The Absorption of Carbon Dioxide by Weak Base Ion Exchange Resins

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A study of the feasibility of using ion exchange resin systems for carbon dioxide absorption from gas streams was completed with the conclusion that such a system could compete very successfully with atmospheric control systems now in use. A detailed study of such a system based on polyethylenimine showed that this material is superior to any of the commercially available weak base resins tested. The kinetic data obtained correlated very well when a model was postulated that was based on diffusive transfer through a gas film, a water film, and the resin particle in series, with diffusion within the resin particle as the rate determining step.

The purpose of this investigation was to determine the feasibility of using ion exchange resin systems for carbon dioxide absorption from gas streams. With the advent of vehicles such as submarines and spacecraft which remove man from his natural environment for long periods of time, special methods are necessary to sustain him in a small, finite atmosphere. In particular, it is important that the water and carbon dioxide continuously introduced into the atmosphere be continuously and efficiently removed.

For various reasons, present practices are inadequate. Monoethanolamine scrubbers, currently in use in submarines, utilize a toxic, volatile, combustible liquid and require high power loads. Lithium hydroxide scrubbers involve an irreversible reaction, thus requiring large inventories of fresh material.

The weak base, ion exchange resins investigated herein have potential advantages over present atmosphere control methods in that they are inert, stable, have large capacities for carbon dioxide and water, and are easy to regenerate. This study is important from a theoretical point of view as well, since insofar as we know, it represents the first time that solid state, ion exchange materials have been utilized for gas absorption of this nature.

The groundwork for this investigation was laid by Robins (*1*), who found that dilute solutions of poly-N-methylethylenimine and other similar materials could absorb carbon dioxide, and by Saber (*2*), who was able to synthesize a solid resin from polyethylenimine (PEI) that, when in the basic state, has a strong acid capacity of over 9 meq./g. of resin. (By comparison, potassium hydroxide has a strong acid capacity of 17.9 meq./g.)

The study involved the determination of the behavior of several resin systems, including PEI and some commercial resins, under a variety of conditions of temperature, carbon dioxide concentration, and humidity, and a detailed analysis of the absorption data to develop a reasonable model for the mechanism by which carbon dioxide was absorbed.

EXPERIMENTAL WORK

Resin Preparation

The monomer unit of PEI is $+\, CH_2 - CH_2 - NH\, +$, which arises from the opening of the three membered ethylenimine ring. For steric reasons, only every second nitrogen group can be activated (accounting for the strong acid capacity of one half the potassium hydroxide value). The activated unit can thus be written as $+\, CH_2 - CH_2 - NH - CH_2 - CH_2 - NH_2{}^+ - +$.

The PEI resin was prepared according to the method of Saber (*2*) by dissolving PEI in methanol and reacting it at 90°C. for 1 hr. with epichlorohydrin (ECH), with a 4.2 PEI/ECH molar ratio. The resulting viscous liquid was dried, pulverized, and extracted with methanol to remove uncross-linked PEI. The resulting material was dried and sieved, with the 28- to 48-mesh cut retained for study.

Since an acid base neutralization reaction is required for resin operation, the higher the initial *p*H of the material, the higher its capacity. Therefore, all resins were soaked for a minimum of 12 hr. in an agitated 1 M potassium hydroxide solution to convert them to the hydroxide form. This potassium hydroxide solution was decanted and the particles washed with distilled water down to *p*H 11 to remove excess potassium hydroxide. In addition, Robins (*1*) found that chloride ion catalyzes the hydration of carbon dioxide. Thus, the final step in resin preparation was to soak them in 1 M potassium chloride solution.

Other resins studied include Dowex WGR (in which reactive nitrogen groups arise from tetraethylene pentamine), Dowex-3, Dowex-4, and Rohm & Haas Amberlite IRA-93, a styrene-divinyl benzene copolymer containing tertiary amine groups.

To determine the suitability of these materials as carbon dioxide absorbents, the strong acid capacity was measured by

TABLE 1. STRONG ACID CAPACITY AT 20°C.

Resin	Capacity, meq./dry g.
Dowex-3	3.1
Dowex-4	3.5
IRA-93	4.4
Dowex-WGR	5.8
PEI-ECH	9.1

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titration with 0.2N hydrochloric acid. The results are shown in Table 1. With the exception of IRA-93, for which Rohm & Haas data were used, each point in Table 1 represents an average of two replicate runs, with differences between the two runs in each case being less than 5% of the reported value.

