}$  for  $\tau$  in Eq. 2. The predicted  $k_{L}$  values were then compared to the  $k_{L}$  data measured under identical turbulence and interfacial conditions. The plot of  $k_{L}$  calculated from  $T_{A}$  versus measured  $k_{L}$  is shown in Figure 27 and  $k_{L}$  calculated from  $T_{M}$  versus measured  $k_{L}$  is shown in Figure 28.

In Figures 27 and 28, it is obvious that prediction of  $k_L$  for a 1-OD monolayer covered gas/liquid interface by a surface renewal model results in very large discrepancies between experimental and calculated  $k_L$  values. However, the cleaned interface results show excellent correlation between  $k_L$  values calculated from the Higbie (1935) model and experimental determinations. Therefore, it may be concluded that surface renewal models are appropriate for clean interfaces but do not apply for film-covered interfaces. The most likely hydrodynamical interpretation of this result is that turbulence eddies do not completely renew the surface of a liquid where the interface is covered by an organic monolayer. This conclusion is supported by qualitative examination of the fluorescence fluctuation time series for CO<sub>2</sub> invasion through a clean and film-covered interface shown in Figures 13 and 15 respectively.



Figure 27. Application of the Higbie (1935) surface renewal model 1. Plot of k<sub>c</sub> calculated by substitution of T<sub>A</sub> for r in Eq. 2 vs. k<sub>c</sub> measured in the bulk experiments under similar turbulence conditions. Key for rayon/vacuum cleaned interface data is:  $\Box - z_c = 150$  um,  $\Delta - z_c = 300$  um,  $\Diamond - z_c = 450$  um. Key for the 1-0D monolayer covered interface data is:  $O - z_c = 300$  um. Solid line is slope of 1 with zero intercept.



Figure 28. Application of the Higbie (1935) surface renewal model. Plot of  $k_{\rm L}$  calculated by substitution of  $T_{\rm M}$  for  $\tau$  in Eq. 2 vs.  $k_{\rm L}$ measured in the bulk experiments under similar turbulence conditions. Data key is identical to Figure 27.

In Figure 13, the peak heights of the normalized fluorescence intensity fluctuations aperiodically return to a value of one where one is defined to be the average signal intensity at the starting pH. Since  $CO_2$  invasion will decrease pH and fluorescence intensity, the implication of this increase in signal to initial levels is that the sampling volume was completely replaced by fluid with pH at or near the starting pH. If this were not the case and the fluid in the interface was only being renewed up to some non-zero depth  $z_e$ , the peak height would not return to a normalized value of one. This increase in signal also demonstrates that the sampling spot size was small enough to resolve the smallest spatial scales present because the entire sampling area was renewed.

The surface concentration fluctuation data provides qualitative evidence that surface renewal was occurring at the rayon/vacuum cleaned gas/liquid interface. Therefore, Figure 13 represents direct experimental evidence in support of the applicability of surface renewal theory for gas/liquid interfacial mass transport. A result of this interpretation is that  $k_l$  values predicted by surface renewal models ought to correlate with experimental measurements. This is observed for the rayon/vacuum cleaned data of Figures 27 and 28.

A least-squares linear regression which force fit a straight line with zero y-intercept was performed on each rayon/vacuum cleaned data set. This type of regression was used since the theoretical slope and y-intercept are one and zero, respectively. It is assumed that if the Higbie (1935) model is accurate, a slope of one with zero intercept

would be observed for cleaned-interface data plotted as in Figures 27 and 28. Therefore, the slopes of the linear regressions from Figure 27 and 28 were tested for statistically significant deviation from one by use of a t-ratio (Bennett and Franklin, 1954). This shows that prediction of  $k_{\rm L}$  by  $T_{\rm M}$  results in a slope which is not statistically different from one at the 0.05 level. In contrast, the slope of the line from prediction of  $k_{\rm L}$  by  $T_{\rm A}$  is seen to be significantly different from one at the 0.05 level.

The results from the linear regression would seem to suggest that use of  $T_{\mu}$  in the Higbie (1935) model for a clean gas/liquid interface results in accurate prediction of  $k_{\rm L}$  over the range of turbulence conditions studied. However, qualitative inspection of Figure 28 shows that  $k_{\rm L}$  was predicted accurately for higher turbulence intensities but overestimated for low regime. This overestimation of  $k_{\rm L}$  was also observed for the 1-OD film data for all turbulence intensities which suggests that for low turbulence intensities, the rayon/vacuum cleaned interface behaved similarly to a film-covered interface. This interpretation of the data in Figure 28 supports the explanation that the transition in slope observed in the bulk  $k_{\rm L}$  measurements (Figure 21) was due to a transition in fluid mechanical dependence of the transport process. Additional evidence for this hypothesis is provided by the results in the following chapter.

Explanation of the poor prediction of measured transport rates for the case of the 1-OD film data is provided by examination of the 1-OD monolayer CO<sub>2</sub> invasion fluorescence fluctuation time series. In

contrast to the rayon/vacuum cleaned time series shown in Figure 13, it shows that after the initial decay of the fluorescence signal, the maximum recorded relative signal level never rises above 0.6. This implies that the aqueous surface microlayer was not completely renewed by the turbulence eddies. Therefore, surface renewal models would not be expected to apply. This is observed in both Figures 27 and 28 in the poor correlation of predicted with measured k<sub>1</sub> values.

Further interpretation of the results of the application of the Higbie model must be made with caution. Since Q and L at the  $CO_2/H_2O$  interface were not measured directly,  $T_m$  and  $T_u$  there are estimated by use of calculated values for Q and L in Eqs. 24 and 25. Therefore, the true  $T_m$  and  $T_u$  at the  $CO_2/H_2O$  interface are not known. As a result, it is not known definitively if  $T_m$  is the true  $T_u$  and  $T_A$  is the true  $T_m$  present at the  $CO_2/H_2O$  interface. Therefore, there is a certain ambiguity in the interpretation of  $T_A$  and  $T_M$ .

If  $T_A$  and  $T_M$  are accurate estimates of the true turbulence timescales, this data provides additional evidence that the dissipation model provides a more accurate representation of the gas/liquid exchange process than the large-eddy model. It has already been observed that if Eq. 24, or symbolically  $T_m$ , is substituted into Eq. 2 for T, the functional form of the large eddy model, Eq. 9, is obtained. Similarly, if Eq. 25 or  $T_u$ , is substituted for T, the dissipation model, or Eq. 11, results. Therefore, if  $T_M$  is an estimate of the true  $T_u$ , correlation of  $T_M$  with both  $k_L$  and the calculated value for  $T_u$  implies that the dissipation model provides a
hydrodynamically correct model of the gas/liquid transport process. The observation that  $T_A$  does not predict  $k_L$  accurately but is correlated with the calculated value for  $T_m$  suggests that the large-eddy model is not a realistic description of the exchange process. This data provides additional evidence for the conclusion that prediction of  $k_L$  by Eq. 11 is to be preferred over Eq. 9.

Since it has already been observed that the fluorescence intensity fluctuations tracked the motion of the water in the aqueous microlayer,  $f_T(T)$  is approximated by  $f_T(T)$ . The Danckwerts (1951) model could be applied by substitution of  $f_T(T)$  for  $f_T(T)$  in Eq. 3 and the result integrated to find  $F_t(t)$ . From this result an empirical  $\phi_t(t)$ could be calculated from Eq. 4. However, determination of  $k_L$  by direct numerical integration of Eq. 6 using the empirical form for  $\phi_t(t)$ is troublesome since the integrand is singular at the origin.

In order to apply Eq. 6,  $f_{\rm T}({\rm T})$  is fit to an eighth order polynomial of the form

 $f_{T}(T) = (p_{0} + p_{1}T + ... + p_{n}T^{n} + ... + p_{8}T^{8})$ (42) where the  $p_{n}$  are the coefficients of the polynomial approximation calculated so that  $f_{T}(T)$  is normalized with respect to the interval T = 0 to  $T_{m}$  where  $T_{m}$  is the maximum peak width observed. Although physical intuition suggests that there is zero probability of observing a peak with zero width, a constant term  $p_{0}$  was fit to  $f_{T}(T)$ . Inclusion of  $p_{0}$  simplified the regression since it allowed a standard least squares polynomial regression routine to be used. Definition of  $f_{T}(T)$  in the manner of Eq. 42 leads to Eq. 3 having an analytic

solution for  $F_t(t)$  of the form

$$F_{t}(t) = (p_{0}t + p_{1}t^{2}/2 + ... + p_{n}t^{n+1}/(n+1) + ... + p_{8}t^{9}/9)$$
(43)

This result is used in Eqs. 3 and 4 to calculate  $\phi_{c}(t)$  which is

$$\phi_{t}(t) = N^{-1}(1 - (p_{0}t + p_{1}t^{2}/2 + ... + p_{n}t^{n+1}/(n+1) + ... + p_{8}t^{9}/9)) \quad (44)$$

where the normalization constant N is now defined by integration of  $\phi_t(t)$  from zero to  $t_m$ , where  $t_m$  is the maximum lifetime and is equal to  $T_m$ . N has the explicit form

$$N = t_{m} - (p_{0}t_{m}^{2}/2 + p_{1}t_{m}^{3}/6 + ... + p_{n}t_{m}^{n+2}/((n+1)(n+2)) + ... + p_{8}t_{m}^{10}/90)$$
(45)

Substitution of  $\phi_t(t)$  defined as described by Eq. 44 into Eq. 6 allows the integration to be performed analytically over the finite limits 0 and  $t_m$ . The result for  $k_i$  is

$$k_{L} = (D/\pi)^{1/2} N^{1} (2t_{m}^{1/2} - (2p_{0}t_{m}^{3/2}/3 + p_{1}t_{m}^{5/2}/5 + ... + p_{n}t_{m}^{n+3/2}/((n+1)(n+3/2)) + ... + 2p_{8}t_{m}^{19/2}/171))$$
(46)

The initial polynomial fit to  $f_T(T)$  as given by Eq. 42 was performed with the polynomial least squares routine POLFIT.FOR (Bevington, 1969) by the FORTRAN-77 (Microsoft v3.31, Microsoft, Redmond, WA) program AVGFIT.FOR which is listed in Appendix A. The subsequent calculation of  $k_L$  was done by the TurboPascal (V3.01, Borland International, Scotts Valley, CA) program KADANCK.PAS which is listed in Appendix A.

The results from the application of the Danckwerts (1951) model are shown in Figure 29. There is excellent correlation of predicted and measured  $k_L$  for the rayon/vacuum cleaned data. The 1-OD results show poor prediction of the experimentally determined  $k_L$  values.



Figure 29. Application of the Danckwerts (1951) surface renewal model. Plot of k<sub>L</sub> calculated by use of  $f_T(T)$  and the procedure described in Section 4.C. vs. k<sub>L</sub> measured in the bulk experiments under similar turbulence conditions. Key for rayon/vacuum cleaned interface data is:  $\Box - z_c = 150$  um,  $\Delta - z_c = 300$  um,  $\Diamond - z_c = 450$  um. Key for the 1-OD monolayer covered interface data is:  $\Box - z_c = 300$  um. Solid line is slope of 1 with zero intercept.

These results are in agreement with those from the application of the Higbie (1935) model. Both show that surface renewal models provide an appropriate physical description of the transport process for a clean gas/liquid interface. In addition, they also support the conclusion that surface renewal models do not apply for gas transport through film-covered gas/liquid interfaces.

In a manner similar to that used for the Higbie (1935) model results, a least-squares linear regression which force fit a straight line with zero y-intercept was performed on the rayon/vacuum cleaned data set. The results from this procedure show that the data resulting from the application of the Danckwerts (1951) model has a slope which is significantly different from one at the 0.05 level. This is in contrast to the application of the Higbie (1935) model which predicted  $k_L$  by use of  $T_M$ . This former result has a slope which is not significantly different from one. However, it should not be concluded that prediction of  $k_L$  by use of  $T_M$  in the Higbie model is more accurate overall than by use of the Danckwerts (1951) model based on the results from the linear regressions.

Qualitative comparison of Figures 27 and 28 shows that the Higble (1935) model predicts  $k_{\rm L}$  more accurately for higher turbulence intensities while the Danckwerts (1951) model is more accurate at lower turbulence intensities. It is possible that the underestimation of  $k_{\rm L}$  for higher turbulence intensities by the Danckwerts model is an artifact of the data analysis procedure. If this is the case it implies that the Danckwerts (1951) model may provide a more realistic

conclude that this was occurring on the basis of these results alone. In the next chapter, the results from the calculation of eddy approach distances from the fluorescence fluctuation time series such as shown in Figures 13 and 15 for both clean and 1-OD monolayer covered interfaces are discussed. These results support the explanations and interpretations given in this chapter.

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description of the gas/liquid transport process over a broader range of turbulence conditions. This result makes sense based on physical intuition since it is unreasonable to assume that each eddy resides at the interface for the same length of time. Empirically, this result is supported by the  $f_T(T)$  shown in Figure 23. If only one peak width were observed at the  $CO_2/H_2O$  interface, these distributions should resemble Dirac delta functions centered on the dominant peak width.

This underestimation of  $k_1$  for the Danckwerts (1951) model may have arisen through the digitization of the fluorescence fluctuation time series and subsequent analysis. The digital sampling itself filtered out frequencies above the Nyquist frequency limit which is defined as one half of the sampling rate (Bendat and Piersol, 1971). This filtering is mathematically equivalent to the rejection of events with small timescales. In addition, the algorithm used to calculate peak widths could not detect peak widths below a cutoff timescale defined by 2icts. Also, the regression procedure used to determine data slopes for determining peak beginnings and peak endings acted as a low-pass filter in the frequency domain of the time series. While these parameters were calculated to minimize loss of these fast peaks, some attenuation of the low timescale (high frequency) part of the data was unavoidable. Since the events with small timescale are most efficient in promoting mass transport, their loss could have resulted in an underprediction of  $k_1$  by the Danckwerts (1951) model.

This underprediction is not observed for the low turbulence intensity data since the fluctuation frequencies were much lower.

Therefore, the Nyquist limit of the data sampling rate is not as close to the observed fluctuation frequencies. Also, the signal to noise ratio is better in the data sets with lower turbulence intensity than with higher turbulence. This allows more accurate peak width determination.

4.D. Interfacial [CO2] Fluctuation Measurement Conclusions

Figures 25 and 26 provide evidence that the empirical relations of Hopfinger and Toly (1976), which describe Q and L for grid-generated aqueous phase turbulence, may be applied to the present experimental apparatus. This is demonstrated by the correlation between the calculated turbulence timescales and measured concentration fluctuation timescales. Further verification of this could be achieved by independent measurement of Q and L by future efforts in the present experimental apparatus.

Figures 28 and 29 show that  $k_{\rm L}$  may be calculated using a surface renewal model with directly measured surface element timescales for a clean gas/liquid interface using either the Higbie (1935) or Danckwerts (1951) model. These measurements also suggest that gas/liquid transport models based on the dissipation scales are more accurate than those based on the macro scales. The obvious correlation of  $k_{\rm L}$ values calculated with both the Higbie (1935) and Danckwerts (1951) models with measured  $k_{\rm L}$  data demonstrate that surface renewal models of gas/liquid transport adequately described the hydrodynamical dependence of k<sub>l</sub> for high turbulence intensities and clean gas/liquid interfaces. This is a step forward in the understanding of the basic mechanisms of gas/liquid mass transport since it represents the first time that surface renewal models have been tested with directly measured timescale data. However, these results should not be interpreted to mean that surface renewal models apply universally to gas/liquid interfaces without regard to interfacial cleanliness and/or turbulence intensity. The 1-0D film-covered interface and low turbulence intensity rayon/vacuum cleaned results suggest that film-covered interfaces and low turbulence intensity regimes cannot be described by surface renewal models.

It was hypothesized from qualitative examination of the fluorescence fluctuation time series that the presence of a 1-OD monolayer prevents the turbulence eddies from completely renewing the gas/liquid interface. Incomplete surface renewal may also have caused the poor prediction of  $k_L$  for the low turbulence intensity cleaned-interface results. If this were the case it would explain the failure of surface renewal models to predict  $k_L$  for low turbulence intensities and at film-covered interfaces. However, it is not possible to conclude that this was occurring on the basis of these results alone. In the next chapter, the results from the calculation of eddy approach distances from the fluorescence fluctuation time series such as shown in Figures 13 and 15 for both clean and 1-OD monolayer covered interfaces are discussed. These results support the explanations and interpretations given in this chapter.

#### 5. Eddy Approach Distance Calculations

#### 5.A. Introduction

The measurements of  $k_{L}$  and surface fluorescence timescales as a function of turbulence intensity discussed in Chapters 3 and 4, respectively, suggested that the hydrodynamical dependence of the gas/liquid mass transport process is different for clean and film-covered interfaces. These same results also provided evidence that there is a difference in the fluid mechanical dependence of  $k_{L}$  between low and high turbulence intensities for a clean  $CO_2/H_2O$  interface. It was hypothesized that these changes might be explained by a transition from stagnant film behavior at the interface to renewal of the liquid surface by the turbulence eddies. However, this could not be proven conclusively by either the bulk  $k_{L}$  data of Chapter 3 or the surface lifetime data of Chapter 4.

Definitive verification of this explanation might be provided by information regarding the approach of turbulence eddies towards the gas/liquid interface. Measurement of eddy approach distances would show the conditions under which the turbulence eddies are fully renewing the gas/liquid interface as well as the regimes under which the liquid surface is not renewed. The basic measurements necessary to obtain the eddy approach data might include direct measurement of the  $[CO_2]$  gradient in the aqueous surface microlayer for clean and filmcovered liquid surfaces either as a function of the various turbulence parameters. If each eddy has a characteristic [CO<sub>2</sub>] profile, the eddy approach distances could be calculated from the surface gradient data.

Unfortunately, attempts to measure the  $[CO_2]$  gradient directly in the present apparatus using the LIF-DCFS technique were unsuccessful. This failure was due to the presence of small waves on the  $CO_2/H_2O$ interface. These waves were generated by the oscillatory motion of the grid and the turbulence eddies themselves. While they were not thought to have affected the surface fluorescence measurements, the vertical motion of the interface caused by such low-amplitude waves prevented imaging a small enough section of the aqueous surface microlayer to resolve the turbulence eddies.

Even though direct measurement of the surface  $[CO_2]$  gradient was not possible, it was found that the eddy approach distances could be estimated from surface fluorescence fluctuation time series data such as shown in Figures 13 and 15 using an idealized description of the pH profile in the aqueous surface microlayer. The details of this procedure are described in the following section. The results from these calculations support the hydrodynamical transition interpretation of both the bulk  $k_L$  and surface lifetime data presented in Chapters 3 and 4 respectively. In addition, the eddy approach distances are used in the Whitman (1923) film model and with the surface fluctuation timescales in the surface penetration model of Harriott (1962) to predict  $k_L$ . This allows the first test of these models with experimentally determined input parameters.

# 5.B. Calculational Procedure

Surface fluorescence fluctuation time series such as those shown in Figures 13 and 15 represent measurements of depth-integrated fluorescence intensity fluctuations. Therefore, the instantaneous fluorescence signal observed,  $F_{\rm T}$  (ADC-counts) may be written as

$$F_{\tau} = \int_{0}^{z_c} F(z) dz$$
(47)

where F(z) (ADC-counts cm<sup>-1</sup>) is the fluorescence intensity at z and F(z)dz (ADC-counts) is the fluorescence signal from the layer of water with depth z and thickness dz. F(z) is defined by the pH gradient in the aqueous surface microlayer, pH(z) and the excitation intensity, I(z). Therefore, use of Eq. 33 shows F(z) is

 $F(z) = k(pH(z))I_0 10^{-ecz}$ (48) where I(z) is determined by Eq. 33 and k(pH(z)) (ADC-counts watts<sup>-1</sup>) is defined as the depth-dependent fluorescence intensity coupling constant. k(pH(z)) represents the fluorescence radiation observed from water with depth z and pH is defined by pH(z) for unit incident excitation intensity. Substitution of Eq. 48 in Eq. 47 gives

$$F_{\tau} = \int_{0}^{z_c} \mathbf{k}'(\mathbf{p}\mathbf{H}(z))\mathbf{10}^{-\mathbf{e}cz} dz$$
(49)

where k'(pH(z)) denotes the quantity  $I_0k(pH(z))$ .

