GAS EXCHANGE IN RELATION TO OTHER AIR/SEA INTERACTION PHENOMENA

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I. INTRODUCTION

The transfer of atmospheric pollutants to the ocean finds increasing interest. This is true in view of its practical importance, as well as due to the fact that pollutant transfer (gases, vapours, aerosol particles)might also contribute to the general understanding of air/ sea interaction (transfer of momentum, heat, water vapour, etc). - A report on some aspects of pollutant transfer has been given previously (1971) by one of the present authors [3,4].

II. TRANSFER VELOCITY AND TRANSFER RESISTANCE: Choice of Notation.

The transfer of "matter"[+] from the air to the sea, i.e. from an elevation of, say,ten meters above the water level, into the water, e.g. down to a few meters depth below the surface is primarily accomplished by two competing transport mechanisms (eddy diffusion and molecular diffusion). Since eddies cannot penetrate the interface, molecular diffusion is the only transport mechanism through those layers which are directly adjacent to the interface, whilst eddy diffusion prevails at greater distance.

The flux density j of the "substance" in question through any of the individual layers which are to be penetrated by the transfer process is usually proportional to the concentration difference Δc across

(1) this layer, i.e. $j \sim \Delta c$. This virtually is true for trace substances, but not so for momentum and heat, since concentration gradients of these particular quantities may actively cause advective or turbulent transport through the layer in question (see e.g. [1/93]).

Where eq. (1) holds we may say that the transfer resistance R [sec/cm]

(2) defined by $R = \Delta c/j$ is independent of Δc. If we then arbitrarily divide the region on both sides of the interface into a number of sublayers, and if we know there are no internal sources or sinks, this means that the flux density is constant through all these layers. Of course, all individual Δc_i across the individual layers add up to the total concentration difference Δc_{total} across the whole sandwich and there-

(2a) fore it follows from $R_i = \Delta c_i/j$ (cf. (2)) that $R_{total} = \Sigma R_i$, as with electric resistancies connected in series.

By introduction of the concept of resistance the treatment of transfer processes is greatly facilitated: although, or rather because the transfer bottle-neck for different substances may be situated in different layers, the R value of a particular layer may be measured

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[+] this term may include all quantities under a specific conservation law (such as heat, momentum etc.), since, clearly, these quantities behave matter-like during transfer.

for one substance and used for another one, either directly or after multiplication with a known factor [2/184].

We shall find that a model "sandwich" of only a limited number of individual layers and of basicly, but not strictly logarithmic spacing, will be suited best for our purpose. Of course, ultimately, using a great number of very thin layers would mean defining a diffusion constant D(z), variing with distance z from the interface. By defining an average diffusion constant $\bar{D}$ for an individual layer we have the relation $R=1/\bar{D}$ where R the resistance and l the thickness of this layer. - Further, the inverse of R namely the transfer veloc-

(3) ity w [cm/sec]$=1/R$ may also prove useful in illustrating the intensity of substance transfer through a layer with the transfer resistance R. This w is the velocity of a fictitious piston pushing the substance through the resistance layer from either side.

It should be stressed that both, resistance R and transfer velocity w, always apply to a specific layer (between e.g. z_1 and z_2) and strictly therefore should be put as $R(z_1,z_2)$ or $w(z_1,z_2)$, we may, however, where misunderstanding seems unlikely, omit the boundaries. We shall also often use the "total" transfer resistance R_{total} between e.g. 10 meters above and, say, 1 meter below the water level. R_{total} or the corresponding tranfer velocity do not critically depend on the exact values of these boundaries.

III. THE (LIQUID) FILM MODEL. - The effect of "solubility" and the influence of gas phase resistance.

For a layer through which molecular diffusion is the only transport process it follows from eqs. (2) and (3) that $w=D/l$ or $R= 1/D$, where D= molecular diffusion constant. Since gas phase molecular diffusion is by four orders of magnitude faster than in a liquid the bottle-neck with inter-phase gas transfer is in the liquid, although the molecular diffusion layer in the liquid is rather thin (below one milli-meter). Gas transfer is, however, the more enhanced the higher its solubility in the liquid is [2/182] . This led Münnich (1971) [3/7, 4/146] to the conclusion that substances of extremely low volatility like DDT should behave like water vapour, which due to its large liquid/gas phase partition factor (high "solubility" α) sees practically no resistance in the liquid phase, is transferred much faster than less soluble gases, and has its bottle-neck in the gas phase boundary layer. The same argument has been used by Eggleton (1970 and 1975) [5,6].

