# On the Exchange of Carbon Dioxide between the Atmosphere and the Sea

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## Abstract

The physical and chemical processes responsible for exchange of carbon dioxide between the atmosphere and the sea are analyzed. It is shown that the rate of transfer is considerably decreased due to the finite rate of hydration of $CO_2$ in water. This is the case both for a smooth water surface where molecular diffusion plays a rôle in the first few hundredths of a millimeter as well as for a rough sea where turbulence extends all the way to the surface. A general agreement is found between the transfer rate deduced in this way and the rate of exchange estimated on the basis of the $C^{14}/C^{12}$ ratio in the atmosphere and the sea.
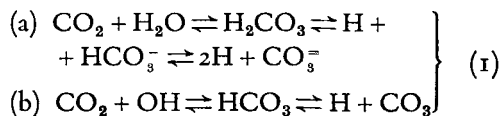
## 1. Introduction

Recent studies of the exchange of carbon dioxide between the atmosphere and the sea (REVELLE and SUESS, 1957; CRAIG, 1957; ARNOLD and ANDERSON, 1957; BOLIN and ERIKSSON, 1959) using measurements of radiocarbon in the atmosphere and the sea have given a residence time for carbon dioxide in the atmosphere of 3—7 years. This result has been obtained considering the atmosphere and the sea as well mixed reservoirs (the latter one divided into an upper and a lower part) and assuming the exchange between them being directly proportional to the concentrations. The value of the residence time is roughly proportional to the difference of $C^{14}/C^{12}$ in the atmosphere and the surface layers of the ocean (after correction for fractionation). A large number of new measurements has recently become available (BROECKER et al., 1959) and they agree in general with the previous measurement reported by REVELLE and SUESS (l.c.). Considerable variations occur, however, for example between the surface waters around the Antarctica and the Northern Atlantic. We shall here accept a value for this average residence time of about 5 years

but keep in mind that this is an average value applicable to the ocean as a whole.

Obviously the model of the atmosphere and the sea adopted in these studies is a gross oversimplification of actual conditions and it therefore seems desirable to investigate a little more in detail the processes that bring about this exchange. It is of particular interest to analyze the proposal by ERIKSSON (1959), that the comparatively slow rate of hydration is of importance.

## 2. Chemical and physical processes governing the exchange

The carbon system of the sea consists of dissolved carbon dioxide, carbonic acid, bicarbonate and carbonate ions, which are all in approximate equilibrium. We may write (BUCH ET AL., 1932)

$$\left.\begin{array}{l} \text{(a) } CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H + \\ \qquad + HCO_3^- \rightleftharpoons 2H + CO_3^= \\ \text{(b) } CO_2 + OH \rightleftharpoons HCO_3 \rightleftharpoons H + CO_3 \end{array}\right\} \quad (1)$$

The first reaction is the only one of importance for $pH \leq 8$ and the latter one is the

dominating process for pH ≥ 10 (cf. Mills and Urey, 1940). When dealing with the ocean surface (pH = 8.0—8.2) we may disregard the second one.

The dissociation of carbonic acid into bicarbonate ions and further into carbonate ions is a fast process and may for all practical purposes be considered as instantaneous. The hydration (and dehydration) expressed by the first reaction in (1 a) proceeds with a finite speed, which is a function of pH and temperature. It has been determined experimentally (Mills and Urey, 1940, Roughton, 1941) for neutral solutions for temperatures ranging between 0° C and 35° C. Denoting the rate of hydration by $\alpha_1$ and dehydration by $\alpha_2$ we have

$$K = \frac{\alpha_2}{\alpha_1} \qquad (2)$$

where $K$ is the equilibrium constant. Table 1 gives values for these quantities as a function of temperature.

**Table 1**

| Temp. °C | $\alpha_1$ sec$^{-1}$ | $\alpha_2$ sec$^{-1}$ | $K$ |
|---|---|---|---|
| 0° | 0.002 | 2 | 1000 |
| 27° | 0.028 | 31 | 1100 |
| 37° | 0.10 | 80 | 800 |

It is probably not permissible to neglect reaction (1 b) completely at the ocean surface and the rates given in table 1 may therefore be somewhat too small. We shall use a value of $\alpha_1 = 0.03$ sec$^{-1}$ in the following. It will be seen, however, that the value does not enter critically into any of the results deduced.