In Eq. 49, pH(z) is determined by the dynamics of the turbulence

phase,  $pH_b$ . Therefore, since each eddy renews the fluid in the surface layer up to  $z_e$ , for the lower region

$$pH(z) = pH_b; \quad z \ge z_e \tag{50}$$

It should be noted that each turbulence eddy has a distinct  $z_e$ . In addition,  $z_e$  varies stochastically from eddy to eddy due to the statistical nature of the hydrodynamics of turbulence. Therefore,  $z_e$  is not equivalent to  $\delta$  in the Whitman (1923) film model.

The upper layer of the interfacial region extends over the range

 $0 \le z < z_e$ . In this region it is assumed that the water is saturated with  $CO_2$ . This uniform  $[CO_2]$  leads to a constant pH(z) in the upper layer defined as

 $pH(z) = pH_s; \quad 0 \le z < z_e$ (51) where  $pH_s$  is the aqueous pH for  $C(z) = C_s$  where C(z) is the concentration gradient in the interfacial layer.

The two-layer model is shown diagramatically in Figure 30. Defined in terms of momentum and mass viscous sublayers, the lower region may be thought of as the momentum viscous sublayer. Below the depth defined by  $z_e$ , mass transport is mainly due to the motion of the turbulence present. Transport in the interfacial region is not defined since C(z) is uniform. However, in reality it is understood that the gas must move into this region mainly by molecular diffusion. Therefore, the interfacial region may be loosely viewed as the molecular diffusion sublayer. The major difference in this interpretation from that standardly used is that in the two-layer model, eddy motions may persist up to the interfacial plane.

The two-layer model provides a very idealized view of pH(z). While the approximation that  $pH(z) = pH_b$  in the lower region is thought to be fairly realistic, it is understood that pH(z) in the upper region will not be constant, but will be affected by molecular diffusion of all aqueous phase carbonic acid species in addition to the hydration of  $CO_2$  to  $H_2CO_3$ . Strictly speaking, therefore, pH(z) in the upper region should be determined by solving a set of coupled partial differential equations which incorporate the  $CO_2$  hydration



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Figure 30. Schematic diagram of the two-layer model. The top trace is a plot pH(z). The bottom plot is the corresponding C(z). Also shown for reference is  $z_c$ .

kinetics of Eq. 34. Unfortunately, this more realistic definition of pH(z) is sufficiently complex that  $z_e$  cannot be determined by a closed form analytic solution of Eq. 49. Even the relatively simple form for pH(z) defined by a linear pH gradient in the interfacial region leads to a form for  $z_e$  which is prohibitively complex computationally. In contrast, the two-layer model for pH(z) leads to an analytic solution of Eq. 49 for  $z_e$ . Therefore, the two-layer model was chosen for use in spite of its relative simplicity. As will be discussed below, evidence in support of this choice is that the two-layer model gives estimates of  $z_e$  which are reasonable in terms of commonly accepted viscous sublayer depths (Kitaigorodskii, 1984).

Incorporation of the model shows that Eq. 49 can be rewritten as

$$F_{T} = \int_{0}^{z_{e}} k'(pH_{s}) 10^{-ecz} dz + \int_{z_{e}}^{z_{c}} k'(pH_{b}) 10^{-ecz} dz$$
(52)

Since k'(pH(z)) is a function of pH only and pH is constant in each layer,  $k'(pH_s)$  and  $k'(pH_b)$  are both constants. Therefore, Eq. 52 is analytically integrable and  $F_\tau$  is seen to be

$$F_{\tau} = (1 - \exp[-bz_{e}])k'_{s}/b + (\exp[-bz_{e}] - 0.01)k'_{b}/b$$
(53)  
where  $k'_{s} = k'(pH_{s}), k'_{e} = k'(pH_{b}), \text{ and}$ 

$$b = 2.303ec$$
 (54)

and by definition of  $z_c$ ,  $\exp[-bz_c] = 0.01$ .

The fluorescence intensity fluctuation data (e.g. Figures 13 and 15) were normalized by the maximum fluorescence intensity  $F_{T,0}$  (ADC-counts) measured during the course of an experiment. However,  $F_{T}$  as

written in Eq. 53 is not normalized. Therefore, solution of Eq. 53 for  $z_e$  by use of the normalized experimental fluorescence intensities requires that  $F_T$  be normalized by  $F_{T,0}$ .

The maximum fluorescence intensity is observed when the pH of the solution is at its maximum value, i.e.,  $pH_0$ . Since increasing  $[CO_2]$  lowers pH,  $pH_0$  occurs prior to the start of  $CO_2$  invasion or when  $\{CO_2\} = 0$ . In addition, a constant  $\{CO_2\}$  implies constant pH. Therefore, before  $CO_2$  invasion begins there is no pH gradient anywhere in the aqueous phase and pH(z) there is

$$pH(z) = pH_0; \quad 0 \le z \tag{55}$$

Therefore,  $F_{T,0}$  is defined by Eq. 49 to be

$$F_{T,0} = \int_{0}^{z_c} k'(pH_0) \exp[-bz] dz$$
(56)

Eq. 56 may be integrated to give

$$F_{1,0} = 0.99 k' (pH_0) / b$$
(57)

where the constant 0.99 follows from the definition of  $z_{\rm c}$ .

Division of Eq. 53 by Eq. 57 shows that the normalized fluorescence intensity  $\hat{F}_{\rm T}$  is given by

 $\hat{F}_{T} = (1/0.99)(k'_{s}/k'_{0} - 0.01k'_{e}/k'_{0} + (k'_{e}/k'_{0} - k'_{s}/k'_{0})\exp[-bz_{e}]) \quad (58)$ where  $k'_{0} = k'(pH_{0})$ .

Integration of Eq. 49 once with  $k'(pH(z)) = pH_s$  and again with  $k'(pH(z)) = pH_0$  shows that the ratio  $k'_s/k'_0$  is equal to the ratio of the fluorescence intensities at  $pH_s$  and  $pH_0$ . Similar integration performed with  $k'(pH(z)) = pH_b$  shows that  $k'_e/k'_0$  is equal to the ratio

of the intensities at  $pH_b$  and  $pH_0$ . These intensity ratios are predictable for any two pH values by use of a fluorescence vs. pH calibration curve of the form shown in Eq. 37. Therefore all the variables in Eq. 58 are known except  $z_e$ . Rearrangement of Eq. 58 shows that  $z_e$  is given by

$$z_{e} = (-1/b) \ln\{(0.99\hat{F}_{T} + 0.01/A_{e} - 1/A_{s})/(1/A_{e} - 1/A_{s})\}$$
(59)

where

$$A_{e} = k_{0}^{\prime} / k_{e}^{\prime} \tag{60}$$

and

$$A_{s} = k_{0}'/k_{s}'$$
(61)

Eq. 59 allows calculation of  $z_e$  by a simple formula which is easily applied by use of a computer.

In Eq. 59, b is known from measurements of the optical density of the solution and the concentration of OG.  $\hat{F}_{T}$  is defined to be the maximum normalized fluorescence intensity observed during a given surface renewal event. These events are seen as the peaks in the normalized fluorescence fluctuation time series shown in Figures 13 and 15. Calculation of  $A_{e}$  and  $A_{s}$  requires knowledge of  $pH_{0}$ ,  $pH_{s}$ , and  $pH_{b}$ .  $pH_{0}$  is easily determined by measurement of initial pH with a pH electrode.  $pH_{s}$  is calculated from  $pH_{0}$  and the measured atmospheric pressure. However, determination of  $pH_{b}$  is more complex because it changes over the course of an experiment.

Since the decrease in pH of the bulk aqueous phase is caused by the increase in  $[CO_2]$ , the flux of  $CO_2$  into the water column determines pH<sub>b</sub> during the course of an experiment. For a gas/liquid transport system such as  $CO_2/H_2O$  in this pH range, the average flux of  $CO_2$  into the water is assumed to be described by Eq. 1. For this case the mean change in  $[CO_2]$  with time is given by Eq. 32. Rearrangement of Eq. 32 shows that  $C_b(t)$  is given by

$$C_{b}(t) = C_{s}(1 - \exp[k_{1}t/H])$$
 (62)

Since  $C_s$ ,  $k_L$ , t, and H are known,  $C_b(t)$  can be estimated from Eq. 62. This allows the mean  $pH_b$  to be calculated by solution of the aqueous phase charge balance equation (Appendix B). However, due to smallscale concentration inhomogeneities in the tank, the actual pH of the arriving eddy may be different from  $pH_b$  calculated by use of Eq. 62. However, the results suggest that this was not a major problem in the calculation.

Calculation of  $\hat{F}_{T}$ ,  $A_{e}$ , and  $A_{s}$  were done using the FORTRAN IV-RT program APPRCH.FOR by application of Eqs. 60, 61, and 62. These results were then used by the subroutine APCALC.FOR to determine  $z_{e}$  through the use of Eq. 59. Both of these programs are listed in Appendix A.

5.C. Eddy Approach Distance Calculation Results and Discussion

Since no new experimental techniques were necessary, the data used in the eddy approach distance calculations were collected as part of the interfacial [CO<sub>2</sub>] fluctuation experiments. The twelve experiments selected for use in the calculations had known, accurate pH vs. fluorescence calibration curves and spanned the range of turbulence and interfacial conditions of interest. The relevant parameters for these experiments are  $z_c = 300$  um with  $\omega = 3.3$  to 5.8 Hz, Z = 7.5 or 12.5 cm, and s' = 2.5 cm. From the twelve experiments, eight were performed with rayon/vacuum cleaned interfaces and four were performed with a 1-OD monolayer present on the water surface.

Following the calculational procedure described in Section 5.B.,  $\hat{F}_{\rm T}$  was found for every relative fluorescence intensity peak detected by PWIDTH.FOR for each of the twelve experiments. After all peaks detected in an individual experiment had been analyzed, the average approach distance  $\tilde{z}_{\rm e}$  (um), was calculated by the subroutine APPAVG.FOR which was called through APPRCH.FOR. The rayon/vacuum cleaned data shown in Figure 15 have  $\tilde{z}_{\rm e} = 40$  um and the 1-OD monolayer data shown in Figure 13 have  $\tilde{z}_{\rm e} = 70$  um.

To allow additional analysis and application of these results, the  $z_e$  data was sorted into bins to allow estimation of an eddy approach distance distribution,  $f_z(z_e)$  for each experiment. This was done by the FORTRAN IV-RT subroutine APSORT.FOR (listed in Appendix A) which was called by APPRCH.FOR. Figure 31 shows  $f_z(z_e)$  measured for high and low turbulence intensity rayon/vacuum cleaned interfaces. Figure 32 shows  $f_z(z_e)$  for similar turbulence conditions but with 1-OD monolayer covered interfaces.

In the case of the rayon/vacuum cleaned interface experiments,  $f_z(z_e)$  for the high turbulence intensity data shows that most of the eddies have  $z_e = 0$  um. This means that in this case, the majority of the eddies fully renew the gas/liquid interface. For the low



Figure 31. The calculated eddy approach distance density function  $f_z(z_e)$  for high and low turbulence intensity rayon/vacuum cleaned interfaces. The solid line is the high turbulence intensity data which had  $z_e = 300$  um and grid parameters  $\omega = 5.8$  Hz, Z = 7.5 cm, and s' = 2.5 cm. The dashed line is the low turbulence intensity data which had  $z_e = 300$  um and grid parameters  $\omega = 4.2$  Hz, Z = 12.5 cm, and s' = 2.5 cm.



Figure 32. The calculated eddy approach distance density function  $f_z(z_e)$  for high and low turbulence intensity 1-OD monolayer covered interfaces. The solid line is the high turbulence intensity data which had  $z_c = 300$  um and grid parameters  $\omega = 5.8$  Hz, Z = 7.5 cm, and s' = 2.5 cm. The dashed line is the low turbulence intensity data which had  $z_c = 300$  um and grid parameters  $\omega = 4.2$  Hz, Z = 12.5 cm, and s' = 2.5 cm.

turbulence intensity situation,  $f_z(z_e)$  is seen to flatten out and show a greater number of eddies with  $z_e > 0$  um and fewer with  $z_e = 0$  um. This suggests that as the turbulence intensity decreases, fewer eddies have the dynamic thrust necessary to fully renew the liquid surface. However, even at the lowest turbulence intensities studied the eddies fully renew the cleaned aqueous surface a significant fraction of the time. These results quantitatively show why surface renewal models of gas/liquid mass transport provide an accurate physical description of the gas exchange process at clean gas/liquid interfaces. Also, if the trend observed in  $f_z(z_e)$  continues as the turbulence intensity decreases further, the results imply that surface renewal models might become inapplicable for even lower turbulence intensities due to incomplete renewal of the liquid surface by the eddies.

The change in  $f_{g}(z_{e})$  shown in Figure 31 also supports the interpretation that the break in the slope observed in the cleaned-interface bulk  $k_{L}$  data in Figure 21 was due to a change in the hydrodynamics of the transport process. Similarly, Figure 31 also supports the explanation that the overprediction of  $k_{L}$  for low turbulence intensities by the Higbie (1935) surface renewal model was caused by incomplete renewal of the liquid surface by the turbulence eddies. In both Figures 21 and 28, the anomalous behavior is thought to be due to transitions from full surface renewal to partial renewal or film-like behavior of the aqueous surface as the turbulence intensity decreased. Figure 31 shows that the eddies are less likely to fully renew the interface at low turbulence intensities. The observed behavior in

both Figures 21 and 28 is explained if all of the eddies failed to renew the interface at some lower turbulence intensity.

In contrast to the rayon/vacuum cleaned results,  $f_z(z_e)$  for the high turbulence intensity 1-0D monolayer data shown in Figure 32 shows that no eddies are seen to have  $z_e = 0$  um. This implies that complete surface renewal is never observed at the film-covered interface. For the low turbulence intensity data, although there is little change in the shape of  $f_z(z_e)$ , the peak is shifted towards larger  $z_e$ . This is expected since in the presence of a damping monolayer, less energetic eddies would not be able to penetrate as far into the viscous sublayer. This quantitatively demonstrates why surface renewal models are unable to predict  $k_L$  measured at 1-0D monolayer covered interfaces. In particular, since complete surface renewal does not occur there, surface renewal models do not provide a valid physical description of the transport process.

The qualitative interpretation of the fluorescence fluctuation peak heights presented in Section 4.D. for the rayon/vacuum cleaned and 1-OD monolayer covered interfaces is verified by comparison of Figure 31 with Figure 32. In Section 4.D., it was argued that the peak height served as a qualitative indicator of the extent of renewal of the aqueous surface. This observation is supported by the data presented in this chapter because the high turbulence intensity rayon/vacuum cleaned interface showed eddies completely renewing the aqueous surface. In contrast, eddies at the 1-OD monolayer covered surface were never observed to completely renew the interface.

# 5.D. Prediction of k,

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In addition to supporting earlier hypotheses made concerning the bulk  $k_{\rm L}$  and surface timescale data in Chapters 3 and 4 respectively,  $\dot{z}_{\rm e}$  and  $f_{z}(z_{\rm e})$  are used to predict  $k_{\rm L}$  with the Whitman (1923) film model and Harriott (1962) surface penetration model respectively. This allows the first test of these models using empirically determined input parameters. This provides additional information on the hydrodynamical dependence of the transport process under the conditions studied.

# 5.D.1. Application of the Whitman Stagnant Film Model

The Whitman (1923) stagnant film model was tested by substituting  $\ddot{z}_{\rm e}$  for  $\delta$  in Eq. 14 where D is 1.76 x 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup> as given by Ackgerman and Gainer (1972). The predicted k<sub>L</sub> values were then compared to experimental determinations carried out as discussed in Section 3.B. under similar interfacial and turbulence conditions. The results are shown in Figure 33.

The 1-OD monolayer covered  $\bar{z}_e$  data show excellent prediction of the experimentally determined  $k_l$  values for both high and low turbulence intensities. The rayon-vacuum cleaned interface  $\bar{z}_e$  data show fair prediction for the low turbulence intensities but poor prediction for the high turbulence intensities. This suggests that at low turbulence intensities, the hydrodynamics of the eddies at the rayon/vacuum



Figure 33. Application of the Whitman (1923) model. Plot of  $k_{\rm L}$  calculated by substitution of  $\dot{z}_{\rm e}$  for  $\delta$  in Eq. 14 vs.  $k_{\rm L}$  measured in the bulk experiments under similar turbulence and interfacial conditions. Data key is:  $\Omega$  - rayon/vacuum cleaned interface,  $z_{\rm c}$  = 300 um,  $\Omega$  - 1-0D monolayer covered interface,  $z_{\rm c}$  = 300 um.

cleaned aqueous interface were similar to a film-covered interface. This result agrees with the observations made in Chapters 3 and 4 and the conclusions drawn in the previous section.

Overall, this test shows that the Whitman (1923) stagnant film model may be used to predict  $k_{\rm L}$  provided the gas/liquid interface is film-covered and  $\tilde{z}_{\rm e}$  is known. This implies that for this situation the stagnant film model provides a reasonable description of the liquid-phase fluid mechanics of the transport process. These results also show that application of the stagnant film model to a cleaned aqueous surface leads to inaccurate prediction of  $k_{\rm L}$  even when  $\tilde{z}_{\rm e}$  is known. This suggests that stagnant film models are not appropriately applied to gas transport at clean liquid surfaces.

The success of the stagnant film model in accurate prediction of  $k_{\rm L}$  for the 1-OD monolayer covered interface situations is somewhat puzzling. The Whitman (1923) model predicts that  $k_{\rm L}$  should scale linearly with D. However, Dickey et al. (1984) has shown that for an uncleaned water surface,  $k_{\rm L}$  scales as D<sup>1/2</sup>. It is not possible to determine how the data shown in Figure 33 scales with D since only one gas was used in the current experiments. Therefore, this problem remains unresolved at the present time.

S.D.2. Application of the Harriott Surface Penetration Model

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# 5.D.2.A. Calculational Procedure

It was hoped that the experimentally determined  $f_z(z_e)$  and  $f_T(T)$  could be substituted for  $f_h(h)$  and  $f_T(T)$  respectively in the Harriott (1962) and Bullin and Dukler (1972) surface penetration models. However, for  $f_z(z_e)$  and  $f_T(T)$  to be equal to  $f_h(h)$  and  $f_T(T)$  respectively,  $z_e$  and T would have to be statistically independent. This independence was tested by plotting  $z_e$  vs. T for all fluorescence fluctuation events observed in an individual experiment. If  $z_e$  and T are uncorrelated, the data points would be evenly distributed over the range  $z_{\min} \leq z_e \leq z_{\max}$  and  $T_{\min} \leq T \leq T_m$ . Observation of clustering of the points in any particular region of that rectangle would demonstrate the existence of any correlations between  $z_e$  and T. A plot of this type prepared based upon the surface fluorescence fluctuation data in Figure 13 is presented in Figure 34.

The distribution of points shows a correlation between high T and low  $z_e$ . For low T,  $z_e$  appears to be evenly distributed between  $z_{min}$ and  $z_{max}$ . Since larger eddies in general have larger timescales, these data suggests that larger turbulence eddies are more likely to completely renew the aqueous surface than the smaller eddies. This interpretation seems reasonable in light of the larger dynamic thrust of larger eddies. However it should not be assumed that because the larger eddies are more likely to completely renew the surface that



Figure 34. Test of correlation between  $z_e$  and T. Plot of  $z_e$  vs. T from the fluorescence fluctuation data shown in Figure 13.

they are most important in determining  $k_{L}$ . Indeed, larger eddies also have larger T values, and this makes them less efficient in promoting gas/liquid transport than the smaller eddies for a given  $z_{e}$ . It should also be noted that there are fewer large eddies than small eddies and this also lessened their impact on  $k_{i}$ .