Although a high capacity is desirable for the work, the lower capacity materials could not be ruled out until the relative rates of absorption were determined.

RESIN CHARACTERIZATION

Absorption

The 28- to 48-mesh resin beads were packed to a depth of 1 ft. in a column of borosilicate glass of 44 mm. I.D. with a 2 mm. thick wall. Since the resin particles were low in density and moist, it was necessary to design the bed to prevent gas channeling. This was done by forcing the gas to follow a tortuous path through the bed by use of 6-mesh Du Pont "Vexar" screens and brass separators dividing the column into 1-in. sections. A few random holes were drilled into each separator (less than 25% of the surface was perforated). A 65-mesh screen was cemented over the holes to prevent transfer of particles from one section to another, and the separators were sealed against the walls by O ring gaskets.

The column was assembled as follows: The bottom plate was put into place and the first "Vexar" screen laid flat on top of it. Additions of wet resin and a small amount of 1M potassium chloride solution were alternated with mechanical vibration until the meshes were completely filled. These steps were repeated until eight screens were filled, each screen rotated between 30 and 45 deg. with respect to its predecessor. A perforated brass plate was then worked down the column until it contacted the completed section, whereupon the next section was begun.

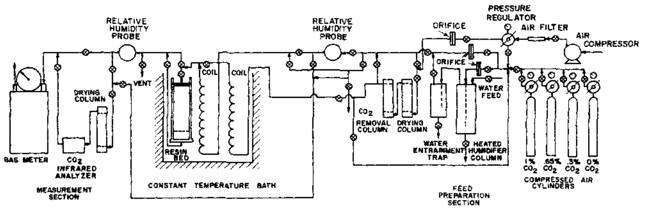

Fig. 1. Experimental apparatus for absorption studies.

The column was drained of excess liquid and placed in a constant temperature bath, and the resin was prepared for study by passing 100% relative humidity, carbon dioxide free air at the same temperature through the column until no evolution of carbon dioxide was detected. During a run, prepared mixtures of bone dry air containing fixed amounts of carbon dioxide were humidified to a desired level by bubbling through water (initially carbon dioxide free but at carbon dioxide equilibrium prior to opening the valves to the column), were brought to column temperature, and were passed through the column. The inlet and outlet gas humidity were measured by wide-range probes. The outlet carbon dioxide concentration was monitored by use of an infrared analyzer, the gas being first passed through a Drierite column for complete water removal. Intermittent readings of cumulative gas flow (by use of a dry test meter) and bath temperature were also taken. A run was considered completed when the inlet and outlet carbon dioxide concentrations coincided. A diagram of the apparatus is shown on Figure 1.

REGENERATION

The procedure followed here was essentially the same as for an absorption run, except that carbon dioxide free air of the proper humidity was used. Normally, a regeneration run would be made at the same temperature as the preceding absorption run, and regeneration would thereafter be completed at 70°C to remove the last traces of carbon dioxide. At the conclusion of a regeneration run, the bed was wetted down with potassium chloride solution at *p*H 11 to prepare it for the next absorption run.

RANGE OF VARIABLES

Experiments were performed at temperatures ranging from 0° to 70°C., relative humidities ranging from 0 to 100%, and carbon dioxide contents from 0 to 1.00%.

RESULTS

All resins tested behaved in a similar manner, with the exception that the PEI-ECH resin showed substantially higher capacity for carbon dioxide than did the others. The results reported below will, therefore, be almost exclusively for PEI-ECH, with some comparisons to Dowex WGR, which had the next highest capacity for carbon dioxide.

