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GAS TRANSFER AT AIR-WATER INTERFACES

by

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MANAGEMENT PERSPECTIVE

The transfer of gases across the air-water interface is a complex process. It is important to understand this process to address properly the issue of non-point sources (i.e., from the atmosphere) of toxics to water bodies. This report summarizes what information is available in the literature on the subject and lays out an experimental research plan to address those topics which require further clarification. Construction of the experimental apparatus has begun, and experiments will be started early in 1988.

Dr. J. Lawrence
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PERSPECTIVE - GESTION

Le transfert des gaz de part et d'autre de l'interface atmosphère-eau est un processus fort complexe, qu'il importe de comprendre pour étudier adéquatement les sources non ponctuelles de substances toxiques (dépôts atmosphériques) contaminant les plans d'eau. Le rapport résume les données publiées à ce sujet et propose un plan de recherche expérimentale pour les questions qui doivent être élucidées. On a commencé à fabriquer le matériel requis et les essais seront amorcés au début de 1988.

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ABSTRACT

Mass flux of different chemical compounds across the air-water interface is determined generally by the resistance to transfer in the thin viscous sublayer of the controlling phase. Various turbulence creating mechanisms such as wind stress applied at the interface, wave breaking and wave motion itself determine the degree of turbulence which influence the thickness of the viscous sublayer. This report presents a literature review on the gas transfer at air-water interfaces and describes a planned experimental program to determine the mechanisms and rates of the gas transfer.

RÉSUMÉ

Le transport massique de divers composés chimiques de part et d'autre de l'interface atmosphère-eau est généralement déterminé par leur résistance au transfert dans la mince couche visqueuse sous-jacente à la couche aqueuse. Divers mécanismes, comme la tension exercée à l'interface par le vent, le déferlement des vagues et leurs mouvements proprement dits, sont à l'origine de la turbulence et déterminent dans quelle mesure celle-ci influera sur l'épaisseur de la sous-couche visqueuse. Le rapport examine la documentation portant sur le transfert des gaz à l'interface atmosphère-eau et décrit un plan de recherche visant à déterminer les mécanismes et les taux de transfert des gaz.

1.0 INTRODUCTION

Gas transfer at air-water interfaces is a complex process; it plays an important role in the geobiochemical cycling system. In particular, the exchange of gases such as oxygen and carbon dioxide is very important because both are involved in animal and plant life. Furthermore, the latter may influence the heat budget of the earth. On the other hand there are some other gases that have environmental impacts such as PCB's and other atmospheric pollutants. Atmospheric deposition accounts for greater than 80% of the PCB input to Lake Michigan (Eisenreich et al., 1981). According to a model study, there are 5000 kg/yr of wet deposition and 4000 kg/yr of dry deposition of PCB's to Lake Michigan (Doskey and Andren, 1980; Murphy and Rzeszutko, 1977); 2800 kg/yr of the 4000 kg/yr is reported to be deposited in vapour form. For Lake Superior the total input at the air-water interface is calculated as 8900 to 11600 kg/yr,of which dry deposition amounts to 6070 to 8000 kg/yr; of which 6000 kg/yr is estimated to be in vapour form (Eisenreich et al., 1981).

This report presents a literature review on gas transfer at air-water interfaces. It also describes a planned experimental program to determine the mechanisms and rates of the gas transfer.

The volatilization or absorbtion rate of gaseous compounds is determined generally by one of the controlling phases. If most of the resistance to gas transfer occurs below the interface the transfer is called liquid phase controlled; in the reverse case it is called gas phase controlled. As a rule, relatively insoluble gases are under liquid phase control (O_2, N_2, CO_2, CO); while water-soluble gases are under gas phase control (H_2O, SO_2, SO_3).

Gas transfer depends on the degree of turbulence intensity in the controlling phase. In a thermally non-stratified water body, in the absence of bubbles and aerosols, turbulence is caused by the surface elements as a result of the wind shear applied at the air-water interface. If the transfer is under liquid phase control,

the air-water interface should be considered as seen from below; while in the reverse case it should be considered as seen from above.

Besides the wind shear applied at the air-water interface, the interface itself may be considered as a source of turbulence. Concerning liquid phase controlled transfer, Kitaigorodskii (1984) proposed a mechanism in which the dissipation of energy from breaking waves is considered as a source of energy flux towards the interface, which results in the formation of near-surface turbulence. Coantic (1986) postulated that in the presence of a strong shear at the interface, the phase difference between velocity components of capillary waves deviates from 90° and causes an additional transfer mechanism. Donelan (1983) presented a mixing length model which takes into account the effect of turbulence caused by the interface as a function of the flow regime for gas transfer under gas phase control.

The effect of a "dirty" interface on gas transfer under liquid phase control is of great importance. There are two main effects: (i) as a physical barrier (Broecker et al., 1978; Jaehne et al., 1984; Hunt, 1984), it forms an obstacle for gas transfer and suppresses the waves and eddies responsible for gas transfer, (ii) as a chemical barrier (Strachan, personal communication), it may influence the chemical characteristics of the gases of interest (a change in the vapor pressure in the air causes an alteration in the Henry's constant).

2.0 FUNDAMENTAL GAS TRANSFER MODELS

There are various models that describe gas transfer at air-water interfaces. A few fundamental ones that give simple physical insight to this complicated process will be presented.

2.1 Film Model

The first conceptual gas transfer model was constructed by Whitman (1923) and applied later by various researchers to environmental processes (Liss and Slater, 1974; Mackay and Yeun, 1983). The film model assumes that there is one gas film above the interface and one liquid film below it. Furthermore, it is assumed that the bulk of the gas and that of the liquid have no significant concentration gradients. Since gas transfer occurs through the film by molecular diffusion Fick's law is applicable:

$$F = - D(\partial c/\partial z) \tag{1}$$

where F is gas flux, D is molecular diffusivity and c is the gas concentration and z is the vertical coordinate-position upwards. Eq.1 can be expressed in a more general form:

$$F = k\ \Delta c \tag{2}$$

where $k = D/\Delta z$ is the mass transfer velocity. The film (whether liquid or gas) is very thin and the concentration changes linearly through this layer of thickness (Δz). The mass transfer velocity depends mainly on the degree of turbulence intensity and the Schmidt number, $Sc = \nu/D$, where ν is the kinematic viscosity. An increase of the turbulence intensity will result in a decrease of the thickness of the film (molecular diffusion sub-layer) which means enhancement of the mass transfer velocity and consequently the gas flux.

The main purpose of the film model is to allow estimation of resistances in the gas film and the liquid film. Fig.1 presents the film model schematically. In the presence of two films at the air-water interface eq.1 can be written as follows (Liss and Slater, 1974):

$$F = k_g(c_g - c_{sg}) = k_l(c_{sl} - c_l) \tag{3}$$

where k_g and k_l are mass transfer velocities for the gas and liquid phases. By relating the concentrations of the gas for both phases at the interface by Henry's law, one obtains,

$$c_{sg} = H_c\, c_{sl} \tag{4}$$

where H_c is Henry's dimensionless constant. It is related to the Henry's constant as follows:

$$H = H_c\, R\, T \tag{5}$$

where R is the universal gas constant and T is the absolute temperature. Using eqs.3 and 4 gas flux can be written as

$$F = K_g\,(c_g - H_c\, c_l) = K_l\,(c_g\,/H_c - c_l) \tag{6}$$

where

$$1/K_g = 1/k_g + H_c/k_l \tag{7a}$$

$$1/K_l = 1/k_l + 1/(H_c\, k_l) \tag{7b}$$

Eqs. 7a and 7b can be written in terms of resistance, r, instead of conductivity, k,

$$R_g = r_g + H_c\, r_l \tag{8a}$$

$$R_l = r_l + r_g/H_c \tag{8b}$$

If $r_g \gg H_c r_l$, the gas of interest is under gas phase control; while in the reverse case it is under liquid phase control.

2.2 Penetration Model

Higbie (1935) assumed the existence of a infinitely deep water body where the thickness of the film depends on the square root of a characteristic exposure time. It was assumed that at the end of this time all the elements at the surface are replaced by other elements of the bulk of the liquid or the gas (fig.2).

The solution to the diffusion equation is the well-known error-function-complement:

$$c_{sl} - c = (c_{sl} - c_l)\ \mathrm{erfc}(z/2\sqrt{Dt}) \tag{9}$$

Using Fick's law (eq.1) at the air-water interface and this solution (eq.9), the gas flux is found as (for gas transfer under liquid phase control),

$$F = -D\ (\partial c/\partial z)_{z=0} = \sqrt{D/\pi t}\ (c_{sl} - c_l) \tag{10}$$

The integration of eq.10 from 0 to the exposure time t_* gives for the mass transfer velocity:

$$k = 2\sqrt{D/\pi t_*} \tag{11}$$

2.3 Renewal Model

Danckwerts (1951) found that the constant exposure time concept of Higbie was not realistic. Instead of it, he proposed a surface renewal concept where times of exposure of different surface elements are different. Danckwerts' model assumes that the probability of replacement of any surface element is independent of its age at the surface. Mathematically, the fraction of the surface renewed is expressed as an exponential function that depends on the surface renewal rate, s and the time elapsed, t (fig.3),

$$f = 1 - \exp(-st) \tag{12}$$

Using Fick's law at the air-water interface and the error-function-complement and taking into account the surface renewal distribution, the mass transfer velocity is found as follows,

$$k = \sqrt{D\ s} \tag{13}$$

Despite the apparent conceptual advance (with respect to the Higbie's model), the only result is to identify the time scale as the reciprocal of the renewal rate rather than $\pi/4$ times the time interval between periodic replacements (Brumley, 1983).

2.4 Film - Penetration Model

Dobbins (1956) proposed the film penetration model in which the gas concentration varied from c_{sl} at the interface to c_l in the bulk of the liquid as a function of a surface renewal rate. Thus, in this model, Whitman's film concept and Danckwerts' (1951) surface renewal concept were incorporated together. The mass transfer velocity is obtained as follows:

$$k = \sqrt{D\ s}\ \coth\sqrt{s(\Delta z)^2/D} \tag{14}$$

Dobbins' formulation gives the result of the surface renewal model for large renewal rates (the second term approaches unity); while at smaller renewal rates, it gives the result of the film model (the second term approaches $\sqrt{D/(s(\Delta z)^2)}$).