Since the correlation observed in Figure 34 was found to be typical of the  $z_{\mu}$  and T data for all the eddy approach distance experiments, it is concluded here that  $f_z(z_e)$  and  $f_T(T)$  are not statistically independent. This means they cannot be used directly in the models of Harriott (1962) and Bullin and Dukler (1972). However, each peak from a particular fluorescence fluctuation time series may be assumed to have been caused by a turbulence eddy with timescale T and approach distance  $z_{\mu}$ . Therefore the result from an individual fluorescence fluctuation experiment is a series of the form  $(z_{e,n}, T_n)$ . Each series represents one realization of the joint probability density function for  $z_e$  and T  $f_{z,T}(z_e, T)$  from that particular experiment. As such, the empirical series of  $(z_{e,n}, T_n)$  can be used directly in the model of Harriott (1962) in place of the series  $(h_0, \tau_0)$  drawn from the independent distributions  $f_h(h)$  and  $f_1(I)$ . However, there is no convergence condition placed on the averaged k, calculated by use of the empirical series. After all data pairs  $(z_{e,n}, T_n)$  have been analyzed, the k<sub>l,n</sub> are summed and averaged. It is assumed here that this average is an accurate estimate of the true  $k_{\mu}$ . However, before the Harriott (1962) model can be used to calculate  $k_{L}$  in the present experimental apparatus one further modification is necessary.

The model of Harriott (1962) assumes that each arriving eddy has zero solute concentration. Since the aqueous  $[CO_2]$  in the bulk phase was non-zero and increased with time over the course of an experiment, the Harriott (1962) model was modified to account for non-zero solute concentration in the arriving eddy. Therefore,  $Q_n$  is now given by

$$Q_{n} = C_{s} (4DT_{n}/\pi)^{1/2} - \int_{0}^{z_{e(n-1)}} C_{(n-1)}(\xi) \operatorname{erfc}(\xi/(4DT_{n})^{1/2}) d\xi - \frac{1}{2} \int_{0}^{z_{e(n-1)}} C_{b(n-1)} \operatorname{erfc}(\xi/(4DT_{n})^{1/2}) d\xi$$
(63)

where  $\xi$  (cm) is a dummy integration variable,  $C_{b(n+1)}$  is the solute concentration in the arriving eddy, and  $C_n(z)$  is defined as

$$C_{n}(z) = C_{s} \operatorname{erfc}(z^{2}/4DT_{n})^{1/2} + (4\pi DT_{n})^{-1/2} x$$

$$\begin{cases} z_{e(n-1)} \\ \int C_{(n-1)}(\xi) \{ \exp[-(\xi-z)^{2}/4DT_{n}] - \exp[-(\xi+z)^{2}/4DT_{n}] \} d\xi + \\ 0 \\ H \\ \int C_{b(n-1)} \{ \exp[-(\xi-z)^{2}/4DT_{n}] - \exp[-(\xi+z)^{2}/4DT_{n}] \} d\xi \end{cases}; z < z_{e,n} \quad (64)$$

$$z_{e(n-1)}$$

$$C_{n}(z) = C_{b,n}; \quad \text{for } z > z_{e,n}$$
(65)

where

$$C_{b,n} = C_{b(n+1)} + Q_n / H$$
(66)

For  $Q_n$  defined by Eq. 63 and  $C_n(z)$  given by Eqs. 64 and 65

$$k_{L,n} = Q_n / (T_n (C_s - C_{b,n}))$$
(67)

These modifications to the Harriott (1962) model allow the increase in aqueous  $\{CO_2\}$  to be incorporated into the calculation of  $k_{\rm L}$ .

Application of Eqs. 63, 64, 65, 66, and 67 was carried out by the FORTRAN-77 (V3.31, Microsoft Corp., Redmond, WA) program SURPENT.FOR on an IBM-PC compatible computer equipped with an 8087 math coprocessor (Intel Corp., Santa Clara, CA). SURPENT.FOR is listed in Appendix A. The integrals involved in Eqs. 63 and 64 were numerically integrated by the Numerical Recipes (Press et al., 1986) subroutine QSIMP.FOR which is listed in Appendix A.

The algorithm used to calculate  $k_{\rm L}$  was adapted from Harriott (1962). Initially,  $C_{\rm b,0}$  and  $C_0(z)$  were set equal to 0.  $Q_1$  was then computed from Eq. 63. Then  $C_1(z)$  was calculated from Eq. 64 and  $C_{\rm b,1}$  calculated from Eq. 66. The process proceeded iteratively from this point. Since  $C_{\rm n}(z)$  was defined by integration of  $C_{\rm n-1}(z)$ , the calculation of  $C_{\rm n}(z)$  through direct application of Eq. 63 was very complicated in principle. A computational shortcut was provided by fitting  $C_{\rm n}(z)$  to a function of the form

$$C_{0}(z) = \exp[a_{0} + a_{1}z + a_{2}z^{2} + a_{3}z^{3}]$$
(68)

This was done by a least-squares third order polynomial to the function  $\ln(C_n(z))$  using the Numerical Recipes (Press et al., 1986) singular value decomposition algorithm SVDFIT.FOR. This procedure simplified the coding and calculation of  $Q_n$  and  $C_n(z)$  since it removed the implicit double integration present in Eqs. 63 and 64.

### 5.D.2.B. Results and Discussion

The Harriott (1962) model was used to calculate k, through the

procedure described in the previous section for all experiments where the series  $(z_{en}, T_n)$  was calculated. The calculated  $k_L$  values were then compared to the experimentally determined results based on similarity of turbulence conditions present in the tank. The results are shown in Figure 35.

In the case of the 1-OD monolayer covered interface, the results in Figure 35 show that the surface penetration model of Harriott (1962) applied as described above predicts  $k_{\rm L}$  excellently over the entire turbulence range studied. This implies that the model provides an accurate physical description of the gas transport process at a film-covered gas/liquid interface. This is an important result since it allows an understanding of the basic fluid mechanics associated with the transport process in terms of a realistic hydrodynamical model.

In Figure 35, the rayon/vacuum cleaned interface data shows some scatter for the highest turbulence intensity but excellent correlation for the lower intensities. As in the case of the 1-OD data, this correlation suggests that the surface penetration model provides a realistic description of the hydrodynamics associated with gas exchange at a clean gas/liquid interface. The high turbulence intensity cleaned interface data point which shows serious underprediction of  $k_{\rm L}$  may have resulted from interfacial contamination in spite of the steps taken to ensure a clean aqueous surface. This interpretation is further verified by observation that  $\bar{z}_{\rm e}$  for that experiment was large compared to the other high turbulence intensity cleaned interface  $\bar{z}_{\rm a}$ 



Figure 35. Application of the Harriott (1962) surface penetration model. Plot of  $k_{\rm L}$  calculated by use of the empirical series  $(z_{\rm en}, T_{\rm n})$  and the procedure described in Section 5.D. vs.  $k_{\rm L}$  measured in the bulk experiments under similar turbulence and interfacial conditions. Data key is:  $\Box$  - rayon/vacuum cleaned interface,  $z_{\rm c} = 300$  um, O - 1-OD monolayer covered interface,  $z_{\rm c} = 300$  um.

results. If this interpretation is correct, this outlying data point emphasizes the necessity of carefully cleaning the liquid surfaces in gas exchange experiments.

A linear regression with a forced zero intercept was performed to determine if the slope of all the data in Figure 35 was significantly different from unity. This test showed that the slope of the combined rayon/vacuum cleaned and 1-OD monolayer covered interface data is less than one. However, linear regression of the 1-OD monolayer covered interface data alone showed that its slope is not significantly different from one. Therefore, while the overall correlation of predicted to measured  $k_L$  is very good, it was concluded that the Harriott (1962) surface penetration model underpredicted  $k_L$  for the rayon/vacuum cleaned interface data.

A possible explanation of this discrepancy may be provided if there were small amounts of surface active impurities present in the OG dye. If these contaminants were present in spite of the OG purification procedure used, they may have formed a weak or solvated monolayer or film (Gaines, 1966) at the  $H_2O/CO_2$  interface. However it should not be concluded that this adventitious film was identical in nature to a 1-OD monolayer. Since some turbulence eddies were observed to renew the aqueous surface fully in all of the rayon/vacuum cleaned experiments, the hydrodynamical characteristics of the spontaneously formed film were very different from the 1-OD monolayer. However, if it were indeed present its affect on  $z_e$  is seen in the underprediction of  $k_1$  by the surface penetration model. Further evidence in support of this explanation may be found by observing that the rayon/vacuum cleaned data point that showed the largest discrepancy was the first in a series of experiments performed with the same aqueous solution. The initial sparging of the aqueous solution by the small He bubbles to bring the initial  $[CO_2]$  to zero served to concentrate surface active material present in solution at the  $H_2O/CO_2$  interface (Scott, 1975). Therefore, while the rayon/vacuum cleaning procedure helped keep the films present at the aqueous surface in the subsequent experiments at a minimum, in the initial experiment performed, the aqueous phase may still have had some surface active material present. This concentration of contaminant would have decreased as successive experiments were performed due to removal of the surface water by the rayon/vacuum cleaning technique. Presumably therefore, the formation of the adventitious film and its effects would have decreased as well.

Figure 36 shows the quantity:  $\{k_{l}(measured) - k_{l}(predicted)\}\$ plotted vs. experiment number for the rayon/vacuum cleaned interface experiments. As hypothesized in the preceding paragraph, the difference between measured and predicted  $k_{l}$  is larger for the earlier experiments. This suggests that the adventitious film interpretation of the underprediction of  $k_{l}$  by the Harriott (1962) model is correct and there was some impurity present in the solution which tended to form a weak film at the aqueous surface. Therefore, the underprediction of  $k_{l}$  should not be interpreted as a failure of the surface penetration model.



Figure 36. Test for the presence of surface active impurities in the OG dye. The rayon/vacuum cleaned results from the application of the Harriott (1962) surface penetration model are shown as a plot of  $\{k_{L} (Measured) - k_{L} (Calculated)\}$  vs. experiment number from the data of Figure 35.

In light of the information provided by Figure 36, Figure 35 is very encouraging in that it shows  $k_{\rm L}$  may be predicted by a surface penetration model for either clean or film-covered interfaces. This is an important result since it demonstrates that the fundamental fluid mechanics controlling the gas/liquid transport process in these two dissimilar cases can be described in terms of the same hydrodynamical parameters.

Application of the Bullin and Dukler (1972) model would have required its reformulation in terms of the joint probability density function  $f_{z,T}(z_e,T)$  for  $z_e$  and T. While this could have been done it was felt that this effort would not provide any information not already obtained by application of the Harriott (1962) model. Therefore, the Bullin and Dukler (1972) model was left untested.

#### 5.E. Conclusions

The calculation of  $z_e$  and  $f_z(z_e)$  from the surface fluorescence fluctuation time series represented the first empirical determination of these parameters for a free gas/liquid interface. In addition, the turbulence present was assumed to be isotropic with calculated Q and L. The  $z_e$  data provided new information regarding the interaction of turbulence eddies with clean and film-covered liquid surfaces. In the case of a clean gas/liquid interface, high intensity turbulence eddies were seen to renew the liquid surface most of the time due to the low shear stress. Low intensity turbulence eddies did not renew the
gas/liquid interface as often due to their lower dynamic thrust. Turbulence eddies at a 1-OD monolayer covered interface were never observed to renew the liquid surface re-gardless of turbulence intensity. This was presumably due to the 1-OD monolayer damping the turbulence motion through an increase in shear stress at the interface.

The observed behavior of the turbulence eddies close to clean and film-covered liquid surfaces agreed with that hypothesized by Davies (1972) and Hunt and Graham (1978) among others. Since that theorized behavior had not been verified experimentally for a gas/liquid interface prior to this work, the measurement of  $z_e$  represents a step forward in the understanding of the dynamics of aqueous turbulence eddies close to a free surface.

Applied to the modeling of gas/liquid mass transport, the  $z_e$  data has shown that surface renewal models provide an accurate physical description of the process for clean liquid surfaces. The approach distance calculations have also shown that the Whitman (1923) film model provides an appropriate physical description of the transport process for an interface covered by a mono-molecular film. This result is of importance since it demonstrates that the two models cannot be used interchangeably to describe gas exchange. Surface renewal theory and the film model describe gas/liquid mass transport under very different interfacial conditions. Neither should be viewed as a "unified" model of gas/liquid mass transport.

In addition to providing new hydrodynamical information and insight into the applicability of surface renewal and film models, the calculated  $z_e$  have allowed testing and verification of a surface penetration model of gas/liquid gas transport. Through the use of the empirically determined input parameters  $z_e$  and T, this model was able to accurately describe the variation of  $k_l$  with Q and L at both filmcovered and clean gas/liquid interfaces. This result is of great importance since the relevant parameters for accurately quantifying the process under the two different interfacial regimes are known. In this sense, surface penetration models were seen to provide a very general model for the gas/liquid mass transport process.

The major failing of the Harriott (1962) model is that it offers no method for predicting  $k_{\rm L}$  from fluid mechanical variables. Both  $z_{\rm e}$ and T must be empirically determined for application of the model as presently formulated. Therefore, its utility in a predictive sense is somewhat limited since there are few measurements of  $f_z(z_{\rm e})$  and  $f_{\rm T}({\rm T})$ . It does offer a means to calculate  $k_{\rm L}$  from empirically determined eddy approach distance and timescale distributions.

# 6. Gas Exchange at Natural Water Surfaces

## 6.A. Introduction

The ultimate goal of research such as this is to facilitate the prediction of  $k_{L}$  in oceans, lakes and other bodies of water. The results presented in Chapters 3, 4, and 5 provide mechanistic information regarding the interaction of aqueous phase turbulence with gas/liquid mass transport. However, there is still much that must be determined before  $k_{L}$  for the open ocean may be accurately predicted. In bodies of water such as the ocean, the process of gas exchange is much more complicated than in the laboratory. The stress of the wind on the water surface creates waves, currents, and turbulence. In addition, there may be organic surface films, bubbles, and turbulence generated by mechanisms unrelated to the wind stress. All of these processes may affect gas transport and should be accounted for in a comprehensive environmental gas/liquid transport model. However, their inclusion in a realistic gas/liquid mass transport model is not easily accomplished.

Of the phenomena mentioned above, those processes directly related to the wind stress are most important in controlling  $k_{L}$ . The mechanical energy transferred from the wind to the water is responsible for much of the mixing which occurs in the upper layer of the ocean (Niiler, 1975; Phillips, 1977). As such, the role of wind in generating aqueous phase turbulence and in turn, promoting gas transfer, is central to the prediction of  $k_L$  for the ocean and other bodies of water exposed to the atmosphere. Therefore, it seems logical to determine the hydrodynamical mechanism(s) which are of importance in wind-driven gas exchange. This is a necessary first step in understanding the complex environmental gas transport process.

Since the results presented in Chapters 3, 4, and 5 provide a cohesive hydrodynamical view of gas/liquid transport under a variety of conditions, it would be useful to compare wind tunnel measurements of  $k_{l}$  to the present results for  $k_{l}$  determined in the grid-stirred tank. This comparison might show if any of the three gas exchange models discussed (i.e. surface renewal, surface penetration, or stagnant film) describes the hydrodynamical dependence of wind-driven gas exchange. Of these, it would seem most logical to use a surface penetration model since they provide an accurate physical description of the gas/liquid transport process for a wide range of conditions. However, their predictive power is limited by knowledge of the input parameters h and T.

Unfortunately, measurement of h and  $\tau$  for wind-generated turbulence has not yet been accomplished. In addition, there is currently no a-priori method of calculating these variables from externally measured parameters such as wind speed. Therefore, use of a model such as that of Harriott (1962) in the comparison of wind tunnel and stirred-tank results is not feasible at the present time. However,

under the appropriate set of turbulence and interfacial conditions, either surface renewal theory or the stagnant film model might be useful.

The empirical stagnant film model of Davies (1972) suffers from the inability to estimate the fluid mechanical variables from the relevant aerodynamic parameters. Also there are no direct measurements of  $\delta$  for wind-generated turbulence. This means that the Whitman (1923) stagnant film model provides no systematic method of relating wind-driven and mechanically stirred transport. Therefore, these stagnant film models will be of little use in the proposed comparison.

Methods of calculating surface renewal timescales from wind speeds do exist. O'Conner (1983) developed a wind-driven surface renewal model where s is calculated using  $T_m$ . However, the experimental results presented in the previous chapters suggest that it is  $T_u$  not  $T_m$  which is the appropriate scale in defining s. Therefore, an alternative model should be used in this comparison.

Cohen (1983) developed a dissipation scale surface renewal model for gas transport at clean water surfaces which calculates  $k_{\rm L}$  using aerodynamic rather than hydrodynamic input parameters. Therefore it was used to compare the present measurements of  $k_{\rm L}$  in a grid-stirred tank to transport data from wind/wave tunnels. This comparison suggests that for a clean liquid surface, the hydrodynamical dependence of the transport process is similar for wind-driven and grid-stirred gas/liquid mass transport.

The model of Kitaigorodskii (1984) describes the transport pro-

cess in terms of separate diffusive sublayers for mass and momentum. This model provides a description of the transport process which agrees physically with the behavior observed experimentally for a 1-OD monolayer covered interface. Unfortunately, the Kitaigorodskii (1984) model,was derived to describe transport at clean water surfaces. It is not clear how to resolve this at the present time. In addition, the model assumes that all turbulence present in the water is generated by breaking wind-waves. In the proposed comparison, situations where wave breaking was observed were not considered to avoid flux enhancement associated with bubble formation. This is an unfortunate situation since the Kitaigorodskii (1984) model provides one of the better descriptions of wind-driven gas exchange currently available.

# 6.B. Wind-Driven Gas/Liquid Mass Transport

Tanks stirred by oscillating grids trade simulation of realistic environmental wind/wave conditions for known levels of aqueous phase turbulence. Since wind tunnels simulate environmental conditions more closely, it seems desirable to compare  $k_{\rm L}$  measurements made in them to the present stirred-tank results. The dissipation model of Cohen (1983) may be used to relate the present data to the wind tunnel experiments of Broecker et al. (1978), Liss et al. (1981), Mackay and Yeun (1983), Merlivat and Memery (1983), and Jähne et al. (1984).

Cohen (1983) divides  $\varepsilon$  into a mechanically generated component  $\varepsilon_s$ , a wave generated component  $\varepsilon_s$ , and a component due to the wind

induced drift current  $\epsilon_d$  with

$$\varepsilon_{\rm W} = 0.4 v A^4 k^4 \Theta^2 \tag{69}$$

$$\epsilon_{d} = 3.25 \times 10^{-4} (U_{w}^{*})^{4} / v$$
(70)

where A (cm) is the wave amplitude, k (cm<sup>-1</sup>) and  $\theta$  (s<sup>-1</sup>) are the radian wave number and frequency respectively, and  $U_{\mu}^{*}$  (cm s<sup>-1</sup>) is the water side friction velocity. By assuming continuity of stress at the interface  $U_{\mu}^{*}$  may be written as

$$U_{\mu}^{*} = (\rho_{a} / \rho_{\mu})^{1/2} U_{a}^{*}$$
(71)

where  $\rho_a$  (g cm<sup>-3</sup>) and  $\rho_u$  (g cm<sup>-3</sup>) are the densities of air and water respectively, and  $U_a^*$  (cm s<sup>-1</sup>) is the air side friction velocity. This model assumes that there are no breaking waves. Cohen (1983) showed that if  $\varepsilon_s = 0$  and  $U_u^* > 2$  cm s<sup>-1</sup>, then  $\varepsilon_d >> \varepsilon_u$  and  $\varepsilon$  is determined mainly by  $\varepsilon_d$ . Therefore for higher wind speeds, the functional form of the Lamont and Scott (1970) model,  $(\varepsilon/v)^{1/4}$  may be calculated by use of  $\varepsilon_d$  alone. For lower wind speeds, calculation of  $(\varepsilon/v)^{1/4}$  requires both  $\varepsilon_d$  and  $\varepsilon_u$ . However, if  $\varepsilon_u$  is neglected and it is assumed that  $\varepsilon = \varepsilon_d$  for  $U_u^* < 2$  cm s<sup>-1</sup>,  $(\varepsilon/v)^{1/4}$  is not drastically underestimated.