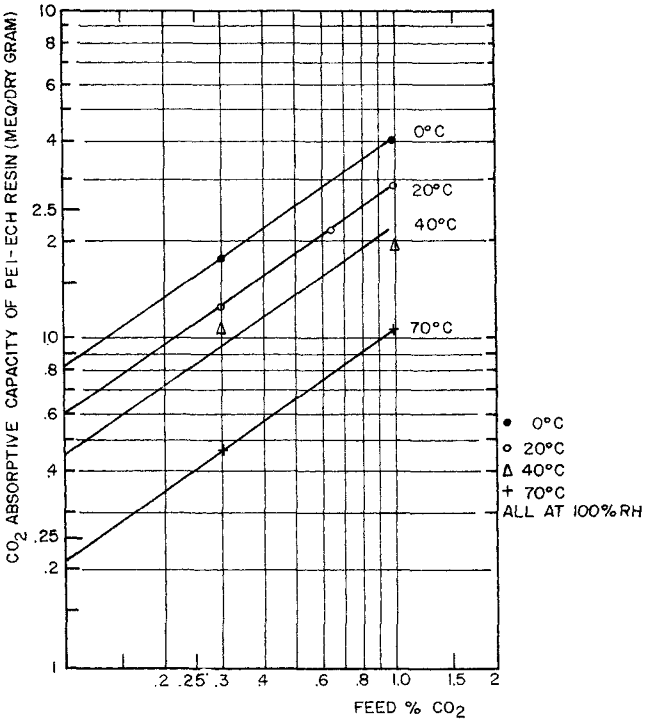

Fig. 2. Equilibrium capacity of resin as a function of temperature and feed gas composition.

For the equilibrium carbon dioxide studies at 100% relative humidity, data were taken at 0°, 20°, 40°, and 70°C. At 20°C., five points were taken, three at 1% carbon dioxide and one each at 0.65 and 0.3% carbon dioxide. At the other temperatures, two points were taken, one at 1% carbon dioxide and one at 0.3% carbon dioxide.

The results obtained were plotted, at the four temperature levels chosen, against feed percent carbon dioxide on Figure 2. The straight lines were assumed in accordance with Equation 1. Dowex WGR had capacities consistently about one half these values, and capacities at lower humidities turned out to be proportional to the humidity. Data on dilute polymer systems in the literature (*1*) indicate that this relationship should follow the Katchalsky and Spitnik modification of the Henderson-Hesselbach equation (*3*), and, accordingly, an equilibrium constant was defined by

$$K = C/(\mathrm{RH})\,(P_{\mathrm{CO}_2}{}^{n}) \qquad (1)$$

Since $n \neq 1$, difficulties arise when an attempt is made to attribute the usual thermodynamic significance to this equilibrium constant, for it has been established (*4*) that ion exchange equilibrium constants are concentration dependent. Since

$$C = sd\,P_{\mathrm{CO}_2} \qquad (2)$$

Equation (1) may be rewritten as

$$K = sd\,P_{\mathrm{CO}_2}{}^{1-n}\,(\mathrm{RH})^{-1} \qquad (3)$$

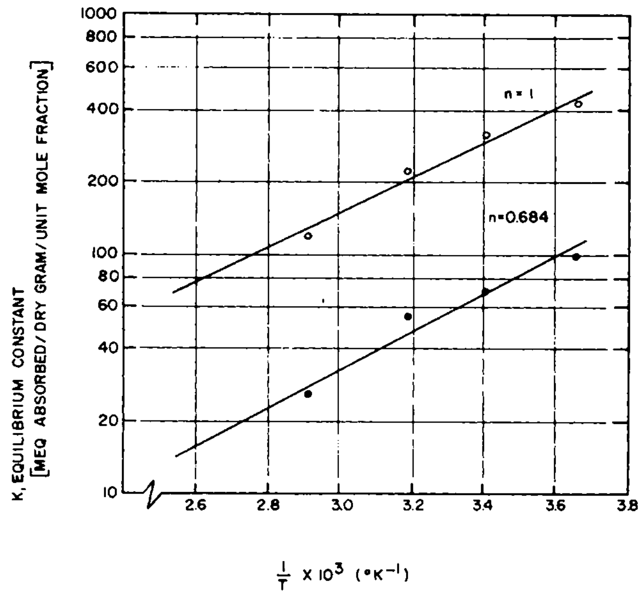

Fig. 3. Equilibrium constant as a function of temperature.

By using regression analysis on the eleven points taken at the four different temperatures, the best value for n was found to be $n = 0.68$ (for Dowex WGR, $n = 0.62$). Figure 3 shows a plot of ln K vs. $1/T$ and indicates a reasonable correlation with temperature. The validity of the straight line correlation assumed is supported by a calculated correlation coefficient of 0.9375. These results may be well expressed by

$$K = 0.0715 \exp\,(-3{,}616/RT) \qquad (4)$$

Data on the rate of uptake of carbon dioxide at various temperatures and concentration levels were correlated by use of a model in which the rate is diffusion controlled. Indications that such a model might work were obtained when it was found that variations in gas flow rate from 0.05 to 0.3 std. cu.ft./min. had no effect on the mass uptake curve.