Fig. 1 summarizes the experimental evidence on gas tranfer and gives an impression of the degree to which the real situation can be approximated by a simple one- or two-layer transfer resistance model. Good reviews of the simple film models can be found in Liss (1973) [7], Broecker and Peng (1974) [8], and Liss and Slater (1974) [2].

Apart from the influence of solubility which affects the gas phase residence time of a trace gas only - the liquid phase residence time (evasion rate) is not influenced [8/31] - the gas to gas differences in the transfer rates as predicted by the film model are rather small, in agreement with the experimental results. This is due to the fact, that the molecular diffusion constants do not vary over a wide range, and, consequently, there seems to be no need for more sophisticated models [8/23 , 2/181].

log R [sec/cm]

| | | -5 | -4 | -3 | -2 | -1 | 0 | +1 | +2 | +3 |

GAS PHASE

- turbulent layer between 100 m and 10 m: ● (at about -1)
- turbulent layer between 10 m and 1 cm: (shaded around -1/0)
- viscous gas boundary layer: (shaded around -1)
- reflection at the interface: no reflection (shaded around -4 to -3)

LIQUID PHASE

- (organic) liquid surface film: (shaded -4 to +1, dot at -1)
- viscous liquid boundary layer: $\alpha = 10^5$ (H₂O) at -3; $\alpha = 1$ (CO₂) at +2
- turbulent layer

log transfer resistance log R [sec/cm]

| -5 | -4 | -3 | -2 | -1 | 0 | +1 | +2 | +3 |

log transfer velocity log w [cm/sec]

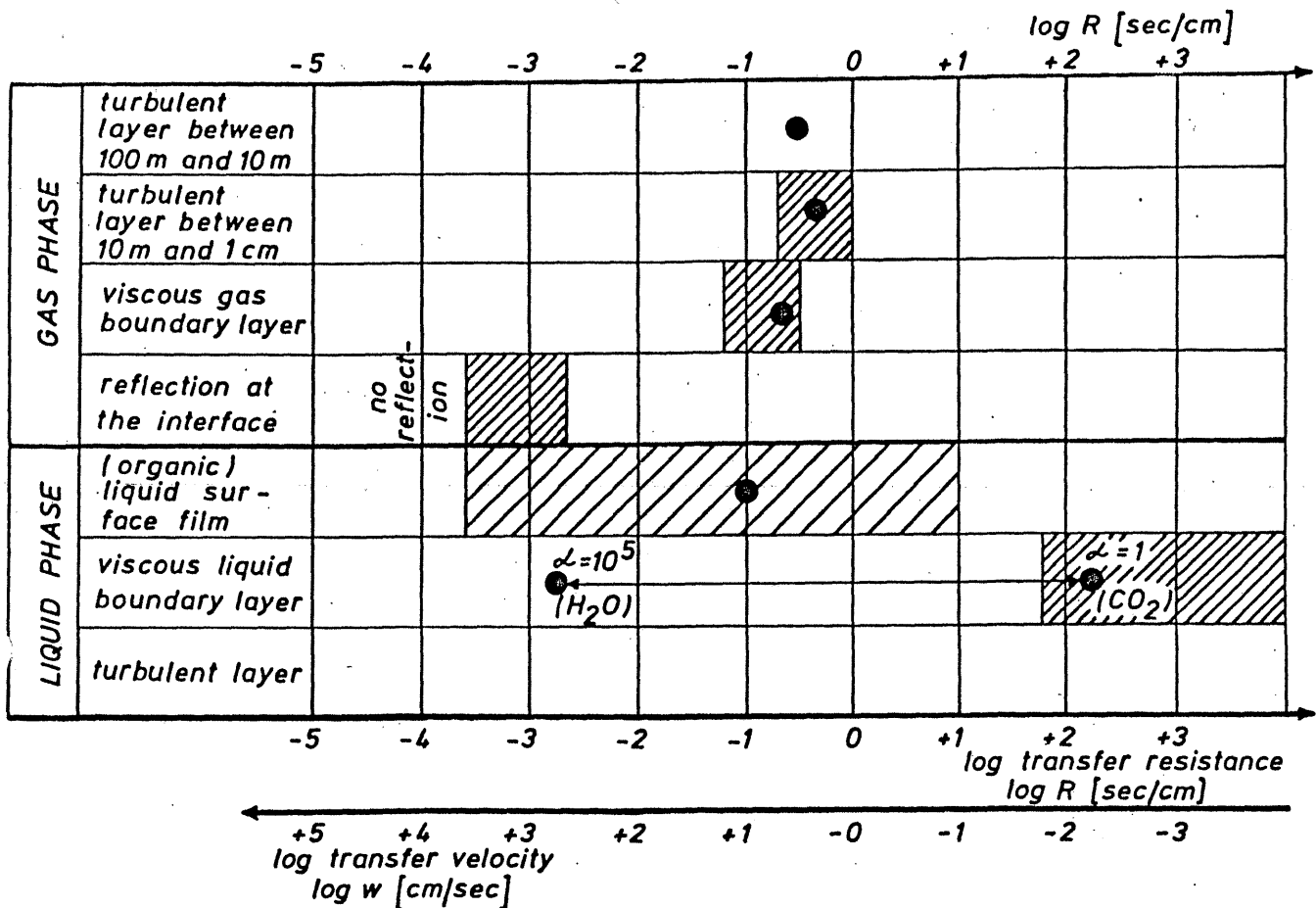| +5 | +4 | +3 | +2 | +1 | -0 | -1 | -2 | -3 |

