EFFECT OF WAVES AT THE INTERFACIAL BOUNDARY ON THE
DESORPTION OF A GAS FROM THE BULK OF A LIQUID

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An experimental investigation has been made of the effects of artificially excited two-dimensional gravity waves on the process of interfacial mass transfer during desorption of CO_2 from a layer of liquid of uniform depth. A simple dimensionless relationship is proposed for calculating mass transfer coefficients during the use of such means for intensifying processes.

At the present time the problem of gas transfer through the free surfaces of reservoirs to the atmosphere is attracting considerable attention in investigations being carried out in a number of fields [1-4]. Carbon dioxide dissolved in the oceans is involved in biochemical exchanges, leading to the formation of organics, food chains, fuel resources, etc. In the atmosphere the CO_2 transmits the shortwave part of the spectrum and traps the longwave thermal radiation of the earth. The ecological problems of natural and artificial water reservoirs are also connected with the mass transfer of the gases CO_2 and O_2 which are only slightly soluble in water through the microporous boundaries. Under natural conditions the interaction of the atmosphere with the surface of a reservoir during mass transfer can influence the physical-chemical and thermophysical properties of the liquid and the hydro- and aerodynamical conditions close to the interface. It is a complicated matter to determine the role of each process under such conditions. The results of investigations on gas transfer between the oceans and the atmosphere obtained by different authors under natural conditions [3, 5, 6] therefore show considerable divergences from one another and do not permit the establishment of fundamental relationships for the variation of the mass transfer coefficients with the state of the wavy interface with the gas, as a general rule. In addition, according to some of the data [3, 4, 7, 8] the waves can intensify mass transfer by several times over.

In experiments with wind waves in laboratory equipment of the "trough" type it has also not been possible to correctly isolate the effect of the wave mechanism in the intensification of interfacial mass transfer, since in this case the waves are three-dimensional as a rule and are covered by capillary ripples, while the interfacial boundary appears to be saturated by bubbles of air captured by the waves.

As a result of what has been said above, a study has been made in the present work in a laboratory apparatus of the "trough" type of the effects of standing and traveling gravity waves and wave ripples produced by a mechanical wave generator on the mass-transfer coefficient from a layer of liquid of uniform depth.

The main part of the equipment was the working section, or container with the liquid. It consisted of a rectangular space of length 1 m, width 0.3 m, and depth 0.5 m, with a maximum volume of contained liquid of 140 liters. Distilled water was poured into this volume, and was then saturated with CO_2 gas by bubbling through tubes with outlets placed on the bottom of the tank and connected through a manometer to a CO_2 cylinder.

A movable bottom was used in the equipment for investigating the effect of the liquid depth on the rate of desorption of CO_2 under identical dynamic characteristics of the interface. The depth of the liquid volume during the experiments could be varied from 500 to 50 mm by means of this movable bottom.

The waves were excited by a planar wave generator having a height of 0.035 m, a length of 0.28 m, and placed at the end of the basin. The liquid level in the unperturbed state was fixed at the middle of the wave generator. In order to set up periodic waves on the

Fig. 1   Fig. 2
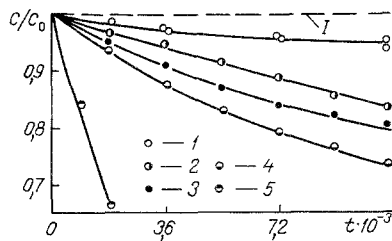
Fig. 1. Effect of the method of exciting the liquid surface on mass transfer, H = 0.47 m: 1) smooth surface; 2) excitation by needle; 3) standing wave of λ = 145 mm, A = 2 mm; 4) traveling wave, λ = 130 mm, A = 3 mm; 5) disruption of the liquid by the wave generator, breakdown of waves. t in seconds.
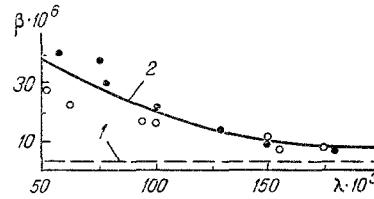
Fig. 2. Effect of the wavelength on the coefficient of the transfer of CO_2 through the surface, A = 2-3.5 mm: 1) calculation according to the model proposed in [4]; 2) calculation according to Eq. (4); solid points: H = 0.47 m; open points: H = 0.3 m.

surface of the liquid the wave generator was given a reciprocating motion. At the opposite end of the tank the waves were damped by using a perforated plate. This method is effective in the wavelength range λ = 10-150 mm. At larger wavelengths standing waves occurred. The use of this arrangement made it possible to produce perturbations at the wave generator with frequencies in the range 1.5-10 Hz and amplitudes of the motion of 0.8-15 mm. By this method of exciting the surface it was possible to produce waves with lengths of 15-210 mm and amplitudes of 1-20 mm.

