Gas–Liquid Mass Transfer in Stirred Tanks

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Most methods for determining mass transfer coefficients ($k_L a_B$) between gas bubbles and liquid in stirred vessels involve adsorption or desorption and measuring liquid-phase concentrations (Albal et al., 1983; Joosten et al., 1977; Kralj and Sinic, 1984). A common procedure is to bubble the gas continuously through a batch liquid whose concentration is measured with a suitable electrode. Another approach is the dynamic method of monitoring the rate of evolution from a liquid saturated with the desorbing gas. Van't Riet (1979) has reviewed various procedures. Recently, Kojima et al. (1987) developed a different method, based upon the continuous flow of gas and liquid, that does not require measurement of the concentration in the vessel.

Method

This note describes a new pseudosteady-state chemical approach that eliminates the need for liquid-phase concentrations. The method is illustrated with data for the rate of evolution of carbon dioxide from a batch aqueous solution of Na_2CO_3 sparged with helium, as determined from the analysis of the effluent gas. With careful control of the pH of the solution and initial removal of dissolved gases from the liquid, the concentration of CO_2 in the effluent gas remains constant over a long enough time period for accurate measurement of $k_L a_B$. Also, it is shown that the kinetics of the reactions

$$H_2O + CO_2(aq) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+ \qquad (1)$$

$$HCO_3^- \rightleftharpoons CO_3^= + H^+ \qquad (2)$$

are fast with respect to mass transfer. Hence, the rate of evolution from the carbonate solution is controlled by mass transfer from liquid to gas bubble

$$CO_2(aq) \rightleftharpoons CO_2(g) \qquad (3)$$

The applicability of the method depends upon two premises:

1. The concentration of carbon dioxide in the gas, $[CO_2]_g$ is constant over a sufficient length of time for measurements to be made (pseudosteady state)
2. The concentration of $[CO_2]_{aq}$ in the solution is the equilibrium value determined from reactions 1 and 2

If the pH is too low, much CO_2 is evolved and $(CO_2)_{aq}$ is rapidly reduced. If the pH is too high, insufficient CO_2 is evolved for an accurate measurement of $[CO_2]_g$. Also, the initial amount of Na_2CO_3 must be substantial.

The rate of mass transfer from liquid to gas bubble according to Eq. 3 may be written

$$r = k_L a_B \{[CO_2]_{aq} - [CO_2]^i_{aq}\} = k_L a_B \left\{ \frac{[CO_2]_{aq} - [CO_2]_g}{H} \right\} \qquad (4)$$

where in the second equality the concentration in the liquid at the interface is assumed to be in equilibrium with that in the bulk gas bubble—the usual assumption for a slightly soluble gas. Both premises of the method can be checked experimentally.

Pseudosteady state

For a constant flow rate of inert feed gas (pure helium in our experiments), a constant measured $[CO_2]_g$ over a period of time indicates that r is constant. Then Eq. 4 requires that $[CO_2]_{aq}$ also be constant with time since Henry's constant H is invariant at constant temperature. Figure 1 for a typical run shows that the response line (62.15 mv) is essentially constant over a period of more than 3 min.

Equilibrium solution concentrations

The second premise can be examined by measuring the rate of evolution of CO_2 over a range of stirring speeds and extrapolating to infinite rpm. The procedure is to calculate $[HCO_3^-]$ by assuming that Eqs. 1 and 2 are at equilibrium and then check

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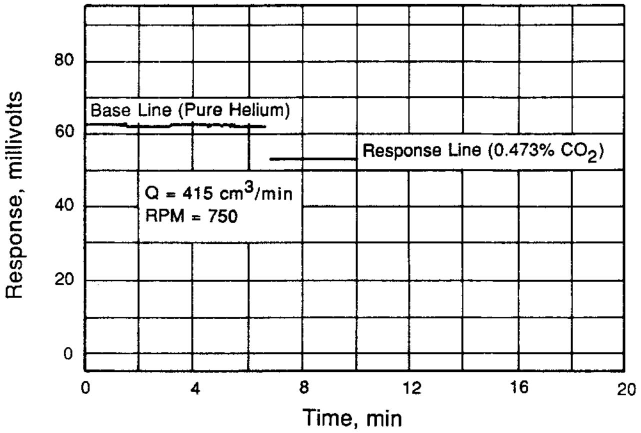

