STUDY OF MASS TRANSFER IN A SYSTEM OF GAS BUBBLES AND A LIQUID

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The dissolution of a system of CO_2 bubbles in water and aqueous solutions of dextrose has been studied experimentally. The interfacial surface area is calculated, and the mass-transfer coefficient β is determined. A relation is found among β, the bubble diameter, the physical properties of the liquid, and the rate at which the gas is bubbled through the liquid. A criterial equation is proposed for β.

There is no generally accepted theory for mass transfer between a system of gas bubbles and a liquid [1]. Even for a solitary bubble in a liquid at Reynolds numbers $N_{Re} > 1$, the familiar theoretical models for mass transfer do not conform to experimental data, as was shown in [2]. For the dissolution of a solitary CO_2 bubble in water, as an example, the β value calculated from the Levich equation [3] is 11–12 times as great as the experimental values [2, 4]. For this reason, the mass-transfer dependence and the value of β are determined experimentally.

The results of experimental studies of mass transfer between a system of bubbles in a liquid are usually expressed as a dependence of the quantity βF or its analog on the parameters of the process [5–7]. This manner of exhibiting the experimental data does not reveal the mechanism for mass transfer (i.e., whether it is related to a limitation by the interfacial area F or by β); it precludes an evaluation of the effect of the transfer conditions on the transfer rate; and it hinders the use of experimental data to analyze mass transfer under other conditons.

In this paper, information reported previously [8] on the motion and deformation of solitary bubbles is used to calculate the interfacial area F.

1. The experiments were carried out in a transparent column 2 m high having a transverse cross section of $S = 0.2 \times 0.2\ m^2$. Figure 1 shows the experimental column 1, the line from tank 2, the intermediate reservoir 3, the regulating valve 4, the grid 5, the diaphragm rheometer 6, the manometer 7, the membrane 8, the fitting 9, and the thermometer 10. Carbon dioxide of 99.8% purity is fed from tank 2 through the intermediate reservoir 3 with control valve 4 to a chamber under a copper grid 5 with 16 apertures $d = 0.15 \cdot 10^{-2}$ m in diameter (useful cross section of 0.07%). The height H to which the column is filled with liquid was varied from 0.7 to 2.0 m, and the liquid volume V° in the column was varied from 0.028 to 0.080 m^3. We assume the specific gas flow rate to be $\theta = Q_1/V^\circ\ (0.30–1.60) \cdot 10^{-3}\ m^3/m^3 \cdot sec$, where Q_1 is the volume flow rate at the entrance to the column.

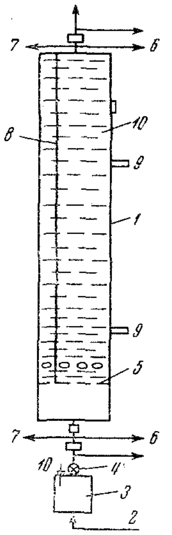

Fig. 1.

Distilled water (1) and aqueous solutions of dextrose of various densities (rows 2, 3, and 4 in the table) were used in the experiments. The solution density ρ(kg/m^3) was measured with densimeters having a scale division of 1 kg/m^3. The kinematic viscosity ν(m^2/sec) was determined on a VPZh-1 viscosimeter with a capillary diameter of 0.86 mm. The CO_2 diffusion coefficients D (m^2/sec) in the water and the dextrose solutions and the solubility constants φ_0 (kmole/μN) were determined from the data of [2] for the corresponding solution densities ρ. The surface tension σ(N/m) of water was taken from [9]. For the dextrose solutions, the value of σ was evaluated on the basis of the parachor value [10]. All the liquid properties were determined at the experimental temperature of 20° C.

