discussions on the mechanism of adsorption. This work was supported in part by Grants from the General Motors Corporation, Mobil Oil, and a National Science Foundation Energy Related Traineeship.

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Batch Absorption of CO₂ by Free and Microencapsulated Carbonic Anhydrase

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The rates of absorption of CO_2 into aqueous buffered solutions containing free carbonic anhydrase and carbonic anhydrase microencapsulated in cellulose nitrate microcapsules were measured in a slurry reactor. Using a pseudo-steady-state model to describe the absorption process, it was possible to determine gas–liquid mass transfer coefficients and the effectiveness factor for the microencapsulated enzyme from the experimental data.

Introduction

Batch absorption techniques are important in the measurement of reaction rate constants by manometric methods (Dixon, 1974). This problem is of general interest in the study of transients in multiphase chemically reacting systems and in the analysis of slurry adsorbers (Mehta and Calvert, 1967; Misic and Smith, 1971; Komiyama and Smith, 1975) and reactors. In this paper, we study the batch absorption of CO_2 into aqueous buffered solutions containing the enzyme carbonic anhydrase both free in solution and microencapsulated in cellulose nitrate microcapsules.

The pseudo-steady-state approach of Danckwerts (1970) for describing batch absorption systems is used to analyze the data. By assuming that the amount of reaction taking place in the near vicinity of the gas bubbles is negligible in comparison with the amount of reaction taking place in the bulk liquid, one can derive simple expressions for the rate of change of the bulk concentration of the reacting species in terms of mass transfer coefficients. Previous workers have assumed that the flux of dissolved gas through the free liquid surface in the absorber is negligible in comparison to the flux of gas from the gas bubbles to the liquid. In our experimental system, this assumption is found to be quite accurate. Since the ratio

of catalyst particle volume to free liquid volume in the reactor used is very small, steady-state effectiveness factors can describe the rate of reaction of the microencapsulated enzyme in this unsteady-state system.

We measure the rate of absorption of CO_2 into an aqueous Veronal buffer solution containing the enzyme carbonic anhydrase in homogeneous solution, as well as in cellulose nitrate microcapsules by following the change in pH of the solution as a function of time. The rate and equilibrium constants for all the chemical reactions taking place in this system have been studied previously. The nonenzymatic reactions have been well summarized by Danckwerts and Sharma (1966) and Suchdeo and Schultz (1974) among others. Roughton and Booth (1946) and Lindskog et al. (1971) have reported the enzymatic rate parameters and several of the enzyme properties. Chang (1972) has reported the microencapsulation of carbonic anhydrase in cellulose nitrate microcapsules, but little quantitative information is available on the effectiveness of the microcapsules in enhancing CO_2 absorption. Using equilibrium and rate constants from the literature, we calculate the change in pH of the solution as a function of time with only one parameter, the liquid phase mass transfer coefficient from the bubble to the liquid. Values of this pa-

slurry absorbers by Misic and Smith (1971) and Komiyama and Smith (1975). Using the estimated mass transfer coefficients, we then evaluate the effectiveness factor for the microencapsulated enzyme. In the next section, we discuss the assumptions involved in the model used to study the batch absorption of a pure gaseous component i accompanied by homogeneous chemical reaction in the liquid phase and heterogeneous reaction within catalyst particles.

Theory

Consider a slurry reaction system where a gas of pure component i is continuously dispersed through a solution with which it can react. Reactions with absorbed gas can take place in the homogeneous phase, as well as in the heterogeneous phase (catalyst particles). The macroscopic mass balance (Slattery, 1972) for component i, using the liquid volume V_L as the control volume is given by

$$\frac{d}{dt} \int_{V_L} c_i dV = - \int_{A_L} c_i(\mathbf{v}_i - \mathbf{w}) \cdot \mathbf{n} dA + \int_{V_L} r_i dV \quad (1)$$

where c_i is the molar concentration of component i in the liquid phase, r_i is the intrinsic rate of reaction of i in the liquid, $\mathbf{v}_i$ is the mass average velocity of component i, and $\mathbf{w}$ is the velocity of the control volume interfacial area A_L relative to a stationary coordinate system. The total area of the control volume A_L consists of the gas–liquid interfacial area A_g, the free surface liquid area A_f, and the particle-liquid area A_p.