The postulated model consists of the following steps:

1. Transfer of carbon dioxide from the bulk gas stream across the gaseous boundary layer to a thin liquid film surrounding the spherical resin particle, governed by the equation

$$\text{rate} = k_G\left(P_{\mathrm{CO}_2} - \frac{C_L}{s}\right) \qquad (5)$$

2. Transfer of carbon dioxide across the liquid film to the surface of the solid, governed by the equation

$$\text{rate} = k_L\left(C_L - \frac{C_R}{d}\right) \qquad (6)$$

3. Slow diffusion of carbon dioxide from the surface towards the interior of the particle, governed by Fick's law with a constant diffusion coefficient (with spherical coordinates):

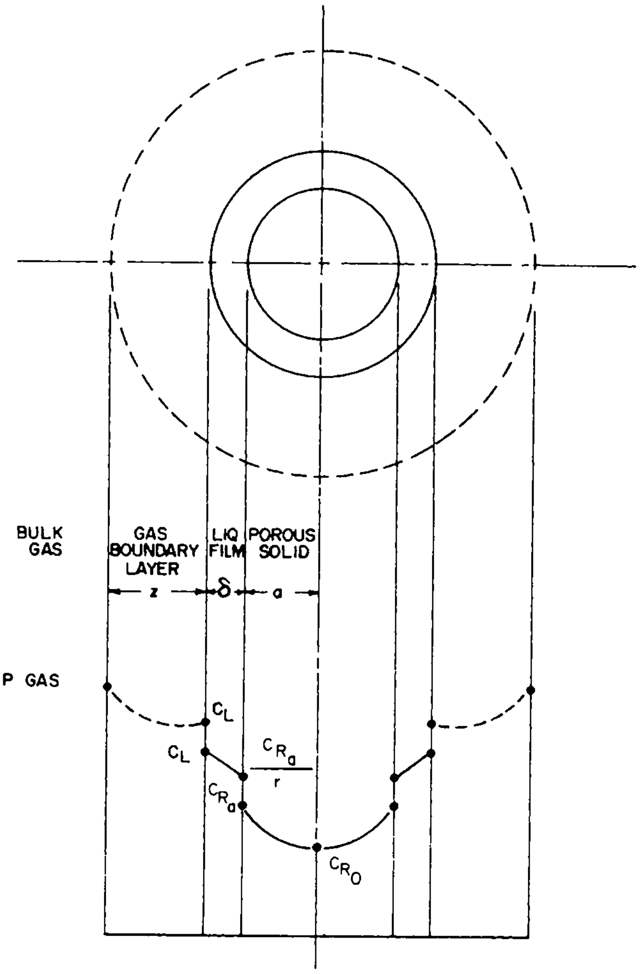

Fig. 4. Model of process and suggested concentration profiles.

$$\frac{\partial C_R}{\partial t} = D\nabla^2 C_R - \text{rate of removal by chemical reaction [see Equation (14)]} \qquad (7)$$

4. Rapid reaction of carbon dioxide with resin inside of particle by

$$R_3\mathrm{NH}^+\ \mathrm{OH}^- + \mathrm{CO}_2 + \mathrm{H_2O} \rightarrow R_3\mathrm{NH}^+\ \mathrm{HCO_3}^- + \mathrm{H_2O} \qquad (8)$$

The model and accompanying profiles are shown in Figure 4. If the material balances are written about the gas boundary layer and the liquid film, and if rate Equations (5) and (6) are taken into account, the concentration of carbon dioxide at the surface of the resin particle is found to be

$$(C_R)_{\text{surface}} - (C_{R0})_{\text{surface}} = [ds\, P_{CO_2} - (C_{R0})_{\text{surface}}] \left[1 - \exp\left(\frac{-\eta t}{2\xi}\right)\right] \quad (9)$$

where

$$\eta = \frac{3k_G k_L}{a\delta ds} \quad (10)$$

$$2\xi = \frac{k_G}{s\delta} + \frac{k_L}{\delta} + \frac{3k_L}{ad} = \frac{adk_G + k_L\,(3\delta s + ads)}{a\delta ds} \quad (11)$$

The terms η and ξ are obtained from the material balance equation written for the liquid film as

$$\frac{\partial^2 C_L}{\partial t} + \left(\frac{k_G}{s\delta} + \frac{k_L}{\delta} + \frac{3k_L}{ad}\right)\frac{\partial C_L}{\partial t} + \left(\frac{3k_G\, k_L}{a\delta ds}\right) C_L = \left(\frac{3k_G\, k_L}{a\delta d}\right) P_{\text{Gas}} \quad (12)$$

In order to obtain Equation (9), one must assume that $\eta << \xi^2$. The justification for this assumption is presented below.