Fig. 1: Transfer resistance R and transfer velocity w of individual
layers in the gas phase and in the liquid phase, and their
relative importance. Representative values under marine con-
ditions are denoted by dots, the shaded areas give an idea
of the range to be expected. One e.g. sees immediately, that
true reflection of molecules at the interface does not play a
role. - The resistance of the viscous liquid boundary layer
strongly depends on the air/liquid equilibrium partition
factor (Henry's law constant H in Liss's notation $\lfloor 2/181 \rfloor$ or
on the "solubility" $\alpha = 1/H$) of the trace substance in ques-
tion. - If Ohm's law eq. (2a) shall be valid across phase
boundaries note that reference should be made as to which
phase all R's and w's are normalized, i.e. in which medium
the pistons are thought to work. We have chosen the atmosphere
to be the reference medium; therefore the transfer velocity
through e.g. the liquid boundary film is $w = \alpha D/l$ or $R = 1/w =$
$= 1/\alpha D$ (l = film thickness). Normalizing to the liquid phase
would give $w^* = D/l$ or $R^* = 1/D$; the advantage of this notation
is that w^*, the velocity of a piston transporting the same
amount of gas, but "working" in the liquid phase, does not
contain α , and this means that the in- and evasion time
+) $\tau = h/w^*$ of gases dissolved in liquids is independent of gas
solubility. This is due to the fact that in this case the
exchange bottle-neck is situated in the same phase, a fact
which greatly facilitates the discussion of gas exchange ex-
periments based on measurements of the gas concentration
change in the liquid. $w/w^* = \alpha$ also means of course: no net
gas transport in solution equilibrium.

+) h = depth of water in container

IV. THE DANCKWERTS (Residence-Time-) MODEL FOR THE LIQUID FILM.

This model has been used by one of the authors since 1960 (Münnich [9,10,3], originally not knowing of Danckwerts's work (1951) [e.g. 11,12,13]. The preference for this model originated from the fact that it shows a way to explain why there is a quasi-stagnant film close to the interface see [11/1461]. Münnich's approach to Danckwerts[+] model was slightly different: his starting point was diffusive penetration of a radioactive tracer (like radon) or of a reactive gas into a reactive liquid. If the gas concentration is sufficiently small (as e.g. with CO_2 at atmospheric level in 1molar NaOH) the decay constant by reaction is independent of CO_2 concentration [14/9] as it is in radioactive decay. For the trace substance penetrating into the liquid by molecular diffusion he then opened a second decay channel represented by eddies carrying the tracer-loaded liquid into the bulk, and replacing it by liquid being free of tracer [9,3/6]. Mathematical evaluation of this model leads to the following relations [14/8,9,3/6, 16/123]:
statistical distribution of the tracer concentration c(z) with depth z

(8) $c(z)/c(0) = \exp(-z/\bar{z})$, where the effective film thickness $l = \bar{z} = \sqrt{D\tau}$ [++] ;
c(0) is the tracer concentration immediately at the interface (on the liquid side, which means $c(0) = \alpha \cdot c_{gas\ phase}$). Thus the only difference from the simple film model is that now the film thickness $l = \sqrt{D\tau}$ changes with the molecular diffusion constant, and this has the

(9) consequence that the transfer velocity $w = D/l = \sqrt{D/\tau}$ increases only with the square root of D.