The area integral in eq 1 can be written as (Bird et al., 1960)

$$\int_{A_L} c_i(\mathbf{v}_i - \mathbf{w}) \cdot \mathbf{n} dA = \int_{A_L} c_i(\mathbf{v}^* - \mathbf{w}) \cdot \mathbf{n} dA$$
$$+ \int_{A_L} \mathbf{J}_i^* \cdot \mathbf{n} dA \quad (2)$$

where $\mathbf{J}_i^*$ is the molar diffusive flux of component i relative to the molar average velocity $\mathbf{v}^*$. For dilute solutions one can assume $\mathbf{v}^* \approx \mathbf{w}$ and eq 2 then becomes

$$\int_{A_L} c_i(\mathbf{v}_i - \mathbf{w}) \cdot \mathbf{n} dA \approx A_g\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_g$$
$$+ A_f\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_f + A_p\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_p \quad (3)$$

where the brackets denote area averages. If the liquid is well stirred, one can assume that the concentration c_i is uniform throughout V_L. If the liquid volume remains constant with time, combination of eq 1 and 2 results in

$$\frac{dc_i}{dt} = -S_g\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_g - S_f\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_f - S_p\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_p + r_i$$

$$(4)$$

where the surface areas per unit volume of liquid are defined as

$$S_g = A_g/V_L; \quad S_f = A_f/V_L; \quad S_p = A_p/V_L \quad (5)$$

and the initial condition is $c_i(0) = c_{i0}$. The estimation of the fluxes of eq 4 is a problem central to the theory of diffusion with chemical reaction. When the system is in steady state, one can calculate an enhancement factor to take into account the effect of chemical reaction on the rate of absorption of the gas. This can be done by means of several models including the film theory, penetration theory, and the surface renewal theory. This approach, strictly speaking, is not valid for transient systems since the bulk concentration of component i is continually changing. This in turn will affect the mass

taking place in the film surrounding the gas bubbles is very small in comparison to the amount of reaction taking place in the bulk fluid. This pseudo-steady-state situation allows the fluxes in eq 4 between gas and liquid phases to be expressed in terms of mass transfer coefficients and suitable driving forces

$$- \langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_g = k_L(c_i^* - c_i) \quad (6)$$

$$- \langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_f = k_{Lf}(c_{if}^* - c_i) \quad (7)$$

In eq 6 and 7 k_L and k_{Lf} represent mass transfer coefficients between gas bubble and bulk liquid and between bulk liquid and free surface, respectively. The quantity c_i^* is the liquid phase concentration of component i in equilibrium with the gas-phase concentration in the gas bubbles while c_{if}^* is the same concentration in equilibrium with the gas phase concentration of component i at the free interphase. The concentration c_i^* can be calculated using the Henry's law constant He (Smith and Van Ness, 1975)

$$c_i^* = pc/\text{He} \quad (8)$$

where p is the partial pressure of component i in the gas and c is the total liquid phase molar concentration.

For the reaction taking place in the solid catalyst, one can show that

$$- S_p\langle \mathbf{J}_i^* \cdot \mathbf{n} \rangle_p = \eta \left(\frac{V_p}{V_L}\right) \hat{r}_{ib} \quad (9)$$

where V_p is the volume of particles, $\hat{r}_{ib}$ is the reaction rate in the solid at bulk fluid conditions and η is an effectiveness factor defined as the actual rate of reaction divided by the rate at bulk fluid conditions. Lewis and Paynter (1971) have shown that the steady-state η will be valid under unsteady-state conditions if the ratio of catalyst to liquid volume is small. In our experiments, this ratio was made 2×10^{-3}. Combination of eq 4, 6, 7, and 9 results in

$$\frac{dc_i}{dt} = S_g k_L(c_i^* - c_i) - S_f k_{Lf}(c_i - c_{if}^*)$$

$$+ \eta \left(\frac{V_p}{V_L}\right) \hat{r}_{ib} + r_i \quad (10)$$

The pseudo-steady state assumption allows one to use the effectiveness factor calculated for steady-state conditions. For linear reaction kinetics, η is independent of the concentration of the reactant. For more complex rate expressions, η will be a function of c_i. The way η is defined includes the effect of the liquid phase mass transfer resistance at the liquid–particle interface (Fink et al., 1973; Wadiak and Carbonell, 1975a,b). Recent work on the batch absorption of gases in slurries has neglected the second term on the right-hand side of eq 10, that dealing with the mass transfer of dissolved gas from the liquid to the free surface. We will do the same in this work, thus reducing eq 10 to the form

$$\frac{dc_i}{dt} = S_g k_L(c_i^* - c_i) + \eta \left(\frac{V_p}{V_L}\right) \hat{r}_{ib} + r_i \quad (11)$$

This is the starting point for our analysis of CO_2 absorption.

