LOW-COST EXPERIMENTS IN MASS TRANSFER

Part 8. Absorption of Carbon Dioxide from a Single Bubble

M.H.I. BAIRD, I. NIRDOSH*
McMaster University • Hamilton, Ontario, Canada L8S 4L7

Efficient gas-liquid contact for mass transfer purposes can be obtained by creating a dispersion of gas bubbles, as (for example) in a bubble column reactor, a stirred-tank reactor, or a bubble-cap plate distillation column.[1] An earlier paper in this series described an experiment to measure mass transfer in a bubble column.[2] For a more basic approach, an experiment can be done with a single gas bubble of known size that allows for a more precise comparison of the results with predictions based on transport phenomena and fluid mechanics.

From the point of view of an inexpensive undergraduate laboratory experiment, there are some problems associated with measurements on a freely rising gas bubble. The terminal velocity of a freely rising bubble is typically about 20 cm/s, so a tall column must be constructed to measure mass transfer over a reasonable period of rise time. Careful account must also be taken of mass transfer end effects at the points of bubble release and collection. The experimentation and analysis require more time than is available in a typical undergraduate laboratory course.

If some way can be found to observe the mass transfer from a bubble while it is held stationary in a downflowing stream of liquid, the experiment is considerably simplified. This paper describes such an experiment in which a cylindrical bubble of carbon dioxide, which is moderately soluble in water, is held stationary in a downflow of water in a vertical tube. The mass transfer rate is calculated from the measured rate at which the bubble volume decreases with time.

STABILITY OF A GAS BUBBLE IN A VERTICAL TUBE

It has been found that good results are obtained with internal tube diameters in the range of 7 to 10 mm. Only a moderate flow of water is needed to hold the gas bubble stationary, and it takes up an elongated cylindrical shape as indicated in Figure 1.

Rao and Baird[3] have studied the relationship between the downward critical superficial velocity of the liquid phase (u_c) for bubble stabilization and the tube diameter and other properties of the liquid. Data for several different tube diameters and liquids can be correlated in terms of the Froude number and the Eötvos number

$$Fr^{0.5} = 0.163\,\ell n(Eo) - 0.222 \qquad (1)$$

where

$$Fr = \frac{u_c^2}{(2gr)} \qquad \text{and} \qquad Eo = \frac{4r^2\rho g}{\sigma}$$

Equation (1) has been found to hold for 3.9<Eo<50 and is independent of the length of the bubble, provided this exceeds about one tube diameter. Table 1 shows the four different values of tube radius r that have been studied in the experiment at McMaster University, with the corresponding values of u_c estimated from Eq. (1).

If a single vertical tube is used, the superficial liquid velocity, u, must be controlled precisely at the appropriate value of u_c from Eq. (1) in order to hold the bubble stationary, requiring constant attention and small flow adjustments with a needle valve. In order to avoid this limitation and to allow four different tube radii to be studied, a glass tube has been made up of four 12-cm long sections A to D (see Table 1), with the radius decreasing with height as shown in Figure

Malcolm Baird received his PhD in chemical engineering from Cambridge University in 1960. After some industrial experience and a post-doctoral fellowship at the University of Edinburgh, he came to McMaster University. His research interests are liquid-liquid extraction, oscillatory fluid flows, and hydrodynamic modeling of metallurgical processes.
Inder Nirdosh received his BSc and MSc in chemical engineering from Panjab University (India) and his PhD from Birmingham University (United Kingdom). He joined Lakehead University in 1981, and his research interests are in the fields of mineral processing and electrochemical engineering.

* Address: Lakehead University, Thunder Bay, Ontario, Canada P7B 5E1

2. Water is fed down through the tube at a measured flow rate as shown.

In this type of multisectioned tube, a cylindrical gas bubble tends to stabilize in one of the four sections, depending on the flow rate of water supplied. For example, for any flow rate of water between 0.896 and 1.80 mL/s, a cylindrical bubble will tend to rise to the top of section B since the water flow is less than 1.80 mL/s; but it cannot rise into section A since the water flow rate exceeds 0.896 mL/s. Thus it can be seen that a bubble can be held stationary in any section by setting the flow rate at any required value between certain limits, without the experimenter having to worry about the effect of any slight drift in the water flow rate upon the bubble position.