2.5 Eddy Diffusivity Models

There are a variety of models which are based on the eddy diffusivity approach. According to this approach, the gas flux is

constant with depth. Furthermore, the turbulent diffusivity is assumed to be diminished dramatically towards the interface. In order to compensate this decrease in diffusivity, the concentration gradient increases. In other words, the attenuation of the diffusivity towards the interface implies higher concentration gradients. Gas flux across the air-water interface is expressed as follows:

$$F = -D(\partial c/\partial z)_{z=0} = k_l\ (c_{sl}-c_l) = -(D+D_t)(\partial c/\partial z) \qquad (15)$$

where D_t is the turbulent eddy diffusivity. King (1966) solved the diffusion equation by using the total diffusivity coefficient, $D_T = D+D_t$, where he assumed that $D_t = az^n$ with $a = fn\ (L,T,n)$ and n is a parameter to be determined (L and T are length and time scales to be determined). Mass transfer velocity is obtained as follows:

$$k = D^{1-1/n}(a^{1+1/n}/\pi)\ \ \sin(\pi/n) \qquad (16)$$

With small n values the mass transfer velocity approaches the result of the surface renewal method and large n values gives the results of the film model.

Another kind of application of the eddy diffusivity model is obtained by expressing the turbulent diffusivity as a function of mixing length. Concerning gas transfer under gas phase control, Donelan (1983) used the mixing length proposed by Riley et al. (1982),

$$l = l_s + \kappa z\ (1 - \exp(-zu_*/13\nu))^2 \qquad (17)$$

where l_s is surface roughness length which depends on the roughness Reynolds number and is zero for smooth flow. In the constant flux layer, the velocity profile is given by,

$$\rho(\nu+\nu_t)(dU/dz) = -\tau = \rho u_*^2 \tag{18}$$

where $\nu_t = l^2(dU/dz)$ is the turbulent viscosity. Donelan (1983) related this mixing length for the velocity profile to the concentration profile by a Schmidt number dependence,

$$l_g = m\ Sc^n l_s + Sc^{-1/2}\kappa z(1-\exp(-zu_*/13\nu))^2 \tag{19}$$

where l_g is the gas mixing length, κ is the von Karman constant, m and n are empirical constants. Using this gas mixing length, the concentration profile can be written as follows,

$$(D+D_t)(dc/dz) = -F = \rho\ u_* g_* = C_g\ \Delta U\ \Delta c \tag{20}$$

where $D_t = l_g^2\ (dc/dz)$ is the turbulent diffusivity, g_* is the scaling parameter of the concentration profile similar to u_* in the velocity profile. Integration of eq. 20 with eq. 19 gives the mass transfer velocity, k,

$$k = C_g\ \Delta U = ((D+l_g^2\ (dU/dz))(dc/dz)(1/\Delta c) \tag{21}$$

where C_g is the Stanton number, ΔU and Δc are velocity and concentration differences between the surface and the level to which integration is carried out (inside the turbulent boundary layer).

The conceptual achievement of the eddy diffusivity model is that the discontinuity of the concentration profile between the film and the bulk of the fluid is avoided.

2.6 Eddy - Structure Models

Eddy - structure models are based on the idealized interfacial configuration of turbulence "eddy-structures" neglecting any damping phenomena (Theofanus, 1984). In this respect, they are distinguished from eddy diffusivity models and film models where eddy motions are damped towards the air-water interface. On the other hand, eddy-structure models can be treated in terms of the surface renewal theory of Danckwerts (1951).

2.6.1 Large-Eddy Model

Fortescue and Pearson (1967) assumed that gas transfer at the interface is dominated by eddies circulating in square roll cells with dimension L, with sinusoidal velocity both in horizontal and vertical directions (fig.4). The cell dimension L was assumed to be equal to the integral length scale of the turbulent flow field and the amplitude of the velocity was equal to twice the root-mean-square (rms) turbulent velocity. Eddies that are responsible for the gas transfer were identified with energy containing eddies of the spectrum. Molecular but not turbulent diffusion was assumed to occur as surface renewal theory predicts.

Fortescue and Pearson solved the diffusion equation numerically for the system described above and calculated mass transfer velocity as follows,

$$k_1 = 1.46 \sqrt{(D\ q/\ L)} \qquad (22)$$

where q is the rms of the average kinetic energy.

2.6.2 Small - Eddy Model

Lammon and Scott (1970) used the same approach as Fortescue and Pearson (fig.4), but instead of the energy containing eddies they assumed that eddies travel towards the interface and are reflected back into the bulk of the fluid and the mass is transferred by molecular diffusion near the surface. In order to take into account the effect of all the eddies, they used the Kovasznay turbulent energy spectrum, but the most efficient eddies in terms of their contribution to mass transfer, were the smallest (i.e. viscosity dominated). The following expression for the mass transfer velocity is obtained:

$$k = (0.40)\ (\varepsilon\nu)^{1/4}\ Sc^{-1/2} \qquad (23)$$

3.0 MASS TRANSFER VELOCITY CORRELATIONS; EXPERIMENTAL RESULTS

Experimental studies concerning gas transfer at the air-water interfaces of stagnant water bodies may be classified according to the type of turbulence creating mechanism and the controlling phase of the transfer process.

For thermally neutral conditions, the main turbulence creating mechanism under the gas controlled phase is the application of a wind shear at the interface. The roughness of the air-water interface as seen from above, creates turbulence. For the same conditions under the liquid controlled phase, the roughness as seen from below creates turbulence. Other kinds of turbulence creating mechanism for this phase are : (i) bottom created turbulence; (ii) turbulence created artificially in the body of the fluid. In both these cases shear at the interface is zero and the turbulence

diffuses to the interface from below. However, there are other kinds of experiments with or without any turbulence creating mechanism during which the air-water interface boundary conditions are altered (e.g. by the use of surfactants, surface breaking methods).

In this review, emphasis will be given to the liquid phase controlling processes. However, important developments concerning air phase control will be mentioned as well.

3.1 Turbulence Creating Mechanism: Wind Shear Applied at the Interface

Until the early 1980's, many laboratory studies of gas transfer at the air-water interface have been realized in which the majority dealt with liquid phase controlled mechanisms. The results of these studies indicated that gas transfer can be examined from two different views: (i) wind, (ii) waves.

Liss (1983) presented a review figure in which the results of major gas transfer studies concerning wind influence on the mass transfer velocity are summarized (fig.5). All the data reveal that (despite the differences in wind-wave tunnel dimensions) the mass transfer velocity has a tendency to increase with wind speed.

Kanwisher(1963) conducted experiments by blowing air on the surface of a water body contained in a tank of modest size (1.0 x 0.5 x 0.5 m); wind speed was measured at 10 cm above the surface. At low speeds no significant effect of the wind on the mass transfer velocity (of CO_2) was detected. It is only at a critical value of wind speed where the enhancement of the mass transfer velocity starts (2 - 3 m/s). Kanwisher stated that this critical wind speed is the speed where capillary waves start to form; the mass transfer velocity is estimated to be proportional to the square of the wind speed.

Liss (1973) used a water tank (0.60 x 0.30 x 0.30 m) and a wind - wave tunnel (4.50 x 0.30 x 0.10 m) to determine mass transfer velocities of O_2, CO_2, and H_2O. Experiments performed in the water tank revealed the enhancement of the mass transfer velocity when the air-water interface was broken by means of a surface breaker (a device used to break the liquid surface by providing an upward jet of water below the water surface). The average increase in the mass transfer velocity of O_2, produced artificially, was 95% whereas the increase concerning H_2O was only 55%. This result is consistent with the fact that O_2 is controlled by the liquid phase while H_2O is controlled by the gas phase.

In Liss' wind-wave tunnel experiments those gases were used in order to determine the dependency of the mass transfer velocity on the wind speed (O_2 experiments were invasion experiments, while CO_2 and H_2O experiments were evasion experiments). Concerning O_2 and CO_2, there is a gradual increase of the mass transfer velocity until 5 m/s (here fig.6a). At this speed, the mass transfer velocity starts to increase. Liss ascribes the reason that the mass transfer velocity of CO_2 is higher than that of O_2 to chemical mechanisms: "the pH range in the experiments was from 6.2 to 6.6. Results from the laboratory tank experiments would indicate that at these 'high' pH values, enhancement of the CO_2 exchange is possible (...). Comparison of fig.6a which is for CO_2 and O_2 exchange at high pH, with the graph given by Hoover and Berkshire (1969) for CO_2 exchange at low and high pH, reveals that they are remarkably similar. This similarity independently confirms that enhancement of CO_2 exchange can occur under calm conditions when the pH is in the range where some of the dissolved inorganic carbon occurs as ionic forms".

On the other hand, the enhancement of the mass transfer velocity from 5 m/s is estimated to be proportional to the square of the friction velocity as Kanwisher did. The increasing wind speed seems

to be more effective for the gases under liquid-phase control. The mass transfer velocity of H_2O varies linearly as a function of wind speed (fig.6b). Liss (1973) did not examine the waves as a factor in the enhancement of the mass transfer velocity for gases under liquid phase control; it is emphasized that " (in discussing) results used in the present study it has been assumed that the interface is flat".

Broecker et al. (1978) made experiments with a larger wind-wave tunnel (18.0 x 1.0 x 1.0 m); the water depth was 0.5 m. They did two sets of experiments, one with a free surface, the other with a surfactant. The surfactant (oleyl alcohol) used was not a physical barrier for CO_2 (perhaps a chemical barrier ?); its function was to dampen the waves. Broecker et al.'s results concerning free surfaces seem to match other data except Liss' (1973) data (fig.7); however they are slightly greater. Broecker et al. explain it by the different water depths of various studies:"the greatest difference is between our data and those of Liss (1973) and Hoover and Berkshire (1969), whose tunnels had a water depth of only 10 or 25 cm. The measurements of Downing and Truesdale (1955) (depth=38 cm) show less variation, and those of Kanwisher (1963) (depth=50 cm) are most similar to ours (depth=50 cm)". Broecker et al. (1978) emphasized the functional difference of their results and others; Liss obtained a square dependency on the wind speed in the range $u < 6$ m/s while Broecker et al. obtained a linear one.