Experimental Section

Experiments were first performed by absorbing CO_2 into aqueous Veronal buffer solutions in the absence of enzyme. A diagram of the apparatus is shown in Figure 1. A 400-mL glass beaker containing 300 mL of a 0.03 M Veronal buffer solution (pH 9.7) was immersed in a constant-temperature
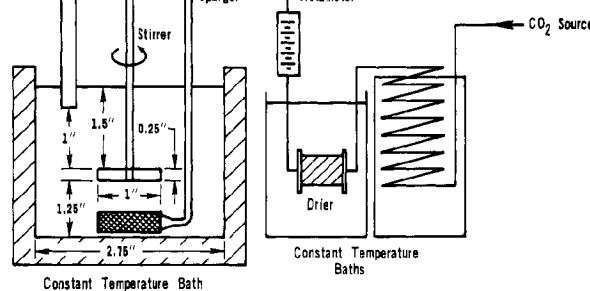
Figure 1. Experimental apparatus (not drawn to scale).

bath at 5 °C. A glass or stainless steel stirrer and a pH combination electrode were placed in the beaker as shown in Figure 1. A gas sparger was introduced into the solution with CO_2 gas flowing at flow rates of either 41 cm^3/min or 61 cm^3/min at 5 °C and 1 atm depending on the experiment. Simultaneously, the time and pH of the solution were recorded at every 0.1 pH interval change. The stirrer speed was measured at 840 rpm using a stroboscope.

A second set of experiments was performed with 1 mg of carbonic anhydrase (bovine, Sigma Chem. Co.) mixed in the same buffer solution, and the corresponding change in pH with time was recorded.
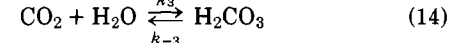
Cellulose nitrate microcapsules containing carbonic anhydrase were made by the procedure described by Paine and Carbonell (1975), with a few modifications. The aqueous hemoglobin solution was filtered using a Whatman No. 1 filter paper, and the separation of the microcapsules was expedited by centrifugation on a bench scale centrifuge. The microcapsules were rinsed 5 to 6 times in the same Veronal buffer. Approximately 50 mg of enzyme was added in 2.5 mL of the hemoglobin solution, resulting in an enzyme concentration of 20 mg/mL.

Approximately 0.6 mL of microcapsules was added to the 300 mL of 0.03 M Veronal solution and the same procedure of measuring the change in pH as a function of time was followed. The experiments using the free and microencapsulated enzyme were done with a gas flow rate of 41 cm^3/min. The volume of microcapsules was measured using a calibrated centrifuge tube. A void fraction of 0.33 was assumed.

The CO_2 source was 99.5% pure liquid CO_2. Tygon tubing of $\frac{1}{4}$-in. i.d. was used for gas transferral. The gas flowed into two ice baths in $\frac{1}{4}$-in. o.d. stainless steel tubing. The gas flowed through a total of 25 coils wound at a $4\frac{1}{2}$-in. diameter and through a Pyrex drying tube containing Drierite filler inserted in an ice bath. Two Whatman GF/A filter disks were used to prevent dust particles of Drierite from reaching the sparger. The gas was then passed through a rotameter that had been calibrated by using a standard soap bubble meter at 5 °C and 1 atm. The sparger was a Kimax #12C sparger. The constant temperature bath used is a Neslab Model RTE-8, and the pH meter is a Leeds and Northrup Model 74-10 with a standard combination electrode.