Figure 1. Typical response curve.

this assumption with the measured rate data. To calculate $[HCO_3^-]_{eq}$, first an overall mass balance for carbon is written over a time interval, t:

$$M_o = [Na_2CO_3]_o = [CO_2]_{aq} + [CO_3^=] + [HCO_3^-] + [CO_2]_g \frac{Qt}{V} \quad (5)$$

where $[Na_2CO_3]_o$ is the initial concentration of $CO_3^=$ and the last term represents the total CO_2 evolved during the time t. Using the equilibrium constants for reactions 1 and 2 to eliminate $[HCO_3^-]$ and $[CO_3^=]$ and taking $[CO_2]_g = H[CO_2]_{aq}$, Eq. 5 yields for $[CO_2]_{aq}$

$$[CO_2]_{aq} = \frac{M_o}{1 + \frac{K_2K_1}{[H^+]^2} + \frac{K_1}{[H^+]} + \frac{Qt}{V}H} \quad (6)$$

The corresponding expression for $[HCO_3^-]$ is

$$[HCO_3^-]_{eq} = \frac{K_1[CO_2]_{aq}}{H^+} \quad (7)$$

K_1 and K_2 were evaluated at 303 K from the following expressions involving the ionic strength I and temperature T.

For K_1 (from Harned and Owen, 1958):

$$-\log K_1 = -\log K_1^0 - \frac{2AI^{1/2}}{1 + I^{1/2}} + BI \quad (8)$$

$$\log K_1^0 = \frac{-3{,}404.71}{T} + 14.84 - 0.03279T$$

$$A = 0.4883 + 0.7554 \times 10^{-3}(T - 273) + 0.1743 \times 10^{-5}(T - 273)^2 + 0.1167 \times 10^{-7}(T - 273)^3$$

$$B = 0.066 + 1.92 \times 10^{-3}(T - 273) - 0.0176 \times 10^{-3}(T - 273)^2$$

For K_2 (from Näsänen, 1946):

$$-\log K_2 = -\log K_2^0 - \frac{2.02I^{1/2}}{1 + CI^{1/2}} - DI \quad (9)$$

$$\log K_2^0 = 6.498 - 2{,}902/T + 0.0238T$$

For K_2 no values of C and D were found for Na_2CO_3. Hence, the values for NaCl were used ($C = 1.49$, $D = 0.055$). Calculations show that completely neglecting the effect of ionic strength on the equilibrium concentrations changes k_La_B by 50%. It is estimated that using Eqs. 8 and 9 reduces this error in k_La_B to less than 10%.

Henry's constant, H, for carbon dioxide was calculated for our mixed electrolyte solution by the method of Onda et al. (1970). This approach modifies the solubility in pure water ($H = 1.36$ at 303 K, from Stumm and Morgan, 1981) for the effect of ionic strength of the Na_2CO_3 and H_2SO_4. This reduces the solubility so that $H = 2.13$.

The conditions chosen for our experiments were 303 K, pH = 9.00, $M_o = 0.50$ mol/L, and $I = 1.309$ mol/L. With these values, the resulting concentrations and equilibrium constants calculated with Eqs. 6–9 are:

$$[CO_2]_{aq} = 3.18 \times 10^{-4}\ \text{mol/L}$$
$$[HCO_3^-]_{aq} = 0.381\ \text{mol/L}$$
$$[CO_3^=] = 0.118\ \text{mol/L}$$
$$[SO_4^=] = 0.191\ \text{mol/L}$$
$$K_1 = 1.20 \times 10^{-6}\ \text{mol/L}$$
$$K_2 = 3.10 \times 10^{-10}\ \text{mol/L}$$

The term QtH/V in Eq. 6 for a time of 3 min is only 0.4% of the sum of the other three terms in the denominator.