The dissociation equilibrium between $H_2CO_3$ and the bicarbonate and carbonate ions is, on the other hand, very sensitive to the pH (cf. Harvey, 1955, Bolin and Eriksson, 1959). Since we here shall be considering steady state processes, we need not, however, be concerned with this in the following.

The transfer of carbon dioxide through the atmosphere and the sea takes place by turbulent processes except possibly in the intermediate vicinity of the sea surface where molecular diffusion may play a role at least in the case of a smooth surface. The transfer across the sea surface is dependent on the

number of molecules colliding with the interphase and being retained in the water when coming from the air and *vice versa*.

Transfer in the *atmosphere* has been studied in connection with evaporation (cf. Sverdrup, 1951). It has been shown that the observed rates can be explained if considering a boundary layer with molecular diffusion above which the turbulent transfer is dominating. The characteristics of this boundary layer are not very well known and it is doubtful whether it exists at all in case of a rough sea surface. Its thickness is of the order of 1—10 mm except in calm weather. Very little is also known about a corresponding boundary layer in the *sea*. The rate of molecular diffusion of a gas through water is, however, about $10^4$ times less than the corresponding rate of diffusion through a gas at standard pressure and temperature. Thus if the thickness of the boundary layer in the sea were considerably more than $10^{-4}$ of the thickness of the boundary layer in the air, i.e. more than about 1 μ and the solubility close to unity or less the diffusion through this water layer would be much more decisive in determining the rate of transfer between the atmosphere and the sea, than molecular diffusion through the lowest layer of the atmosphere. Now we know that the residence time for water in the atmosphere, obviously controlled by mixing processes in the atmosphere, is only about 10 days as compared with about five years for carbon dioxide. This fact in itself tells us that the comparatively long residence time for carbon dioxide in the atmosphere depends on slow transfer in the surface layers of the ocean rather than the lowest layers of the atmosphere. We shall indeed find that the transfer is essentially due to transfer of dissolved $CO_2$ in which case the solubility may be considered close to unity and furthermore studies of gas bubbles in sea water (Wyman et al., 1952) indicate a thickness of the molecular boundary layer of about 35 μ. In the following we shall assume that the gas phase above the sea surface is well mixed and consider the processes in the sea as rate determining.

In case of strong winds and a rough sea surface most likely no molecular boundary layer exists. The turbulent eddies reach all the way to the surface which is clearly indicated by the fact that air bubbles may be found

at considerable depth under these conditions. Since the turbulence in this case is induced by the wind, one might even expect the eddy diffusivity to have a maximum at the surface as was found for the eddy viscosity in a case studied by ROSSBY and MONTGOMERY (1935). Values for the eddy diffusivity range between 0.2 and 100 cm² sec⁻¹ (SVERDRUP, 1942).

According to kinetic theory of gases the number of molecules $(S)$ penetrating into the water surface is given by

$$S = 1/4 \, c \cdot v \cdot \bar{v} \qquad (3)$$

where $v$ is the number of molecules per unit volume, $\bar{v}$ is the mean molecular speed and $c$ the fraction of all colliding molecules that is retained in the water. In our case $\bar{v} \approx 10^4$ cm sec⁻¹. The residence time of carbon dioxide in the atmosphere of about 5 years corresponds to a transfer velocity of $7 \cdot 10^{-3}$ cm sec⁻¹ (in terms of $CO_2$ at the pressure prevailing in the atmosphere).[1] Thus the molecular transfer velocity across the sea surface is larger than this observed transfer velocity as long as $c > 4 \cdot 10^{-6}$. Recent studies by MÜNNICH and VOGEL (1959), indicate that the molecular transfer across the surface of a NaOH solution may be considerably greater than 0.1 cm sec⁻¹ indicating that the transfer across the surface is not a limiting factor for the observed rate of transfer. It would, however, be of great interest to determine the constant $c$ in (3) experimentally and not merely know that $c \geq 10^{-5}$ as implied by MÜNNICH and VOGEL's experiment.