Broecker et al. compared their data with and without surfactant (fig.8). It is observed that mass transfer was reduced dramatically in the presence of the surfactant. In both cases, the mass transfer velocity is a function of wind velocity, but with different slopes. In the case where surfactant is used, the increase of the mass transfer velocity follows the tendency in the case without surfactant for wind velocities smaller than 2 m/s where there were no

waves. Broecker et al. had no answer regarding what enhances the mass transfer velocity at wind speeds where waves are present; instead they had a question: "It is still an open question whether the increased mass transfer rate with development of a wave field is due to the increased surface area at the air-water interface, or whether it is a result of an increased turbulence in near surface boundary layer".

According to MacIntyre (1971), surface dilatations (local change of area) due to the capillary waves can increase the mass transfer by a factor of 3.5: the average thickness of the viscous boundary layer in this model is reduced as a result of the surface dilatation and not because of the turbulence in the near surface region. Broecker et al. estimate that both effects are responsible for the enhancement of mass transfer in the presence of waves, because a factor of 5 is observed in their experiments rather than 3.5.

Jaehne et al. (1979) did experiments with a circular channel (40 cm = inner diameter, 10 cm = water depth) with N_2 and CO_2. Fig.9 shows that there is a jump at around 6 m/s for CO_2 (invasion) and at 7 m/s for N_2 (evasion) (both at 20 C): this discontinuity is accompanied by another discontinuity at the same critical velocity if friction velocity is plotted against wind speed (fig.10). The wave pattern is reported to change abruptly at this speed: there is a passage from a near calm sea surface (wave amplitude < 0.2 cm) to rough irregular waves of several centimeters.

There is no data concerning friction velocity in other studies; furthermore, every study has different geometrical characteristics concerning wind-wave tunnels and wind speed is measured at different heights. All these factors make a serious comparison among studies impossible. Neverthless, there is one common point in all these studies: there is an enhancement of the

mass transfer velocity with the onset of capillary waves, which make the surface rough; there is no information about the roughness in Jaehne et al. (1979), but it seems to be that "roughness" is based on a subjective visual evaluation (which side of the surface is considered is not emphasized either).

Despite all these inconsistencies in these pioneer works, where waves are not investigated systematically, Broecker et al. (1979) and Jaehne et al. (1979) deserve to be given special attention together; this will make the role of waves in gas transfer evident (fig.11). On this figure, besides Broecker et al.'s linear tunnel data and Jaehne et al.'s circular data, there is data from Jaehne's circular tunnel but this time parted by a beach. There is no excessive jump in mass transfer velocity; there are two slopes, one corresponding to the regime without waves, and the other with waves as observed in Broecker et al.'s study, but the enhancement is bigger; if the effect of fetch is excluded this discrepancy is hard to be explain unless there are different conditions associated with the cleanness of the surface. Jaehne et al. didn't give any quantitative information on waves (wave age, wave breaking, etc), but they emphasized that the influence of the wave spectrum should be studied in order to get a precise picture of the gas transfer enhancement mechanism.

Mackay and Yeun (1983) realized the first experimental wind-wave tunnel study (6.0 x 0.61 x 0.60 m) with various organic compounds with relatively high Henry's law constants (mostly under liquid phase control). Despite the fact that there is neither qualitative nor quantitaive information about waves, their results concerning both gas phase controlled and liquid phase controlled gases verified some of the classical studies as far as general tendencies are concerned (Liss, 1973; Kanwisher, 1963) (fig.12.a-b).

In this review, no attempt is made to try to explain why different data sets disagree; instead Liss' (1983) statement is respected: " the surprising agreement among the studies should, perhaps be stressed". This agreement seems to be that enhancement of the mass transfer velocity coincides with the onset of waves.

3.2 Turbulence Creating Mechanism: Oscillating Horizontal Grid (Zero Shear at the Air Water Interface)

There are two basic experimental studies on gas transfer at the air-water interface in the presence of turbulence created in the body of the fluid (with zero shear at the interface): Dickey et al. (1984) and Pankow et al. (1984). It is not surprising to see that both assumed the existence of the eddy-structure model (ch.2.6) where the idea of the damping of the turbulence towards the interface is excluded. Such an assumption implies the verification of the available surface renewal models: Fortescue and Pearson's (1967) large eddy model (ch.2.6.1) and Lammon and Scott's (1970) small eddy model (ch.2.6.2).

Dickey et al. (1984) made experiments with a water tank (0.62 x 0.62 x 0.76 m) where turbulence was created by an oscillating horizontal grid. Streak photography methods were used in order to determine instantaneous fluid velocity vectors from which turbulent parameters (velocities, length scales, dissipation rates) are calculated. Mass transfer experiments were also performed using CO_2, CH_4, Rn, O_2, N_2. It was assumed that the eddies closest to the interface control gas transfer. The surface renewal rate, s, is calculated as the ratio of the turbulent velocity, q, to the integral length scale, L. Estimation of turbulent parameters close to the interface is realized through extrapolation - according to the surface renewal models, turbulence is not attenuated towards the

interface. Fig.13 shows the dependence of the mass transfer velocity to $k = \sqrt{Ds}$.

Dickey et al. (1984) plotted the mass transfer velocity as a function of, $D^{1/2}\varepsilon^{1/4}$, where $\varepsilon \alpha q^3/L$ is the energy dissipation (fig.14) referring to the suggestion of Lamont and Scott (1970), that the gas transfer coefficient is proportional to the square root of the molecular diffusivity and to the 1/4 power of turbulent dissipation rate. Results seem to be consistent with such a formulation. However, the functional form of the energy dissipation model on their fig. 5 (here fig. 14) does not have unit of velocity (m/day).

Pankow et al. (1984) generated turbulence in the same way as Dickey et al. (1984) did, but they determined the turbulence parameters by using Hopfinger and Toly's (1976) empirical equations:

$$u_{rms} = 0.26\ \omega\ p^{1.5}\ M^{0.5}\ z^{-1}\ (cm/s) \tag{24a}$$

$$L = 0.10\ z \tag{24b}$$

where ω is the oscillation frequency, p is oscillation stroke amplitude, M is the mesh spacing and z is the distance from the oscillating grid. Assuming that the turbulence was isotropic they estimated turbulent velocity as $q = \sqrt{3}\ u_{rms}$. Surface renewal was calculated as in Dickey et al.:s=q/L. Fig.15 shows the dependence of the mass transfer velocity on the root of surface renewal rate, s,for two different integral length scales (two different grid positions with respect to the surface): "Although it appears that there is some correlation, additional experimentation is needed". The major drawback of Pankow et al.'s study originates from the fact that they determined turbulent parameters from empirical relations. Brumley (1984) made detailed measurements concerning near surface turbulence created by an

oscillating grid. His results, especially those concerning vertical fluctuations deviate considerably from Hopfinger and Toly's results: they have the tendency to be attenuated at the interface (fig.16).

3.3 Waves As An Active Source For Near-Surface Turbulence

So far, there has been no systematic experimental study of wave effects on gas transfer. Jaehne et al.'s (1987) study is the only one that examined and tried to explain the enhancement of gas transfer in terms of wave parameters.

According to Jaehne et al. (1987), the enhancement of mass transfer velocity is due to the change of the sea surface from a rigid surface (smooth) to a free surface, rather than a passage from a smooth regime to a rough regime. The passage to a free surface coincides with the formation of capillary waves, but Jaehne et al. assume that all the waves, not only capillary waves, are responsible for the enhancement of gas transfer. They outline 'a turbulent wave dissipation model' in which all the energy put into the wave field is transferred into near-surface turbulence; " since the energy cascade starts at the largest length scale in the wave field, large scales must also influence the mass transfer process "; so, a parameter which characterizes the 'free surface' is needed: the wave slope which characterizes the stability of the surface is proposed for this task. Figs. 17.a-b, 18.a-b, 19.a-b show mass transfer velocity as a function of mean wave slope of all the waves for three different wave tunnels. Jaehne et al. comment that mean square slope of all the waves describes the behavior of mass transfer velocity better than the mean wave slope of capillary waves only. In all these tunnels, variations of the mean square wave slope of all the waves as a function of mass transfer velocity have very similar values which is surprising because the shapes of wave slope spectra are quite different (fig.20).

It was already mentioned (ch.1) that there are two recent theories that consider waves as an active source for near surface turbulence: Kitaigorodskii (1984) and Coantic (1986).

Kitaigorodskii (1984) proposed a new model in which he assumed that the breaking of waves generates turbulent patches, which form the main source of near-surface turbulence and cause an enhancement of the mass transfer. He assumed the existence of a constant flux of energy (injected by breaking) towards the air-water interface:

$$-\overline{b'w'} + \nu(db/dz) = \int \varepsilon_\nu dz \qquad (25)$$

where b is turbulent energy, ν is viscosity and $\varepsilon\nu$ is the energy dissipation in this layer, $\varepsilon_o = \int \varepsilon_\nu dz$ (ε_o is the energy available to increase wave amplitude but lost by wave breaking). With the boundary condition,

$$\overline{b'w'} - \nu(db/dz) = 0 \qquad (26)$$

Eq.25 can be written as

$$-\overline{b'w'} + (db/dz) = \varepsilon_\nu(o)z = (\nu_{tb} + \nu)(db/dz) \qquad (27)$$

where ν_{tb} is the coefficient of vertical turbulent diffusion for turbulent energy, b. In other words, Kitaigorodskii introduced the concept of a viscous sublayer for the vertical transport of mean kinetic energy of turbulence and assumed that the thickness of this sublayer and the molecular diffusion sublayer is dependent on the flux of energy and not on the flux of momentum. The trouble with this model is that the injections of energy are assumed to take place "not uniformly at all scales but largely at a predominant scale, which must

be proportional to the amplitude of the breaking waves"; because data coming from various studies indicate that enhancement of gas transfer occours already with the onset of capillary waves. It is probable that wave breaking influences gas transfer, but we need data to decide on the scale of breaking waves responsible for the enhancement of the gas flux and to calculate the extra amount of the gas flux.