Cohen (1983) showed that for  $U_{\mu}^{*} = 0.5 \text{ cm s}^{-1}$ ,  $\varepsilon_{\mu} = 0.45\varepsilon_{d}$ . Neglecting this term in calculating  $\varepsilon$  led to an 18% underestimation of  $(\varepsilon/v)^{1/4}$  which is acceptable for the present comparisons. In support of this assumption, substitution of Eq. 70 into Eq. 15 shows that  $k_{L}$  should correlate linearly with  $U_{\mu}^{*}$ . This result has been derived separately by Munnich and Flothman (1975) and Deacon (1977) and also observed experimentally (Cohen, 1983). This model was used to compare the present data for  $CO_2$  in a grid-stirred tank to the wind tunnel data of Broecker et al. (1978) for  $CO_2$ , Liss et al. (1981) for  $O_2$ , Mackay and Yeun (1983) for benzene, toluene and 1,2-dichloropropane, Merlivat and Memery (1983) for  $N_2O$ , and Jähne et al. (1984) for  $CO_2$ . For the wind tunnel data,  $\varepsilon$  was calculated from reported values of  $U_g^*$  or  $U_w^*$  and Eqs. 70 and 71. The  $k_L$  data for the different experiments were normalized to  $S_c = 600$  as in Jähne et al. (1984) to correct for differences in D and T. These values were then plotted vs.  $(\varepsilon/v)^{1/4}$  and the results are shown in Figure 37.

The data sets for clean gas/liquid interfaces of Broecker et al. (1978), Liss et al. (1981), Merlivat and Memery (1983) and Jähne et al. (1984) all correlate reasonably well with the rayon/vacuum cleaned grid results. While there is considerable scatter among the data sets, Figure 37 is very encouraging. It suggests that Cohen's model may be used to relate stirred tank results to wind tunnel experiments provided the aqueous surface is free of surface films. This supports the hypothesis that wind-driven gas/liquid transport has the same hydrodynamical dependence as gas exchange in the presence of mechanically-stirred turbulence. However, the current data do not provide definitive proof of this conclusion.

The data of Mackay and Yeun (1983) and the lens paper-cleaned grid results are systematically lower than the other data sets but are in very good agreement with each other. As noted Chapters 3, there is evidence that the  $CO_2$ /water interfaces in the lens paper-cleaned



Figure 37: Plot of k data normalized to  $S_c = 600 \text{ vs.} (c/v)^{1/4}$  for the present grid data and wind tunnel results. For the wind tunnel data,  $\varepsilon$  was calculated from the model of Cohen (1983) using (20) and (21). The data shown are:  $\blacklozenge$  - CO<sub>2</sub>, rayon/vacuum cleaned interface, present grid data;  $\blacksquare$  - CO<sub>2</sub>, lens paper cleaned interface, present grid data; • - CO,, 1-OD monolayer covered interface, present grid O - CO2, circular wind tunnel, film covered interface, Jahne data; et al. (1984); O - CO<sub>2</sub>, linear wind tunnel, clean interface, Broecker et al. (1978); + - 0, linear wind tunnel, clean interface, Liss et al. (1981); 👌 - Benzene, toluene, 1,2-dichloropropane, linear wind tunnel, clean interface, Mackay and Yeun (1983); ▼ - N,O, linear wind tunnel, clean interface, Merlivat and Memery (1983); CO,, circular wind tunnels, clean interface, Jahne et al. (1984);  $\Delta$  - CO<sub>2</sub>, linear wind tunnel, clean interface, Jähne et al. (1984).

experiments were contaminated by surface films. The data set of Mackay and Yeun (1983) is unique in that it is the only data set included in this comparison which studied the transfer of organic material from an aqueous to a gaseous phase. The organic material added to the aqueous phase might have had surface active contaminants present which affected the transport rates through the formation of a surface film. If this were the case, it would explain the observed agreement of the Mackay and Yeun (1983) data with the lens paper cleaned set.

The 1-OD film results from the grid-stirred tank are in rough agreement with the film-covered wind tunnel results of Jähne et al. (1984). Also, the slopes of the two film-covered interface data sets are approximately the same. This suggests that the hydrodynamical dependence is similar in both cases. However, this analysis is not conclusive since it has been shown in this thesis that surface renewal models do not apply to film-covered liquid surfaces.

In general, the model of Cohen (1983) shows hope of being able to relate wind tunnel experiments to studies done with mechanically generated turbulence provided it is known that the interface in both situations is free of surface films. This is one step further in the understanding of the mechanism of wind-driven gas/liquid exchange. This preliminary result shows the gas-exchange process in the two types of experiments may possibly be described by the same surface renewal model over a limited range of conditions (i.e. clean liquid surface, high turbulence intensity, no breaking waves). The model of Kitalgorodskii (1984) or Kerman (1984) for gas-exchange in the presence of breaking wind waves might be useful to further extend these results to more realistic environmental conditions.

6.C. Implications For Modeling Air/Sea Gas Exchange

The open ocean is a very complex system. The air/sea interface is known to be at least partially covered by an organic film of undetermined composition and origin (Williams et al., 1986). The intermittent presence of this film greatly complicates calculation of  $k_{\rm L}$ for an air/sea exchange process. Depending on surface conditions, either surface renewal or film-like behavior might be observed. Therefore, it cannot be known a-priori which, if either model would apply for a given set of air and sea conditions. Use of a surface penetration model would solve the ambiguity posed by the presence or absence of films. As already mentioned however,  $f_{\rm h}(h)$  and  $f_{\rm T}({\rm T})$ remain unmeasured in the open ocean.

In addition to the uncertainty as to which transport model is most applicable for a given set of conditions such as wind speed, temperature etc., there are the effects of bubbles and waves to be considered as well. Recent studies have shown that bubbles may play a significant role in gas transport (Merlivat and Memery, 1983; Jahne et al., 1985; Memery and Merlivat, 1985). However, it is unclear at this point how to best incorporate the effect of bubbles into a comprehensive gas exchange model. In short, while the results presented here resolve certain mechanistic questions pertaining to wind-driven gas exchange, the problem is far from solved. The many types of chemical and physical conditions which may occur in environmental air/water systems creates many difficulties in the accurate calculation of  $k_{\rm L}$  for all situations of interest. Before  $k_{\rm L}$  may be calculated reliably, more information is necessary concerning the extent and strength of organic films at the air/sea interface. Information concerning bubble production mechanisms and populations for the variety of conditions found in the environment such as discussed by Thorpe (1982; 1984A; 1984B) will also be of use.

It must be acknowledged therefore, that the current state of knowledge of the process does not allow reliable estimation of air/sea gas transport coefficients for all environmental conditions. However, use of the Cohen (1983) model and the present  $k_{\rm L}$  data has provided information concerning the hydrodynamical mechanism of environmental gas exchange for a limited range of conditions. This information suggests that hydrodynamic surface renewal gas/liquid transport models may be applied to environmental gas exchange provided the water surface is not covered by a film. If an organic film exists at the air/sea interface, h and  $\tau$  must be measured so that a stagnant film model or a surface penetration model may be used to calculate  $k_{\rm L}$ . While these results do not allow a general theory of gas exchange to be formulated, they do provide insight into which parameters are of importance.

It is hoped that as this complex system becomes better understood, it will be parametrizable in terms of easily measured physical variables. Complete understanding of all factors involved in environmental gas/liquid transport might allow formulation of a comprehensive model of the process. With this type of model, it might then be possible to calculate  $k_L$  for any given set of physical and chemical conditions.

While the data presented in Figure 37 do not allow a comprehensive model to be formulated directly, possible paths to pursue have been suggested. Further experimentation in this area may verify the preliminary conclusion that wind-driven and mechanically-stirred transport may be described in terms of the same hydrodynamical parameters. If this could be done it may be possible to extend a surface penetration model to describe wind-driven gas exchange. This would be a major step forward since this type of model provides a very general description of the transport process. However, due to lack of knowledge concerning the variation of the input parameters h and  $\tau$  with wind speed precludes this at this time.

## 7. Conclusions

The results presented in this thesis provide a comprehensive investigation of the effects and relation of liquid-phase turbulence to gas/liquid mass transport. The results also provide information on the effects of organic films on the transport process and the associated hydrodynamics. The use of the LIF-DCFS technique has allowed non-invasive study of the gas exchange process with very fine spatial and temporal resolution. The turbulence generated by the oscillating grid has allowed the process to be studied under reproducible turbulence conditions with estimated intensity and scale. These two techniques used in combination have provided a means to study the complicated process of gas/liquid mass transport under controlled chemical and hydrodynamical conditions. This has allowed measurement of parameters not previously possible.

The information generated has shown that a coherent understanding of the transport process is possible for a wide range of turbulence and interfacial conditions. This is an important result since the ultimate goal of research such as this is the prediction of transport rates and/or fluxes of gases for environmental bodies of water. In these environmental situations, a variety of turbulence and interfacial conditions is known to exist. Therefore it is crucial to understand how different interfacial and turbulence conditions can affect the gas/liquid mass transport process.

Specifically, the results from the bulk k, measurement experi-

ments have shown that the dissipation scale hydrodynamic gas/liquid exchange model formulated by Lamont and Scott (1970) provides a reasonable description of the variation of  $k_{\rm L}$  with  $\varepsilon$  for a clean gas/liquid interface. The results also suggest that the large eddy hydrodynamic surface renewal model of Fortescue and Pearson (1967) does not provide an accurate description of the exchange process. The 1-OD monolayer bulk  $k_{\rm L}$  data shows that the empirical film-covered interface hydrodynamic gas/liquid transport model of Davies (1972) does not provide an adequate description of the transport process. In addition, these results show that the hydrodynamic surface renewal model is not applicable to gas exchange at a 1-OD monolayer covered interface.

The bulk k<sub>l</sub> results also show that the rate of the transport process is extremely sensitive to the presence of surface films. This demonstrates that study of gas/liquid transport under known interfacial conditions requires careful preparation of the liquid surface. The results show that there are fundamental differences in the hydrodynamical mechanisms of gas exchange for clean and film-covered interfaces. This has important implications towards the modeling of environmental gas exchange since some of these aqueous surfaces will have organic films present. Therefore, a single simple model will not be sufficient to describe all situations of interest.

The surface fluorescence fluctuation timescale measurements suggest that the turbulence scales calculated by use of Eqs. 21, 22, and 23 are fairly accurate. This is seen by the correlation of the measured fluorescence timescales with the calculated turbulence timescales  $T_m$  and  $T_u$ . The fact that such good agreement was seen between the experimental and calculated timescales shows that Eqs. 21, 22, and 23 give reasonable estimates for Q and L. However, this result must be stated with caution as Q and L were not determined by direct measurement for the experimental apparatus used.

A more important facet from the surface fluorescence fluctuation timescale experiments is the use of the measured timescales in the surface renewal models of Higbie (1935) and Danckwerts (1951). This has shown that either model may be used to predict  $k_L$  for clean gas/liquid interfaces. These results also show that neither of the two surface renewal models is an appropriate choice to describe gas transport at a 1-OD monolayer covered interface. The surface fluorescence fluctuation timescale measurements results suggest that surface renewal models provide a realistic description of the hydrodynamics associated with gas exchange at a clean liquid surface. The results also suggest that surface renewal models do not provide a realistic description of mass transport at a 1-OD monolayer covered interface. However, these conclusions cannot be proven using these data alone.

The eddy approach distance calculations allowed the first test of surface penetration theory as formulated by Harriott (1962). Use of this model allows the gas/liquid transport process at clean and filmcovered liquid interfaces to be described by the same hydrodynamical parameters. This is not possible with any of the other gas transport models tested. It is felt that this result is of great interest since

it demonstrates that the fundamental fluid mechanics governing gas/liquid mass transport is the same for film-covered and clean interfaces.

The eddy approach distance calculations demonstrate that complete renewal of the liquid surface frequently can be observed for a clean interface. They also show that there is no surface renewal at a 1-OD monolayer covered surface over the range of turbulence intensities studied. This supports the tentative conclusions made concerning the conditions under which the surface renewal and stagnant film models discussed above are applicable. It also provides empirical verification of the idea that stagnant film and surface renewal models are complementary rather than mutually exclusive (Toor and Marchello, 1958).

The results from the eddy approach distance calculations provide verification of several hypotheses concerning the present data. In addition, they answer several long-standing questions regarding the hydrodynamical mechanisms of gas/liquid mass transport. It may be concluded on the basis of this data that stagnant film models such as that of Whitman (1923) do not provide a realistic description of a liquid-phase rate controlled transport process at a clean gas/liquid interface. Therefore, they should never be used to predict  $k_L$  in these situations. However, surface renewal models are seen to describe the physical reality of gas exchange at a clean gas/liquid interface. It is, therefore, these models that should be used to calculate  $k_L$  for this case. However, this does not in any way imply

that surface renewal models may be applied to all gas/liquid transport systems.

Since the eddy approach calculation results suggest that complete renewal of the surface is never observed at a film-covered interface, surface renewal models should not be used to predict  $k_{\rm L}$  for these regimes. Gas exchange at interfaces where surface films are present is best described by surface penetration models. If it can be assumed that the results of Section 5.D.1. are correct, stagnant film type models may be used if h is known. Then  $k_{\rm L}$  is calculated by substitution of the average eddy approach distance for  $\delta$  in the Whitman (1923) model. Application of surface penetration models requires knowledge of both h and T.

In closing, these experiments have demonstrated that the gas/liquid mass transport process is very complex. However in spite of this complexity, the present results do provide a coherent view of the process over a range of physical and chemical conditions for mechanically generated liquid phase turbulence. While the process is not completely understood for all situations of interest, it is felt that this research has made significant progress towards a more complete understanding. The chemical and physical conditions under which several commonly used gas/liquid transport models are applicable have been determined. Gas transport at clean and film-covered interfaces is now known to be describable in terms of the same hydrodynamical parameters by the surface penetration model of Harriott (1962).

This understanding of the hydrodynamical mechanisms controlling

gas transport, viewed in concert with the ability of the Cohen (1983) model to relate wind-driven transport to that driven by mechanically generated turbulence provides a better understanding of the winddriven gas exchange process. Therefore, these results show hope that a method to accurately predict environmental transport rates may be found. This present research is a needed step in that direction.

Future relevant experiments might include a detailed, systematic study of the effects of organic films on gas exchange and associated hydrodynamics. Also needed is information on the generation of turbulence by wind. The wind stress will also affect any surface films present through direct action and the creation of surface waves. The effect of waves must also be quantified both for the breaking and nonbreaking case. In the case of breaking waves, gas transport by bubbles must also be considered. All of these phenomena must be understood before environmental gas/líquid transport rates may be calculated accurately for all situations of importance.

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## Appendix A. Computer Code

Programs are listed in the order mentioned in the text.

#### DCFS.FOR

DCFS.FOR calculated  $k_{\rm L}$  for the bulk  $k_{\rm L}$  measurements. It was run on a DEC micro-PDP-11/23 using FORTRAN IV-RT. Subroutines called but not listed here include a running mean filter program to do preliminary data smoothing, RUNMEA.FOR and GETZER.FOR, which was a transcendental equation root finder based on the Numerical Algorithms Group (NAG Mk:8) library subroutine CO5ADF.FOR. Data for use by DCFS.FOR was collected by the program GETEXP.FOR.

C	DCFS	.FOR (DATA ANALYSIS PROGRAM WRITTEN BY W.E.A.)
		IMPLICIT REAL*8 (A, B, C, D, E, F, G, H, U, V, W, X, Y, Z,
	æ	S, P, O, T, R), INTEGER (I, J, K, L, M, N)
		VIRTUAL XDAT1(10000), XDAT2(10000)
		DIMENSION NAME(5), IDATA(4), CAL(2,4), XAVG(75), IEND(2),
	&	PH(2), ZERO(3), XCORR(2), SUMY(2), SUMY2(2), SUMXY(2), CO2(2),
	æ	<pre>FCKONE(2), TCORR(2), EPH(2), ESIG(2), QZERO(3), IPAR(2),</pre>
	&	IDAT(2), INAME(3)
		COMMON CAL, STPH, ENDPH
		EXTERNAL CORF1, CORF2, ECOR1, ECOR2
		ALPH1(X)=((X/CKONE)+1.00000+(CKTWO/X))**(-1.00000)
		ALPH2(X)=(((X**2)/(CKONE*CKTWO))+(X/CKTWO)+1.00000)**(-1.00000)
		ACTIV(X,Y,Z)=10.00000**
	&	(-1.0000*(AL*(2**2.000)*(DSQRT(X)/(1.000+(B*Y*DSQRT(X))))))
		COCAL(X,Y) = (CB-CA+X-Y)/(AONE+2,00000*ATWO)
		PHCAL(X,C1,C2,C3,C4)=C1+C2*X+C3*X**2+C4*X**3
		DATA IPAR/'.P', 'AR'/, IDAT/'.D', 'AT'/
С.	. ENTER 6 CHAR STRING WHICH IS EXPERIMENTAL NAME (EXAMP. "DC1663")	
С.	THE	N OPENS .PAR AND .DAT FILES IN PROGRAM
		WRITE (5, 10)
_		READ (5, 20) INAME
с.	OPE	N AND READ IN BEGINNING DATA FROM '*****, PAR' FILE
		DO 800 I = I, 3
800	)	NAME(1) = INAME(1)
		NAME(4) = 1PAR(1)
		NAME(0) = IPAR(2)
10		WRILE (J, 12) NAME
LZ		FORMAT (IX, SAZ)
		CALL ASSIGN (IO, NAME, IO, 'OLD', 'RDO', 'NC')
		READ $(10, 21)$ BEGRA, IDIM READ $(10, 20)$ STRU ENDRU
		READ (10, 30) SILR, ENDER DEAD (10, 40) SDATE TTIME
		PEAD (10, 40) SRATE, TITME
		$\begin{array}{c} \text{READ} (10, 40) \text{ ESIG} \\ \text{READ} (10, 40) \text{ EPOM} \text{ DREF} \end{array}$
		$\frac{10}{10}$
		READ (10, 40) EEE, DERES READ (10, 40) EEE
		(10, 40) 3135, DETER

```
READ (10, 50) CAL(1,1), CAL(1,2), CAL(1,3), CAL(1,4)
           READ (10, 180) CIMIN, CIMAX
           READ (10, 50) CAL(2,1), CAL(2,2), CAL(2,3), CAL(2,4)
           READ (10, 180) C2MIN, C2MAX
        CALL CLOSE (10)
        IF (MOD(IDIM, 2) . EQ. 0) IDIM = IDIM + 1
        IF (IDIM .GT, 75) IDIM = 75
        XDIM= 1.00 / DBLE(FLOAT(IDIM))
        STIME=1./SRATE
        TEK=TEMP+273.0000
        PKH=2385.73/TEK-14.0184+.0152642*TEK-SISS*(.28596-6.167E-4*TEK)
        HENRY=10.00**(PKH)
        PKW=(-4470.99/TEK)+6.0875-(0.01706*TEK)
        XKW=10.00**(PKW)
        PKONE=(-3405.41/TEK)+14.8422-(0.0327698*TEK)
        XKONE=10.00**(PKONE)
        PKTWO=(-2894.31/TEK)+6.4530-(0.0237282*TEK)
        XKTWO=10.00**(PKTWO)
        EPSIL=(-1.000*TEK*0.3616838)+186.1657
        AL=1.82E06*(EPSIL*TEK)**(-1.5000)
        B=50.3*(EPSIL*TEK)**(-.50000)
         ACTH=ACTIV(SISS,9.00,1.00)
         ACTOH=ACTIV(SISS, 3.00, 1.00)
         ACTHCO=ACTIV(SISS, 4.00, 1.00)
         ACTCO=ACTIV(SISS, 5.00, 2.00)
         CKONE=(XKONE/(ACTH*ACTHCO))
         CKTWO=((XKTWO*ACTHCO)/(ACTH*ACTCO))
         CKW=(XKW/(ACTH*ACTOH))
        PATM=BPRES/760.0
        SATCO=HENRY*PATM
C . CALCULATE Ca or Cb
      IF (BEGPH .GT. 7.00) GOTO 5
      CA=(10.0**(-1.0*BEGPH)-(CKW/(10.00**(-1.0*BEGPH))))/ACTH
      CB=0.000
      GOTO 15
        CB=((CKW/(10.00**(-1.0*BEGPH)))-10.00**(-1.0*BEGPH))/ACTOH
5
        CA=0.000
С
        BEGIN DATA ENTRY OPEN INPUT AND OUTPUT FILES
15
        NAME(4) = IDAT(1)
        NAME(5) = IDAT(2)
        WRITE (5,12) NAME
        CALL ASSIGN (10, NAME, 10, 'OLD', 'RDO', 'NC')
        DO 900 I=1,2
           J = 14 + I
           WRITE (5, 60) I-1
           READ (5, 70) IEND
           DO 901 K = 1, 2
                NAME(K+3) = IEND(K)
901
           CONTINUE
           CALL ASSIGN (J, NAME, 10, 'NEW', 'NC')
```