MASS TRANSFER RATE PREDICTION

The rate of mass transfer is given by the well-known equation

$$m' = kA\Delta c \qquad (2)$$

The area A is taken to be that of the curved cylindrical surface enclosing the bubble; the nose and tail areas are neglected. Typically, these areas are no more than 5% of the total area. From Figure 1

$$A = 2\pi(r-\delta)L \qquad (3)$$

The concentration driving force, Δc, is taken to be the solubility c^* of carbon dioxide in water, assuming that the downflowing water is free of dissolved gas.

Since carbon dioxide has a low solubility in water, and pure carbon dioxide gas is used, it can be assumed that the mass transfer rate is liquid phase diffusion-controlled.

If τ is the contact time of the moving liquid film at the cylindrical bubble surface, the well-known Higbie penetration model[4] provides an expression for the mass transfer coefficient:

$$k = 2\left(\frac{D}{\pi\tau}\right)^{0.5} \qquad (4)$$

where D is the molecular diffusivity of carbon dioxide in water.

LIQUID-GAS CONTACT TIME

While the gas bubble is stationary in the tube, the water flows downward past it as a moving film. If the surface velocity of the film is u_s, then

$$\tau = \frac{L}{u_s} \qquad (5)$$

Assuming that the film is laminar and that the film thickness, δ, is much less than r (typically $\delta / r \approx 0.05$), the simple ex-

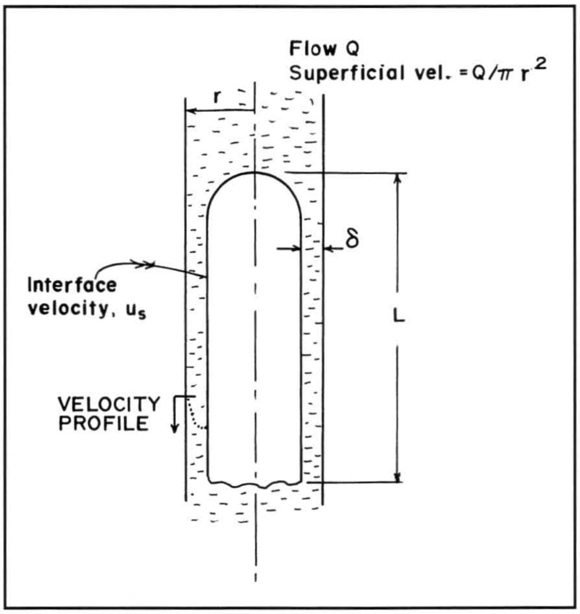

Figure 1. *Cylindrical gas bubble, showing some of the symbols used.*

TABLE 1
Tube Radii, Critical Liquid Velocities, and Water Flow Rates for Bubble Stabilization

Section	A	B	C	D
Internal tube radius, mm	3.51	3.98	4.41	5.05
Eötvos number for water	6.708	8.642	10.59	13.88
Velocity u_c from Eq. (1), mm/s	23.14	36.08	47.82	65.07
Flow rate, $\pi r^2 u_c$, mL/s	0.896	1.80	2.92	5.21

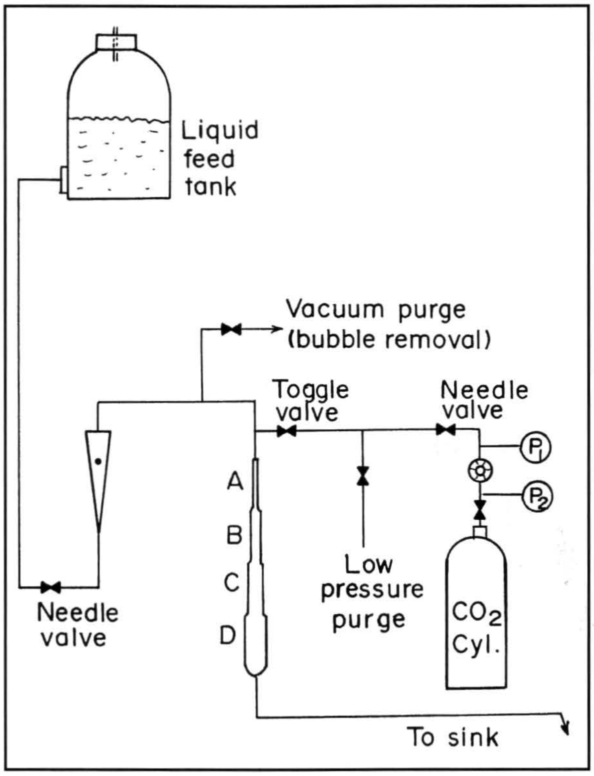

Figure 2. *Experimental arrangement with multisectioned tube.*

pression[5] for the surface velocity of a liquid film flowing down a vertical flat plate