According to Coantic (1986) capillary waves in the presence of a shear flow control gas transfer. When capillary waves appear at a zero shear interface, the horizontal and vertical components of the associated orbital motions are in quadrature. On the other hand, if capillary waves develop at a sheared surface, nonlinear interactions between the orbital motions and the drift current can cause a phase shift away from than 90° between the components of the capillary waves. Coantic mentions that similar effects have already been observed under gravity waves (Shonting, 1970). The reason that capillary waves are considered is that the characteristic scale of these waves is comparable to diffusive sublayer thicknesses.

3.4 Comparison of Data Observed Using Different Turbulence Creating Mechanisms

Cohen (1983) divided the dissipation term in Lammon and Scott's equation (eq.23) into different parts such as ε_s, mechanically generated (in the body of the fluid); ε_w, wave generated; ε_d, wind-induced drift current generated, where;

$$\varepsilon_w = 0.4\nu A^4\kappa^4\sigma^2 \tag{28a}$$

$$\varepsilon_d = 3.25 \times 10^{-4}(u_{*w})^4/\nu \tag{28b}$$

where A is the wave amplitude, κ is the radian wave number, σ is the radian frequency. This model assumed that there was no wave breaking. .Asher and Pankow (1986) used this formulation to compare their data and some of the well established wind tunnel data (fig.21): although there is considerable scatter between different studies some data sets show some agreement.

Broecker et al. (1978), Merlivat and Memery (1983) and Jaehne et al. (1984) correlate well with the rayon/vacuum cleaned oscillating grid results of Asher and Pankow. The 1-OD (octadecanol) film results are reported to be in rough agreement with the results of Jaehne et al. (1984) where the surface was covered with film.

Cohen's (1983) study provides the opportunity to compare data from different turbulence causing mechanisms.

4.0 PROPOSED EXPERIMENTAL PROGRAMME

An experimental programme is designed to study gas transfer of both liquid phase and gas phase controlled gases. The following measurements will be conducted:

a) Total stress transmitted from the air to the water should be calculated; turbulent air velocity (horizontal and vertical components) in the constant stress layer will be measured with an x-film anemometer.

b) Turbulent intensity in the water should be calculated; turbulent water velocity will be measured with a laser doppler velocimeter (horizontal and vertical components) or a hot film anemometer.

c) Thermal stratification should be calculated; temperature at a reference level in air, in water and at the interface will be measured by a cold wire and a thermister.

d) Wave energy spectrum should be calculated; wave heights will be measured in the time domain with a capacitance wave gauge and a laser displacement gauge.

e) Wave slope spectrum should be calculated; wave slopes will be measured in the time domain with a laser slope gauge.

f) Mass transfer velocity of the compound of interest in the air should be calculated; concentration of the compound in the air will be measured by a special device (for the analysis, Lakes Research Branch is responsible).

g) Mass transfer velocity of the compound of interest in the water should be calculated; concentration of the compound in the water will be measured by a special device (for the analysis, Lakes Research Branch is responsible).

The following physicochemical information should be supplied by Lakes Research Branch:

a) molecular diffusivity of the gases of interest in air and in water,

b) kinematic viscosity of the gases of interest in air and in water,

c) Henry's constant of the gases of interest.

The strategy of this experimental programme is, first, to measure such parameters in order to compare our data and all the data from other studies, then, to test the validity of both eddy-diffusivity and eddy-structure models and finally to determine critical variables that influence gas transfer at air-water interfaces associated with additional mechanisms causing near surface turbulence.

In order to compare all the results coming from different studies a dissipation term shall be calculated. This dissipation term should characterize dissipation at the level of eddies closest to the surface, which control gas transfer. It could be determined by measuring the dissipation as a function of height (for processes both under liquid phase and gas phase control) and extrapolating these values to the surface (Dickey et al. (1984) assuming that these dissipation values characterize dissipation of the eddies of interest.

Experimentally, dissipation can be determined by two ways. In the absence of thermal gradients, for a stationary, horizontally uniform turbulent field with unidirectionnal mean flow, the energy balance of the fluctuating motion can be described as follows (Townsend, 1976):

$$(\partial/\partial z)((1/2\ \overline{q^2 w'} + \overline{p'w'}) = -\ \overline{u'w'}(\partial u/\partial z) - \varepsilon \qquad (29)$$

where p' is the pressure fluctuation. Assuming that the complete divergence term is much smaller than the production and dissipation terms, one can write:

$$\varepsilon = -\overline{u'w'}\ (\partial u/\partial z) \qquad (30)$$

Dissipation can be determined as well from the spectrum of horizontal turbulent velocities, in the inertial subrange (Large and Pond, 1981).

Determination of the dissipation will permit verification of some surface renewal model (Fortescue and Pearson, 1966; Lammon and Scott, 1970) formulations based on the eddy-structure model approach. On the other hand, measurement of friction velocity in the constant stress layer will permit verification of various shear turbulence models based on the eddy diffusivity approach (Deacon, 1977; Kitaigorodskii, 1979).

Sources of turbulence both in the air and in the water other than the wind shear should be determined in order to have a precise picture concerning gas transfer. A classical approach is to make experiments with the same free stream air velocity once without a surfactant and once with a surfactant dissolved in the water and to locate sources such as wave breaking and wave-turbulence interaction, but the presence of the surfactant will influence the process of gas transfer not only physically but also chemically (personal communication, Strachan). A solution to this situation could be to make two different sets of experiments:

a) experiments without surfactant designed to measure turbulent parameters and chemical parameters,

b) experiments with surfactants designed to measure only turbulent parameters.

The aim of such a programme is not to reveal directly the change of behavior of gas flux but to detect the influences caused by wave-turbulence interaction and/or wave breaking indirectly. Concerning liquid phase controlled gas transfer, in the experiment without a surfactant, dissipation values (or rms of turbulent velocities) will be determined as functions of air velocity and depth. At a given depth, dissipation (or rms of turbulent velocities) is expected to increase as a function of air velocity. It would be interesting to examine the behaviour of dissipation (rms of turbulent velocities) with a surfactant. It could be expected that an abrupt enhancement of mass transfer velocity would be accompanied by an increase of turbulent parameters in the experiments without surfactant. On the other hand, experiments with surfactant are expected to give information indirectly about the location of additional sources of turbulence.

Kitaigorodskii et al. (1983) compared their results with Dillon et al. (1981) and made the following comments: "Our measurements in the upper 1 m (just above Dillon's layer) show a much higher dissipation, suggesting that in this layer there are sources of turbulence in addition to shear. We consider that this source of turbulent energy can come only from the wave motion - either through breaking or wave-turbulence interaction. The picture that emerges from these considerations is one of a two layer structure; the upper layer, with thickness of order $10\xi_{rms}$, where ξ is wave height, is a region of intense turbulence generation by waves, while below this region the more classical notion of a constant stress layer is appropriate". The existence of those sources causing additional near surface turbulence is highly probable, but the difficulty seems to be to distinguish between those sources.

Systematic data is needed to comment about the additional sources of turbulence both in air and in water in order to detect and to distinguish them.

In addition, wave-slope (which gives information about the stability of the wave surface in order to detect the change from a rigid surface to a free surface and ultimately to wave breaking), fetch length and wave age (characterizing the stage of wave development) will be examined in order to detect their influence, if any, on the mass transfer velocity.

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FIGURE CAPTIONS

Figure 1. Two-layer model of an air-water interface (from Liss and Slater, 1974).

Figure 2. Penetration and Renewal Models (from Brumley, 1983).

Figure 3. Distribution of turbulence eddies in the surface according to the postulates of Higbie (1935) and Danckwerts (1951). In the Higbie theory, each element of the surface resides for a time t* before being swept away and replaced by fresh liquid. In the Danckwerts theory, the probability of replacement of any liquid element is independent of the time for which it has already resided at the surface (from Davies, 1972).

Figure 4. Large- and Small-Eddy Roll Cell Models (from Brumley, 1983).

Figure 5. Relationship between air-water gas transfer velocity and wind velocity found in various wind tunnel studies. The depth of water in the tunnel is shown in the key. Heights above the water surface at which the plotted wind velocities were measured are: 5 cm (Downing and Truesdale); 10 cm (Kanwisher, Liss), 17 cm (Liss et al.), 60 cm (Broecker, et. al.); height of wind measurement not reported by Hoover and Berkshire or Merlivat (from Liss, 1983).

Figure 6a Graph of the variation of the exchange constants for oxygen and carbon dioxide, with wind velocity measured at a height of 10 cm above the water surface (u_{10}). •——• $K_l(O_2)$, +----+ $K_l(CO_2)$ cm hr^{-1} (from Liss, 1973).

Figure 6b Graph of the variation of the exchange constant for vapour ($K_g(H_2O)$, with the wind velocity measured at a height of 10 cm above the water surface (U_{10}) (from Liss, 1973).

Figure 7. Comparison of the functional dependence between the exchange coefficient of CO_2 and the wind speed with other investigations. V_{ref} was measured h cm above the undisturbed air-water interface, h = 5 (Downing and Truesdale), h = 10 cm (Kanwisher, Liss), h = 60 (Broecker). No value of h was reported by Hoover and Berkshire (from Broecker, 1978).

Figure 8. Effect of wind velocity on exchange rate of CO_2 with (o) and without (x) contaminating the tank water with a monolayer of oleyl alcohol, (from Broecker, 1978).

Figure 9. CO_2 gas transfer velocity at high wind speed (...). A periodic change of the wave pattern from rough to smooth surface was observed at the filled points (from Jaehne et. al. 1979).

Figure 10. Friction velocity U_* as a function of wind speed in the evasion experiments at 20°C. Compare Fig. 9 for the gas exchange values at the same experimental conditions. Straight line theoretical values for smooth surface (from Jaehne et. al., 1979).

Figure 11. Relationship between air-water transfer velocity for CO_2 and wind velocity in the Heidelberg circular wind tunnel. Results are for evasion of gas, with and without a beach in the water channel. Also shown are data from a linear wind tunnel (Broecker et. al., 1978) (from Jaehne et. al., 1979).