As has been mentioned already, the concept of competing disintegration channels makes the Danckwerts model handy to include more than one mechanism influencing the gas exchange rate (e.g. chemical reaction, wind induced turbulence, temperature induced convection etc.). For strongly reacting gases (CO_2 in NaOH [14/9,10/214], SO_2 in water [2/182]) film thickness is not influenced by turbulence (and vice versa [15/280]) since the decay constant $1/\tau = 1/\tau(reaction) + 1/\tau(turbulence)$ is controlled exclusively by the reaction rate.

It is evident that strict validity of Danckwerts model depends on the following conditions:
1) molecular diffusion is the only multi-stage (i.e. diffusion-like) process operating. If eddy diffusion would work as such to an appreciable extent it would have to be added to the molecular diffusion constant D.
2) Danckwerts model treats turbulent transport as a single-stage process. This is appropriate for the larger eddies which in fact replace tracer-loaded water from the film by pure water from the bulk liquid. The predicted dependence of w on decreasing molecular diffusion constant D predicted by eq.(9) is only correct if smaller eddies do not exist. If they would do, they would as long as molecular diffusion is large and we according to eq. (8) have a thick boundary film, only compete with molecular diffusion (see preceding paragraph), and they probably would not be very efficient in doing this. If, however, molecular diffusion becomes much smaller, their relative importance increases of course, and in addition (the boundary film according to eq. (8) is much thinner now) they may now, despite their small diameter, contribute to the single stage transfer, namely replace loaded water by pure water. This means they increase $1/\tau$ (decrease τ). Due to $l = \bar{z} = \sqrt{D\tau}$ this is equivalent to 1 decreasing stronger and $w = D/l$ de-

+) Danckwerts's emphasis is primarily on the age distribution of the surface elements of the liquid [11/1462, 13/102].

++) the intensity of the single-stage removal of tracer by the eddies is reflected by $1/\tau$, the probability of occurrence per unit time

creasing less than predicted by Danckwerts model, even if the de-
creasing molecular diffusion constant is not influenced appreciably
by additive turbulent diffusion (see fig. 2).
Note, however, that molecular diffusion of momentum (kinematic viscos-
ity) has a tendency to efficiently damp the small eddies
and consequently the assumption that there are no eddies with diameter
$\lesssim z_{momentum} = \sqrt{D_M \tau}$, might be a good one and a tracer diffusing more slow]
than momentum might in fact experience the same residence time τ as does
momentum.

3) Danckwerts model assumes a residence time τ independent of the dis-
tance z from the interface. There are cases $\lfloor 3/7, 17/544 \rfloor$ where one
might suspect that the residence time increases towards the interface
(see p. 9). The extreme case would be that $\tau \rightarrow \infty$ for some distance
$z < z_0$, and this is equivalent to assuming a simple film of fixed thick-
ness in addition to a Danckwerts regime. In this case the fixed film
plays no role for large molecular diffusion constants, from a certain
D downward, however, the total film thickness then decreases less
than predicted by Danckwerts and eventually remains constant. This
then means that the transfer velocity approximates the slope for the
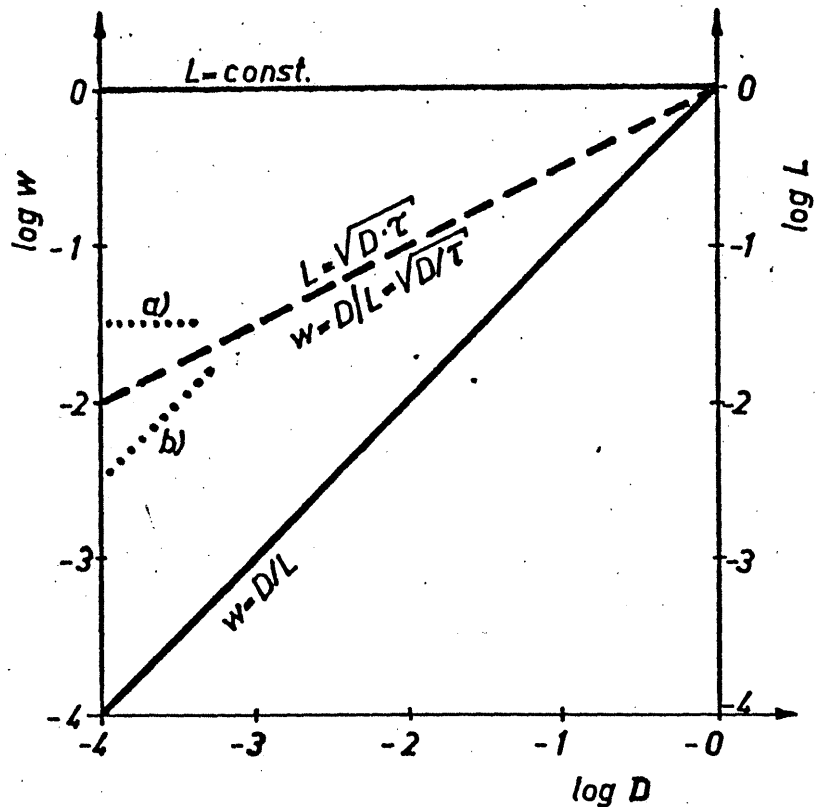simple film model.