		$\rho\ 10^{-3}$	$\nu\ 10^4$	$D\ 10^9$	$\varphi_0^{10132.5}$	$\sigma\ 10^3$
Water	1	0.998	0.009	1.9	3.50	72.75
Aqueous solutions of dextrose	2	1.095	0.015	1.37	2.92	73.01
	3	1.150	0.035	1.07	2.45	74.89
	4	1.175	0.054	0.94	2.18	75.51

Most of the resistance to CO_2 dissolution in water and in the aqueous dextrose solutions is concentrated in the liquid phase [2, 4], and the mass-transfer coefficient β is given by

$$\langle\beta\rangle = \frac{q}{\langle F\rangle (C_0 - \langle C\rangle)}, \tag{1.1}$$

where q(kmole/sec) is the mass-transfer rate F(m^2) is the interfacial area; C_0 (kmole/m^3) is the gas concentration in the liquid or the equilibrium concentration in the gas phase, and ⟨C⟩ (kmole/m^3) is the gas concentration in the liquid, averaged over the time during which the mass transfer takes place.

The reaction $CO_2 + H_2O \rightleftarrows H_2CO_3$ occurs very slowly (the rate constant is 0.025 liter/mole · sec at 25° C [11]) and has a negligibly small effect on the dissolution rate. The steady-state mass-transfer rate is defined as the difference between the molar gas flow rates at the entrance and exit of the system, $Q_{1,0}C_1$ and $Q_{2,0}C_2$, respectively, reduced to 293° K and a pressure of 101.325 kN/m^2:

$$q = Q_{1,0}C_1 - Q_{2,0}C_2, \tag{1.2}$$

where Q is the volume gas flow rate and C is the molar concentration of CO_2 in the gas.

The gas which entered the column during the experiments was assumed dry, and that which left it was assumed completely saturated with water vapor. The gas flow rates Q_1 and Q_2 at the entrance and exit of the column were measured by diaphragm rheometers 6 to 2.5%, while the gas pressure before the diaphragms was measured by liquid manometers 7.

For relatively insoluble gases the difference $C_0 - \langle C\rangle$ is governed primarily by the value of C_0, so the quantity ⟨C⟩ in Eq. (1.1) may with sufficient accuracy be treated as the arithmetic mean for the CO_2 concentrations in the liquid before and after the experiment, C' and C", respectively:

$$\langle C\rangle = 0.5\,(C' + C''). \tag{1.3}$$

The quantities C' and C" were found as the average results of a base titration of two liquid samples drawn off into 100-ml pycnometers from different column heights through the fitting 9. The relative error of this analysis was 6%.

The CO_2 solubility in water and in the aqueous dextrose solutions obeys Henry's law fairly well [2, 4]:

$$C_0 = \varphi_0 \langle p\rangle, \tag{1.4}$$

where φ_0 (kmole/Nm) is the Henry constant, and ⟨p⟩ (N/m^2) is the CO_2 partial pressure, averaged over the height of the liquid column. For a system of large bubbles distributed uniformly through the liquid, we have

$$\langle p\rangle = y\,(p + 0.5\,Hg\rho), \tag{1.5}$$

where y is the mole fraction of CO_2 in the gas phase, p is the absolute pressure above the liquid, ρ is the liquid density, and g is the acceleration due to gravity.

From the experimentally determined q and ⟨C⟩, the quantity ⟨βF⟩ can be determined. The area ⟨F⟩ is calculated to determine ⟨β⟩. In the general case, the total surface area of the bubbles is

$$\langle F\rangle = N\int_0^H P(h)\,F(h)\,dh, \qquad (1.6)$$

where N is the number of bubbles existing in the liquid simultaneously, F(h) is the surface area of a single bubble at height, and P(h) is the differential distribution of bubbles with respect to height.

In a previous study [8], it was found that when a bubble of diameter $d = 0.65 \cdot 10^{-2}$ m rises to a height of 2 m, its diameter increases to $0.78 \cdot 10^{-2}$ m, while its ascent velocity decreases from 23.1 to 22.7 m/sec. Accordingly, we can use $u \approx \text{const}$, finding

$$P(h) = \frac{1}{H}, \qquad \langle F\rangle = \frac{N}{H}\int_0^H F(h)\,dh. \qquad (1.7)$$

The surface area of a bubble considered to be an oblate spheroid can be expressed in terms of the volume V:

$$F(h) = \varphi V^{2/3}(h), \qquad \varphi = 3.42\,\frac{(m^2+1)^{1/2}}{m^{1/3}}, \qquad m = \frac{a}{b}, \qquad (1.8)$$

where a is the frontal bubble diameter and b is the bubble height. The parameter m is a function of the initial bubble deformation m^* and the time (sec) elapsed since the start of the ascent [8]. For water, e.g., we have

$$m = m^* - 0.08\tau \qquad (\tau < 7.5\ \text{sec}) \qquad (1.9)$$

For the dextrose solutions, the numerical coefficient of τ in this dependence was calculated to lie within the range 0.12–0.43.