The previous discussion is valid for a smooth water surface. In case of a rough sea with breaking waves droplets in the air and bubbles in the water probably take same part in the exchange of $CO_2$. This is, however, not of principle importance since in such a case the turbulence in the atmosphere and the sea is so violent and still plays the most important rôle. This can be seen from the fact that the amount of $CO_2$-gas in a bubble

is about the same as the amount of dissolved $CO_2$-gas in the same water volume. In the case of bubbles penetrating into the sea turbulent motion extends to the surface and due to the great solubility of $CO_2$ in water much more $CO_2$ is transferred by this turbulent motion of the *water* than the comparatively very small quantities of gas present in form of bubbles. With regard to droplets in the air we recall that the residence time for carbon dioxide in the air of about five years means a transfer across the sea surface equal to the total amount of $CO_2$ present in a 20 m deep layer of the ocean every year. Due to the slow hydration process it takes of the order of minutes to establish an equilibrium between the drops and the surrounding air. Only very small drops that stay an appreciable time in the air therefore are of importance. Assuming for the moment that all transfer were due to exchange between the drops and the surrounding air. This would imply a transfer of sea salt into the atmosphere at such a rate that even if assuming the highest observed air concentration of salt (see Station Vinga, EGNÉR, ERIKSSON, 1955) the amount of salt present in a layer of about 25 m were transferred into the atmosphere in a second. This is obviously unrealistic.

In the previous discussion we have already used the word residence time several times. In the case of exchange between *well-mixed* reservoirs this concept is uniquely defined as the inverse of the exchange coefficient (cf. e.g. CRAIG, 1957). Obviously the residence time for molecules in incompletely mixed reservoirs is a function of the initial position of the molecule considered. Thus molecules immediately above the sea surface on an average stay a much shorter time in the atmosphere than those in the middle of the troposphere. An *average* residence time is of course a function of the internal mixing in the atmosphere and the rapidity of the molecular transfer across the sea surface. According to our previous discussion the latter implies a transfer velocity larger than 0.1 cm sec⁻¹ or a residence time less than three months and the internal mixing of the troposphere has a characteristic time scale of one to two months (LAL, PETERS, 1959). The five years' residence time for carbon dioxide in the

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[1] We shall use the term transfer velocity in the following as the depth of a column of the gas at prevailing pressure in the gas phase that is transferred across a horizontal surface (usually the sea surface) per unit time. Clearly a transfer velocity in the water in the case of a steady state is the velocity defined above divided by the solubility of the gas in water (cf. equ. 7). Solubility of $CO_2$ gas will be assumed to be unity in the following.

atmosphere must then mean that only a small fraction of molecules entering the sea surface ever have a chance to be transferred into the main part of the sea, i.e. beyond a very thin boundary layer. The residence time as deduced from $C^{14}/C^{12}$ measurements therefore is the average time for bringing a molecule from the *interior* of one reservoir to the *interior* of the other. The residence time for carbon dioxide *in the atmosphere* defined in this way is essentially dependent on incomplete or slow mixing *in the sea*.

### 3. Molecular and turbulent transfer of carbon dioxide in the sea

The transfer of carbon dioxide in the ocean has been studied by DINGLE (1954). He treated, however, the hydration process as a one-way reaction and furthermore a thorough discussion of the molecular and eddy diffusivity is lacking. The residence time of about one day arrived at is not compatible with our previous discussion. We shall here reconsider the problem. In accordance with our previous discussion we shall assume complete mixing in the atmosphere and an immediate adjustment of conditions at the sea surface.

Consider an infinite surface, horizontal homogeneity of the water and no net vertical velocity. We denote by $n'$ the amount of dissolved carbon dioxide and by $n''$ the sum of the remaining inorganic carbon compounds in the water. We shall assume that the dissociation in (1 a) is very fast. The rate constant $(\alpha_2^*)$ expressing the rate of transfer of $H_2CO_2$, $HCO_3$ and $CO_3$ into dissolved $CO_2$ then is given by

$$\alpha_2^* = \alpha_2 \frac{1}{K} \frac{N'}{N-N'} \qquad (4)$$

where $N'$ and $N$ denote equilibrium values for dissolved $CO_2$ and total amount of carbon in the system. Considering now the vertical distribution of $n'$ and $n''$ being dependent both on the chemical reaction (1 a) and molecular or turbulent diffusion we obtain