Figure 12a k_g data corrected to a Schmidt number of 0.6 plotts vs wind speed (from Mackay and Yeun, 1983).

Figure 12b k_l data corrected to a Schmidt number of 1000 plotted vs wind speed (from Mackey and Yeun, 1983).

Figure 13. Relationship between the gas transfer coefficient and the square root of the product of molecular diffusivity and surface renewal rate. The solid line shows the least square fit to the data, (m is the slope, R^2 the correlation coefficient), and the dashed portion is the extrapolation of this line. Horizontal bars are drawn through data points from Run #1 and indicate the range of values for this run (from Dickey et. al., 1984).

Figure 14. Relationship between the gas transfer coefficient and the functional form of the energy dissipation model of Lammon and Scott (1970) (from Dickey et. al., 1984).

Figure 15. k_l vs $(U'/l)^{1/2}$ for several experiments. (□) symbol for l = 1.05 cm, (+) symbol for 0.50 cm (from Pankow et. al., 1984).

Figure 16. Vertical Velocity Fluctuation profile (cube-root depth scale) (from Brumley, 1983).

Figure 17. a-b Summary of the mass transfer results and wave slope data from the small circular facility, Heidelberg (...). (a) Summary of all gas tracer results corrected to a Schmidt number of 600. (b) Mean square slope (open symbols) and mean square slope of the capillary waves (>14 Hz) (solid symbols). Symbols with crosses (mean square slope) or asterisks (capillary wave slope) denote measurements at a contaminated water surface (from Jaehne et. al., 1987).

Figure 18. a-b Summary of the mass transfer results and wave slope data from the large circular facility, Heidelberg. See Fig. 17 for detailed explanation (from Jaehne et. al., 1987).

Figure 19. a-b Summary of the mass transfer results and wave slope data from the large IMST tunnel, Marseille. (a) Rn gas exchange results corrected to a Schmidt number of 600 (b) Mean square slope (open symbols) and mean square slope of the capillary waves (>14 Hz) (solid symbols). The wave data are obtained at four fetches: circles, 4.6 m; squares, 9.4 m; tilted squares, 24 m; and triangles, 30.9 m (from Jaehne et. al., 1987).

Figure 20. Typical wave slope spectra for the three wind-wave facilities used for the gas exchange experiments in equal-area graphs with a logarithmic frequency ordinate (from Jaehn et. al., 1987).

Figure 21. Plot of normalized data k_l data vs $(\varepsilon/\nu)^{1/4}$ for the present grid data and wind tunnel results. ε for the wind tunnel data was calculated from the model of Cohen (1983). The data shown are ◆, CO_2, rayon/vacuum cleaned interface, present grid data; ■, CO_2, lens paper cleaned interface, present grid data; ●, CO_2 1-octadecanol film, present grid data; o, CO_2, circular wind tunnel, film covered interface, Jaehne et. al., 1984; □, CO_2 linear wind tunnel, clean interface, Broecker et. al. (1978); +, O_2, linear wind tunnel, clean interface, Liss et. al. (1981); ◇, Benzene, toluene, 1,2-dichloropropane, linear wind tunnel, clean interface, Mackay and Yeun (1983); ▼, N_2O, linear wind tunnel, clean interface, Merlivat and Memery (1983); ▲, CO_2, circular wind tunnels, clean interface, Jaehne et. al. (1984); Δ, CO_2, linear wind tunnel, clean interface, Jaehne et. al. (1984) (from Aesher and Pankow, 1986).

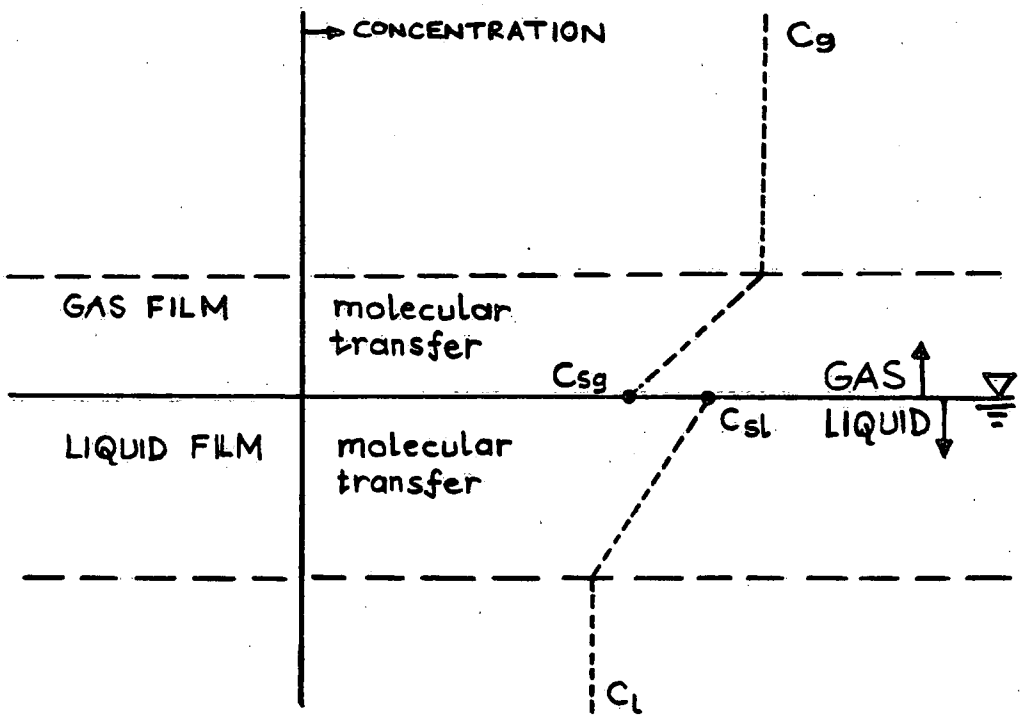
CONCENTRATION
Cg
GAS FILM
molecular transfer
Csg
GAS
Csl
LIQUID
LIQUID FILM
molecular transfer
Cl

FIG. 1

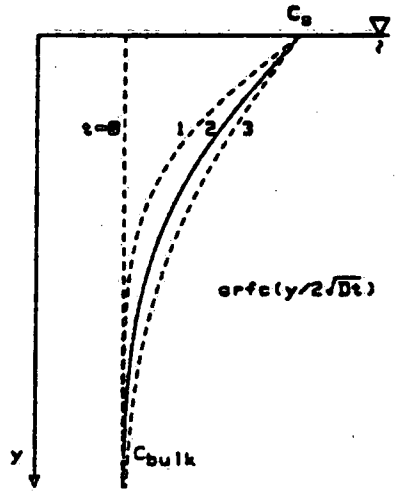
C_s
t
t=0
1
2
3
erfc(y/2√Dt)
y
C_{bulk}

FIG.2

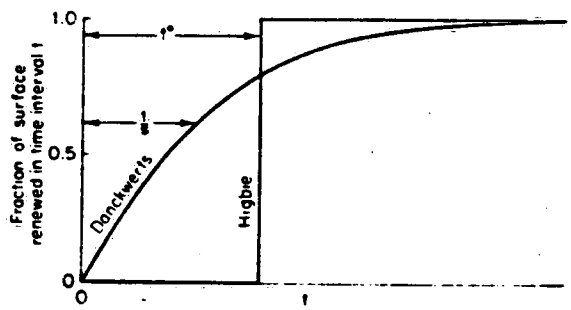
1.0
0.5
0
Fraction of surface renewed in time interval t
t*
t/2
Danckwerts
Higbie
0
t

FIG.3

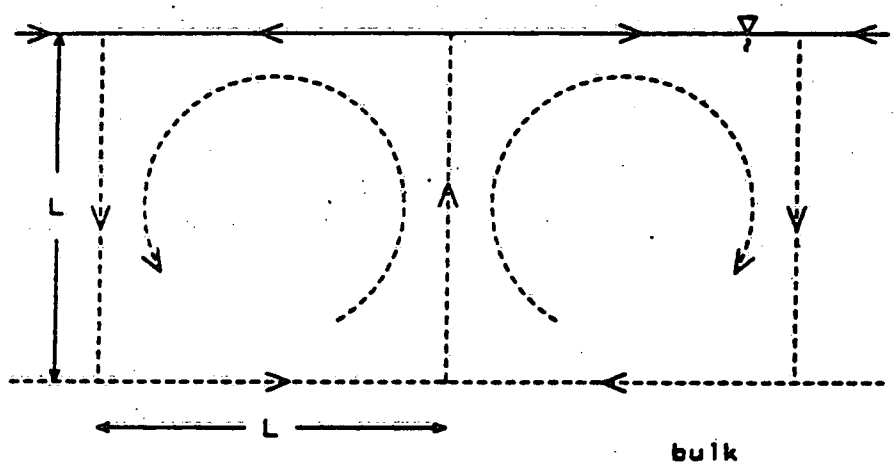
L
L
bulk

FIG.4

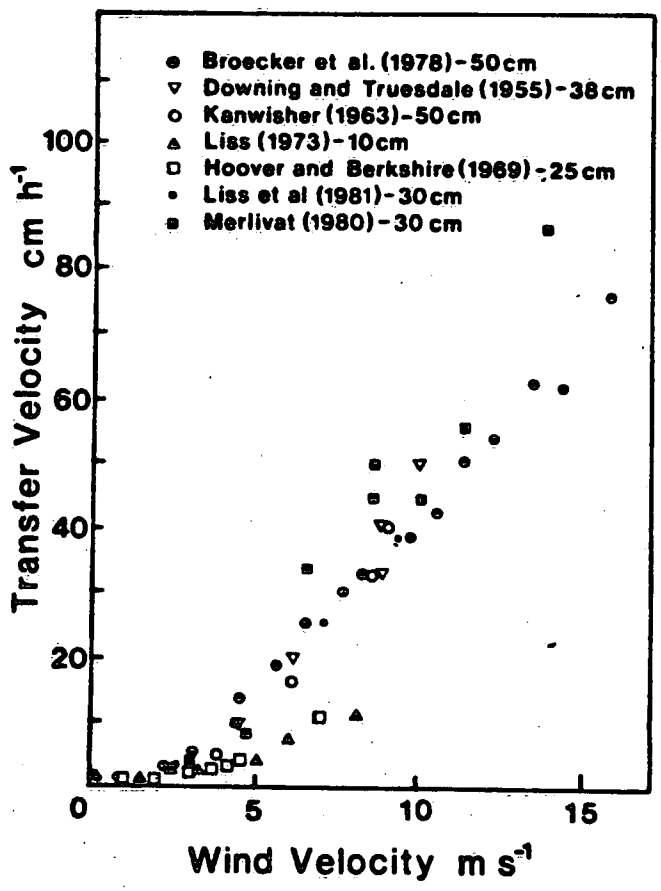
Broecker et al. (1978) - 50 cm
Downing and Truesdale (1955) - 38 cm
Kanwisher (1963) - 50 cm
Liss (1973) - 10 cm
Hoover and Berkshire (1969) - 25 cm
Liss et al (1981) - 30 cm
Merlivat (1980) - 30 cm
Transfer Velocity cm h⁻¹
Wind Velocity m s⁻¹
0
5
10
15
20
40
60
80
100