The waves excited on the surface of the liquid could be of two types: gravity waves or capillary waves. It is known that the phase velocity of gravity waves in a basin of depth H is [9]:

$$c_\phi = \left[\frac{g\lambda}{2\pi} \left(\frac{e^{2\pi H/\lambda} - e^{-2\pi H/\lambda}}{e^{2\pi H/\lambda} + e^{-2\pi H/\lambda}} \right) \right]^{1/2}. \tag{1}$$

For waves which are long compared with the depth of the liquid (λ > 14H) the asymptotic shallow-water approximation is obtained. The wave velocity is then $c_\phi = \sqrt{gH}$. Since the minimum value of the depth in the experiments was 0.05 m, it can be assumed that in the case of travelling gravity waves of length $\lambda \sim$ 60-200 mm the deep-water limit was always satisfied. In this case,

$$c_\phi = (g\lambda/2\pi)^{1/2}, \tag{2}$$

and $\omega = (gk)^{1/2}$.

Since the waves were generated in a basin of finite dimensions, standing waves occur at certain definite wavelengths. The corresponding resonance frequency was equal to $\omega_x = \sqrt{gr} \cdot (n/\ell)^{1/2}$, where n is the number of the harmonic, and ℓ is the length of the basin. In the experiments standing waves of the higher harmonics (n = 4-6) occurred.

In experiments with a vertical needle wave generator surface waves with lengths λ < 50 mm were generated. In this case surface tension always had a considerable effect on the motion of the waves, and the dispersion relationship assumed the form

$$c_\phi = \left[\left(g + \frac{\sigma k^2}{\rho} \right)/k \right]^{1/2}, \tag{3}$$

and the condition for the existence of purely gravity waves was as follows: $\lambda > 2\pi(\sigma/\rho g)^{1/2}$. Since the experiments were carried out in water, it follows that λ > 0.017 m.

Thus, in the experiments with the forced excitation of the surface by a horizontal wave generator, gravity waves resulted in the deep water. The characteristics of the mechanical excitation of the waves is not related to an air flow above the surface, and therefore this could be easily controlled on the one hand, and on the other hand, the results could be used for modeling the effects of two-dimensional wind waves. Such experiments made it possible
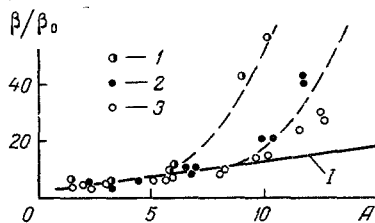
Fig. 3   Fig. 4

Fig. 3. Effect of the amplitude of the gravity waves on the intensity of CO_2 gas transfer through perturbed surfaces: 1) H = 0.15 m; 2) H = 0.3 m; 3) H = 0.47 m; λ = 60-70 mm; I: calculation according to Eq. (4).
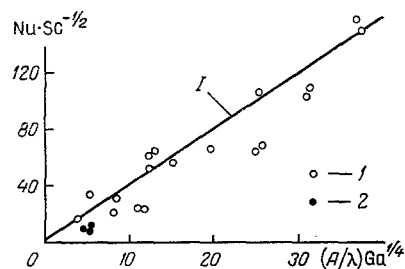
Fig. 4. Generalization of the experimental data on the effects of surface waves on the desorption of CO_2 from a layer of liquid of depths H = 0.47 m and H = 0.3 m: 1) gravity waves; 2) capillary ripples; I: calculation according to Eq. (5).

to clearly isolate the effects of the wave characteristics on the desorption of CO_2 from the bulk of the liquid.

The measurement of the distribution of the local concentrations of CO_2 in the bulk of the liquid was carried out by two methods: by titrimetric analysis and by a conductometric method. The first is a traditional method; here samples of the liquid were taken from different locations by means of a syringe, and were then subjected to chemical analysis. The second method is based on the dependence of the electrical conductivity of the electrolyte solution of the carbon dioxide concentration. This method and the local platinum probes which are used, together with the associated other equipment, are described in detail in [10]. It need only be noted that the maximum error in determining the mass-transfer coefficient by these methods is related in principle to errors in the thermometric analysis, and does not exceed 3%. At the same time, the method has the advantage that when it is used there is no longer any need to remove samples, and it gives the possibility of continuously controlling the process from the electrical signals at the output of the conductometric amplifier. In the experiments the CO_2 concentrations were 50-600 mg/liter, so that the condition $c_s \ll c \ll c_p$ was always satisfied, where $c_s \simeq 0.57$ mg/liter in the equilibrium concentration, and $c_p \simeq 1730$ mg/liter is the saturation concentration of CO_2 in water.