$$\left. \begin{aligned} \frac{\partial n'}{\partial t} &= -\alpha_1 n' + \alpha_2^* n'' + \frac{\partial}{\partial z}\left(A \frac{\partial n'}{\partial z}\right) \\ \frac{\partial n''}{\partial t} &= \quad \alpha_1 n' - \alpha_2^* n'' + \frac{\partial}{\partial z}\left(A \frac{\partial n''}{\partial z}\right) \end{aligned} \right\} \quad (5)$$

where $A$ is the molecular or eddy diffusivity. The boundary conditions at the sea surface express the fact that only the dissolved carbon dioxide is in exchange with the atmosphere. Thus

(a) $\qquad -A \dfrac{\partial n'}{\partial z} = \beta_1 n' - \beta_2 n_a$

$$\left. \vphantom{\begin{aligned}1\\1\\1\end{aligned}} \right\} \quad z = 0 \qquad (6)$$

(b) $\qquad -A \dfrac{\partial n''}{\partial z} = 0$

Here the coefficients $\beta_1$ and $\beta_2$ express the number of molecules leaving the water or penetrating into it respectively and $n_a$ is the concentration in the gas phase. In case of an equilibrium we have $\partial n'/\partial z = 0$ and thus

$$n' = \frac{\beta_2}{\beta_1} n_a = n'_0 \qquad (7)$$

$\beta_2/\beta_1$ is an expression for the solubility of carbon dioxide. If the coefficient $c$ in equ. (3) is large (cf. sec. 2) the left side of equ. (6 a) is small compared with the two terms on the right side and we may use the boundary condition (7) also in case of a net transfer taking place. In addition we shall assume complete mixing below a certain depth, $d$ and thus have

$$\left. \begin{aligned} n' = n'_d \qquad n'' = n''_d \qquad z = -d \\ \alpha_1 n'_d = \alpha_2 n''_d \end{aligned} \right\} \quad (8)$$

The complete time-dependent problem as outlined above leads to a nonhomogeneous partial differential equation of fourth order with variable coefficients. We shall here only treat a few special cases which still are of considerable interest.

### a. Molecular diffusion through a boundary layer

Let us assume that the turbulence in the interior of the water mass is intense enough to maintain any necessary transport and that all gradients of $n'$ and $n''$ are confined to a boundary layer through which molecular diffusion is predominant. Consider furthermore a steady state, where the transfer still is too small to affect conditions in the air $(n_0')$ or in the turbulent part of the fluid $(n_d'$ and $n_d'')$ over

the time interval considered. The equations (5) are transferred into

$$-\alpha_1 n' + \alpha_2^* n'' + \varkappa \frac{\partial^2 n'}{\partial z^2} = 0$$

$$\alpha_1 n' - \alpha_2^* n'' + \varkappa \frac{\partial^2 n''}{\partial z^2} = 0$$

(9)

with the boundary conditions (6 b) (7) and (8). $\varkappa$ is the molecular diffusivity and $d$ now denotes the thickness of the boundary layer. We here deduce the following expression for the flux of total amount of carbon dioxide towards the interior of the fluid

$$F = \frac{n_0' - n_d'}{d} \cdot \frac{\alpha_1 + \alpha_2^*}{\alpha_1} \cdot \gamma d \cdot$$

$$\cdot \frac{e^{\gamma d} + e^{-\gamma d}}{e^{\gamma d}\left(1 + \frac{\alpha_2^*}{\alpha_1}\gamma d\right) - e^{-\gamma d}\left(1 - \frac{\alpha_2^*}{\alpha_1}\gamma d\right)}$$

(10)

where

$$\gamma^2 = \frac{\alpha_1 + \alpha_2^*}{\varkappa}$$

(11)

Obviously the flux depends upon the total gradient imposed $(n_0' - n_d') \cdot d^{-1}$ and $\gamma d$ which expresses the ratio of the rate of hydration and dehydration to the rate of molecular diffusion through a layer of thickness $d$. We have the two limiting cases $\gamma d \to \infty$ (diffusion is slow compared to hydration) and $\gamma d \to 0$ (diffusion through the layer considered is fast compared to the rate of hydration). We get

$$\lim_{\gamma d \to \infty} F = F_\infty = \varkappa \frac{n_0' - n_d'}{d} \cdot \frac{\alpha_1 + \alpha_2^*}{\alpha_2^*}$$