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WRITE (J, 80) 1-1
900
        CONTINUE
        WRITE (5, 71)
        READ (5, 70) IEND
        DO 1000 I = 1, 2
           NAME(I+3) = IEND(I)
1000
        CONTINUE
        CALL ASSIGN (12, NAME, 10, 'NEW', 'NC')
        WRITE (12, 72) NAME
C . READ IN ZERO LEVELS (SING. PREC. IN DATA FILE)
        READ (10, *)
        READ (10, 90) NAME, QZERO
        WRITE (5, 90) NAME, QZERO
        ZERO(1) = DBLE(QZERO(1))
        ZERO(2) = DBLE(QZERO(2))
        ZERO(3) = DBLE(QZERO(3))
        DO 100 I = 1, 3
           ILIM(I) = INT (100.00 * QZERO(I))
100
        CONTINUE
C . READ ALL DATA INTO ARRAY XDATA
        I = 1
665
        READ (10, 110, ERR=25, END=25) IDATA
        IBADP = 0
        IF (IDATA(2) .GT. ILIM(1)) IBADP=111
        IF (IDATA(3) .GT. ILIM(2)) IBADP=111
        IF (IDATA(4) .LT. ILIM(3)) IBADP=111
        IF (IBADP .EQ. 0) GOTO 675
        WRITE (12,110) IDATA
        IF (I .EQ. 1) GOTO 665
        XDAT1(I) = XDAT1(I-1)
        XDAT2(I) = XDAT2(I-1)
        I = I + 1
        GOTO 665
675
        PVAL = 0.01 * (DBLE (FLOAT (IDATA(4)))) - ZERO(3)
        POWCO = PREF / PVAL
        XDAT1(I) =
     & DABS ((0.01 * (DBLE (FLOAT (IDATA(2)))) -ZERO(1)) * POWCO)
        XDAT2(I) =
     & DABS ((0.01 * (DBLE (FLOAT (IDATA(3)))) -ZERO(2)) * POWCO)
        I = I + 1
        IF (I .GT. 10000) WRITE (5, 240)
        IF (I .GT. 10000) CALL EXIT
        GOTO 665
25
        CALL CLOSE (10)
        IPNT = I - 1
        CALL RUNMEA (XDAT1, IPNT, XAVG, IDIM)
        CALL RUNMEA (XDAT2, IPNT, XAVG, IDIM)
C . CALCULATE RATIO CORRECTIONS FOR INITIAL DATA
        DO 300 I=1,2
           XDATA = XDAT1(1)
```

IF (I . EQ. 2) XDATA = XDAT2(1) PH(I) = PHCAL(XDATA, CAL(I,1), CAL(I,2), CAL(I,3), CAL(I,4))WRITE (5,170) I-1, STPH, PH(1) XCORR(I) = 1.0WRITE (5,160) READ (5,\*) ITST IF (ITST .NE. 1) GOTO 300 EPS = 1.0D - 10ETA = 5.0D-09IFL = 0IF (I .EQ. 1) CALL GETZER (C1MIN, C1MAX, EPS, ETA, CORF1, XSIG, IFL) & IF (I .EQ. 2) & CALL GETZER (C2MIN, C2MAX, EPS, ETA, CORF2, XSIG, IFL) IF (IFL .NE. 0) GOTO 55 XCORR(I) = XSIG / XDATA300 CONTINUE С CALCULATE SIGNAL LOSS CORRECTION TERMS POWCO = PREF / (EPOW - ZERO(3))DO 400 I=1,2 ESIG(I) = (ESIG(I) + ZERO(I)) \* POWCO \* XCORR(I)EPH(I) = PHCAL(ESIG(I), CAL(I,1), CAL(I,2), CAL(I,3), CAL(I,4))WRITE (5, 170) I-1, ENDPH, EPH(I) TCORR(I) = 0.0D0WRITE (5,190) READ (5, \*) ITST IF (ITST .NE. 1) GOTO 400 EPS = 1.0D-10ETA = 5.0D - 09IFAIL=0 IF (I .EQ. 1) CALL GETZER (CIMIN, CIMAX, EPS, ETA, ECORI, XSIG, IFAIL) & IF (IFAIL .NE. 0) GOTO 55 IFAIL=0 IF (I .EQ. 2) & CALL GETZER (C2MIN, C2MAX, EPS, ETA, ECOR2, XSIG, IFAIL) IF (IFAIL .NE. 0) GOTO 55 TCORR(I) = ((XSIG / ESIG(I)) - 1.0D0) / TTIME400 CONTINUE C . INITIALIZE ALL SUMS FOR REGRESSION CALCULATIONS TO FIND KA SUM=0.0 SUMX=0.0 SUMY(1) = 0.0SUMY(2)=0.0SUMX2=0.0SUMY2(1) = 0.0SUMY2(2) = 0.0SUMXY(1)=0.0SUMXY(2)=0.0NPTS=0

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IPT=0 WRITE (5,1) XCORR, TCORR C . FIND SIGNIFICANT CHANGE IN DATA DO 500 I = 2, IPNT IF (XDAT1(I) / XDAT1(1) .LT. .97 .AND. XDAT2(I) / XDAT2(1) .LT. .97) GOTO 35 & 500 CONTINUE C . BEGINNING OF DATA ANALYSIS 35 NPTS = IDO 600 I = NPTS, IPNT TIME = DBLE (FLOAT (1)) \* STIMESUM = SUM + 1.0D0SUMX = SUMX + TIMESUMX2 = SUMX2 + TIME \* TIMEDO 601 J = 1, 2 YDATA = XDAT1(I) \* XCORR(J) \* (1.0 + TIME \* TCORR(J))IF (J . EQ. 2) YDATA = XDAT2(I) \* XCORR(J) \* (1.0 + TIME \* TCORR(J))& PH(J) =& PHCAL(YDATA, CAL(J, 1), CAL(J, 2), CAL(J, 3), CAL(J, 4))CONCH = DEXP (-2.3025851 \* PH(J)) / ACTHAONE = ALPH1(CONCH) ATWO = ALPH2(CONCH)CONCOH = CKW / CONCHCO2(J) = COCAL (CONCH, CONCOH)FCKONE(J)=0.0D0IF (SATCO-CO2(J) .GT. 0.0D0) & FCKONE(J) = -1.0 \* DLOG ((SATCO - CO2(J)) / SATCO)SUMY(J) = SUMY(J) + FCKONE(J)SUMY2(J) = SUMY2(J) + FCKONE(J) \* FCKONE(J)SUMXY(J) = SUMXY(J) + FCKONE(J) \* TIME601 CONTINUE ICHK = IIF (MOD(ICHK, 25) .NE. 0) GOTO 600 WRITE (5, 120) TIME, XDAT1(1), PH(1), CO2(1), FCKONE(1) WRITE (15, 120) TIME, XDAT1(I), PH(1), CO2(1), FCKONE(1) WRITE (5, 120) TIME, XDAT2(I), PH(2), CO2(2), FCKONE(2) WRITE (16, 120) TIME, XDAT2(I), PH(2), CO2(2), FCKONE(2) 600 CONTINUE DO 700 I=1,2 J = 14 + IDELTA = SUM \* SUMX2 - SUMX \* SUMX A = (SUMX2 \* SUMY(I) - SUMX \* SUMXY(I)) / DELTAB = (SUMXY(I) \* SUM - SUMX \* SUMY(I)) / DELTAC = DBLE (FLOAT (IPNT - NPTS - 2)) VARNCE = (SUMY2(1)+A\*A\*SUM+B\*B\*SUMX2-2.\*(A\*SUMY(1)+B\*SUMXY(1)-& A\*B\*SUMX))/C SIGMA=SQRT(VARNCE\*SUMX2/DELTA) SIGMB=SQRT(VARNCE\*SUM/DELTA) R=(SUM\*SUMXY(I)-SUMX\*SUMY(I))/SQRT(DELTA\*(SUM\*SUMY2(I)-

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SUMY(I)\*SUMY(I))) £. XRTA = B \* DEPTHBVAL = A + BTIME \* BEVAL = A + TTIME \* BWRITE (J,130) BTIME, BVAL, TTIME, EVAL WRITE (J,140) XRTA, A, SIGMA, B, SIGMB, R, VARNCE WRITE (J,210) SATCO IF (I .EQ. 1) WRITE (5,220) XRTA, R IF (I .EQ. 2) WRITE (5,230) XRTA, R 700 CONTINUE CALL CLOSE (15) CALL CLOSE (16) CALL CLOSE (12) CALL EXIT 1 FORMAT (2F10.3/2E17.7) 10 FORMAT (1X, 'ENTER EXPERIMENT CODE (6 CHARS. MAX.):') 20 FORMAT (3A2) 21 FORMAT(14X, F10.3, 14X, I10) 30 FORMAT (10X, F6.3, 8X, F6.3) 40 FORMAT (10X, F9.4, 11X, F9.4) 50 FORMAT (1X, 4E17.7) 60 FORMAT (1X, 'ENTER FILE EXTENSION (".\*\*\*") FOR CHANNEL #: 'I2) 70 FORMAT (2A2) 71 FORMAT (' ENTER ERROR LOGGING FILE EXTENSION (FORM: .\*\*\*)') 72 FORMAT (/5X'FILENAME: '2X, 5A2/) FORMAT (5X, 'TIME', 2X, 'CHAN. ', I1, 6X, 'PH', 6X, '[CO2]', 6X'-LOG') 80 90 FORMAT (1X, 5A2, 3F10.3) 110 FORMAT (1X,4110) 120 FORMAT (3X, F8.2, F9.1, 3X, F6.3, 2E13.3) 130 FORMAT (1X, ' &'/2E17.7/2E17.7) 140 FORMAT(' \$'/' \$.. KA='E15.8/' \$'16X'REGRESSION PARAMETERS:' /' \$'16X'Y-INT='E17.7,3X'SIGMA A='E17.7/' \$'16X'SLOPE='E17.7 & ,3X,'SIGMA B='E17.7/ & \$'16X'C, COEFF='F8.5/' \$'16X'STD. ERR.='E17.7) & 150 FORMAT (' ERROR IN SIG. CORR SUBROUTINE') 160 FORMAT (1X, 'DO YOU WANT TO WEIGHT DATA TO INIT. SIG. LEVEL?'/ 1X, 'TYPE 1 FOR "YES"') & 170 FORMAT (1X, 'CHANNEL : '12, 5X'MEAS. PH: 'F10.3, 5X, 'CALC. PH: 'F10.3) 180 FORMAT (10X, F10, 3, 15X, F10.3) 190 FORMAT (1X'USE TIME CORRECTION FACTORS? (1 FOR YES)') FORMAT (' \$'5X'[ CO2 ] SAT. ='E17.7) 210 220 FORMAT (' UPPER BEAM TRANSPORT COEFF. ='2E17.7) 230 FORMAT (' LOWER BEAM TRANSPORT COEFF. ='2E17.7) 240 FORMAT (' TOO MANY DATA POINTS FOR DCFS.FOR (10000 MAX.)') 250 FORMAT (' ERROR OCCURED IN DATA READ AT POINT #'I5) WRITE (5,150) 55 CALL CLOSE (10) CALL CLOSE (15) CALL CLOSE (16) CALL CLOSE (12)

CALL EXIT 45 WRITE (5,250) I CALL CLOSE (10) CALL CLOSE (15) CALL CLOSE (16) CALL CLOSE (12) CALL EXIT END DOUBLE PRECISION FUNCTION CORF1(X) IMPLICIT REAL\*8(C,S,E,X) DIMENSION CAL(2,4) COMMON CAL, STPH CORF1=CAL(1,1)+CAL(1,2)\*X+CAL(1,3)\*X\*\*2+CAL(1,4)\*X\*\*3-STPH RETURN END DOUBLE PRECISION FUNCTION CORF2(X) IMPLICIT REAL\*8(C,S,E,X) DIMENSION CAL(2,4) COMMON CAL, STPH CORF2=CAL(2,1)+CAL(2,2)\*X+CAL(2,3)\*X\*\*2+CAL(2,4)\*X\*\*3-STPH RETURN END DOUBLE PRECISION FUNCTION ECOR1(X) IMPLICIT REAL\*8(C,S,E,X) DIMENSION CAL(2,4) COMMON CAL, STPH, ENDPH ECOR1=CAL(1,1)+CAL(1,2)\*X+CAL(1,3)\*X\*\*2+CAL(1,4)\*X\*\*3-ENDPH RETURN END DOUBLE PRECISION FUNCTION ECOR2(X) IMPLICIT REAL\*8(C,S,E,X) DIMENSION CAL(2,4) COMMON CAL, STPH, ENDPH ECOR2=CAL(2,1)+CAL(2,2)\*X+CAL(2,3)\*X\*\*2+CAL(2,4)\*X\*\*3-ENDPH RETURN END

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## CO2KIN.FOR

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CO2KIN.FOR integrated the CO<sub>2</sub> kinetics defined by Eq. 34 for an aqueous solution containing DCFS, HOPSA and CO<sub>2</sub>. The aqueous phase pH was calculated by the function CHHODC.FOR which is listed after CO2KIN.FOR. CHHODC.FOR is a linear bisection root finder similar in form to GETZER.FOR.

\_\_\_\_\_

IMPLICIT REAL\*8 (A,B,C,D,E,F,G,H,U,V,W,X,Y,Z,S,P,O,Q,T,R), & INTEGER (I,J,K,L,M,N) EXTERNAL CTFUNC,CTOUT,CHHODC DIMENSION W(1,7),CT(1)

COMMON AO, CA, CB, CS, DC, RK13, RK31, XKA, XKD2, XKD3, XK1, & XK2, XKW, IUNIT, XSTEP ACTIV(X, Y, Z) = 10.00000 \*\*& (-1.0000\*(AL\*(2\*\*2.000)\*(DSQRT(X)/(1.000+(B\*Y\*DSQRT(X)))))) IUNIT=10 CALL ASSIGN (10, 'CO2KIN.INP', 10, 'RDO') READ (10,\*) STPH, TEMP, SISS READ (10,\*) RK31, RK13, PATM READ (10,\*) TIME, TEND, TOL, XPTS READ (10,\*) VHOP, CHOP, VDCFS, CDCFS, VOL CALL CLOSE (10) AO=VHOP\*CHOP/VOL DC=VDCFS\*CDCFS/VOL TEK=TEMP+273.0000 PKH=2385.73/TEK-14.0184+.0152642\*TEK-SISS\*(.28596-6.167E-4\*TEK) HENRY=10.00\*\*(PKH)PKW=(-4470.99/TEK)+6.0875-(0.01706\*TEK) XK1W=10.00\*\*(PKW) PKONE=(-3405.41/TEK)+14.8422-(0.0327698\*TEK) XKONE=650.0\*(10.00\*\*(PKONE)) PKTWO=(-2894.31/TEK)+6.4530-(0.0237282\*TEK) XKTWO=10.00\*\*(PKTWO) EPSIL=(-1.000\*TEK\*0.3616838)+186.1657 AL=1.82E06\*(EPSIL\*TEK)\*\*(-1.5000) B=50.3\*(EPSIL\*TEK)\*\*(-.50000) ACTH=ACTIV(SISS, 9.00, 1.00)ACTOH=ACTIV(SISS, 3.00, 1.00) ACTHCO=ACTIV(SISS, 4.00, 1.00) ACTCO=ACTIV(SISS, 5.00, 2.00) XKA=10.\*\*(-7.3)XKD2=10.\*\*(-3.5) XKD3=10.\*\*(-5.0)XK1=(XKONE/(ACTH\*ACTHCO)) XK2=((XKTWO\*ACTHCO)/(ACTH\*ACTCO)) XKW=(XK1W/(ACTH\*ACTOH)) CS=HENRY\*PATM XH=(10.\*\*(-1.\*STPH))/ACTH CDAN=A0\*(XKA/(XH+XKA))CDCF1=DC\*(XH\*XKD2/(XH\*XH + XKD2\*XH + XKD2\*XKD3)) CDCF2=DC-CDCF1 IF (STPH .GT. 6.65) GOTO 5 CA= XH - XKW/XH - CDAN + 2.0\*DC - CDCF1 - 2.0\*CDCF2 CB = 0.000GOTO 15 CB= XKW/XH - XH + CDAN + CDCF1 + 2.0\*CDCF2 - 2.0\*DC CA = 0.000CALL ASSIGN (IUNIT, 'CO2KIN.OUP', 10, 'NEW', 'NC') WRITE (IUNIT, 50) STPH, TEMP, SISS FORMAT (1X'START PH='F6.3,5X, 'TEMP.= 'F4.1,5X, 'I='F6.3) WRITE (IUNIT,60) RK31, RK13, CS

5

15

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WRITE (5,60) RK31, RK13, CS
60
        FORMAT (1X, 'K31 = 'F7.4, 5X, 'K13 = 'E10.3, 5X, '(C02) SAT. = 'E10.3)
        WRITE(IUNIT, 70) XKA, XK1, XK2, XKW
70
        FORMAT(1X, 'KA='E10.3, 5X'K1='E10.3, 5X, 'K2='E10.3, 5X, 'KW='E10.3)
        WRITE (IUNIT, 80) TOL, TIME, TEND, XPTS
80
        FORMAT(1X, 'TOL ='D10.2, 5X, 'TIME1 ='E10.2, 5X'TIME2 ='E10.2, 5X
     &
                'POINTS = F4.0
        WRITE (IUNIT, 130) A0, DC, XKD2, XKD3
        WRITE (5,130) A0, DC, XKD2, XKD3
130
        FORMAT (1X, '[HOPSA] = 'E10.3, 5X'[DCFS] = 'E10.3/
     &
                 1X, 'K2-DCFS = 'E10.3, 5X'K3-DCFS = 'E10.3)
           XSTEP=(TEND-TIME)/XPTS
           WRITE (IUNIT.20)
           WRITE (5,20)
20
           FORMAT (4X'TIME'5X'pCT'6X'pH')
           IFAIL=1
           INUM=1
            IR=0
            CALL D02BBF(TIME, TEND, INUM, CT, TOL, IR, CTFUNC, CTOUT, W, IFAIL)
            IF (TOL .LT. 0) WRITE (5,120)
120
            FORMAT (2X'RANGE TOO SHORT FOR TOL')
        CALL CLOSE (IUNIT)
        CALL EXIT
        END
        SUBROUTINE CTFUNC(T,C,F)
        IMPLICIT REAL*8 (A, C, D, F, R, T, X, Y)
        COMMON AO, CA, CB, CS, DC, RK13, RK31, XKA, XKD2, XKD3, XK1,
     & XK2, XKW, IUNIT, XSTEP
        DIMENSION F(1), C(1)
        EXTERNAL CHHODC
        F(1) = RK31*(CS - C(1)) -
               RK13*(CHHODC(C(1))**2)*XK1*C(1)/
     &
     &
               ((CHHODC(C(1))**2)+XK1*CHHODC(C(1))+XK1*XK2)
        RETURN
        END
        SUBROUTINE CTOUT(X,CT)
        IMPLICIT REAL*8 (A,C,D,F,H,P,R,T,X,Y)
        DIMENSION CT(1)
        COMMON AO, CA, CB, CS, DC, RK13, RK31, XKA, XKD2, XKD3, XK1,
     & XK2, XKW, IUNIT, XSTEP
        EXTERNAL CHHODC
        XH = CHHODC(CT(1))
        PCT=0.D0
        IF (CT(1) .GT. 0.D0) PCT=-1.*DLOG10(CT(1))
        PH=-1.*DLOG10(XH)
        T=X
           WRITE (IUNIT, 40) T, PCT, PH
           WRITE (5,40) T,PCT,PH
           FORMAT (D10.3,2F7.2)
        X=X+XSTEP
```

# RETURN END CHHODC . FOR

This function solved the aqueous solution charge balance equation for  $[H^+]$  by an iterative bisection and interpolation procedure. The form of the charge balance equation used is described in Appendix B.