FIG.5

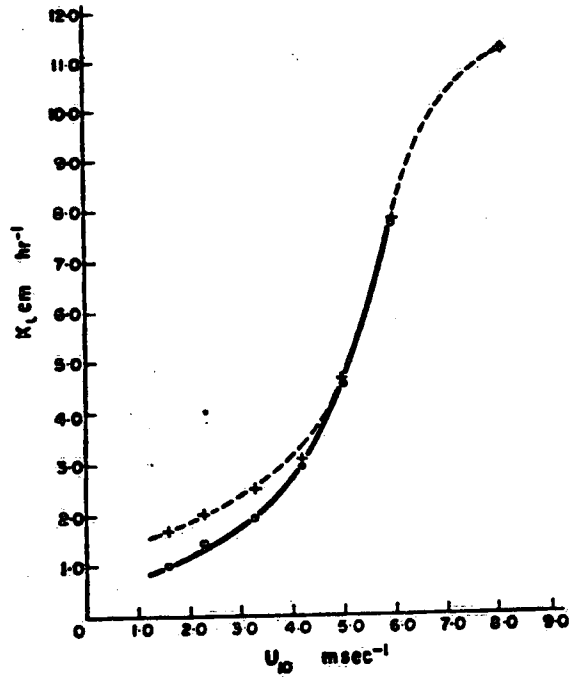
12·0
11·0
10·0
9·0
8·0
7·0
6·0
5·0
4·0
3·0
2·0
1·0
0
K_L cm hr^{-1}
1·0 2·0 3·0 4·0 5·0 6·0 7·0 8·0 9·0
U_{10} msec^{-1}

FIG. 6a

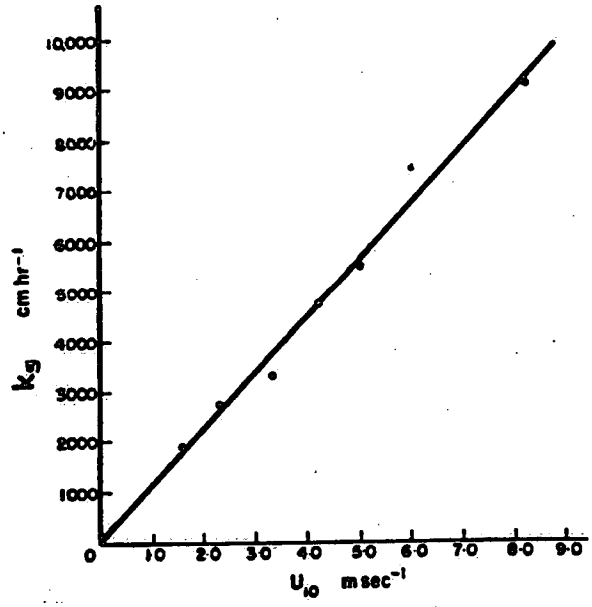
10,000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
k_g cm hr^{-1}
1·0 2·0 3·0 4·0 5·0 6·0 7·0 8·0 9·0
U_{10} msec^{-1}

FIG. 6b

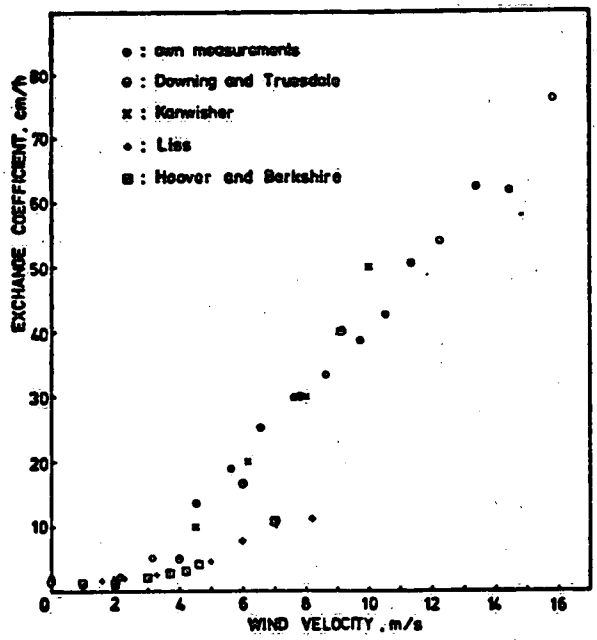
• : own measurements
o : Downing and Truesdale
x : Kanwisher
◆ : Liss
▪ : Hoover and Berkshire
EXCHANGE COEFFICIENT, cm/h
WIND VELOCITY, m/s

FIG. 7

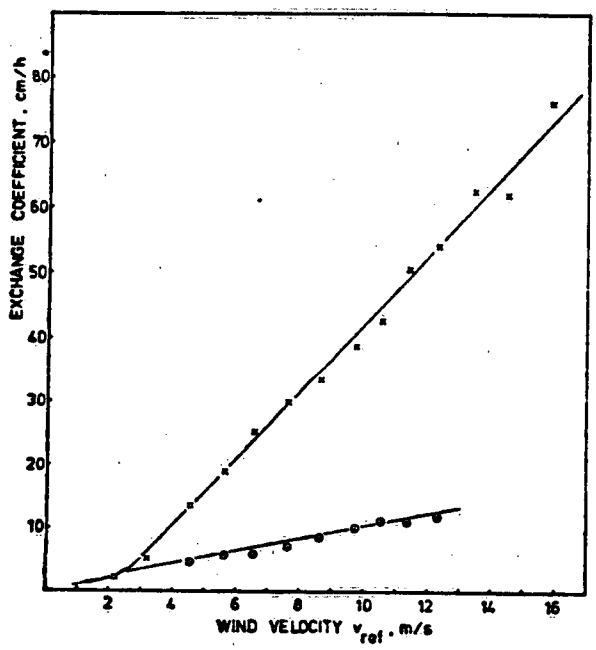
EXCHANGE COEFFICIENT, cm/h
WIND VELOCITY v_{ref}, m/s

FIG. 8

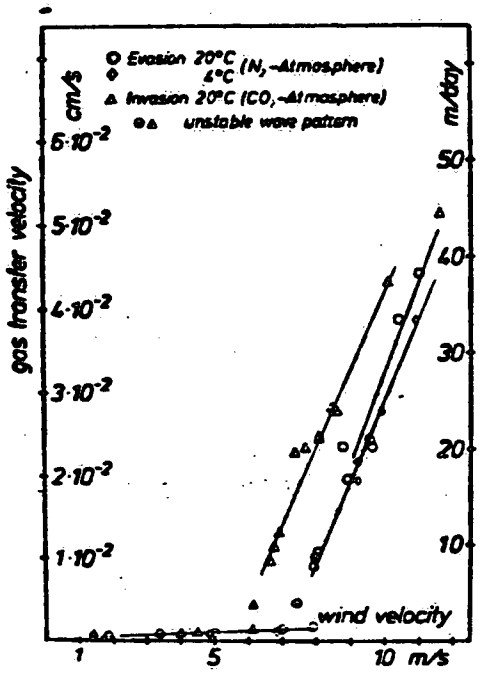
Evasion 20°C (N₂-Atmosphere)
4°C
Invasion 20°C (CO₂-Atmosphere)
unstable wave pattern
gas transfer velocity
cm/s
m/day
6·10⁻²
5·10⁻²
4·10⁻²
3·10⁻²
2·10⁻²
1·10⁻²
50
40
30
20
10
wind velocity
1
5
10 m/s

FIG. 9

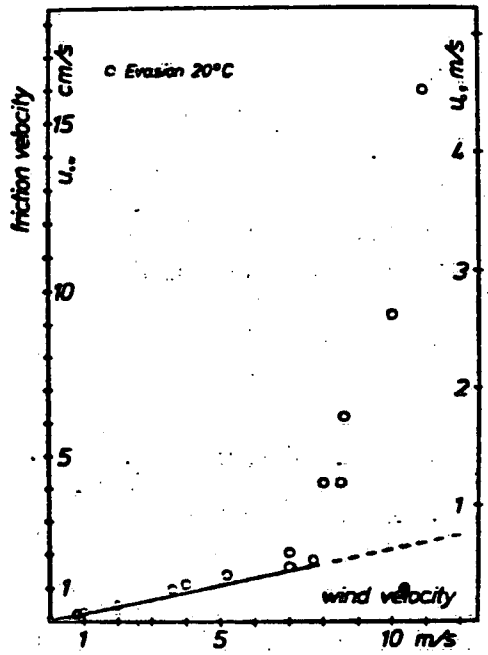
Evasion 20°C
friction velocity
u* cm/s
u*, m/s
15
10
5
1
4
3
2
1
wind velocity
1
5
10 m/s