Significance of kinetics

Dissolved carbon dioxide is produced by reaction 1 and leaves the liquid by evolution into the gas bubbles. Hence, a mass balance of CO_2 on the liquid phase is

$$\frac{d[CO_2]_{aq}}{dt} = -k_La_B\frac{[CO_2]_{aq} - [CO_2]_g}{H} + k_{-1}\{[HCO_3^-][H^+] - K_1[CO_2]_{aq}\} \quad (10)$$

Since $[CO_2]_{aq}$ is constant over the time of a run, Eq. 10 reduces to

$$r = k_La_B\frac{[CO_2]_{aq} - [CO_2]_g}{H} = k_{-1}\{[HCO_3^-][H^+] - K_1[CO_2]_{aq}\} \quad (11)$$

Rearranging this expression to separate k_La_B and k_{-1} from known quantities (eliminating $[CO_2]_{aq}$) yields

$$R = \frac{[HCO_3^-][H^+] - K_1[CO_2]_g/H}{r} = \frac{1}{k_{-1}} + \frac{K_1}{k_La_B} \quad (12)$$

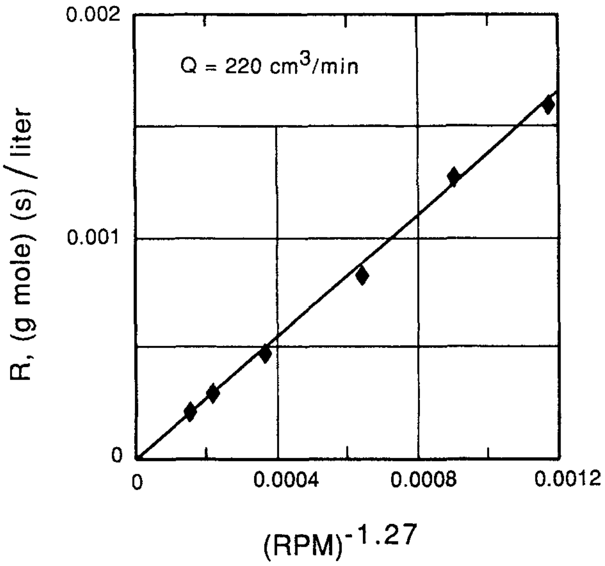

Figure 2. Plot of R vs. rpm$^{-1.27}$: Eq. 14.

For experiments at constant pH and temperature, all quantities on the lefthand side of Eq. 12, and therefore R, are known. The rate is given in terms of measured quantities by

$$r = \frac{Q[CO_2]_g}{V} \tag{13}$$

For data obtained for various stirrer speeds, the only variable on the righthand side of Eq. 12 is k_La_B and it is expected that this mass transfer coefficient is a power function of the speed. Then Eq. 12 may be written

$$R = \frac{1}{k_{-1}} + \frac{K_1}{a(\text{rpm})^b} \tag{14}$$

The reliability of Eq. 14 can be tested by noting if a straight line is obtained by plotting the data as R vs. $(\text{rpm})^{-b}$. Further, the intercept of the line gives the reciprocal of the rate constant, k_{-1}. Over the whole range of operating conditions, Table 1, the data established a straight line with an intercept of essentially zero. Figure 2 for $Q = 220$ cm^3/min is typical of the results. Thus, for our conditions the kinetics of reaction 1 do not affect the rate of CO_2 evolution. Then k_La_B can be calculated by combining Eqs. 4 and 13 to yield

$$k_La_B = \frac{Q[CO_2]_g}{V\{[CO_2]_{aq} - [CO_2]_g/H\}} \tag{15}$$

Here $[CO_2]_{aq} = 3.18 \times 10^{-4}$ mol/L.