DOUBLE PRECISION FUNCTION CHHODC(CVAL) IMPLICIT REAL\*8 (A, B, C, D, E, F, H, R, S, X, Y, Z) COMMON AO, CA, CB, CS, DC, RK13, RK31, XKA, XKD2, XKD3, XK1, & XK2, XKW, IUNIT, XSTEP INTEGER IFAIL, IFAIL1, IND, IR, POIAAF DIMENSION C(17)  $CONCH(H) = H + CB - CA - AO \times (XKA/(H + XKA)) - XKW/H -$ & CVAL\*((XK1\*H+2.\*XK1\*XK2)/(H\*\*2+H\*XK1+XK1\*XK2))+ & DC\*(2.-(H\*XKD2+2.\*XKD2\*XKD3)/(H\*\*2+H\*XKD2+XKD2\*XKD3)) DATA SRNAME /8H CHFUNC / THIS FUNCTION COMPUTES (H+) FOR A GIVEN [CO2] AND INITIAL DYE С С CONCENTRATION. THE DYE'S TOTAL CONC. IS GIVEN IN 'AO' AND ITS KA С IS GIVEN IN 'XKA'. IT RETURNS THE C VALUE FOR [H+] AS CH. NO ASSUMPTIONS WERE MADE IN THE CALCULATION С SO IT IS VALID FOR ANY PH AND [CO2]. С TO USE THIS FUNCTION MUST DEFINE ALL VARIABLES IN COMMON BLOCK IN C THE VARIABLES 'CS', 'RK13', 'RK31', 'IUNIT', AND CALLING PROGRAM. С 'XSTEP' С ARE NOT USED AND MAY BE DUMMIES IN THE CALLING PROGRAM. CH.FOR С FUNCTIONS EQUIVALENTLY TO THE SNAG ROUTINE 'GETZER'. IT MUST BE С COMPILED WITH THE ROUTINES 'ZERPRT', 'XO2AAF' AND 'PO1AAF' TO WORK. C THE VARIABLES DEFINED IN CH. FOR ARE: С A: MINIMUM VALUE FOR H С B: MAXIMUM VALUE FOR H ZERO MUST LIE BETWEEN A AND B С EPS: CONTROLS ACCURACY TO WHICH ROOT IS FOUND С ETA: A SECOND FORM OF ACCURACY CONTROL. SEE DOC. FOR GETZER.FOR A=1.D-14 B=1.D0 EPS=1.D-14 ETA=0.D0 IFAIL1 = 1С INPUT ERROR IF (A.EQ.B .OR. EPS.LE.O.DO) GO TO 120 X = AFX = CONCH(X)IFAIL1 = 0ZERO AT INITIAL POINT С IF (DABS(FX).LT.ETA .OR. FX.EQ.O.DO) GO TO 120 Y = XC(1) = FXX = BFX = CONCH(X)

С ZERO AT INITIAL POINT IF (DABS(FX).LT.ETA .OR. FX.EQ.O.DO) GO TO 120 IFAIL1 = 1С NO ROOT IN RANGE IF (DSIGN(1.D0,FX).EQ.DSIGN(1.D0,C(1))) GO TO 120 IR = 0IND = -120 CALL ZERPRT(X, Y, FX, EPS, IR, C, IND, IFAIL1) IF (IND.EQ.0) GO TO 40 FX = CONCH(X)IF (DABS(FX),GE.ETA .AND. FX.NE.O.DO) GO TO 20 С ZERO HIT EXACTLY IFAIL1 = 0GO TO 120 40 IF (IFAIL1.EQ.0) GO TO 120 GO TO (60, 60, 60, 100, 80), IFAIL1 С IMPOSSIBLE EXIT 60 IFAIL1 = 4GO TO 120 С TOO MUCH ACCURACY REQUESTED 80 IFAIL1 = 2GO TO 120 С PROBABLY A POLE 100 IFAIL1 = 3120 IFAIL = P01AAF(IFAIL, IFAIL1, SRNAME) CHHODC=X RETURN END

# ------

#### PWIDTH.FOR

\_\_\_

PWIDTH.FOR detected fluorescence fluctuation peaks in experimental time series such as shown in Figure 13 and 15. The algorithm used was as described in the text. Not listed are the subroutines PWFIT.FOR which computed the slope at each data point by linear regression, PEAAVG.FOR which calculated  $T_A$  and SLOPE.FOR which calculated  $S_m$  from the background fluorescence fluctuation time series.

IMPLICIT REAL\*4 (A, B, D, E, F, P, R, S, X, Y, Z)
VIRTUAL XDATA(30000)
DIMENSION SLPAR(5), XAVG(75), ZREG(75), YREG(75)
INTEGER\*2 INAME(6), ONAME(5)
INAME(6) = ' '
ONAME(4) = '.P'
ONAME(4) = '.P'
ONAME(5) = 'WD'
CALL ASSIGN (11, 'PWFILE.DAT', 10, 'RDO')
S READ (11, 20, END = 105) (INAME(I), I = 1, 5)
C. READ IN ANALYSIS PARAMETERS FROM FILE: PWFILE.DAT
```
C . THESE PARAMETERS ARE:
C . . . . IFILT = RUNNING MEAN FILTER WIDTH (MUST BE ODD AND < 75)
C . . . . . SMAX = MAXIMUM SLOPE FOR PEAK DETECTION
C . . . . . . . . IF INAME(1) = 'SF' AND SMAX <= 0.
                                                        SMAX CALCULATED
C . . . . . . . . . . . . . . . FROM DATA BY SUBROUTINE 'SLOPE.FOR'. THIS VALUE
C . . . . . . . . . IS USED FOR SUBSEQUENT SETS UNTIL INAME(1) = 'SF'
C . . . . . . . . OR SMAX > 0.0E0
  . . . . ICMAX = MAX NUM PTS FOR S > SMAX FOR PEAK DETECTION
С
        READ (11,*) IFILT, SMAX, ICMAX
        IF (SMAX .LT. 0.0E0 .AND. INAME(1) .NE. 'SF')
     & SMAX = 2.0E0 \times SLPAR(4)
C. IF IFILT = 1 OR O NO FILTERING PERFORMED
C . IF IFILT > 75 THEN IFILT = 75
        IF (IFILT .GT. 75) IFILT = 75
C . START DATA INPUT FOR UNFORMATTED FILES
        TRATE = 0.0E0
        DO 100 I=1,3
100
           ONAME(I) = INAME(I)
        CALL ASSIGN (12, ONAME, 10, 'NEW', 'NC')
        OPEN (UNIT = 10, NAME = INAME, TYPE = 'OLD',
     &
              FORM = 'UNFORMATTED', ERR = 135)
        IPNT = 0
        ISET = 0
        READ (10) FSIG, FPOW
15
        ISET = ISET + 1
        READ (10, END=35) FLAP, FRATE
        WRITE (5, 110) (INAME(I), I = 1, 5), ISET
        TRATE = TRATE + FRATE
        IF (ISET .GT. 1) GOTO 25
        READ (10, ERR=115) I, J, K
        XPR = FLOAT(K) * 0.10E0 - FPOW
        IPNT = 3000 * (ISET - 1) + I
        XDATA(IPNT) = -1.E0 * (FLOAT(J)*0.10E0 - FSIG)
25
           READ (10, ERR=115) I, J, K
           IPNT = 3000 * (ISET - 1) + I
           XPOW = FLOAT(K) \times 0.10E0 - FPOW
           XDATA(IPNT) = -1.0E0 * (0.10E0*FLOAT(J) - FSIG) * XPR/XPOW
           IF (I .EQ. 3000) GOTO 15
        GOTO 25
35
        CALL CLOSE (10)
        IPNTS = IPNT
        TRATE = TRATE / FLOAT (ISET - 1)
        TINT = 1.E0 / TRATE
C . RUNNING MEAN FILTER CALL
        CALL RUNMEA (XDATA, IPNT, XAVG, IFILT)
C. IF INAME(1) = 'SF' THEN SMAX COMPUTED FROM DATA BY CALL TO "SLOPE"
C . THIS VALUE OF SMAX IS USED UNTIL A NEW 'SF' FILE IS ENCOUNTERED
C . "SLOPE" RETURNS SLOPE PARAMETERS IN ARRAY SLPAR IN FOLLOWING ORDER:
C . . . . SLPAR(1) = MIN. SLOPE
C . . . . SLPAR(2) = MAX. SLOPE
```

 $C \dots SLPAR(3) = AVG. SLOPE$ C . . . . SLPAR(4) = STD. DEV OF SLOPE AVG. . . . . . SLPAR(5) UNUSED С С IF (INAME(1) .NE. 'SF' .OR. SMAX .GT. 0.0E0) GOTO 65 CALL SLOPE (IPNT, XDATA, IFILT, ZREG, YREG, SLPAR) SMAX = 2.0E0 \* SLPAR(4). . . IREG = NUM PTS USED IN LIN. REG. TO FIND SLOPE (25 MAX.) С. 65 IREG = (IFILT / 2) + 1IF (IREG .LT. 3) IREG = 3IF (IREG .GT. 75) IREG = 75IPTS = IREGIRG2 = (IREG - 1) / 2IPMAX = IPNTS - IRG2 IPNT = IRG2IBEGP = 0IENDP = 0DO 900 I = 1, IREG ZREG(I) = FLOAT(I)IF (I .EQ. 1) GOTO 900 YREG(I) = XDATA(I-1)900 CONTINUE WRITE (12,70) (SLPAR(I), I = 1, 4) WRITE (12,80) ICMAX, SMAX, IFILT, IREG WRITE (12,90) (INAME(I), I = 1, 5) C . BEGIN LINEAR REGRESSION CALCULATIONS 45 IMAX = 0IEND = 0IEMAX = 055 IPNT = IPNT + 1IF (IPNT .GT. IPMAX) GOTO 95 DO 1000 J = 2, IREG YREG(J-1) = YREG(J)1000 CONTINUE YREG(IREG) = XDATA (IPNT + IRG2)75 CALL PWFIT (ZREG, YREG, IPTS, B) C . INITIAL CHECK FOR SIGN OF SLOPE IF (B .GT. 0.0E0) GOTO 85 C . SLOPE < 0, IF IBEGP NOT SET THEN NOT END OF PEAK RETURN IF (IBEGP .EQ. 0) GOTO 45 C . RESET IVAL = O FOR VALLEY DETECTION IVAL = 0C . ABS (SLOPE) > SMAX, STILL ON BACKSIDE OF PEAK, RETURN IF (ABS(B) .GT. SMAX) IEMAX = IEMAX + 1IF (ABS(B) .GT. SMAX) GOTO 55 C . IF SLOPE < SMAX AND IEMAX > 0 THEN INCREMENT IEND AND TEST C . IF IEND NOT INCREMENTED PROBABLY AT TOP OF A PEAK IF (IEMAX .GT. 0) IEND = IEND + 1C . IF IEND < ICMAX, GET NEXT B WITHOUT INITIALIZATION OF IEND C . IF IEND = ICMAX, END OF PEAK. RESET IBEGP = 0

. . . . . . . .

. -

```
IF (IEND .LT. ICMAX) GOTO 55
        PWIDTH = TINT * (FLOAT (IPNT - IBEGP))
        TSTART = TINT * FLOAT(IBEGP)
        TEND = TINT * FLOAT(IPNT)
        WRITE (12, 30) TSTART, TEND, PWIDTH
        WRITE (5, 30) TSTART, TEND, PWIDTH
        IBEGP = 0
C . RETURN TO INIALIZATION FOR NEXT B AND NEW PEAK
        GOTO 45
C . CHECK TO SEE IF END PEAK PARAMETERS ARE SET
C . IF THEY ARE THEN INCREMENT VALLEY CHECK PARAMETER, IVAL
85
        IF (IEMAX .LT. ICMAX) GOTO 125
        IVAL = IVAL + 1
        IF (IVAL .LT. ICMAX) GOTO 55
C . VALLEY DETECTED, COMPUTE PEAKWIDTH
        PWIDTH = TINT * (FLOAT (IPNT - ICMAX - IBEGP))
        TSTART = TINT * FLOAT(IBEGP)
        TEND = TINT * FLOAT(IPNT - ICMAX)
        WRITE (12, 30) TSTART, TEND, PWIDTH
        WRITE (5, 30) TSTART, TEND, PWIDTH
        IBEGP = IPNT - ICMAX
        IEMAX = 0
        IEND = 0
        IMAX = ICMAX
C . IF B < SMAX AND IBEGP = 0, NO PEAK RETURN FOR NEW B
C . IF B < SMAX AND IBEGP > 0, NEAR TOP OF PEAK, RETURN BUT DO
C . NOT INITIALIZE IMAX, IEND OR IBEGP
125
        IF (B .LT. SMAX .AND, IBEGP .EQ. 0) GOTO 45
        IF (B .LT. SMAX .AND. IBEGP .GT. 0) GOTO 55
        IMAX = IMAX + 1
C . RETURN WITHOUT INIALIZATION OF IMAX FOR IMAX .NE. ICMAX
C . IF IMAX < ICMAX, NO PEAK DETECTED YET
C . IF IMAX > ICMAX, PEAK ALREADY DETECTED
C . DO NOT RESET IBEGP IN EITHER CASE
        IF (IMAX .NE. ICMAX) GOTO 55
C . INITIALIZE PEAK MARKER
        IBEGP = IPNT - ICMAX
C . RETURN TO NEXT B WITHOUT RESET OF ANYTHING
        GOTO 55
95
        CALL CLOSE (12)
C . SORT PEAK WIDTH FILE FOR PLOTTING BY PWGRA.FOR
C . DEFINE SORTING WIDTH AS IFILT * TINT
        WSTEP = FLOAT(IREG) * TINT
        CALL PWSORT (ONAME, WSTEP)
C . RETURN FOR NEXT DATA FILENAME
        GOTO 5
105
        CALL CLOSE (11)
        CALL EXIT
C . DATA READ ERROR TRAP
       WRITE (5,60) ISET, I
115
```

. . . . . . .

		CALL EX	IT			
С.	INPUT FILE ERROR HANDLER					
135		WRITE (	12, 120) INAME			
		WRITE (	5, 120) INAME			
		CALL CL	OSE (12)			
		GOTO 5				
10		FORMAT	(1X, 'SET #'I3, 5X, 'MAXIMUM SLOPE ='E17.7, 5X,			
	&		'MAXIMUM LENGTH ='16)			
20		FORMAT	(1X, 5A2)			
30		FORMAT	(1X, 2F7.2, F7.3)			
40		FORMAT	(1X, 'ICMAX = 'I4)			
60		FORMAT	(1X, 'READ ERRORSET #'12,5X, 'POINT #'14)			
70		FORMAT	(1X, 'SMIN = 'E10.2, 3X, 'SMAX = 'E10.2, 3X, 'SAVG = 'E10.2, 3X,			
	&		'SDEV ='E10.2)			
80		FORMAT	(1X, 'ICMAX = 'I3, 5X, 'SMAX = 'F8.4, 5X, 'IFILT = 'I4,			
	&		5X, 'IREG ='I4)			
90		FORMAT	(5X, 'DATA FILE: '1X, 5A2)			
110		FORMAT	(1X, 'INPUT FILE: '5A2,5X, 'DATA SET #'I2)			
120		FORMAT	(1X, 'FILE: '6A2'COULD NOT BE OPENED. NO ACTION TAKEN')			
		END				

# PWSORT . FOR

. . . . . . . . . . . .