For $\tau < 15$, φ does not change by more than 12% over the height H, so the arithmetic mean $\langle\varphi\rangle$ of the φ values at the beginning and end of the bubble motion may be used in Eq. (1.8). The instantaneous bubble volume is

$$V(h) = V^*(1-Kh)\frac{B}{B-h}, \qquad B = H + \frac{p}{g\rho}, \qquad (1.10)$$

where V^* is the volume of the detaching bubble, and K is a factor which takes into account the decrease in the bubble mass during the ascent. The value of K was calculated from the amount of gas absorbed during the experiment:

$$K = \frac{1}{H}\left(1 - \frac{Q_2}{Q_1}\,\frac{B-H}{B}\right). \qquad (1.11)$$

Substitution of Eqs. (1.8) and (1.10) into (1.7) yields

$$\langle F\rangle = \frac{N}{H}\langle\varphi\rangle V^{*2/3}B^{2/3}\int_0^H\left(\frac{1-Kh}{B-h}\right)^{2/3} dh; \qquad (1.12)$$

This integral was calculated numerically. The quantities N and V^* are related by the obvious relation

$$N = \frac{Q_1 T}{V^*}, \qquad (1.13)$$

where T is the time the bubble remains at height H.

The number of bubbles simultaneously in the column was counted on photographs of a longitudinal cross section of the column, singled out along one series of apertures by a thin opaque membrane 7 (Fig. 1).

At none of the gas flow rates was there any noticeable motion of bubbles in the transverse cross section of the column or bubble circulation in the volume.

At low gas flow rates(i.e., low in comparison with the volume gas content)

$$\psi = \frac{Q_1}{\langle u\rangle S} \leqslant 1.7\cdot 10^{-3}\ \text{m}^3/\text{m}^3,$$

the actual number of bubbles is quite close to that calculated if the volume of the detaching bubble in Eq. (1.13) is found from the condition for the equality of the buoyant force and the surface-tension force:

$$V^* = \frac{\pi d_0 \sigma}{g(\rho - \rho')}, \tag{1.14}$$

where ρ' is the gas density. As the gas flow rate increases ($\psi = 1.7 \cdot 10^{-3}$–$7.7 \cdot 10^{-3}$ m^3/m^3), the deviation between the calculated number of bubbles (curve 1 in Fig. 2) and the actual number of bubbles (points 2) increases. This is apparently due to a change in the volume of the detaching bubble as the gas flow rate increases [12] and to the coalescence of bubbles in the liquid, which is evident from the photographs of different bubble volumes at the same column cross section.

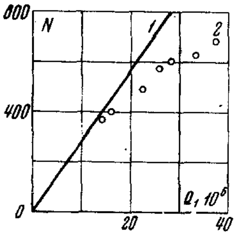

Fig. 2.

Accordingly, ⟨F⟩ was calculated from the nominal bubble detachment volume V_* calculated from Eq. (1.13) for the experimental N. In this manner, the pattern of bubble motion, which is actually quite complicated, is reduced to an approximate model in which the separate bubbles do not coalesce; and their ascent velocity, shape, and surface area can be calculated from the equations for a solitary bubble. The use of this model is justified by the very weak dependence of the bubble ascent velocity on the bubble diameter. The absolute values of this calculated "detachment" diameter d_* lie within the range $(0.5–1.0) \cdot 10^{-2}$ m.