Fig. 2: Dependence of film thickness l and transfer velocity w for
the simple film model (heavy line) and the Danckwerts model
(broken line) on the value of the constant of molecular diffus-
ion. (D, l and w in arbitrary units, $\tau = 1$ assumed). -
If in addition to a Danckwerts film there exists a very thin
fixed thickness film, l eventually becomes constant and l goes
over to branch (a) in the diagram. Transfer velocity then
follows fixed thickness slope (line (b) in the diagram).
On the other hand, if small eddies become single-stage-active
on a very thin Danckwerts film they reduce the film thickness.
For sake of simplicity in using the same diagram for the
discussion of this case, we assume that l follows e.g. branch
(b). This of course means then that the transfer velocity
drops less than predicted by Danckwerts (broken line) and
- in our example - follows line (a).

V. PARAMETERS CONTROLLING RESIDENCE TIME AND FILM THICKNESS.

V-A. WIND STRESS

The most prominent parameter inducing gas exchange is thought to be the wind velocity [7,8,15,18] transferring momentum to the ocean and thus generating oceanic turbulence. Which fraction of total momentum transferred goes directly into the surface film by molecular transfer is still open to discussion [19/12]. It seems to be a reasonable assumption, however, to use the fraction corresponding to hydrodynamically smooth transfer to the ocean, which anyway would mean a considerable percentage of the total (see [20/57]).

If we then assume that this momentum transferred be conducted down by molecular viscosity as a gas tracer would be by molecular diffusion we can calculate the velocity distribution across the viscous surface film if we make an assumption about the film thickness.

(10) By assuming that the flux density $j_M = c_{10} \cdot \rho_a \cdot U_{10}^2 = \rho_a \cdot U_*^2 = \rho_w u_*^2$ is constant through the interface (ρ_a, ρ_w=density of air and water, resp., U_{10}=wind velocity at 10 meters, U_*, u_*=friction velocity in air and in water, resp., c_{10}=smooth drag coeff. $\approx 1 \cdot 10^{-3}$) we know $u_* = U_* / \sqrt{S}$ (where $S = \rho_w / \rho_a$=the "solubility" of momentum in water) from the friction velocity U_* in the atmosphere or from the wind speed U_{10}. In the boundary film we have a linear velocity gradient due to Fick's law $j_M = \rho_w u_*^2 = \rho_w D_M \Delta u / l$; if we then define from this a Reynolds number

(11) $$Re = \Delta u \cdot l / D_M = (u_* / D_M)^2 \cdot l^2$$

D_M=molecular diffusion constant of momentum (kinemetic viscosity)

we see that this viscous flow boundary film cannot exceed a certain thickness without becoming turbulent. By assuming a critical value for the Reynolds number we thus can calculate the laminar film thickness as a function of wind speed.

Inserting reasonable numbers into eqs. (10) and (11) leads to the conclusion that the film thickness calculated in this way is by far too large to be used for the boundary film thickness in the simple gas exchange film model (film thickness assumed in gas exchange is in the order of 50 Microns [2,3,8,10]. This discrepancy is primarily due to the fact, that the molecular diffusion constant D_M of momentum is by a factor of approximetely 600 larger than than the diffusion constants of gases in water, and therefore the simple film model fails to describe the situation adequately. The Danckwerts model on the other hand correctly predicts that the boundary film for gas exchange must be much thinner than the one for momentum transfer.