$$u_s = 0.3054\left(\frac{\rho g Q^2}{\mu r^2}\right)^{\frac{1}{3}} \quad (6)$$

can be used. It can also be shown that the film thickness is

$$\delta = \left(\frac{3\mu Q}{2\pi\rho g r}\right)^{\frac{1}{3}} \quad (7)$$

When Eqs. (3) through (7) are substituted into Eq. (2), a theoretical expression is obtained for the rate of mass transfer in terms of the flow rate of water, the tube radius r, the bubble length L, and the system properties. For many repeated calculations, writing a small computer program is recommended. It is important to note that the theoretical approach depends on several assumptions, including neglect of the nose and tail contributions, the validity of the Higbie penetration model, and the simplification $\delta \ll r$ used in obtaining Eq. (6). It is also assumed that the contact time, τ, (usually less than 0.5 s) is much shorter than the time, t, over which the experiment is carried out.

EXPERIMENTAL MEASUREMENT OF MASS TRANSFER

The procedure is to start the liquid flow at the desired value (Figure 2) and then inject a controlled amount of carbon dioxide from the cylinder by means of the toggle valve as shown. A needle valve is placed just upstream of the injection toggle valve and the gas pressure upstream of the needle valve is regulated at a low gauge pressure, preferably about 10 kPa or 1.5 psig, to avoid excess gas injection. The gas injection technique requires some practice and dexterity, but if a mistake is made (*e.g.,* injection of too much gas), the system can be freed of bubbles by momentarily increasing the water flow or by suction, using the vacuum purge as shown in Figure 2. It is important to ensure that no air remains in the injected carbon dioxide bubble, as this would lead to slower mass transfer.

Once a bubble of suitable length (typically 10 cm) has been injected and stabilized in one of the tube sections, its length will be seen to gradually shrink. This is due to dissolution of carbon dioxide in the water; the rate of shrinkage provides a direct measurement of the mass transfer rate. A millimeter scale mounted behind the vertical glass tube enables the bubble length L to be measured as a function of time. The best arrangement is to have one student calling out the values of L and another keeping a note of the values of L and time; alternatively, a close-up video camera can provide a timed record of the bubble shrinkage.

ANALYSIS OF DATA

The linear rate of shrinkage of the bubble can be related to the volumetric rate of shrinkage and to the rate of mass transfer by

$$-\frac{dV}{dt} = -\pi(r-\delta)^2\frac{dL}{dt} = m'\left(\frac{RT}{MP}\right) \quad (8)$$

The term R is the universal gas constant, and M denotes the molecular weight of carbon dioxide (= 44 kg/kmol).

The theoretical mass transfer rate can be expressed using Eqs. (2) to (5), and hence

$$-\pi(r-\delta)^2\frac{dL}{dt} = 4\pi c^*(r-\delta)\left(\frac{DLu_s}{\pi}\right)^{\frac{1}{2}}\left(\frac{RT}{MP}\right) \quad (9)$$

Note that this expression is in the form

$$-\frac{dL}{dt} = KL^{0.5} \quad (10)$$

which can be integrated to give

$$L^{0.5} = L_0^{0.5} - \frac{Kt}{2} \quad (11)$$

where L_0 is the bubble length initially measured (t=0). Thus, a plot of $L^{1/2}$ versus time should be linear with a negative slope. The slope should be predictable from theory, according to which

$$K = \frac{4c^*\left(\frac{Du_s}{\pi}\right)^{0.5}}{(r-\delta)}\left(\frac{RT}{MP}\right) \quad (12)$$

where u_s and δ are given by Eqs. (6) and (7), respectively.

TYPICAL RESULTS

Some typical data from a student report[6] are shown as a plot of $L^{0.5}$ versus time in Figure 3. The linearity of the plot provides a qualitative support for the penetration model.[4]

The slopes of these plots, -K/2, are determined by linear regression and the experimental values of K can thus be calculated. The corresponding experimental values of K for the four typical cases are compared with the theoretical values (Eq. 12) in Table 2.