Table 1. Operating Conditions

Volume of liquid phase, cm^3	1,000
Volume of reactor, cm^3	1,180
Temperature, K	303
Range of gas flow rate (1 atm, 298 K), cm^3/min	105–1,000
Range of stirring speed, rpm	115–1,000
Concentration of Na_2CO_3, mol/L	0.500
pH of solution	9.00
Concentration of H_2SO_4, mol/L	0.191

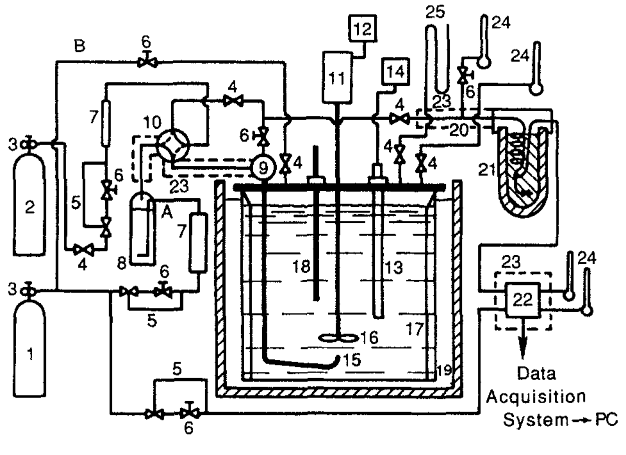

Figure 3. Schematic of apparatus.

1. helium cylinder
2. CO_2 cylinder
3. pressure regulator
4. shut-off valve
5. flow controller
6. needle valve
7. rotameter
8. humidifer
9. three-way valve
10. four-way valve
11. motor
12. stirrer control unit
13. combination electrode
14. pH meter
15. dispersion tube
16. impeller
17. baffle
18. thermometer
19. constant temperature bath
20. flow splitter
21. cold trap
22. thermal conductivity cell
23. heated zone
24. soap bubble meter
25. mercury manometer

Experimental Procedure

The reactor, Figure 3, is a 10 cm ID, 15 cm long Pyrex cylinder equipped with eight stationary Teflon-coated baffles spaced equally around the inner circumference of the cylinder. The baffles extend 0.7 cm inward from the periphery of the cylinder. A flat-bladed impeller is 5.0 cm in diameter and 1.0 cm high. Details of the system are given by Furusawa and Smith (1973). The sparger has a single 0.3 cm ID nozzle and is located 1.0 cm directly below the single impeller.

Pure helium was bubbled through the sparger and the CO_2 concentration in the effluent gas measured in a calibrated TC cell. The continuous voltage from the cell was converted to a digital signal, amplified with a Keithley System 570 data-acquisition work station, and stored in an IBM-PC.

Accurate measurement of the pH was important for obtaining reproducible data. By controlling the pH to 9.00 with an Accumet model 910 meter (gel-filled body combination electrode) the rate r was reproducible within 8%. The concentration of H_2SO_4 required to obtain pH = 9 was calculated from the electroneutrality requirement and equations for K_1, K_2, and $[H^+]\,[OH^-] = K_{H_2O}$. This was an iterative calculation since K_1 and K_2 are functions of the ionic strength.

Anhydrous Na_2CO_3 (certified ACS) and analytic reagent

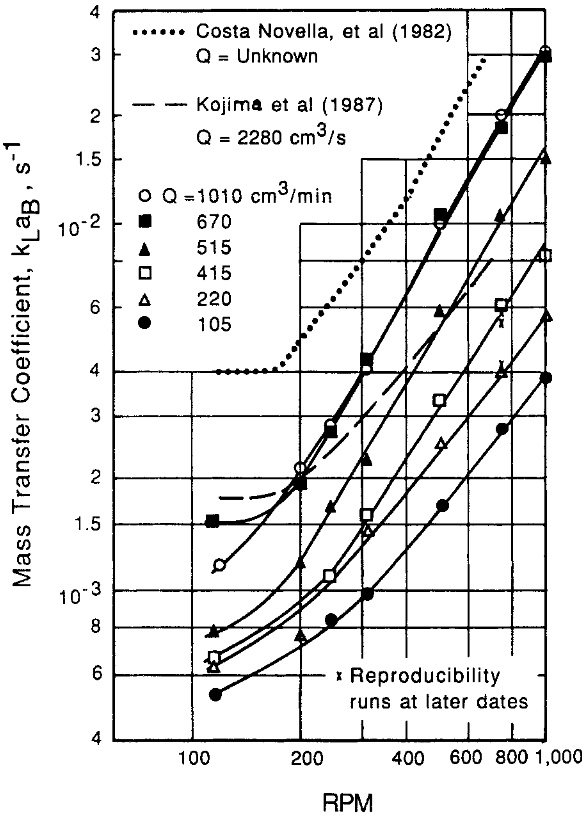

Figure 4. Mass transfer coefficient vs. stirrer speed.