The mass-transfer coefficients were calculated as follows. The mass of gas dissolved in the liquid at the moment t is $m = c_t SH$, while the quantity of gas desorbed during the time $\Delta t = t_2 - t_1$ is $Q = \Delta m / \Delta t = (c_1 - c_2)SH/\Delta t$.

Bearing in mind that $Q = \beta S(\bar{c} - c_s)$, $c_s \ll \bar{c} \ll c_p$, it is found that

$$\beta = \frac{H(c_1 - c_2)}{\bar{c} \cdot \Delta t},$$

where $\bar{c} = (c_1 + c_2)/2$.

Investigations of mass transfer in the case where the interface was not perturbed showed that for relatively small times of the process (10-15 min) a practically constant concentration of CO_2 was established over the depth of the layer, the value of which varied with time. In this case, mass transfer occurred more intensively than according to the theory (see curve I in Fig. 1) for penetration by diffusion only [11], according to which $c/c_0 = 1 - 2(Dt/H^2\pi)^{1/2}$, where c and c_0 are the current and initial concentrations, respectively, and t is the time. This is obviously connected with the effects of thermal convection caused by the cooling of a thin surface layer as a result of evaporation. According to the data of [2, 12], for instance, the thermal currents which arise in this way mix the layer of liquid near the surface into the liquid to a considerable depth. These facts must be taken into account in evaluating the rates of gas transfer in purification plants, basins and reservoirs with unperturbed free liquid surfaces.

Figure 1 also shows the effects of different types of waves excited in the basin on the desorption of CO_2 from the bulk of the liquid. As can be seen from the figure, different excitations of the surface lead to different degrees of intensification of the gas exchange

process through this surface compared to its unperturbed state. Excitation by a needle wave generator increases the rate of gas exchange only slightly compared to the calm state of the surface. The change to a wave generator with a large amplitude and frequency in the horizontal plane leads to the occurrence of liquid spray formation and the generation of breaking waves, and as a result, to a considerable increase in the rate of gas exchange. Different rates of desorption of CO_2 from the bulk of the liquid are found for all the forms of waves produced in the experiments. Thus, for ripple waves the ratio of mass-transfer coefficients is $\beta/\beta_0 = 3.2$, for traveling gravity waves with $\lambda = 130$ mm, $A = 3$ mm, $\beta/\beta_0 = 5.4$, while for standing gravity waves $\beta/\beta_0 = 3.8$, where β_0 is the mass-transfer coefficient for the unperturbed surface.

The effect of the characteristics of the traveling gravity waves on the rate of gas transfer of the CO_2 through the interface is considerable. It follows from the data given in Fig. 2 that a decrease in the wavelength leads to an increase in the mass-transfer coefficients. Thus, for example, a decrease in the wavelength by a factor of 4 (from $\lambda = 200$ to 50 mm) leads to an increase of 6-7 times in β ($H > 0.3$ m). For the long waves ($\lambda > 150$ mm) the value of the mass transfer coefficient approximates to its asymptotic value β_0 for a smooth surface. The wave amplitude also influences the mass transfer intensity (Fig. 3). The small-amplitude waves with $A = 1-1.5$ mm cause an increase in β of 1.5-2 times compared with the value of β_0. Increase of the amplitude by 5 times leads to an increase of 4-6 times in β. If the amplitude of the surface waves is increased further the relationship $\beta = \beta(A)$ becomes quite nonlinear, particularly at small depths of the basin ($H < 0.3$ m). Thus, for example, when waves of $\lambda = 160$ mm, $A = 13$ mm ($H = 0.47$ m) are generated on the surface, it is found that $\beta = 87 \cdot 10^{-6}$ m/sec. For the same waves, but with an amplitude of $A = 2.5$ mm, $\beta = 9.6 \cdot 10^{-6}$ m/sec. The considerable increase in the rate of mass transfer in the case of the high-amplitude waves is caused by spray-formation of the liquid, breaking of the waves, and the formation of internal convection currents in the bulk of the liquid, which have been observed in the experiments. These phenomena have a greater effect on the mass transfer of CO_2 than the purely wave mechanisms.

It should also be noted that as the depth of the reservoir is decreased the intensity of mass transfer increases. Thus, at a depth of $H = 0.05$ m the effect of waves with $\lambda = 75$ mm, $A = 3$ mm leads to a decrease in the initial concentration of CO_2 by a factor of two after 1.5 hours, while at a depth of $H = 0.47$ m this decrease occurs after 3.5 hours. This is obviously related to the existence of convective currents in the bulk of the liquid caused by the mixing action of the wave generator. As the depth of the basin was increased in the range $H > 0.3-0.4$ m, the value of β/β_0 ceased to depend on H. Since depths of $H > 0.3$ m are most characteristic of purification plants, various types of basins, fish tanks, etc., mass transfer of slightly soluble gases through the liquid surfaces in them is governed by the wave processes at the interfaces when this method of intensifying the mass transfer is used.