(12)

$$\lim_{\gamma d \to 0} F = F_0 = \varkappa \frac{n_0' - n_d'}{d}$$

(13)

In the former case the hydration equilibrium is established everywhere $\alpha_1 n' = \alpha_2^* n''$ and the downward transfer is due to diffusion of both dissolved gas and bicarbonate and carbonate ions. In the latter case, on the other hand, no gradients of $n''$ are ever established and the transfer is only due to transfer of dissolved gas. Figure 1 illustrates the principle difference between these two cases with regard to the distribution of $n'$ and $n''$ in the boundary layer. Figure 2 shows the flux
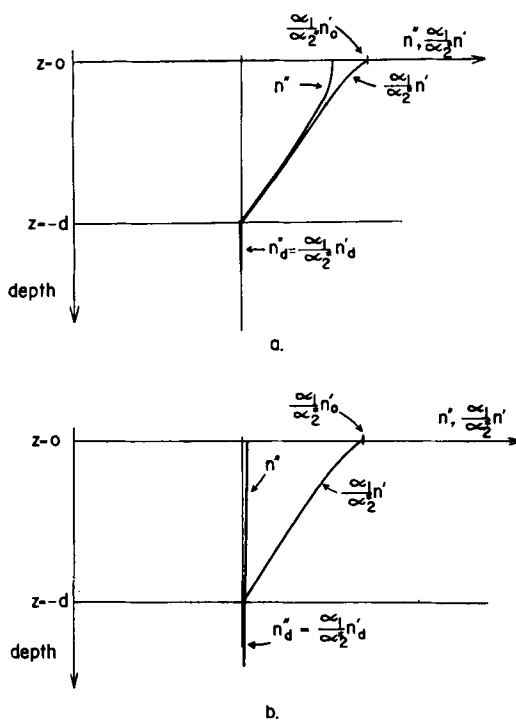


Fig. 1. Distribution of $n'$ and $n''$ as a function of depth in a thin boundary layer with a steady flux of carbon dioxide. (a) shows conditions when $\gamma d$ is large ($\to \infty$), (b) shows conditions when $\gamma d$ is small ($\to 0$).
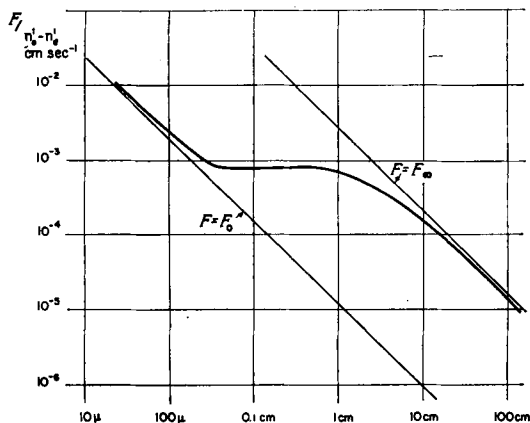


Fig. 2. The steady flux ($F$) of carbon dioxide through a boundary layer ($d$) normalized to a unit difference in concentration between the boundaries of the layer. The straight lines show the asymptotic values given by equations (12) and (13).

as a function of $d$. We have here assumed $\varkappa = 2 \cdot 10^{-5}$ cm$^2$ sec$^{-1}$, $\alpha_1 = 0.03$ sec$^{-1}$ and $\alpha_2 = 150 \cdot \alpha_2^*$ (according to equ. (4) and the

values for $N$ and $N'$ as given by BOLIN and ERIKSSON, 1959). We find $F = F_0$ within 10 % for $d < 130\ \mu$ while $F = F_\infty$ within again 10 % for $d > 20$ cm. We furthermore note that the thickness of the boundary layer should be about 35 $\mu$ to yield a transfer rate corresponding to the residence time of $CO_2$ as obtained from $C^{14}/C^{12}$ data. It is interesting to note that this is equal to the value of 35 $\mu$ derived by WYMAN ET AL. (1952) using a similar model of diffusion of $O_2$ and $N_2$ when studying bubbles in sea water. The exact agreement may be a coincidence since we have not yet considered the relative importance of carbon dioxide transfer in areas with a rough sea surface. The general agreement is, however, no doubt significant.