SUBROUTINE PWSORT(INAME, WSTEP)					
C . INAME GIVES THE FILENAME WITH THE RAW PEAK WIDTH DATA					
C . SORTED DATA IS STORED IN FILE; '*****,AVG'					
C . WSTEP IS THE SORTING INTERVAL DEFINED IN THE CALLING PROGRAM					
C . IF WSTEP $\leq 0.80$ THEN WSTEP = $0.05$					
IMPLICIT REAL*4 (P, W)					
VIRTUAL WIDTH(7500, 2)					
DIMENSION $W1(2)$ , $W2(2)$					
INTEGER INAME(5), ONAME(5)					
IF (WSTEP .LE. $0.0E0$ ) WSTEP = $0.05E0$					
ONAME(4) = '.A'					
ONAME(5) = 'VG'					
WRITE (5,10)					
CALL ASSIGN (20, INAME, 10, 'RDO')					
DO 100 I = 1, 3					
100 $ONAME(1) = INAME(1)$					
CALL ASSIGN (21, ONAME, 10, 'NEW', 'NC')					
WRITE (21,30) INAME					
DO 200 I = 1, 7500					
WIDTH(I,1) = -1.E0					
WIDTH(I,2) = -1.E0					
200 CONTINUE					
READ (20, *)					
READ (20, *)					
READ (20, *)					
IPNT = 0					
5 IF (IPNT .EQ. 7500) GOTO 85					

```
READ (20, *, ERR=95, END=15) XDUM, (WIDTH(IPNT+1,I), I=1,2)
        IPNT = IPNT + 1
        GOTO 5
15
        IF (IPNT .EQ. 0) GOTO 105
        INROW = 7500
        INCOL = 2
        ICOL = 2
        IFAIL = 0
C . CALL TO LB SORTING SUBROUTINE 'MATSOR'
C . THIS VERSION OF MATSOR MUST BE single precision
C . AND THE MAIN DATA ARRAY MUST BE A virtual
        CALL MATSOR (WIDTH, INROW, INCOL, ICOL, W1, W2, IFAIL)
        IF (IFAIL .NE. 0) GOTO 75
        CALL PEAAVG (WIDTH, WSUM, WCNT, WAVG, WDEV)
        WRITE (21, 110) WSUM, WCNT, WAVG, WDEV
        DO 300 I = 1, 7500
           IF (WIDTH(1,2) .NE. -1.E0) GOTO 25
300
        CONTINUE
        WRITE (5,40)
        CALL EXIT
25
        IPT = I
        PNUM = 0.E0
        IBIN = 0
35
        IBIN = IBIN + 1
        WCNT = 0.E0
        WMAX = WSTEP * FLOAT(IBIN)
45
        IF (WIDTH(IPT,2) .GT. WMAX) GOTO 55
        WCNT = WCNT + 1.E0
        IPT = IPT + 1
        IF (IPT .EQ. 7501) GOTO 55
        GOTO 45
55
        WVAL = WMAX - 0.5E0 * WSTEP
        WRITE (21,50) WVAL, WCNT
        IF (IPT .EQ. 7501) GOTO 65
        GOTO 35
65
        CALL CLOSE (20)
        CALL CLOSE (21)
        WRITE (5,80)
        RETURN
75
        WRITE (5,60) IFAIL
        CALL EXIT
85
        WRITE (21,20)
        WRITE (5,20)
        GOTO 15
95
        WRITE (5,90) IPNT
        GOTO 5
105
        WRITE (5,120)
        WRITE (21,120)
        CALL CLOSE (20)
        CALL CLOSE (21)
```

:

		RETURN	
10		FORMAT	(1X,'PWSORT START')
20		FORMAT	(1X, 'WARNING! TOO MANY PEAKS FOUND FOR PWSORT')
30		FORMAT	(1X,5A2/6X,'WIDTH',6X,'COUNT')
40		FORMAT	(1X, ' ERROR NO PEAKS SORTED')
50		FORMAT	(1X,F7.3,F7.0)
60		FORMAT	(1X, 'MATSOR ERROR IFAIL ='14)
70		FORMAT	(1X, 'IBIN OUT OF RANGE')
80		FORMAT	(1X, 'PWSORT FINISH')
90		FORMAT	(1X, 'ERROR READING DATA POINT #'I4)
110		FORMAT	(1X, 'TOTAL PEAK TIME ='F10.3, 5X, '# OF PEAKS ='F10.0/
	&		1X, 'AVERAGE PEAK WIDTH = 'F10.7, 5X, 'STD. DEV. = 'E12.5)
120		FORMAT	(1X, 'NO PEAKS DETECTED')
		END	

## AVGFIT, FOR

5

AVGFIT.FOR performs a least-squares polynomial regression on  $f_{\tau}(T)$ . This determines the best fit polynomial for  $f_{\tau}(T)$ . The regression is performed by the subroutine POLFIT.FOR (Bevington, 1969). The output is used in the program KADANCK.PAS to calculate  $k_{\mu}$ using the procedure outlined in Section 4.C. AVGFIT.FOR is written in FORTRAN-77 (Microsoft v3.31, Microsoft, Redmond, WA).

```
Implicit real*8 (x, y, z)
        Dimension x(200), y(200), ysig(200), zpar(10)
        Character*12 iname, oname, fname
        write (*, '(a\)') ' enter file listing: '
        read (*, '(a)') fname
        write (*, '(a )') ' enter number of terms (10 max.): '
        read (*, *) ireg
        write (*, '(a\)') ' enter fitting mode for sigy: '
        read (*, *) imode
        open (10, file=fname, status='old')
        open (12, file='regdata.txt', status='new')
        read (10, (a, 1x, a)', end = 95) iname, oname
           write (12, '(a)') iname
           open (11, file=iname, status='old')
           do 100 i = 1, 4
                read (11, *)
100
           continue
           x(1) = 0.0
           y(1) = 0.0
           ysig(1) = 0.0
           i = 2
15
           read (11, *, end = 25) x(i), y(i)
                ysig(i) = 1.0d0
                if (imode .eq. 1) ysig(i) = 1.0d0 / dsqrt(y(i))
```

```
i = i + 1
               goto 15
25
          close (11)
          ipnt = i - 1
          call polfit (x, y, y, ipnt, ireg, mode, zpar, xi2, xcof)
          &
          write (12, '(1x,a,f10.4)') 'x-maximum=', x(ipnt)
          open (11, file=oname, status = 'new')
          do 200 i = 1, ipnt
               yreg = zpar(1)
               if (i .eq. 1) write (12, '(a, e17.7)') ' a(0)=', zpar(1)
               do 201 j = 2, ireg
                  if (i .eq. 1) write (12, '(a,i1,a,e17.7)')
                     ' a(', j-1,')=',zpar(j)
    æ
                 yreg = yreg + zpar(j) * (x(i)**(j-1))
201
               continue
               write (11, '(1x,f10.4,2f17.2)') x(i), y(i), yreg
200
          continue
          close (11)
       goto 5
95
       close (12)
       close (10)
       stop
       end
```

```
KADANCK . PAS
```

KADANCK.PAS computed  $k_L$  from Eq. 44 by use of the polynomial coefficients generated by the least squares fitting program AVGFIT.FOR. The program is written in TurboPascal v3.01 (Borland International, Scotts Valley, CA).

```
PROGRAM kadanck (input, output);
(calculates kL from a series of polynomial coefficients for f(t))
\{f(t) = a0 + a1 t + a2 t^2 + ... + a(n)t^n\}
CONST
   npt=200;
  mp=npt;
TYPE
   glmma = ARRAY [1..25] OF real;
   name = string(30];
   filvar = text;
VAR
   npol : integer;
   chisq, kL, power, sum, sumn, xmax, ytest, ytest2 : real;
   ipt, i, i1, i2, imax, j, j2 : integer;
   a : glmma;
   dname, iname, oname : name;
```

```
dfile, ifile, klfile, ofile : filvar;
   fstat : boolean;
   dum10 : string[10];
   dumll : string[11];
PROCEDURE func(x: real; VAR p: glmma; mma: integer);
(* This is essentially FPOLY renamed. *)
VAR
   j: integer;
BEGIN
   p[1] := x;
   FOR j := 2 to mma DO p[j] := p[j-1]*x
END;
function pterm (x : real; i : integer) : real;
(calculates power of x)
var
   n : integer;
   xdum : real;
begin
     if (i > 1) then begin
        xdum := 1.0;
        for n := 1 to i do begin
            xdum := xdum * x
        end;
        pterm := xdum;
     end;
     if (i = 1) then pterm := x;
     if (i = 0) then pterm := 1.0;
end;
function capf (x : real; a : glmma; i : integer) : real;
(evaluates F(t) (integrated f(t)) for polynomial approximation)
var
   xdum : real;
   j, jl : integer;
begín
     xdum := 0.;
     for j := 1 to i do begin
         xdum := xdum + a[j] * pterm(x, j) / j;
     end;
     capf := xdum;
end;
function fterm (x, power : real) : real;
var
   xdum : real;
begin
   xdum := power * \ln(x);
   fterm := exp(xdum);
```

-- ----

end;

```
begin
     {open regression data input file and output file}
     repeat
           write ('enter regression data input filename: ');
           readln (dname);
           assign (dfile, dname);
           {$I-} reset (dfile) ($I+);
           fstat := (ioresult = 0);
           if not fstat then writeln ('cannot file regression file: ', dname);
     until fstat;
     write ('enter kL data output filename: ');
     readln (oname);
     assign (ofile, oname);
     rewrite (ofile);
     (read in polynomial coefficients from program AVGFIT.FOR (POLFIL.FOR))
     write ('please enter number of terms used in fit (25 max.): ');
     readln (npol);
     while not EOF(dfile) do
     begin
           readln (dfile, iname);
           writeln (ofile, iname);
           readln (dfile);
           readln (dfile, dum11, xmax);
           i := 1;
           while not EOF(ifile) and (i <= npol) and fstat do
           begîn
                ($I-) readln (dfile, dum10, a[i]) ($I+);
                fstat := (ioresult = 0);
                i := i + 1;
           end;
           i := i - 1;
           i1 := i - 1;
           i2 := i - 2;
           ipt := i;
           imax := i;
           {integrate polynomial and normalize coefficients}
           sum := capf(xmax, a, npol);
           for i := 1 to npol do a[i] := a[i] / sum;
           writeln (ofile,'normalization constant =', sum:14:3);
(end of integration and normalization)
(calculate phi(theta) and integrate to find normalization)
\{phi(theta) = 1 - F(theta)\}
           sumn := xmax;
           for i := 1 to npol do
           begin
                i1 := i;
                i2 := i + 1;
                sumn := sumn - a[i] * pterm(xmax, i2) / (i1 * i2)
```

```
end;
           writeln (ofile, 'normalization for phi(theta) =', sumn: 15:6);
(end calculation of normalization constant)
{calulate kL by integration of (phi(theta)/sqrt(theta))}
           sum := 2.0 * sqrt(xmax);
           for i := 1 to npol do
           begin
                power := i + 0.5;
                i1 := i;
                sum := sum - a[i] * fterm(xmax, power) / (power * il)
           end;
           sum := sum / summ;
           kL := sqrt(1.76e-05/pi) * sum * 10000.;
           writeln (ofile,'
                               kL =', kL: 16:6);
           writeln (ofile);
           writeln (ofile);
     end;
{end kL calculation}
     close (ofile);
     close (dfile);
end.
```

### APPRCH, FOR

- -

APPRCH.FOR calculated  $z_e$  from the surface fluorescence fluctuation time series such as shown in Figures 13 and 15. The calculation of  $z_e$  was done by the subroutine APCALC.FOR which is listed below. APSORT.FOR was very similar in form to PWSORT.FOR and so was not listed.

```
APPRCH.FOR (5th ORDER REGRESSION, AUTOCALCULATION OF kL)
C PROGRAM APPRCH. FOR
С
  PURPOSE IS TO CALCULATE EDDY PENETRATION DISTRIBUTIONS FROM
  SURFACE TIMESCALE DATA TAKEN WITH ORANGE-G
С
  THIS VERSION CALCULATES Asat BY USING THE MINIMUM SIGNAL OBSERVED
С
  IT ALSO CALCULATES KL INTERNALLY FROM INITIAL AND FINAL pH VALUES
С
  THIS SEEM TO PROVIDE THE MOST REALISTIC APPROACH DISTANCE
С
С
  DISTRIBUTION (FEWEST NEGATIVE DISTANCES).
        IMPLICIT REAL*8 (A, B, C, D, E, G, H, P, Q, R, S, T, U, V, W),
                 REAL*4 (F, X, Y, Z), INTEGER (I, J, K, L, M, N, O)
     &
        VIRTUAL IBEG(1000), IEND(1000), XDATA(30000)
        DIMENSION RA(6), SA(3), XAVG(75), TIME(151), SREG(151),
                  INAME(5), ONAME(5)
     &
        COMMON AO, CA, CB, CS, DC, RKA, RKD2, RKD3, RK1, RK2, RKW, RKL,
               RA, ALPHA, ASAT, HEIGHT, ACTH, STPH
     δ
        EXTERNAL CH, SICAL, COCAL
        ACTIV(R, S, T) = 10.00**
     & (-1.0D0*(AL*(T*T)*(DSQRT(R)/(1.0D0+(B*S*DSQRT(R))))))
```

```
ALPH1(R) = 1.0D0 / ((R / RK1) + 1.0D0 + (RK2 / R))
        ALPH2(R) = 1.0D0 / (((R*R)/(RK1*RK2)) + (R / RK2) + 1.0D0)
Ċ
  OPEN PARAMETER FILE
        CALL ASSIGN (10, 'APPRCH.INP', 10, 'RDO')
S
        READ (10, 10) INAME
        IF (INAME(1) .EQ. 'QU') GOTO 155
        READ (10, *) STPH, ENPH, TEMP, SISS
        READ (10, *) SKL, PATM, (RA(1), I = 1, 6)
        READ (10, *) VHOP, CHOP, VDCFS, CDCFS, VOL, XTOG
        READ (10, *) IFILT, ICMAX
  FINISH READING IN INITIAL PARAMETERS
С
   IF IFILT = 1 OR 0 NO FILTERING PERFORMED
C
  IF IFILT > 75 THEN IFILT = 75
С
        IF (IFILT .GT. 75) IFILT = 75
С
   BEGIN COMPUTATION OF EQUIL. COEFFS., CA, CB, CS, AO
        AO = VHOP * CHOP / VOL
        DC = VDCFS * CDCFS / VOL
        TEK = TEMP + 273.0000
        PATM = PATM / 760.0D0
        PKH = 2385.73 / TEK - 14.0184 + .0152642 * TEK - SISS *
     &
             (.28596 - 6.167E-4 * TEK)
        HENRY = 10.00**(PKH)
        PKW = (-4470.99 / TEK) + 6.0875 - (0.01706 * TEK)
        RK1W = 10.00 * * (PKW)
        PKONE = (-3405.41 / TEK) + 14.8422 - (0.0327698 * TEK)
        RKONE = (10.00 * * (PKONE))
        PKTWO = (-2894.31 / TEK) + 6.4530 - (0.0237282 * TEK)
        RKTWO = 10.00 * * (PKTWO)
        EPSIL = (-1,000 * TEK * 0.3616838) + 186.1657
        AL = 1.82E06 * (EPSIL * TEK) * (-1.5000)
        B = 50.3 * (EPSIL * TEK) * (-.50000)
         ACTH = ACTIV (SISS, 9.00, 1.00)
         ACTOH = ACTIV (SISS, 3.00, 1.00)
         ACTHCO = ACTIV (SISS, 4.00, 1.00)
         ACTCO = ACTIV (SISS, 5.00, 2.00)
         RKA = 10. **(-7.3)
         RKD2 = 10.**(-3.5)
         RKD3 = 10.**(-5.0)
         RK1 = (RKONE / (ACTH * ACTHCO))
         RK2 = ((RKTWO * ACTHCO) / (ACTH * ACTCO))
         RKW = (RK1W / (ACTH * ACTOH))
        CS = HENRY * PATM
        RH = (10.**(-1. * STPH)) / ACTH
        CDAN = AO * (RKA / (RH + RKA))
        CDCF1 = DC * (RH * RKD2 / (RH * RH + RKD2 * RH + RKD2 * RKD3))
        CDCF2 = DC - CDCF1
        IF (STPH .GT. -1.0D0 * DLOG10(DSQRT(RKW))) GOTO 15
        CA = RH - RKW / RH - CDAN + 2.0 * DC - CDCF1 - 2.0 * CDCF2
        CB = 0.000
        GOTO 25
```

CB = RKW / RH - RH + CDAN + CDCF1 + 2.0 \* CDCF2 - 2.0 \* DC15 CA = 0.000C INITIAL CALCULATIONS FOR APCALC.FOR 25 XCOG = XTOG / (452.38 \* SNGL(VOL))ZCUT = (2.0 / (19301.0 \* XCOG)) \* 1.0E04 $ALPHA = DBLE(XCOG) \times 19301.000$ SATPH = -1.0D0 \* DLOG10 (CH(CS)\*ACTH) $\text{HEIGHT} = 1.0003 \times \text{VOL} / (25.4 \times 25.4)$ START DATA INPUT FOR UNFORMATTED FILES С FIRST DATA INPUT IS FOR SB????.DAT FILE TO DETERMINE NORMALIZATION С CALL ASSIGN (11, INAME, 10, 'RDO') IPNT = 0ISET = 0XNORM = 0.0E0READ (11) FSIG, FPOW 35 ISET = ISET + 1IF (ISET .GT. 3) GOTO 55 READ (11, END = 55) FLAP, FRATE IF (ISET .GT. 1) GOTO 45 READ (11, ERR = 135) I, J, K XPR = FLOAT(K) \* 0.10E0 - FPOWIPNT = 3000 \* (ISET - 1) + IXNORM = -1.E0 \* (FLOAT(J)\*0.10E0 - FSIG)45 READ (11, ERR = 135) I, J, K IPNT = 3000 \* (ISET - 1) + IXPOW = FLOAT(K) \* 0.10E0 - FPOWXNORM = XNORM + -1.0E0 \* (0.10E0\*FLOAT(J)-FSIG) \* XPR/XPOWIF (1 .EQ. 3000) GOTO 35 GOTO 45 55 CALL CLOSE (11) XNORM = XNORM / FLOAT(1PNT) END CALCULATION OF FLUORESCENCE NORMALIZATION. CONSTANT IS NOW С С STORED IN THE VARIABLE: XNORM Ċ NOW OPEN FILE "SE????.DAT" TO READ IN TRANSPORT DATA INAME(1) = 'SE'CALL ASSIGN (11, INAME, 10, 'RDO') ZRATE = 0.0E0IPNT = 0ISET = 0READ (11) FSIG, FPOW 65 ISET = ISET + 1READ (11, END = 85) FLAP, FRATE ZRATE = ZRATE + FRATE75 READ (11, ERR = 135) I, J, K IPNT = 3000 \* (ISET - 1) + IXPOW = FLOAT(K) \* 0.10E0 - FPOWXDATA(IPNT) = -1.0E0 \* (0.10E0\*FLOAT(J) - FSIG) \* XPR/XPOWIF (I .EQ. 3000) GOTO 65 GOTO 75 85 CALL CLOSE (11)

```
IPNTS = IPNT
        ZRATE = ZRATE / FLOAT (ISET - 1)
        ZINT = 1.E0 / ZRATE
С
  RUNNING MEAN FILTER CALL
        CALL RUNMEA (XDATA, IPNTS, XAVG, IFILT)
С
  THE NEXT LOOP NORMALIZES THE XDATA ARRAY BY XNORM AND ALSO
C
  FINDS THE FIRST SIGNIFICANT DECREASE IN SIGNAL INTENSITY. THIS IS
  DEFINED AS THE POINT WHERE THE SIGNAL HAS DECREASED TO 0.80 * XNORM
С
С
   AND REMAINS BELOW THAT LEVEL FOR ICMAX POINTS. THE FIRST
  DATA POINT WHERE THIS OCCURS IS STORED AS ISTART. THIS IS USED
С
C
  IN CONJUNCTION WITH THE PEAK WIDTH DATA TO FIND MAXIMUMS
        XMIN = 1.0E0
        DO 200 I = 1, IPNTS
           IDUM = I
           XDATA(I) = XDATA(I) / XNORM
           IF (XMIN .GT. XDATA(I)) XMIN = XDATA(I)
200
        CONTINUE
        ASAT = 1.0D0 / DBLE(XMIN)
        I = 1
        IF (XDATA(1) . GT. 0.8) ICNT = 0
95
           IF (XDATA(I) . LE. 0.8) ICNT = ICNT + 1
           IF (ICNT .EQ. ICMAX) GOTO 105
           I = I + 1
           IF (I .GT. IPNTS) WRITE (5, 20)
           IF (I .GT. IPNTS) CALL EXIT
           GOTO 95
105
        ISTART = I - ICNT
        IF (ISTART LT. 1) ISTART = 1
        TTIME = DBLE(FLOAT(IPNTS - ISTART)) * DBLE(ZINT)
C OPEN FILE: SE????.PWD
  THEN READ IN THE STARTING AND ENDING PEAK TIMES. THESE TIMES ARE
C
С
  CONVERTED TO DATA POINT NUMBER BY USE OF THE PARAMETER "ZINT"
С
   THESE INTEGER VALUES ARE STORED IN THE VIRTUAL ARRAYS IBEG AND IEND
        INAME(4) = ', P'
        INAME(5) = 'WD'
        CALL ASSIGN (11, INAME, 10, 'RDO')
        IPNT = 0
        DO 100 I = 1, 3
           READ (11, *)
100
        CONTINUE
115
        READ (11, *, END = 125, ERR = 135) XBEG, XEND, XDUM
           IPNT = IPNT + 1
           IF (IPNT .GT. 1000) GOTO 125
           IBEG(IPNT) = IFIX(XBEG/ZINT)
           IEND(IPNT) = IFIX(XEND/ZINT)
           GOTO 115
125
        CALL CLOSE (11)
        IPEAK = IPNT
 CALCULATE kL FORM ENDING pH
С
        EH = DEXP (-2.302585093 * ENPH) / ACTH
```