CO$_2$ Absorption Kinetics

The absorption of CO_2 into buffered aqueous solutions containing carbonic anhydrase is accompanied by several chemical reactions (Danckwerts and Sharma, 1966; Suchdeo and Schultz, 1974; Sherwood, 1937)

$$H^+ + V^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HV \tag{12}$$

$$CO_2 + H_2O \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} H_2CO_3 \tag{14}$$

$$CO_2 + OH^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} HCO_3^- \tag{15}$$

$$HCO_3^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} H^+ + CO_3^{2-} \tag{16}$$

$$H^+ + OH^- \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} H_2O \tag{17}$$

$$CO_2 + H_2O \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} H_2CO_3 \tag{18}$$
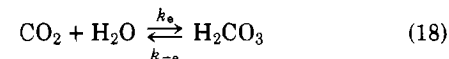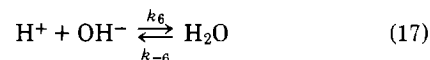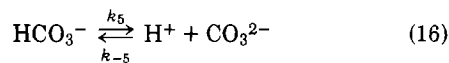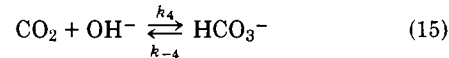
The first reaction is the combination of a hydronium and Veronal ion to yield Veronal. Reaction 14 is the naturally occurring reaction in water, while reaction 18 is the same reaction catalyzed by carbonic anhydrase. Following Suchdeo and Schultz (1974), we assume that reactions 12, 13, 16, and 17 are so fast that the concentrations of reactants and products are related by their equilibrium constants

$$K_1 = \frac{k_1}{k_{-1}} = \frac{c_{HV}}{c_H c_V} \tag{19}$$

$$K_2 = \frac{k_2}{k_{-2}} = \frac{c_{H_2CO_3}}{c_H c_{HCO_3}} \tag{20}$$

$$K_5 = \frac{k_5}{k_{-5}} = \frac{c_H c_{CO_3}}{c_{HCO_3}} \tag{21}$$

and

$$K_6 = \frac{k_6}{k_{-6}} = \frac{c_{H_2O}}{c_H c_{OH}} \tag{22}$$

Reactions 14 and 15 are rate-limiting, and these have equilibrium constants defined as

$$K_3 = \frac{k_3}{k_{-3}} = \frac{c_{H_2CO_3}}{c_{CO_2} c_{H_2O}} \tag{23}$$

and

$$K_4 = \frac{k_4}{k_{-4}} = \frac{c_{HCO_3}}{c_{CO_2} c_{OH}} \tag{24}$$

The forward and reverse enzymatic reactions have been found to be of the Michaelis–Menten type (Roughton and Booth, 1946)

$$r_f = \frac{k_e E_0 c_{CO_2}}{K_m + c_{CO_2}} \tag{25}$$

$$r_b = \frac{k_{-e} E_0 c_{H_2CO_3}}{K_m' + c_{H_2CO_3}} \tag{26}$$

here K_m, K_m' are the Michaelis–Menten constants, k_e, k_{-e} are turnover numbers, and E_0 is the enzyme concentration. Since at equilibrium the forward and backward rates have to be equal and eq 23 must be satisfied, it is easy to show that (Roughton and Booth, 1946)

$$k_e = k_{-e} \tag{27}$$

$$K_m' = K_m K_3 c_{H_2O} \tag{28}$$

First we consider the case where the enzyme is free in solution and there are no microcapsules present. Applying eq 11 to each of the components in the chemical reactions 12–18, we obtain

$$\frac{dc_H}{dt} = k_{-1} c_{HV} - k_1 c_H c_V + k_{-2} c_{H_2CO_3} - k_2 c_H c_{HCO_3}$$
$$+ k_5 c_{HCO_3} - k_{-5} c_H c_{CO_3} + k_{-6} c_{H_2O} - k_6 c_H c_{OH} \tag{29}$$

$$+ k_2 c_H c_{HCO_3} - k_{-2} c_{H_2CO_3} \quad (30)$$

$$\frac{dc_{CO_2}}{dt} = S_g k_L (c_{CO_2}{}^* - c_{CO_2}) + k_{-3} c_{H_2CO_3} - k_3 c_{CO_2} c_{H_2O}$$
$$+ k_{-4} c_{HCO_3} - k_4 c_{CO_2} c_{OH} - r_f + r_b \quad (31)$$

$$\frac{dc_{HCO_3}}{dt} = k_{-2} c_{H_2CO_3} - k_2 c_H c_{HCO_3} + k_4 c_{CO_2} c_{OH} - k_{-4} c_{HCO_3}$$
$$+ k_{-5} c_H c_{CO_3} - k_5 c_{HCO_3} \quad (32)$$