FIG. 10

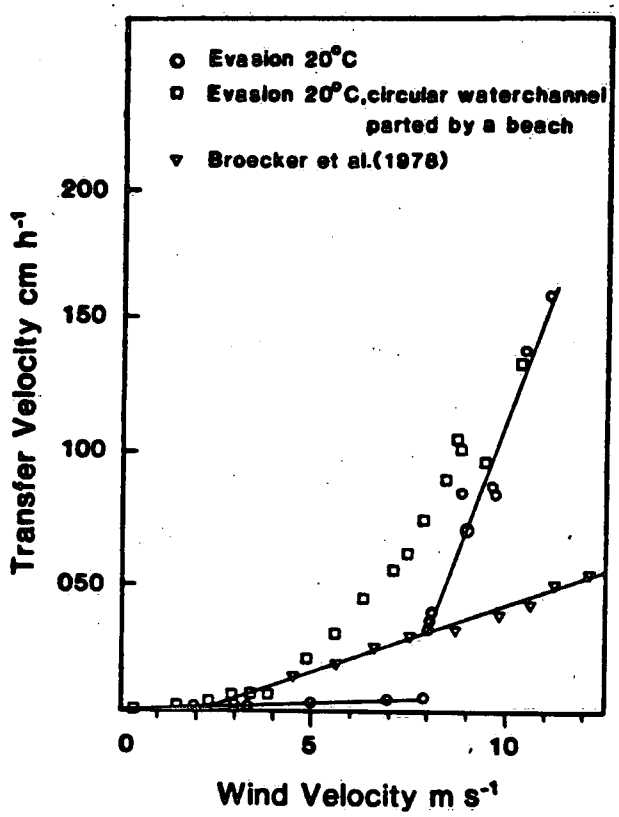
Evasion 20°C
Evasion 20°C,circular waterchannel parted by a beach
Broecker et al.(1978)
Transfer Velocity cm h-1
200
150
100
050
0
5
10
Wind Velocity m s-1

FIG. 11

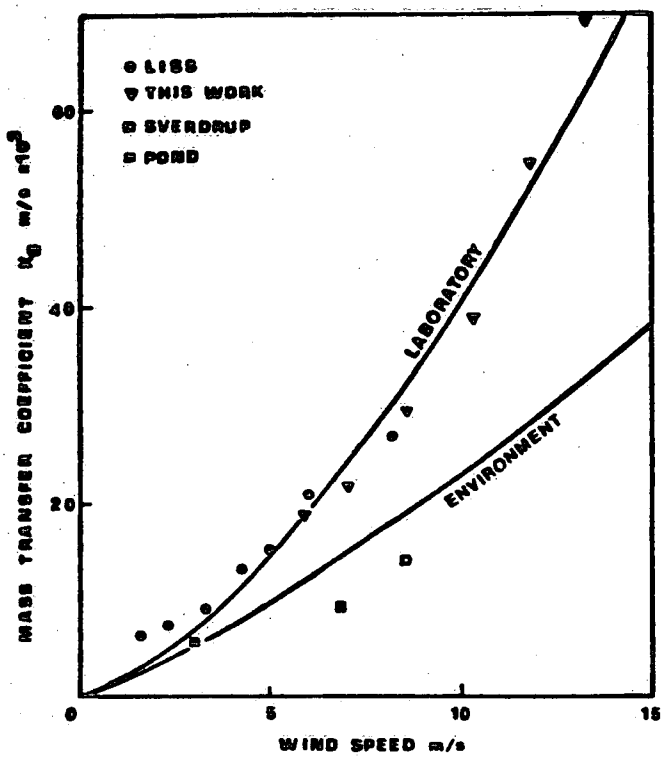

FIG.12 a

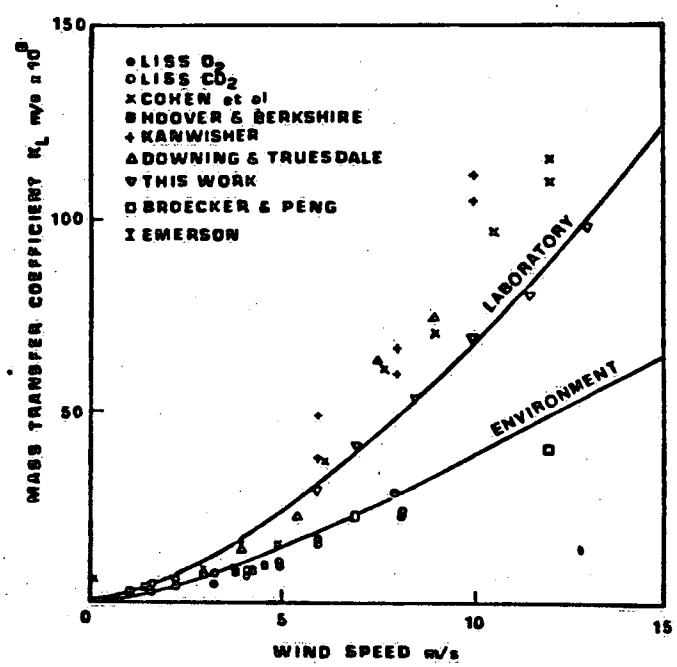

FIG.12 b

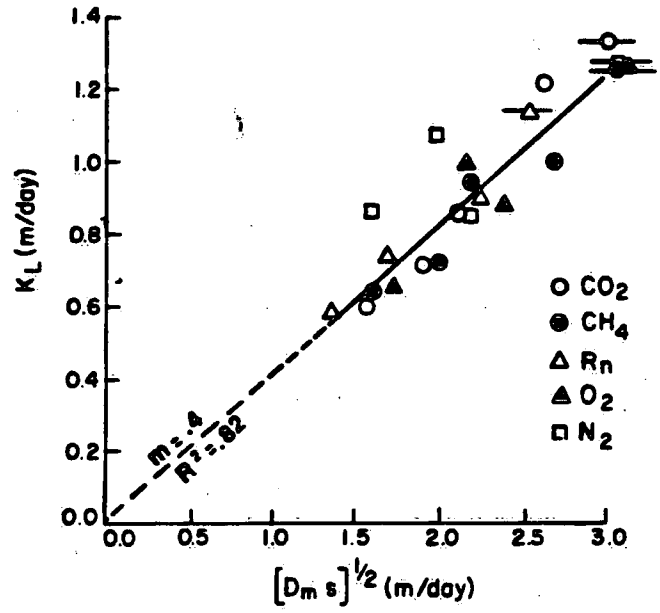
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
K_L (m/day)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
$[D_m s]^{1/2}$ (m/day)
m = .4
R^2 = .82
CO_2
CH_4
Rn
O_2
N_2

FIG. 13

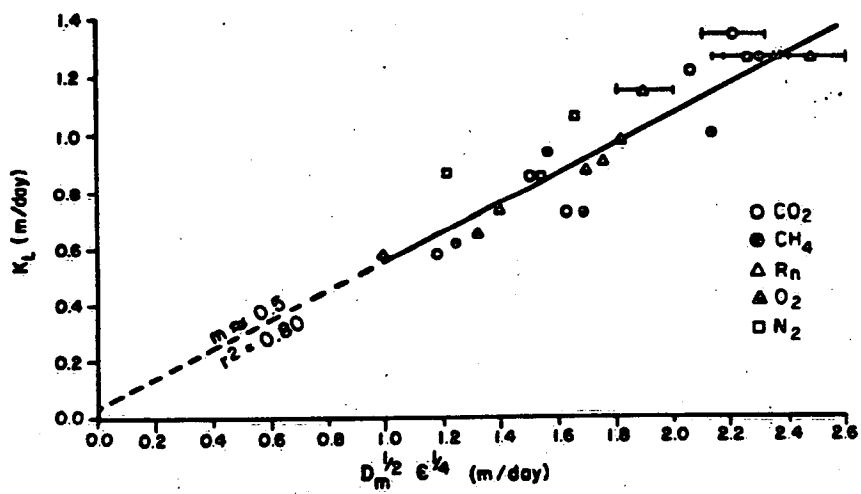
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
K_L (m/day)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
$D_m^{1/2}\ \epsilon^{1/4}$ (m/day)
m ≈ 0.5
r^2 = 0.80
CO_2
CH_4
Rn
O_2
N_2

FIG. 14

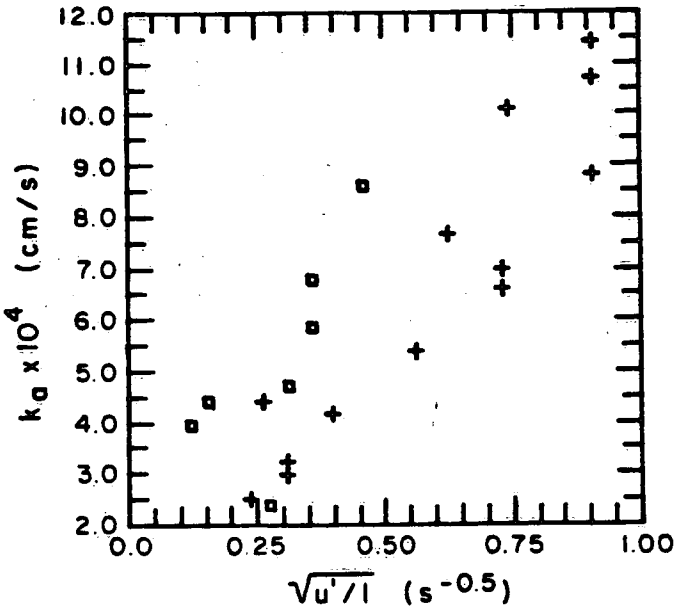
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
$k_a \times 10^4$ (cm/s)
0.0
0.25
0.50
0.75
1.00
$\sqrt{u'/l}$ ($s^{-0.5}$)