The instantaneous bubble ascent velocity is [8]

$$u = 121.50\nu^{0.37} \frac{m^{0.03}}{d^{0.06}}. \tag{1.15}$$

Using $u = dh/d\tau$ in Eq. (1.15), inserting m and d from (1.9) and (1.10), and integrating, we find an equation for the time T the bubble remains in the water:

$$\int_0^H \left(\frac{1-Kh}{B-h}\right)^{0.02} dh = \frac{121.50\nu^{0.37}}{d_*^{0.06} B^{0.02}} \int_0^T (m_* - 0.08\tau)^{0.03}\, d\tau. \tag{1.16}$$

For the experimental conditions, the following relations hold to within 2%:

$$\int_0^T (m_* - 0.08\tau)^{0.03}\, d\tau = T, \qquad \int_0^H \left(\frac{1-Kh}{B-h}\right)^{0.02} dh = H.$$

We thus have

$$T = \frac{H d_*^{0.06} B^{0.02}}{121.50\nu^{0.37}}. \tag{1.17}$$

Combining Eqs. (1.17) and (1.13), we find the approximation

$$V_* = \frac{1.013 H B^{0.02} Q_1}{121.50\nu^{0.37} N}. \tag{1.18}$$

From the value of d_* found, m_* and then $\langle\varphi\rangle$ are determined. The method for calculating m_* was discussed previously [8]. The values of T and V_* for the dextrose solutions were calculated in an analogous manner.

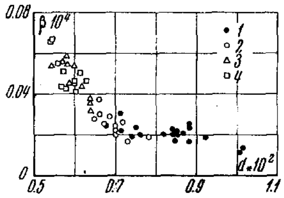

Fig. 3.

The relative error in the β determination did not exceed 15%.

2. A study of the CO_2-dissolution dynamics in water at constant gas flow rate Q_1 showed that the quantity βF remained constant over a wide range of experimental times (45–300 sec) (this confirms the validity of determining βF from the CO_2 concentration in the liquid averaged over the experimental time [Eq. (1.3)]).

It was found experimentally that β falls off sharply with increasing d_* for $d_* < 0.7 \cdot 10^{-2}$ m, and remains essentially constant for $d_* > 0.7 \cdot 10^{-2}$ m (Fig. 3). Here and below, the labels on the points in the figures correspond to the rows in Table 1. This dependence of β on d_* is apparently related to the nature of the liquid motion near the bubble. According to Baird and Davidson [4], the decrease and gradual stabilization of β with increasing d is due to the development and stabilization of a turbulent wake behind the bubble; the concentrations are leveled off in the turbulent wake, and the bubble surface in this region does not take part in the mass transfer.

For both water and the aqueous solutions of dextrose, the experimental change in $\langle \beta F \rangle$ is essentially linearly proportional to the change in the gas flow rate Q_1, because the rate at which $\langle F \rangle$ increases is considerably greater than the rate at which β decreases with increasing average bubble diameter.

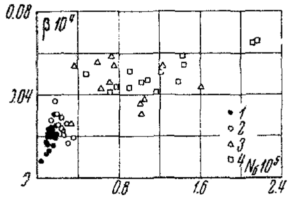

Fig. 4.

For the dissolution of CO_2 in water, the numerical values of β (0.010–0.030 cm/sec) correspond well to experimental data for solitary bubbles [13]. For the dextrose solutions, the β values (0.20–0.065 cm/sec) are close to the data of [2].

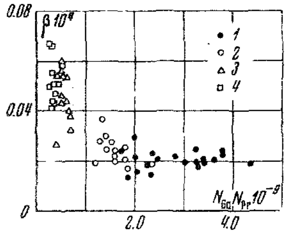

Fig. 5.

Dimensional analysis for this process leads to the following system of governing criteria:

$$N_\delta = \frac{\nu Q_1}{g d_*^2 S}, \quad N_{Ga} N_{Pr} = \frac{g d_*^3}{\nu D}, \quad N_{We} = \frac{\sigma}{g d_*^2 (\rho - \rho')}, \quad N_\Gamma = \frac{H}{d_*}.$$

Here N_δ is the bubbling criterion, N_{Ga} is the Galilean criterion, N_{Pr} is the Prandtl diffusion criterion, N_{We} is the Weber criterion, and N_Γ is the geometric similarity criterion. The β values are seen to become essentially stable at $N_\delta = (0.4\text{–}0.6) \cdot 10^{-5}$ and $N_{Ga} N_{Pr} = 2.0 \times 10^9$ (Figs. 4 and 5). The independence of β from N_δ and $N_{Ga} N_{Pr}$ in this region may be explained in the following manner: as the bubbling rate increases, the volume per bubble increases because of bubble coalescence, while β decreases (according to Fig. 3); this compensates for the β increase because of the development of turbulence in the liquid.