ENCO2 = COCAL(EH)RKL = -1.00D0 \* HEIGHT \* DLOG((CS - ENCO2)/CS) / TTIME SKL = 1.0D04 \* RKLС BEGIN MAIN PROGRAM LOOP TO DETERMINE THE EDDY APPROACH DISTANCES С PROCEDURE IS AS FOLLOWS: С 1. FIND SIGNAL MAXIMUM FOR EACH PEAK DEFINED IN IBEG, IEND С 2. DETERMINE THE EXPERIMENTAL TIME TO THE PEAK MAXIMUM С 3. SEND SMAX, ETIME TO SUBROUTINE "APCALC.FOR" С THE RELEVANT PARAMETERS ARE STORED IN XTIME, XDIST С THIS IS DONE SO THAT THE DATA CAN BE SORTED AND BINNED INTO С A DISTRIBUTION AS DONE FOR THE PEAK WIDTHS С OPEN FILE FOR PRIMARY DATA OUTPUT. PRIMARY FILE WILL BE OF THE С FORM SE????. APP. IT WILL BE A SEQUENTIAL TIME LIST OF С XTIME, XDIST, AND XMAX ONAME(4) = '.A'ONAME(5) = 'PP'DO 400 I = 1, 3 ONAME(I) = INAME(I)400 CONTINUE CALL ASSIGN (12, ONAME, 10, 'NEW', 'NC') WRITE (12, 30) STPH, ENPH, TEMP, SISS, VOL WRITE (12, 40) CA, CB, CS, RK1, RK2 WRITE (12, 50) RKW, SKL, (RA(I), I=1,6) WRITE (12, 60) XTOG, ZCUT, SATPH, ASAT WRITE (12, 70) AO, RKA, DC, RKD2, RKD3 WRITE (12, 130) ENCO2, XNORM, HEIGHT, ISTART WRITE (12, 80) DO 300 I = 1, IPEAK IF (IBEG(I) .LT. ISTART) GOTO 300 XMAX = 0.0E0DO 301 J = IBEG(1), IEND(1) IF (XMAX .GE. XDATA(J)) GOTO 301 XMAX = XDATA(J)JMAX = J301 CONTINUE JCNT = (ICMAX - 1) / 2JDUM = 0SSUM = 0.0D0DO 302 J = JMAX-JCNT, JMAX+JCNT  $SSUM \Rightarrow SSUM + DBLE(XDATA(J))$ 302 CONTINUE SMAX = SSUM / DBLE(FLOAT(ICMAX)) ETIME = DBLE(ZINT \* FLOAT(JMAX)) CALL APCALC (SMAX, ETIME, ADIST, 13) WRITE (12, 90) ETIME, ADIST, SMAX 300 CONTINUE CALL CLOSE (12) SORT APPROACH DISTANCES USING SORTING SUBROUTINE "APSORT" Ċ. THEY ARE THEN BINNED AND STORED INTERNALLY IN APSORT. THE FILENAME C С USED TO STORE THE CALCULATED DISTRIBUTION IS OF THE FORM: SE????.DIS C THE DISTRIBUTION PARAMETER IS CALCULATED FROM Zcut, THE FLUORESCENCE C CUTOFF DEPTH. Zcut IS DIVIDED INTO 30 EQUAL BINS STARTING AT Z=0 um 2BIN = (2CUT / 30.0)CALL APSORT (ONAME, ZBIN) С RETURN FOR NEW INPUT FILE GOTO 5 C . DATA READ ERROR TRAP 135 WRITE (5, 110) INAME, ISET, I CALL EXIT C . INPUT FILE ERROR HANDLER 145 WRITE (5, 120) INAME CALL CLOSE (11) GOTO 5 C END OF PROGRAM ROUTINE 155 CALL CLOSE (10) CALL EXIT C BEGIN FORMAT STATEMENTS C NO EXECUTABLE CODE BELOW THIS POINT 10 FORMAT (1X, 5A2) 20 FORMAT (1X, 'NO DATA BEGINNING FOUND FOR FILE: '5A2) 30 FORMAT(1X, 'ST, PH='F6.3, 5X, 'END PH='F6.3, 5X'TEMP = 'F5.2, 5X 'I = 'F6.4,5X, 'VOL.='F6.2) & 40 FORMAT (1X, 'CA='E8.2, 2X'CB ='E8.2, 2X'CS ='E8.2, 2X'K1 ='E8.2 & ,2X,'K2 = 'E8.2)50 FORMAT (1X, 'KW='E9.2, 2X'KL='E9.2, 2X, 'CAL:', 6(E9.2, 1X)) FORMAT (1X, 'OG='F7.2, 5X, 'Zcut='F5.0, 5X, 'SATPH='F6.3, 60 3X, 'Asat='F9.5) & 70 FORMAT (1X, '[HOPSA] = 'E10.3, 5X, 'KHOPSA = 'E10.3/1X, '[DCFS] = 'E10.3, 5X, 'K2DCFS = 'E10.3, 5X, 'K3DCFS = 'E10.3) & 80 FORMAT (1X, 'TIME', 12X, 'DIST', 8X, 'SMAX') 90 FORMAT (1X, F8.3, 2X, F13.3, 3X, F8.3) 110 FORMAT (1X, 'FILE: '5A2, 'READ ERROR SET #'12,5X, 'POINT #'14) 120 FORMAT (1X, 'FILE: '5A2'COULD NOT BE OPENED. NO ACTION TAKEN') 130 FORMAT (1X, '[CO2] = 'E12.4, 5X, 'NORM. =', F9.3, 5X, 'HEIGHT=', F8.3, æ 5X, 'ISTART = ', 15)END DOUBLE PRECISION FUNCTION SICAL(A) IMPLICIT REAL\*8 (A, C, D, R, S) DIMENSION RA(6) COMMON AO, CA, CB, CS, DC, RKA, RKD2, RKD3, RK1, RK2, RKW, RKL, & RA, ALPHA, ASAT, HEIGHT, ACTH, STPH SICAL = RA(1) + RA(2)\*A + RA(3)\*A\*A + RA(4)\*A\*A\*A +RA(5)\*A\*A\*A\*A + RA(6)\*A\*A\*A\*A\*A & RETURN END DOUBLE PRECISION FUNCTION COCAL(H) IMPLICIT REAL\*8 (A, C, D, H, R, S) DIMENSION RA(6) COMMON AO, CA, CB, CS, DC, RKA, RKD2, RKD3, RK1, RK2, RKW, RKL, RA, ALPHA, ASAT, HEIGHT, ACTH, STPH δź

. . . . . . .

```
COCAL = (H + CB - CA - AO*(RKA/(H+RKA)) - RKW/H +
     & DC*(2. - (H*RKD2 +2.*RKD2*RKD3) / (H*H +H*RKD2 +RKD2*RKD3))) /
     & ((RK1*H+2.*RK1*RK2)/(H*H+H*RK1+RK1*RK2))
        RETURN
        END
APCALC. FOR
        SUBROUTINE APCALC (SMAX, ETIME, ADIST, IUNIT)
        IMPLICIT REAL*8 (A, B, C, D, E, G, H, P, Q, R, S, T, U, V, W),
                 REAL*4 (F, X, Y, Z), INTEGER (I, J, K, L, M, N, O)
     &
        DIMENSION RA(6)
        COMMON AO, CA, CB, CS, DC, RKA, RKD2, RKD3, RK1, RK2, RKW, RKL,
               RA, ALPHA, ASAT, HEIGHT, ACTH, STPH
     &
        EXTERNAL CH, SICAL, COCAL
        CT = CS * (1.0D0 - DEXP(-1.0D0 * RKL * ETIME / HEIGHT))
        CONCH = CH(CT)
        PH = -1.0D0 * DLOG10 (ACTH * CONCH)
        A1 = SICAL(STPH) / SICAL(PH)
        B = (SMAX/0.99 + 0.01D0/A1 - 1.0D0/ASAT) /
            (1.0D0/A1 - 1.0D0/ASAT)
     ٤.
  THE NEXT LINE SETS DEPTH IN CASE B<0 SO THAT APSORT WILL IGNORE POINT
С
        DEPTH = -1234567.0D-04
        IF (B .GT. 0) DEPTH = -1.0D0 \times DLOG(B) / (2.3031 \times ALPHA)
        ADIST = DEPTH * 1.0D04
        WRITE (13, 10) ETIME, PH, CT, SMAX, A1, B, ADIST
        RETURN
        FORMAT (1X, F7.3, 2X, F5.3, 2X, D10.3, 2X, F5.3, 2X, F5.3, 2X,
10
     &
                    F8.3, 2X, F8.3)
        END
```

#### SURPENT . FOR

SURPENT.FOR calculated k using the Harriott (1963) surface penetration model and the algorithm outlined in Section 5.D. This program called QSIMP.FOR, SVDFIT.FOR and ERFC.FOR from the Numerical Recipes (Press et al., 1986) FORTRAN-77 library. The program is written in Microsoft FORTRAN-77 V3.31 and ran on an IBM-PC compatible computer.

implicit real\*8 (a, b, c, d, e, f, h, q, s, t, & u, v, w, x, y, z) dimension acs(5), xray(100), yray(100), sig(100), & u(5,100), v(100,100), w(100) character\*12 iname, oname, inlist common acs, cnl, d, iterm, tn, xdep external erfc, fpar1, fpar2, fpoly, qfun1, qfun2 depth = 3.5d1 hmax = 0.5d-01

```
d = 1.7d - 05
        d0 = 0.0d0
        xpi = 3.1415928
        cs = 10 * * (-4.5)
        iterm = 4
        iont = 15
        hn1 = 0.0d0
        cnl = 0.0d0
        do 100 i = 1, ipnt
           if (i .1e. iterm) acs(i) = 0.0d0
           sig(i) = 1.0d0
100
        continue
        write (*, '(a\)') ' enter input file listing: '
        read (*, '(a)') inlist
        open (10, file=inlist, status='old')
        read (10, '(a)') iname
5
        if (iname .eq. 'exit') then
           close (10)
           stop
        endif
        read (10, '(a)') oname
        open (11, file=iname, status='old')
        open (12, file=oname, status='new')
        ieddy = 0
        xksum = 0.0d0
        xksum2 = 0.0d0
        write (12, '(a)') ' Qn (flux)
                                               kL x 10<sup>4</sup>'
        read (11, *, end = 25) tn, hn
15
           write (*, '(1x, a, 2x, a, i4)') iname, 'ieddy =', ieddy
           write (*, '(a,f8.4,5x,a,f10.3)') ' tn=',tn, 'hn=',hn
           ieddy = ieddy + 1
           if (hn .1t. 0.0d0) hn = 0.0d0
           hn = hn * 1.0d-04
           qnl = 0.0d0
           if (acs(1) .ne. 0.0d0 .and. hn1 .gt. 0.0d0)
     &
            call qsimp (qfun1, d0, hn1, qn1)
           qn2 = 0.0d0
           if (cnl .ne. 0.0d0)
     &
            call gsimp (qfun2, hn1, hmax, qn2)
           qn = cs * dsqrt (4.0d0*d*tn/xpi) - qnl - qn2
           xkl = qn / ((cs - cnl) * tn)
           xk1 = xk1 * 1.0d04
           xksum = xksum + xkl
           xksum2 = xksum2 + xkl * xkl
           write (12, '(el2.4, 5x, f10.4)') qn, xkl
           write (*, '(a,f8.4,5x,a,f10.3/)') ' qn=',qn,'kL=',xkl
           if (hn .eq. 0.0) then
                do 200 i = 1, iterm
                    acs(i) = 0.0d0
200
                continue
```

```
else
                dstep = hn / dble(ipnt)
                xray(1) = 0.0d0
                yray(1) = cs
                do 201 i = 2, ipnt
                   xdep = dble(i) * dstep
                   fp1 = 0.0d0
                   if (acs(1) .ne. 0.0d0 .and. hnl .gt. 0.0d0)
     &
                    call qsimp (fparl, d0, hnl, fpl)
                   fp2 = 0.0d0
                   if (cnl .gt. 0.0d0)
                    call qsimp (fpar2, hn1, hmax, fp2)
     &
                   f2 = cs * erfc(xdep/dsqrt(4.0D0*d*tn)) +
                    (fp1 + fp2) / dsqrt(4.0D0*xpi*d*tn)
     &
                   xray(i) = xdep
                   yray(i) = f2
                continue
201
                do 300 i = 1, ipnt
                   yray(i) = dlog(yray(i))
300
                continue
                call svdfit (xray, yray, sig, ipnt, acs, iterm,
                             u, v, w, 100, 5, xi2, fpoly)
     &
           endíf
           cn1 = cn1 + qn / depth
           hn1 = hn
        goto 15
25
        close (11)
        avgkl = xksum / dble(ieddy)
        sdk1 = dsqrt (xksum2 / dble(ieddy) - avgkl**2)
        write (12, '(a, f10.4, 5x, a, e12.5)') ' kL (avg.) =', avgkl,
        'std. dev.=', sdk1
     &
        close (12)
        goto 5
        end
        double precision function fparl (y)
        implicit real*8 (a, b, c, d, e, f, t, x, y, z)
        dimension acs(5)
        common acs, cnl, d, íterm, tn, xdep
        fml = acs(1) + acs(2) * y
        if (iterm .gt. 2) then
           do 201 j = 3, iterm
                fm1 = fm1 + acs(j) * y**(j-1)
201
           continue
        endíf
        fml = dexp (fml)
        fminl = fml
        fpar1 = fmin1 * (dexp(-1.0D0*((y-xdep)**2)/(4.0D0*d*tn)) -
     δŁ
                          dexp(-1.0D0*((y+xdep)**2)/(4.0D0*d*tn)))
        return
        end
```

```
double precision function fpar2 (y)
   implicit real*8 (a, b, c, d, e, f, t, x, y, z)
   dimension acs(5)
   common acs, cnl, d, iterm, tn, xdep
   fpar2 = cnl * (dexp(-1.0D0*((y-xdep)**2)/(4.0D0*d*tn)) -
                   dexp(-1.0D0*((y+xdep)**2)/(4.0D0*d*tn)))
&
   return
   end
   double precision function qfunl(y)
   implicit real*8 (a, b, c, d, e, f, q, t, x, y, z)
   dimension acs(5)
   common acs, cnl, d, iterm, tn, xdep
   fml = acs(1) + acs(2) * y
   if (iterm .gt. 2) then
      do 201 j = 3, iterm
           fml = fml + acs(j) * y**(j-1)
      continue
   endif
   fm1 = dexp (fm1)
   fminl = fml
   qfunl = fminl * erfc(y / dsqrt(4.0d0 * d * tn))
   return
   end
   double precision function qfun2(y)
   implicit real*8 (a, b, c, d, e, f, q, t, x, y, z)
   dimension acs(5)
   common acs, cnl, d, iterm, tn, xdep
   qfun2 = cn1 * erfc(y / dsqrt(4.0d0 * d * tn))
   return
   end
```

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## Appendix B. The Aqueous Solution Charge Balance Equation

In principle, the  $[H^*]$  of an aqueous solution may be found by solution of the aqueous charge balance equation (Stumm and Morgan, 1981). This requires that the mineral acidity  $C_A$  or mineral basisity  $C_8$  be known. Also necessary are the stoicheometric concentrations of all acids and bases present as well as the concentration of all ions added as salts of the various acids or bases. The final requirement is that the acidity constants for all acids and bases present be known. For a solution containing  $CO_2$ , DCFS, and HOPSA the relevant ionic species are  $H^*$ ,  $OH^+$ ,  $HCO_3^-$ ,  $CO_3^{2-}$ , DCFS<sup>2-</sup>, and HOPSA<sup>-</sup> and any unpaired ions such as Na<sup>+</sup>.

 $C_A$  and  $C_B$  are determined by measurement of initial pH of the solution. All other concentration mat be written as a function of  $[H^*]$  and the acidity constants. These relations are given by

$$[OH] = k_{\mu}/[H]$$
(B1)

$$[HCO_{3}^{-}] = k_{1} [H^{+}] [CO_{2}] / ([H^{+}]^{2} + k_{1} [H^{+}] + k_{1} k_{2})$$
(B2)

$$[CO_3^{2^*}] = k_1 k_2 [CO_2] / ([H^*]^2 + k_1 [H^*] + k_1 k_2)$$
(B3)

$$[DCFS] = C_0 k_{d1} [H^+] / ([H^+]^2 + k_{d1} [H^+] + k_{d1} k_{d2})$$
(B4)

$$[DCFS^{2^{+}}] = C_{D}k_{d1}k_{d2}/([H^{+}]^{2} + k_{d1}[H^{+}] + k_{d1}k_{d2})$$
(B5)

$$[HOPSA^{*}] = C_{H} k_{h1} / ([H^{*}] + k_{h1})$$
(B6)

where  $k_{\mu}$  is the ion product for pure  $H_2O$ ,  $[CO_2]$  is the total concentration of all aqueous phase  $CO_2$  species present defined by

$$[CO_{2}] = [CO_{2}]_{aq} + [H_{2}CO_{3}] + [HCO_{3}] + [CO_{3}^{2}]$$
(B7)

and  ${\bf k_1}$  and  ${\bf k_2}$  are the first and second acidity constants for  ${\bf H_2CO_3}$ 

respectively.  $C_D$  is the total concentration of DCFS species present and is known from the amount added.  $C_H$  is the total concentration of HOPSA and is also known from the initial conditions.  $k_{d1}$  and  $k_{d2}$  are the first and second acidity constants for DCFS and  $k_{h1}$  is the acidity constant for HOPSA.

In the actual solutions used in the experiments, HOPSA was added as its acidic form but the DCFS was added as its disodium salt. This meant that the charge balance equation had to include the  $[Na^{\dagger}]$ resulting from the addition of DCFS. This concentration was easily determined as twice  $C_{\rm p}$ . Therefore, the charge balance equation is

 $2C_{D} + [H^{+}] + C_{B} =$ 

 $C_A + [OH^*] + [HCO_3^*] + 2[CO_3^{2^*}] + [DCFS^*] + 2[DCFS^{2^*}] + [HOPSA^*]$  (B8) Substitution of Eqs. B1, B2, B3, B4, B5, and B6 resulted in an equation which could be solved iteratively for [H<sup>+</sup>]. This is what was coded into the FORTRAN IV-RT subroutine CHHODC.FOR.

Solution of Eq. A9 required that  $k_1$ ,  $k_2$ ,  $k_{d1}$ ,  $k_{d2}$ , and  $k_{h1}$  be known. The acidity constants for CO<sub>2</sub> were taken from Stumm and Morgan (1981).  $k_{d1}$  and  $k_{d2}$  were calculated by Leonhardt et al. (1971).  $k_{h1}$ was measured by Zhujun and Seitz (1984). The  $pk_a$  (-log( $k_a$ )) are

$$pk_1 = 6.3$$
 (B9)

$$pk_2 = 10.3$$
 (B10)

$$pk_{d1} = 3.5$$
 (B11)

$$pk_{d2} = 5.0$$
 (B12)

 $pk_{h1} = 7.4$  (B13)

<u>Vítae</u>

The author was born in 1958 in Seattle, Washington. He attended Lake Washington Senior High (School motto: Better minds through boredom!) in Kirkland, Washington and graduated (to the relief of himself and the staff of LWHS) in 1976. Since injuries sustained in a skiing accident as well as a lack of athletic ability precluded a professional basketball career, the author pursued a B.A. in Chemistry at Reed College in Portland, Oregon starting in 1976. During his undergraduate years, the author came to be known to many as "Bill".

Upon graduation from Reed in 1980, the author spent two years working as a research technician at the Oregon Graduate Center in the Environmental Science Department for James Pankow. In spite of this, Dr. Pankow allowed the author to enroll as a graduate student at the same institution in 1982 (One possible explanation for this action of Dr. Pankow's is that all the expensive equipment had already been broken and no further damage could be done). In any event, the author was given time off for good behavior in 1987. Currently, the author plans to take a post-doctoral research position at Rensselaer Polytechnic Institute (famed for having a name that is very difficult to spell) in Troy, New York. There he will study the static and dynamic properties of organic monolayers on water surfaces using the non-linear spectroscopic technique of second harmonic generation.

The author's research interests include the behavior of turbulence close to gas/liquid interfaces, gas/liquid mass transport and

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