FIG. 15

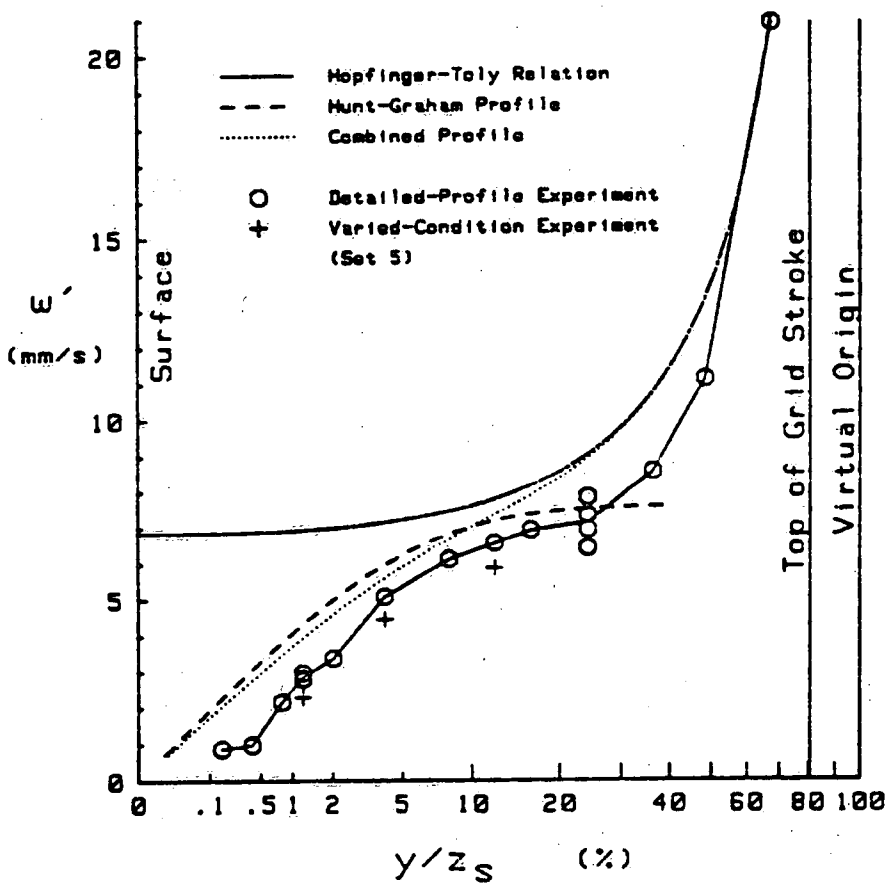
Hopfinger-Toly Relation
Hunt-Graham Profile
Combined Profile
Detailed-Profile Experiment
Varied-Condition Experiment
(Set 5)
Surface
Top of Grid Stroke
Virtual Origin
w'
(mm/s)
20
15
10
5
0
0
.1
.5
1
2
5
10
20
40
60
80
100
y/z_s (%)

FIG. 16

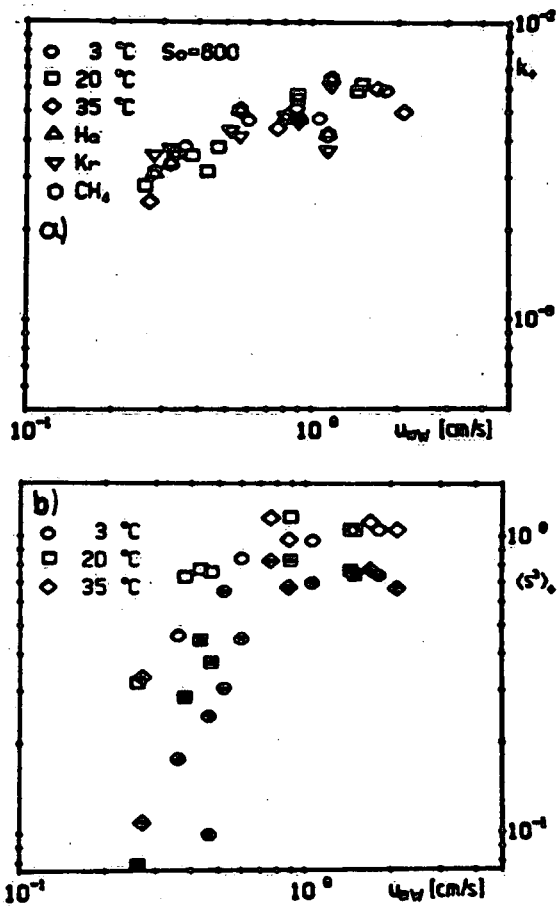

FIG.17 a-b

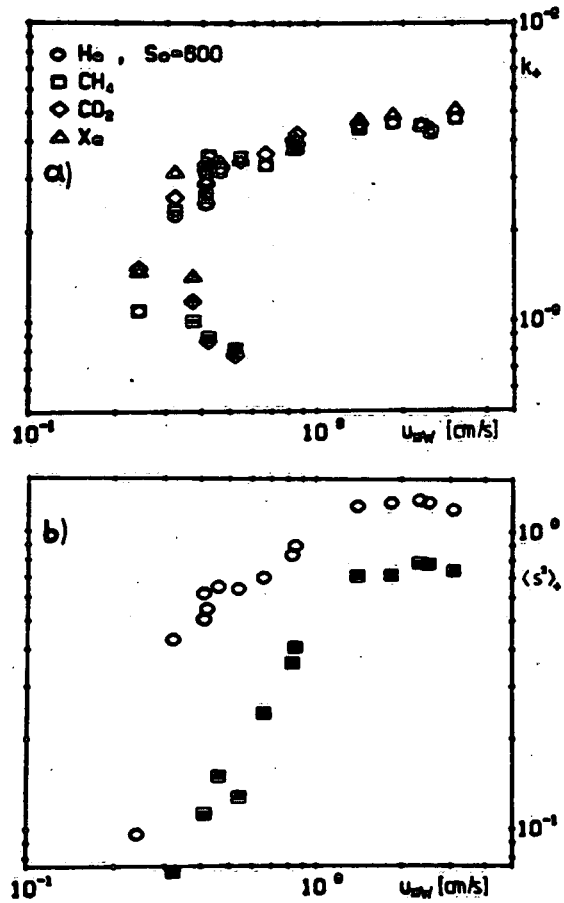

FIG.18 a-b

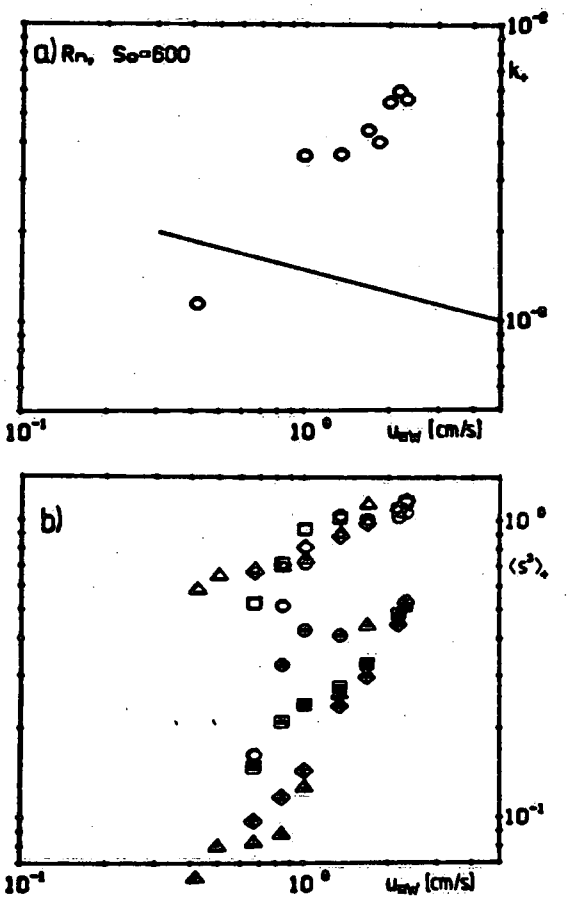
a) Rn, So=600
10^{-2}
k_+
10^{-3}
10^{-1}
10^{0}
u_{sw} [cm/s]
b)
10^{0}
$\langle s^2 \rangle_+$
10^{-1}
10^{-1}
10^{0}
u_{sw} [cm/s]

FIG. 19 a-b

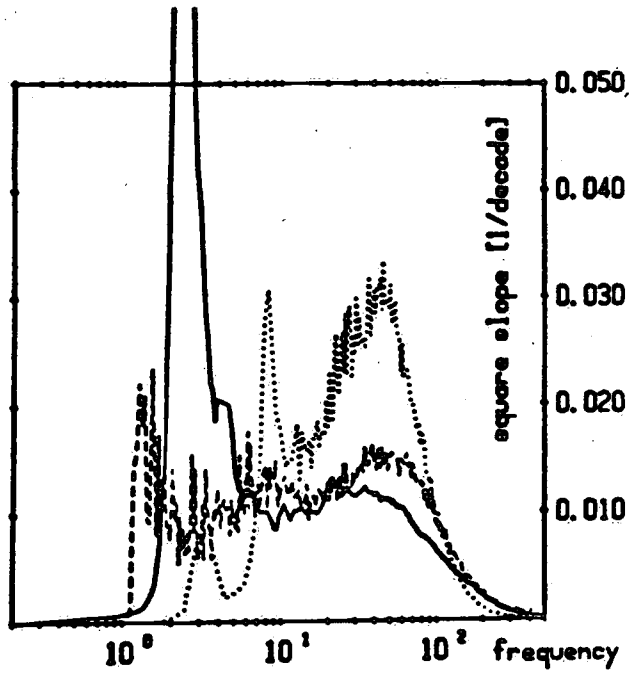
0.050
0.040
0.030
0.020
0.010
square slope [1/decade]
10^0
10^1
10^2
frequency

FIG. 20

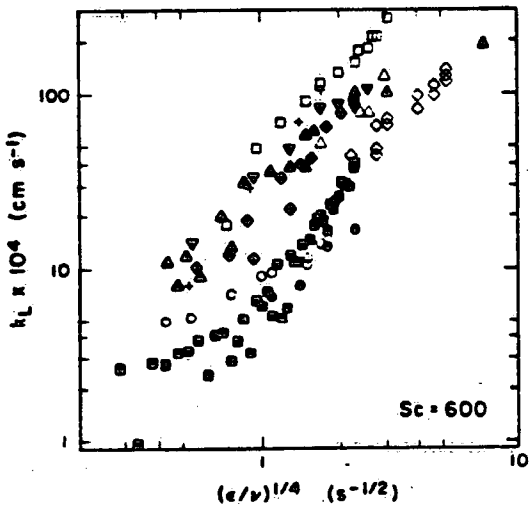
100
10
1
$k_L \times 10^4$ (cm s^{-1})
Sc = 600
1
10
$(\epsilon/\nu)^{1/4}$ (s$^{-1/2}$)

FIG. 21