In his treatment of the $CO_2$-transfer into the ocean DINGLE (1954) assumed that we may put $\alpha_2^\star \equiv 0$ in equation (5). The first of the two equations may then be solved independently of the second yielding

$$F = n'_0 \cdot \sqrt{\alpha_1 \cdot \varkappa} \qquad (14)$$

This gives a transfer velocity of $8 \cdot 10^{-4}$ cm sec$^{-1}$, i.e. much less than the velocities actually observed. The interpretation is obviously that the turbulence in the interior can maintain a steeper gradient of $n'$ than the hydration and thus the thickness of the boundary layer, dependent on the intensity of mixing in the interior of the fluid, is the rate-determining factor. It is interesting to note that for an increasing thickness of the boundary layer the transfer remains constant at $\sqrt{\varkappa \alpha_1} \approx 8 \cdot 10^{-4}$ cm sec$^{-1}$ over a wide range of values for $d$. The decreasing effectiveness of diffusion is compensated by the increasing importance of hydration. Since a stagnant layer within which only molecular transfer takes place can hardly be more than a millimeter thick in the ocean we find that the rate given by (14) is the minimum transfer rate for $CO_2$.

b. Turbulent diffusion of carbon dioxide into a water body

Let us next consider a case in which the diffusivity is equal to the molecular diffusivity $\varkappa$ at the sea surface and then increases linearly towards the interior of the fluid. The results

are, however, not sensitive to the profile. As long as $A = \varkappa$ at the surface (a *smooth surface*) the results apply and we shall in this way be able to make use of our knowledge about turbulence in the sea as deduced from eddy exchange of heat and salt (eddy diffusivity of the order of 10—50 cm$^2$ sec$^{-1}$, cf. SVERDRUP et al., 1942).

We may thus replace $A$ in equation (5) by

$$A = -kz + \varkappa \qquad (z \leq 0) \qquad (15)$$

In steady state our differential equations (5) applied to a layer, $d$, now become

$$\left.\begin{array}{l} -\alpha_1 n' + \alpha_2^\star n'' + \dfrac{\partial}{\partial z}\left[(-kz + \varkappa)\dfrac{\partial n'}{\partial z}\right] = 0 \\[2mm] \alpha_1 n' - \alpha_2^\star n'' + \dfrac{\partial}{\partial z}\left[(-kz + \varkappa)\dfrac{\partial n''}{\partial z}\right] = 0 \end{array}\right\} \quad (16)$$

again with the same boundary conditions as before (6 b), (7) and (8). The solution of this system of equations yields

$$\left.\begin{array}{l} n' = \dfrac{\alpha_2^\star}{\alpha_1 + \alpha_2^\star}[B_0 \ln x + B_1] + \\[2mm] \quad + C_1 J_0(2i\sqrt{bx}) + C_2 Y_0(2i\sqrt{bx}) \\[4mm] n'' = \dfrac{\alpha_1}{\alpha_1 + \alpha_2^\star}[B_0 \ln x + B_1] - \\[2mm] \quad - C_1 J_0(2i\sqrt{bx}) - C_2 Y_0(2i\sqrt{bx}) \end{array}\right\} \quad (17)$$

Here $J_0$ and $Y_0$ are Bessel functions of zero order and of the first and second kind with imaginary argument, $x = -kz + \varkappa$, $b = k^{-2}(\alpha_1 + \alpha_2^\star)$ and $B_0, B_1, C_1$ and $C_2$ are integration constants. For $k = 10^{-3}—1$ cm sec$^{-1}$ and $d = 1—10^3$ cm, we have $C_1 \approx 0$ and we obtain the following expression for the flux

$$F = (n'_0 - n'_d)\frac{\alpha_1 + \alpha_2^\star}{\alpha_1} \cdot$$

$$\cdot k \frac{1}{\dfrac{\alpha_2^\star}{\alpha_1}\ln\dfrac{kd + \varkappa}{\varkappa} - \dfrac{1}{\sqrt{b\varkappa}}\dfrac{Y_0(2i\sqrt{b\varkappa})}{Y_1(2i\sqrt{b\varkappa})}} \quad (18)$$