$$\frac{dc_{CO_3}}{dt} = k_5 c_{HCO_3} - k_{-5} c_H c_{CO_3} \quad (33)$$

$$\frac{dc_{HV}}{dt} = k_1 c_H c_V - k_{-1} c_{HV} \quad (34)$$

$$\frac{dc_{OH}}{dt} = k_{-4} c_{HCO_3} - k_4 c_{CO_2} c_{OH} + k_{-6} c_{H_2O} - k_6 c_H c_{OH}$$
$$\quad (35)$$

$$\frac{dc_{H_2O}}{dt} = k_{-3} c_{H_2CO_3} - k_3 c_{CO_2} c_{H_2O}$$
$$+ k_6 c_H c_{OH} - k_{-6} c_{H_2O} - r_f + r_b \quad (36)$$

The forms of the rate terms r_i in eq 11 have been taken from Danckwerts and Sharma (1966). It is possible to combine eq 29–36 into the four simpler independent expressions

$$\frac{dc_H}{dt} = -\frac{dc_{HV}}{dt} - \frac{dc_{H_2CO_3}}{dt} + \frac{dc_{CO_3}}{dt} - \frac{dc_{H_2O}}{dt} \quad (37)$$

$$\frac{dc_{H_2CO_3}}{dt} = -\frac{dc_{HCO_3}}{dt} - \frac{dc_{OH}}{dt} - \frac{dc_{H_2O}}{dt} - \frac{dc_{CO_3}}{dt} \quad (38)$$

$$\frac{dc_{CO_2}}{dt} = S_g k_L (c_{CO_2}{}^* - c_{CO_2}) + \frac{dc_{OH}}{dt} + \frac{dc_{H_2O}}{dt} \quad (39)$$

$$\frac{dc_{H_2O}}{dt} + \frac{dc_{OH}}{dt} = k_{-3} c_{H_2CO_3} - k_3 c_{CO_2} c_{H_2O} - r_f + r_b$$
$$+ k_{-4} c_{HCO_3} - k_4 c_{CO_2} c_{OH} \quad (40)$$

One can differentiate eq 19–22 to obtain the time derivatives of c_{HV}, c_{HCO_3}, and c_{H_2O}. When these time derivatives and the equilibrium expressions (19–22) are substituted into the equations above, we find that the entire system of reaction equations reduces to three expressions for the concentration of CO_2, H^+, and H_2CO_3

$$\frac{dc_{CO_2}}{dt} = S_g k_L (c_{CO_2}{}^* - c_{CO_2}) - F \quad (41)$$

$$\frac{dc_H}{dt} = \frac{1}{A} \left[\frac{BD}{AC - BD} \left(E + \frac{A}{D} \right) + E \right] F \quad (42)$$

$$\frac{dc_{H_2CO_3}}{dt} = \frac{D}{AC - BD} \left(E + \frac{A}{D} \right) F \quad (43)$$

where

$$A = \left[1 + \frac{c_0 K_1}{(1 + K_1 c_H)^2} + \frac{2 K_5 c_{H_2CO_3}}{K_2 c_H{}^3} + \frac{c_{H_2O}}{(1 + K_6 c_H) c_H} \right] \quad (44)$$

$$B = \frac{K_5}{K_2 c_H{}^2} - 1 \quad (45)$$

$$C = 1 + \frac{K_5}{K_2 c_H{}^2} + \frac{1}{K_2 c_H} \quad (46)$$

$$D = \frac{c_{H_2CO_3}}{K_2 c_H{}^2} + \frac{2 K_5 c_{H_2CO_3}}{K_2 c_H{}^3} \quad (47)$$

$$E = \frac{K_6 c_H}{K_6 c_H + 1} \quad (48)$$

$$F = \left(k_3 + \frac{k_4}{K_6 c_H} \right) c_{CO_2} c_{H_2O} - \left(k_{-3} + \frac{k_{-4}}{K_2 c_H} \right) c_{H_2CO_3}$$
$$+ r_f - r_b \quad (49)$$

and

$$c_0 = c_{HV} + c_V \quad (50)$$

The magnitude of the $K_6 c_H$ term in E, eq 48, is so much greater than 1 for the pH range of these experiments, that in a very good approximation, one can write eq 42 and 43 as

$$\frac{dc_{CO_2}}{dt} = S_g k_L (c_{CO_2}{}^* - c_{CO_2}) - F \quad (51)$$

$$\frac{dc_H}{dt} = \frac{(B + C)}{(AC - BD)} F \quad (52)$$

$$\frac{dc_{H_2CO_3}}{dt} = \frac{(A + D)}{(AC - BD)} F \quad (53)$$

These are the model equations eventually solved numerically.