Once having obtained reasonable predictions for the gas exchange by working along the lines just mentioned we tried to reach this point in a more direct way, i.e. without the necessity of guessing a critical value for the laminar boundary layer Reynolds number. To this end we had a look at the universal velocity profile close to a smooth wall (see e.g. [21/557]). What we did is trying to fit the region close to the wall with a Danckwerts model. For notation see page 7; the best fit curve is shown in Fig. 3 together with the diagram from Schlichtings book [21] where we took the data from. It turns out that the Danckwerts velocity profile fits the universal profile experimental data rather well and in a unique way, which means that we are now in the position to uniquely relate the residence time which is the free parameter in the Danckwerts model directly to the viscosity and the

best Danckwerts-fit to universal profile

$$\boxed{\frac{u(z)}{u_*} = \beta(1-e^{-z/\bar{z}})}$$ with $\bar{z} = \beta z_*$ and $\beta=16$

Dimensionless coordinates X,Y:

$$X = \log(z/z_k)$$
$$Y = u(z)/u_*$$

normalisation lenght $z_* = \dfrac{D_{M(molecular)}}{u_*}$

With $\zeta = \log(z\,[cm])$ and $\zeta_* = \log(z_*[cm])$:

roughness parameter z_0:

$$z_0 = z_*/9 \qquad \text{or} \quad X_0 = \zeta_0 - \zeta_* = -.954$$

normalization lenght z_*:

$$z_* = z_* \qquad \text{or} \quad X_* = \zeta_* - \zeta_* = 0$$

relaxation lenght $\bar{z}$:

$$\bar{z} = 16 z_* \qquad \text{or} \quad \bar{X} = \bar{\zeta} - \zeta_* = 1.205$$

Danckwerts/Prandtl transition z_{DP}:

$$z_{DP} = 67 z_* \qquad \text{or} \quad X_{DP} = \zeta_{DP} - \zeta_* = 1.826$$

Residence time τ of water in viscous boundary layer:

$$\tau = \beta^2 \cdot D_M/u_*^2 \approx 250 \cdot D_M/u_*^2$$
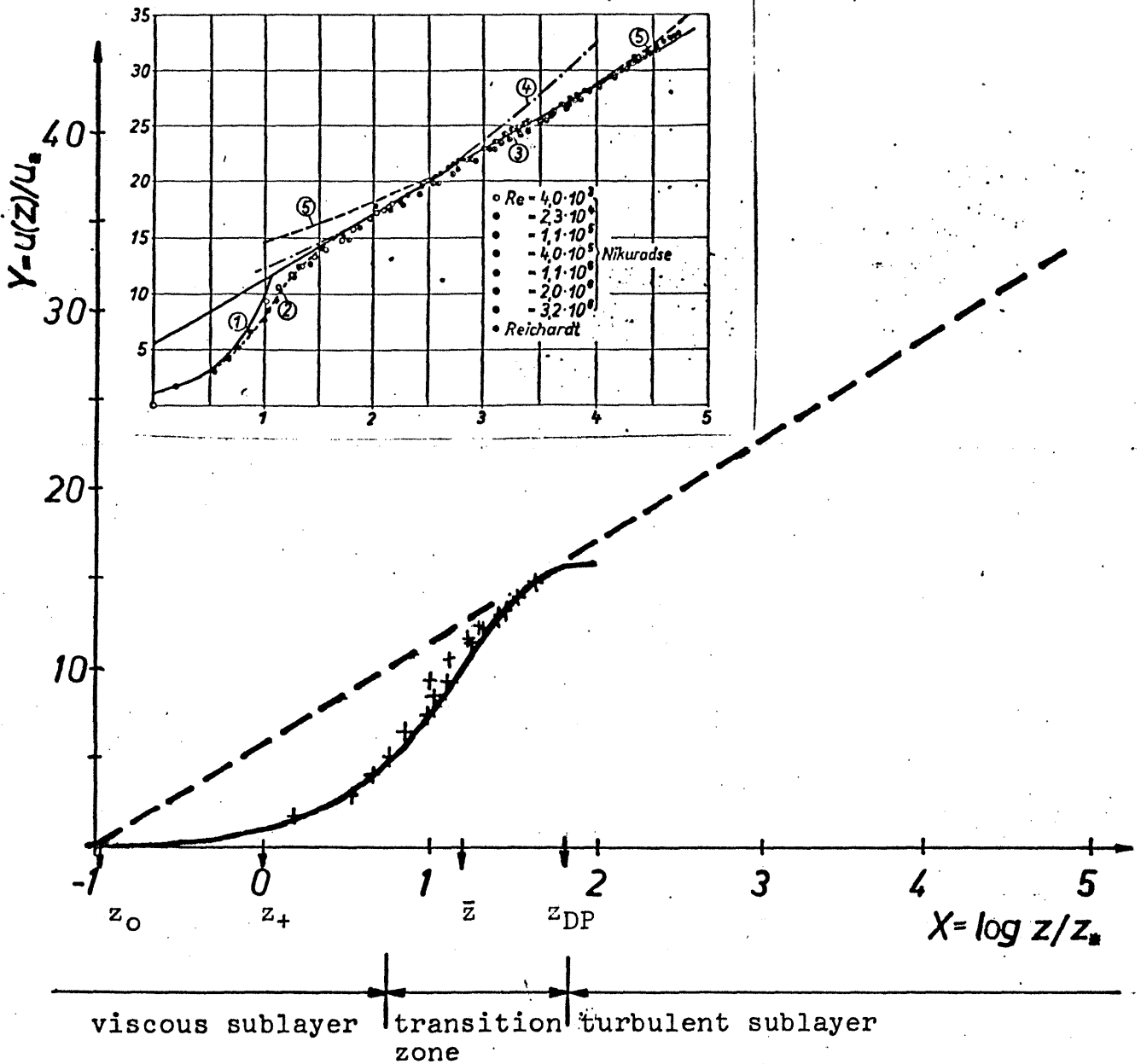
Fig. 3 :