The experimental results conform well to the criterial equation

$$\frac{\beta d_*}{D} = 2.0256 \cdot 10^{10} N_\delta^{0.10} N_\Gamma^{0.16} (N_{Ga} N_{Pr})^{-0.88} N_{We}^{-1.16} \qquad (2.1)$$

for $N_\delta = (0.03\text{–}2.10) \cdot 10^{-5}$, $N_{Ga} N_{Pr} = (0.27\text{–}4.30) \cdot 10^9$, $N_\Gamma = 96\text{–}260$, and $N_{We} = 0.065\text{–}0.226$.

Analysis of Eq. (2.1) shows that as the gas flow rate Q_1 increases (but the bubble diameter remains constant), the mass-transfer rate q is governed primarily by the growth of the interfacial surface area (by the increase of the number of bubbles in the system), and is only slightly intensified by liquid turbulence. With a six-fold increase in the gas flow rate, as an example (or a 3.3-fold increase in the interfacial area$\langle F\rangle$) by a factor of$\langle\beta\rangle$ increases by only a factor of 1.18, and that of $\langle\beta F\rangle$ by a factor of 3.8. This means that mass transfer is governed primarily by the conditions for liquid flow near the bubble, and depends slightly on the degree of turbulence in the liquid volume.

Changes in the bubble diameter d_* have the greatest effect on β. When d_* decreases by a factor of 1.42 (or the surface area increases by the same factor) at constant Q_1, the value of β increases by a factor of 1.78, and that of βF increases by a factor of 2.53. Accordingly, a greater dispersion accelerates mass transfer because of an increase in the interfacial surface area and in the mass-transfer coefficient of β. The role of the latter factor has not previously been taken into account for such systems.

Braginskii et al. [14] calculated an expression for the mass-transfer rate q for the bubbling of a relatively insoluble gas through a liquid on the basis of the Danquerts theory of mass transfer and the Levich model for bubble motion:

$$q \approx 1.72 \frac{H\theta}{\langle d\rangle} \xi^{0.5} N_{We}^{-0.9} N_{Pe}^{-0.5} (C_0 - C) \qquad \left(N_{Pe} = \frac{ud}{D}\right), \tag{2.2}$$

where N_{Pe} is the Peclet diffusion criterion, and ξ is the bubble drag coefficient.

A comparison of the experimental $\langle\beta F\rangle$ divided by the liquid volume V° with the values calculated from Eq. (2.2) shows that the discrepancy exceeds the experimental error. Following the calculation procedure of [14] exactly ($D = 1.9 \cdot 10^{-9}$, $\sigma = 73 \cdot 10^{-3}$, $\rho = 10^3$, $\mu = 1.0$, $\langle d\rangle = 3.6 \cdot 10^{-2}$, $\xi = 0.5$, and $u = 0.34$), we find the average (of 20 experiments) relative error to be $\langle\delta\rangle = 45\%$.

Substitution into (2.2) of the experimental values $\langle u\rangle = 0.23$ and $\xi = 0.8$ found in [8] for $d = 0.8 \cdot 10^{-2}$ increases the average relative error by a factor of five ($\langle\delta\rangle = 225\%$). Apparently only experimental equations in criterial form, like (2.1), can be used at present to treat mass transfer in a continuous bubble layer.

For the reaction C + O → CO, which occurs on the surface of a CO bubble in liquid steel, the value of β calculated from Eq. (2.1) and the initial data of [15] turned out to be 0.043 cm/sec. This is 1/22 the value found in [15] and corresponds closely to Richardson's evaluation of this quantity (0.05 cm/sec) [16].

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