Estimates of all the rate and equilibrium constants in eq 41–49 were obtained from the existing literature. These are shown in Table I. All values are for a temperature of 5 °C and an ionic strength of 0.042 when ionic strength information was available. The ionic strength did not vary significantly from this value throughout our experiments. The total buffer concentration, c_0 is 0.03 M. The value of $c_{CO_2}{}^*$ from eq 8 was 6.279×10^{-2} g-mol/L using $p = 1$ atm. It was not possible to correct the Henry's law constant He to account for the solubility of CO_2 in aqueous solution in the presence of Veronal ion. Values of equilibrium constants were not corrected for values of activity coefficients of ionic species. As a result, there are probably some inaccuracies in the values of the equilibrium and rate constants in Table I.

The enzyme Michaelis–Menten constants K_m and K_m' are also listed in Table I. It was found by Roughton and Booth (1946), that the turnover number k_e depends strongly on the pH of the solution. Lindskog et al. (1971) have summarized these results. From the data available in Lindskog et al. (1971), we derived an empirical equation for k_e as a function of pH

$$k_e = k_e(pH = 9) \left[.261(pH) - 1.349 \right] \quad (54)$$

where k_e (pH = 9) is 6×10^7 min^{-1}. Using these values of the kinetic and equilibrium constants, eq 51–53 were solved nu-
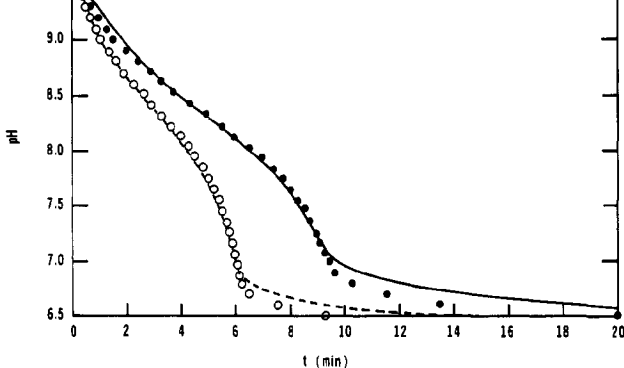
Figure 2. Experimental and calculated values of pH as a function of time. Buffer only, with no enzyme present. Experimental points for gas flow rate of 41 cm³/min (●). Theory (—) with $S_g k_L$ = 0.095 min⁻¹. Experimental points for gas flow rate of 61 cm³/min (○). Theory (- - - -) with $S_g k_L$ = 0.195 min⁻¹.
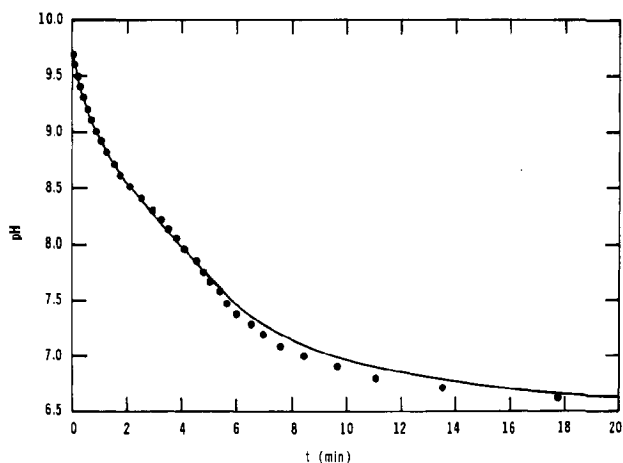

Figure 3. Experimental and calculated values of pH as a function of time. Enzyme (1 mg) in solution. Experimental points for gas flow rate of 41 cm³/min (●). Theory (—) with $S_g k_L$ = 0.090 min⁻¹.

merically using the Runge–Kutta method of fourth-order accuracy (Hildebrand, 1962). The value of $S_g k_L$ was treated as a parameter, chosen to obtain the best possible fit with the experimental data of pH vs. time. The enzyme concentration E_0 in moles per liter was calculated using a molecular weight of 30 000 (Lindskog et al., 1971).