Danckwerts profil of velocity (momentum) fitted to the universal velocity profile by the conditions that velocity gradient for z=0 be as for the linear viscous profile, and that Danckwerts profile meets the log profile with identical slope.

The crosses are experimental data, taken from [21/557].

friction velocity (see page 7). In table 1 a few examples are given where the various parameters of this model are calculated as a function of wind speed U_{10}. The calculated gas transfer velocities are compared with the experimental values listed in the last row of the table

wind speed U_{10}(meter/sec)	3.3	6.7	10.0	13.3
fr.vel.(air) U_* (cm/sec)	10.5	21	32	42
" (water) u_* (cm/sec)	.37	.75	1.1	1.5
film thickness (momentum) $\bar{z}_M$ (mm)	4.3	2.1	1.4	1.1
residence time (sec)	18	4.5	2.0	1.1
transfer vel. w (cm/sec)$\cdot 10^3$ (calculated)	1	2.1	3.1	4.1
transfer vel. w (cm/sec)$\cdot 10^3$ (observed) after Emerson[22]	.5	1.3	2.3	5.0

Table 1 : calculated gas transfer velocity compared with observed data. - values of constants used: kinematic viscosity D_M of water .01 cm^2/sec ; density ratio water/air S= 28.3 smooth drag coefficient $c_{10} \approx 1 \cdot 10^{-3}$; $D_{CO2} = 1.9 \cdot 10^{-5}$ cm^2/sec

The agreement between calculated and observed transfer velocities is surprisingly good in view of the fact that the calculation is based on the assumption of a completely flat interface and the structure of the interface which also changes with wind speed might well influence the tendency of the viscous film to become turbulent, i.e. in our notation to become thinner due to a decreasing critical Reynolds number.

It should be mentioned that the model without influences of that kind does not predict a quadratic increase of gas transfer with wind speed, but a linear one.

Another surprising feature of this model is that there seems to be so little difference between a boundary layer adjacent to a rigid wall or to a completely free interface. One would be inclined to assume that the medium "sticks" to a rigid interface, and that there might therefore exist an additional fixed thickness boundary film close to the wall. It should be kept in mind,however, that the Danckwerts model takes the strong interaction between a wall and its immediate neighbourhood already into account by the fact that the velocity difference between the wall and the adjacent film is the smaller the closer the distance. This is caused by molecular diffusion which is very fast over short distances, and therefore the velocity difference is forced to be small in the time average despite the fact that the residence time is the same even very close to the wall, which means that the eddies in fact reach right to the wall despite to the fact that this on the average is barely noticeable. The situation becomes clear immediately if one replaces eddy transport by another removal mechanism like radioactive decay. It should be stressed that our whole treatment was based on the average situation in the statistical sense.