$Y_1$ being the Bessel function of first order and second kind. As two limiting cases we have

$$F_\infty = (n_0' - n_d') \frac{\alpha_1 + \alpha_2^*}{\alpha_1} k \frac{1}{\ln\left(1 + \dfrac{kd}{\varkappa}\right)} \quad (19)$$

$$F_0 = (n_0' - n_d') k \frac{1}{\ln\left(1 + \dfrac{kd}{\varkappa}\right)} \quad (20)$$

for relatively rapid respectively slow hydration rate as compared with the rate of diffusion. In order to have a transfer velocity of $7 \cdot 10^{-3}$ cm sec$^{-1}$, we must have $k \geq 0.1$ cm sec$^{-1}$ regardless of the value chosen for $d$ between 1 and $10^3$ cm, which in turn means that the mixing at these depths is that intense that no appreciable gradients are necessary to bring about the transfer determined by processes in the vicinity of the sea surface. The value of $k$ thus obtained implies an eddy diffusivity of $A = 10$ cm$^2$ sec$^{-1}$ at the depth of about 1 m. If we permit a thin layer of molecular diffusion at the surface an even more rapid increase of the eddy diffusivity with depth must exist in order to have a transfer velocity of $7 \cdot 10^{-3}$ cm sec$^{-1}$. In any case we are close to the case given by equ. (20), i.e. hydration is of little importance in determining the transfer away from the surface.

In case of a rough sea surface the turbulence elements presumably reach to the surface and no boundary layer with molecular diffusion exists. The turbulence is now intense enough that once a $CO_2$-molecule has been hydrated it will with all likeliness be mixed throughout the mixed layer before being returned to the atmosphere. The rate of transfer of $CO_2$ molecules into the water is then approximately given by equation (14), where, however, we insert the turbulent diffusivity $A$ instead of the molecular one $\varkappa$. For $A = 1$ cm$^2$ sec$^{-1}$ the transfer velocity becomes 0.17 cm sec$^{-1}$ and for $A = 10$ and $100$ cm$^2$ sec$^{-1}$ we obtain respectively 0.6 and 1.7 cm sec$^{-1}$. These values correspond to an atmospheric residence time of 60, 20 and 6 days respectively. These rates are now comparable to the rate of overturning of the mixed layer as a whole, which we know has a characteristic time scale of a month or two indicated by the almost in phase variations of $O_2$ in the ocean and temperature disregarding effects caused by biological activities (cf. REDFIELD, 1948). A value of

$A = 10$ or $100$ cm$^2$ sec$^{-1}$ also implies a characteristic mixing time of a layer 100 m deep of 100 and 10 days respectively.

## 4. Conclusions

It has been shown above that droplets in the air and bubbles in the sea play an insignificant role for the exchange of $CO_2$ between the atmosphere and the sea. Similarly the turbulent and molecular transfer in the atmosphere is rapid as compared to the corresponding processes in the sea. In case of a smooth water surface a transfer velocity of $7 \cdot 10^{-3}$ cm sec$^{-1}$ (corresponding to a residence time for $CO_2$ in the atmosphere of about five years) implies a boundary layer not thicker than about 35 $\mu$ in fair agreement with the thickness of the boundary layer around a bubble as deduced from observation of the rate of solution of bubbles in water. For a rough sea surface the transfer velocity may be 10 to 100 times larger.

By far the greatest part of the ocean surface is smooth but it seems impossible to say what the importance is of the increased transfer in stormy regions. Off hand one would for example expect a smaller difference in the $C^{14}/C^{12}$ ratio between the atmosphere and the sea in a stormy area (after correction for fractionation). The turbulent transfer within the sea also becomes larger in such a case, whereby such an effect may be masked. It would be of great interest to study this ratio in the surface layers of the sea and the atmosphere above. A comparison between the stormy areas around latitude 50° and the relatively calm regions in the subtropics would be of particular interest. An especially interesting phase prevails at present in that the excess radiocarbon introduced by hydrogen bombs is being transferred into the oceans.

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