Figure 2 shows the comparison between the calculated and experimental values of pH as a function of time for CO₂ absorption into the buffer with no enzyme present, at two different gas flow rates: 41 and 61 cm³/min. The values of $S_g k_L$ for these two cases were 0.095 and 0.195 min⁻¹, respectively. The good agreement between theory and experiment justifies the use of eq 11 to describe the absorption process and proves the approximations made in its derivation to be valid, including the pseudo-steady-state approximation, the assumption of negligible reaction in the stagnant film around the gas bubbles, and the neglect of mass transfer at the free surface of the liquid. The slight disagreement for large times near equilibrium is probably due to the above-mentioned inaccuracies in some of the values in Table I as well as experimental error.
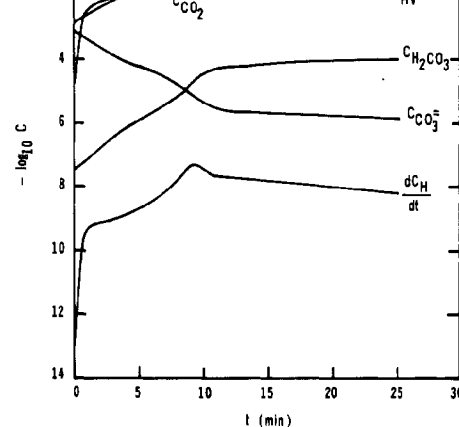
Figure 4. Calculated concentrations of intermediates in buffer system with no enzyme, $S_g k_L$ = 0.095 min⁻¹.

In similar slurry absorbers, Misic and Smith (1971) obtained S_g values of 0.078 to 0.28 cm⁻¹ when the gas flow rates were in the range 42–132 cm³/min. Our values of S_g should be close to these due to the similarities in slurry geometries. Using their figures S_g = 0.076 cm⁻¹ when the gas flow rate is 41 cm³/min and S_g = 0.113 cm⁻¹ when the flow rate is 61 cm³/min, assuming the S_g dependence on flow rate is linear. Using these estimates, we obtain values of k_L = 2 × 10⁻² cm/s and 2.8 × 10⁻² cm/s. These are in excellent agreement with estimates using mass transfer correlations for slurry absorbers.

The Calderbank and Moo-Young (1961) correlation gives estimates of 2.8 × 10⁻² cm/s for bubbles greater than 2.5 mm in diameter and 6.6 × 10⁻³ cm/s for bubbles less than 1 mm in diameter. Hughmark (1967) obtained a correlation that predicts k_L to be approximately 5 × 10⁻² cm/s. The total surface areas around the gas bubbles using these values of S_g are A_g = 22.8 and 84 cm² at the two different flow rates.

In Figure 3 we show the comparison between theory and experiment when 1 mg of carbonic anhydrase is added to the buffer solution. The value of $S_g k_L$ used is 0.09 min⁻¹, since the flow rate of gas was approximately 41 cm³/min, the same as in one of the previous experiments using buffer only. The agreement between theory and experiment is excellent throughout the entire range of pH.

The value of $S_g k_L$ was changed from 0.095 to 0.090 min⁻¹ due to the fact that a slightly narrower impeller was used in these experiments. The value of 0.090 min⁻¹ gave better agreement with experimental data. Values of $S_g k_L$ were found to be very sensitive to changes in absorber geometry.

For times less than 1 min, the absorption term in eq 51 governs the behavior of the system, causing a rapid increase in the concentration of CO₂ in the liquid and a rapid increase in the time derivative of the hydrogen ion concentration. This is shown in Figure 4 where the concentrations of the intermediate species are plotted as a function of time for the buffer experiment without enzyme. After 1 min, the first term in F, eq 49, dominates with both the k_3 and k_4 terms being important. This indicates that in the pH range from 9.4 to about 8.5 reactions 24 and 25 in the buffer are both occurring at approximately equal rates. Below pH 8, the buffer loses much of its buffering capacity and a sudden drop in pH is experienced. This portion of the pH–time curve is extremely sensitive to the choice of $S_g k_L$. The pH vs. time curves are concave upward for very short times and concave downward in the pH range from 8.5 to about 7.5, where they become concave up-

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