It can be seen that the experimental values of the mass transfer rate constant are about 30% below the theoretical values. Students should be encouraged to carefully examine the various assumptions in the theoretical treatment. The assumption that $\delta \ll r$ and the neglect of the nose and tail areas have already been mentioned. Another simplifying assumption is made following Eq. (3), namely that the driving force for mass transfer is the gas solubility. But a material balance for carbon dioxide indicates that in a typical case the exit liquid concentration is as much as 10% of the saturation value. This does not invalidate the theoretical model, because it can be shown that the dissolved carbon dioxide is present in a thin boundary layer near the surface, rather than being uniformly distributed. This concentration profile is accounted for in the derivation of Eq. (4) from the unsteady diffusion equation.[7]

The surface velocity of the falling film (Eq. 6) is calculated on the assumption that the shear stress at the gas-liquid interface is negligible. But there is evidence from the literature[8] that surface tension gradients can cause a deceleration of the liquid surface and the formation of ripples at the rear of a cylindrical gas bubble. This has the effect of reducing the average velocity, therefore increasing the surface contact time and significantly reducing the mass transfer rate. Van Heuven and Beek[8] reported mass transfer rates about 30% below theoretical predictions and attributed the reduction to the surface deceleration effect.

GENERAL CONCLUSIONS

It can be concluded from this experiment that transport phenomena are helpful in understanding the basic mechanism of mass transfer and obtaining an estimate of mass transfer rates from first principles. The derived equation for the mass transfer rate, however, is subject to simplifying assumptions, and therefore the estimate is only approximate.

The experiment is simple and inexpensive to construct and is much less elaborate than the rig used by Van Heuven and Beek,[8] which gave similar results. The most costly items are the rotameter and the needle valve. Some manual dexterity is required on the part of the students, but experience has shown that with a little practice the technique can be made to work.

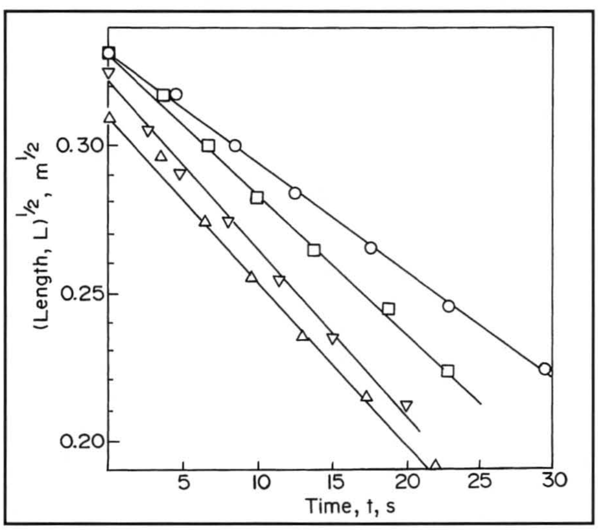

Figure 3. *Typical data on bubble shrinkage.[6]*
○ *Tube radius 3.51 mm, water flow 0.352 mL/s*
□ *Tube radius 3.98 mm, water flow 1.68 mL/s*
▽ *Tube radius 4.41 mm, water flow 2.69 mL/s*
△ *Tube radius 5.05 mm, water flow 3.96 mL/s*

TABLE 2
Typical Observed and Calculated Values[6] of Mass Transfer Rate Constant

Sect.	*Tube Radius (mm)*	*Flow Rate (mL/s)*	*Values of K, $m^{0.5}.s^{-1}$ Observed*	*Calculated*	*Ratio K_{obs}/K_{calc}*
A	3.51	0.352	0.00741	0.01051	0.705
B	3.98	1.68	0.00964	0.01537	0.608
C	4.41	2.69	0.01097	0.01563	0.702
D	5.05	3.96	0.01089	0.01478	0.737

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NOMENCLATURE

A	surface area, m^2
c*	solubility of CO_2 in water, kg/m^3
D	molecular diffusivity, m^2/s
Eo	Eötvos number
Fr	Froude number
g	gravitational acceleration, m/s^2
k	mass transfer coefficient, m/s
K	rate constant, $m^{0.5}$/s
L	bubble length, m
L_0	initial bubble length, m
m′	mass transfer rate, kg/s
M	molecular weight, kg/kmol
P	gas pressure, Pa
Q	liquid flow rate, m^3/s
r	tube internal radius, m
R	universal gas constant, J/(kmol.K)
t	time, s
T	temperature, K
u_c	critical flow velocity, m/s
u_s	bubble surface velocity, m/s
V	bubble volume, m^3
Greek symbols	
δ	liquid film thickness, m
μ	liquid viscosity, Pa.s
ρ	liquid density, kg/m^3
σ	surface tension, N/m
τ	contact time, s
Subscripts	
obs	observed
calc	calculated

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