References

1   Businger, J.A. (1973); Turbulent Transfer in the Atmospheric
    Surface Layer; in: Haugen, D.A. (ed.); Workshop on
    Micrometeorology; American Meteorological Society, Boston,
    pp. 67-100

2   Liss, P.S.; Slater, P.G. (1974); Flux of Gases across the Air-Sea
    Interface; Nature 247, 181-184

3   Münnich, K.O. (1971); Report on the Pollution of the Sea through
    the Atmosphere; IMCO/FAO/UNESCO/WMO/WHO/IAEA,(GESAMP) 3rd
    session, Rome, 22-27 Feb. 1971

4   Münnich, K.O. (1971); Atmosphere/Ocean Relationship in the Global
    Environmental Pollution; in: WMO-No. 312, Special Environmental
    Report No. 2, Meteorology as related to the Human Environment,
    Geneva, pp. 145-147

5   Atkins, D.H.F; Eggleton, A.E.J. (1971); Studies of Atmospheric
    Wash-out and Deposition of γ-BHC, dieldrin and p-p DDT using
    radio labelled pesticides; in: IAEA, Nuclear Techniques in
    Environmental Pollution; Vienna, pp 521-533

6   Eggleton, A.; Atkins D.H. (1975); The role of atmospheric processe
    and the atmosphere-ocean interchange in the life-history of
    halogenated hydrocarbons; presented at the IUGG 16th General
    Assembly, Grenoble.

7   Liss, P.S. (1973); Processes of gas exchange across an air-water
    interface; Deep-Sea Research 20, 221-238

8   Broecker, W.S. Peng, T.H. (1974); Gas exchange rates between air
    and sea; Tellus 26, 21-35

9   Münnich, K.O. (1960); Seasonal variations in C-14 content of
    atmospheric CO_2; presented at the IUGG General Assembly ,
    Helsinki, Aug. 1960

10 Münnich, K.O. (1963); Kreislauf des Radiokohlenstoffs in der
    Natur; Die Naturwissenschaften 6, 211-218

11 Danckwerts, P.V. (1951); Significance of Liquid-Film Coefficients
    in Gas Absorption; Ind. Eng. Chem. 43, 1460-1467

12 Danckwerts, P.V. (1971); Diffusion and masstransfer; in: Sherwood
    et al. (eds.), Proc. Strathclyde Symp.; Gordon and Breach,
    London.

13 Danckwerts, P.V. (1970); Gas-Liquid Reactions; McGraw-Hill, London

14 Münnich, K.O.; Vogel, J.C. (1959); Variations in C-14 content
    during the last years; presented at the C-14-Symposium, Groningen
    Sept. 1959

15 Bolin, B. (1960); On the exchange of carbon dioxide between the
    atmosphere and the sea; Tellus 12, 274-281

16 Broecker, W.S. (1965); An application of natural radon
    problems in ocean circulation; Proceedings of the Symposium
    on diffusion in oceans and fresh waters, Lamont Geological
    Observatory, Palisades, N.Y. 1964.

17 Brutsaert, W. (1975); A theory for local evaporation (or heat
    transfer) from rough and smooth surfaces at ground level;
    Water Resources Res., 11, 543-550

18 Kanwisher, J. (1963); On the exchange of gases between the
    atmosphere and the sea; Deep-Sea Research, 10, 195-207

19 Hasselmann, K. et al. (1973);Measurements of Wind-Wave Growth and
    Swell Decay during the Joint North Sea Wave Project (JONSWAP);
    Ergänzungsheft zur Deutschen Hydrographischen Zeitschrift,
    Reihe A (8°), Nr. 12; Deutsches Hydrographisches Institut,
    Hamburg.

20 Deacon, E.L.; Webb, E.K. (1962); Small-Scale Interactions; in:
    Hill, M.N. (ed.); The Sea, Vol. 1; Wiley, New York, pp. 43-87

21 Schlichting, H. (1965); Grenzschicht-Theorie, 5. Auflage; Braun,
    Karlsruhe.

22 Emerson, S. (1974); Radium-226 and Radon-222 als limnological
    tracers: The carbon dioxide gas exchange rate; thesis,
    Columbia University, Lamont.