To a first approximation, an explanation of the results which have been obtained can be found within the framework of a linear model of the motion of the liquid particles in the gravity waves [9]. Under the influence of a travelling wave the particles rotate with a linear velocity having a constant value $v \sim (k)\exp(2\pi z/\lambda)$ at a distance z from the surface around a circle of radius $R \sim (k/\omega)\exp(2\pi z/\lambda)$. The rotating particles bring fresh portions of liquid to the surface. Thus, there is a renewal of the surface with a characteristic frequency ω. According to the theory of surface renewal, $\beta \sim \sqrt{D\omega}$, so that $\beta \sim \sqrt{D(g(2\pi\lambda))^{1/2}}$. Estimates according to this relationship agree not badly with the experimental data ($A = 1-1.5$ mm) when a suitable choice is made of the coefficient of proportionality. If standing waves occur, the stream lines in them correspond to a family of curves which can be calculated from the relationship $\exp(2\pi z/\lambda)\sin(2\pi z/\lambda) = \text{const}$. It is obvious that such a motion of the liquid particles in a single plane along a straight line will lead to a smaller rate of surface renewal than in the previous case.

The effects of the characteristics of the surface waves on the rate of desorption of the CO_2 from the bulk of the liquid can be taken into account more precisely on the basis of the model proposed in [7], which considers the effects of wind waves. Here it is assumed that the rate of mass transfer is governed by the diffusion processes occurring in the rotating cells. The intensity of the turbulent mixing in the surface layer depends on the amplitudes and lengths of the surface waves. The mixing length ℓ and the velocity fluctuation v of the liquid particles are expressed in terms of the Kolmogorov scales [13]; $v = (v\varepsilon)^{1/4}$; $\ell = (v^3\varepsilon)^{1/4}$. As in [13], the rate of dissipation of energy ε is evaluated from the value of the vorticity beyond the limits of the viscous sublayer at the interface.

According to [7, 13], the relationship between the wave characteristics and the value of ε has the form $\varepsilon \sim A^4 k^4 \omega^2$, and in this case the mass transfer coefficient is calculated from the expression $\beta = 0.4 Sc^{-1/2}(\nu\varepsilon)^{1/4}$.

Let us now use the relationships for the wave characteristics of the traveling waves. By expressing k and ω in terms of the velocities and lengths of the gravity waves, it is found that:

$$\varepsilon = \nu A^4 (2\pi/\lambda)^4 (2\pi c_\phi/\lambda)^4.$$

By taking Eq. (2) into account the following expression is obtained for calculating the mass-transfer coefficient:

$$\beta = 3,98\,(gD^2)^{1/4}\left(\frac{A}{\lambda^{5/4}}\right). \tag{4}$$

As can be seen from Fig. 2, calculations according to Eq. (4) are in agreement with the experimental data and correctly express the trends of the variation of β as the wavelength λ and the amplitude A change.

From Eq. (4) it is possible to obtain the dimensionless expression

$$Nu_\lambda = 3,98\,(A/\lambda)\,Ga^{1/4}\,Sc^{1/2}, \tag{5}$$

where $Nu_\lambda = \beta\lambda/D$; $Sc = \nu/D$. The group $Ga = g\lambda^3/\nu^2$ is a measure of the ratio between the forces of molecular friction and gravity. The range of variation of the Galileo number Ga in the experiments was 10^9–10^{11}, and the values of A/λ varied over the range $A/\lambda = 0.02$–0.1. Correspondingly, the Nusselt numbers Nu_λ varied from 10 to 10^4. The experimental results on the effects of surface waves on mass transfer through the surface are generalized in Fig. 4. This figure also shows the calculations according to Eq. (5). The satisfactory agreement between the calculated and experimental values makes it possible to state that Eq. (5) is applicable for calculating the rates of mass transfer through perturbed surfaces under the conditions indicated above.

NOTATION

β, mass-transfer coefficient, m/sec; c, concentration; D, diffusion coefficient, m^2/sec; λ, wavelength, m; A, wave amplitude, m; c_ϕ, phase velocity of the waves, m/sec; k, wave number, m^{-1}; ω, wave frequency, sec^{-1}; H, basin depth, m; Nu, Nusselt number; Sc, Schmidt number; Ga, Galileo number.

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