grade H_2SO_4, along with distilled water, were used to prepare the liquid solution.

For accurate results it was necessary to degas the solution with helium after it had been added to the reactor. Also, it was important to adjust the pH to exactly 9.00 by bubbling CO_2 through the solution before and after each run. This ensured that M_o and $[CO_2]_{aq}$ were essentially constant during a run and did not vary from run to run.

Results and Discussion

Figure 4 is a logarithmic plot of the results for $k_L a_B$ over the range of stirrer speeds and gas flow rates. The data suggest a linear relationship (with slopes increasing from 1.0 to 1.7 as the gas flow rate increases) except at the lowest stirrer speed (115 rpm). It may be that the assumption of the well-mixed liquid inherent in Eq. 15 is not achieved at the lowest speed. Also, the data indicate no effect of gas flow rate above 670 cm³/min except at the lowest stirrer speed. Check runs were made at a stirrer speed of 750 rpm. The agreement shown in Figure 4 indicates that the method gives reproducible results.

Prior literature (Kojima et al., 1987; Costa Novella et al., 1982; and the Van't Riet review, 1979) indicate that $k_L a_B$ depends upon specific aspects of the stirred system, including design and location of the sparger and baffles, shape and location of the impeller, and diameter and height of the vessel. This has resulted in large differences between reported data. The most recent results for the effect of stirrer speed are apparently those of Kojima et al. and Costa Novella et al., each with different impeller and baffle designs than that of our apparatus. Kojima et al. used a sparger identical to ours but the baffles and impeller were different, and the lowest gas flow rate was 2,280 cm³/min. For this condition they found $k_L a_B$ to increase from $2 \times 10^{-3}\ s^{-1}$ at 120 rpm to 7×10^{-3} at 600 rpm, as shown by the dashed line on Figure 4. The results of Costa Novella et al. for the effect of stirrer speed are shown in Figure 4 by the dotted line. No gas flow rate is given for these values. While a lack of data at the same conditions, and differences in stirred vessel design, make accurate comparisons impossible, the information in Figure 4 suggests that the method described here can give useful results. The procedure should be applicable to other chemical systems where a gas is evolved from the liquid by a chemical reaction of very rapid or known kinetics.

Acknowledgment

A grant from CONICET of Republica Argentina for L. A. Arrua is gratefully acknowledged.

Notation

a_B = gas–liquid interfacial area per unit volume of liquid, cm^{-1}
A, B = empirical constants, Eq. 8
a, b = empirical constants, Eq. 14
C, D = empirical constants, Eq. 9
H = Henry's law constant, $([CO_2]_g/[CO_2]_{aq})_{eq}$
I = ionic strength, mol/L
k_L = liquid-side mass transfer coefficient, cm/s
k_1, k_{-1} = forward and reverse rate constants for reaction 1, s^{-1} and L/s · gmol
K_1 = equilibrium constant of reaction 1, mol/L
K_2 = equilibrium constant of reaction 2, mol/L
M_o = initial concentration of Na_2CO_3 in solution, mol/L
Q = gas flow rate, L/s
r = rate of desorption of CO_2, mol/L · s
R = sum of mass transfer and reaction resistances, Eq. 12, s · mol/L
t = time, s
T = temperature, K
V = volume of liquid phase, L

Subscripts

aq = aqueous phase
eq = equilibrium
g = gas phase

Superscripts

o = infinite dilution
i = gas–liquid interface

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Manuscript received May 24, 1990, and revision received Sept. 6, 1990.