From Equation (9), one can also define the equilibrium value of carbon dioxide concentration at the surface by

$$(C_{R_\infty})_{\text{surface}} = ds\, P_{CO_2} \quad (13)$$

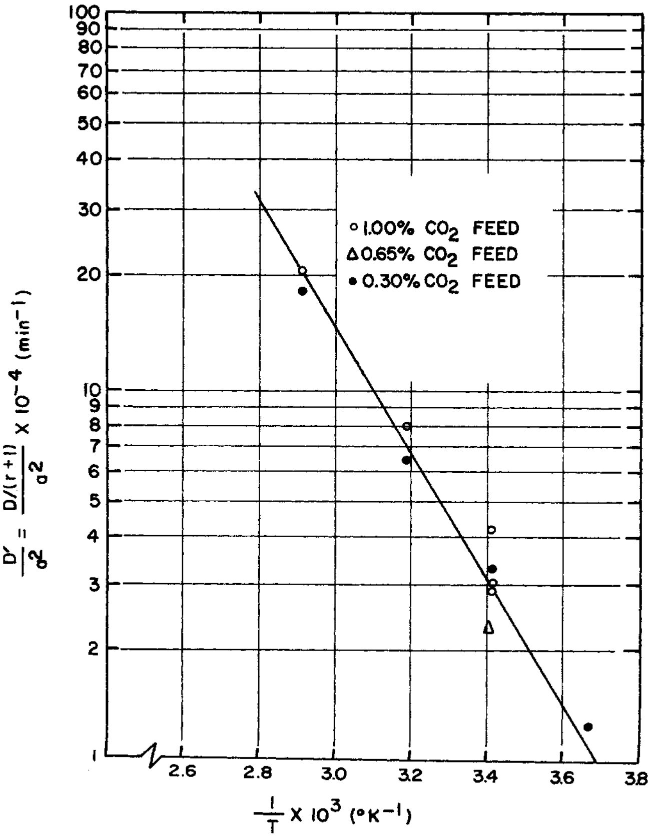

Fig. 5. Fick's law constant (D') as a function of temperature.

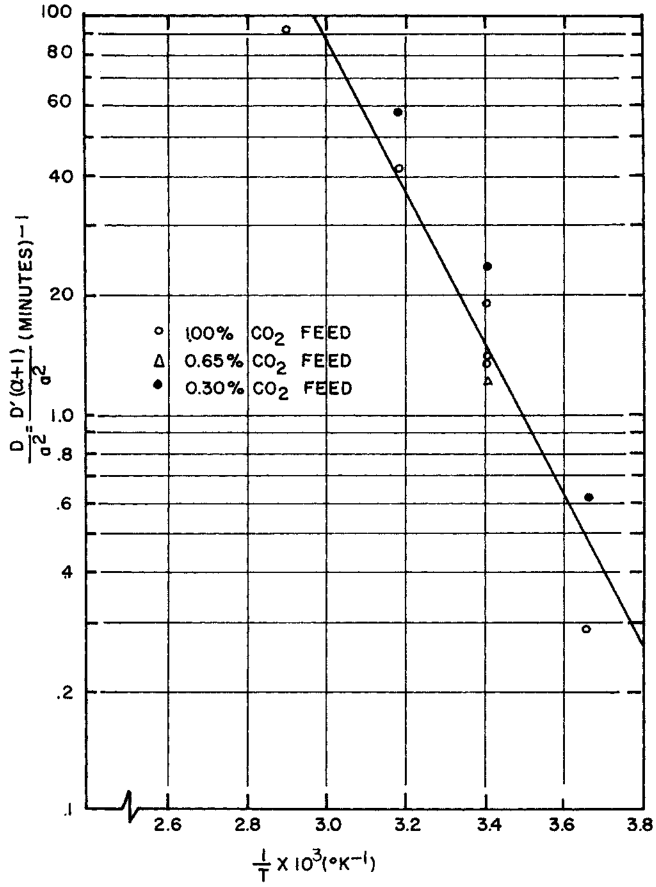

Fig. 6. Diffusion coefficient as a function of temperature.

If it is assumed that the chemical reaction within the particle immobilizes a portion of the diffusing species according to

$$C_{\text{imm}} = \alpha\, C_R \quad (14)$$

and

$$\frac{\partial C_{\text{imm}}}{\partial t} = \frac{\alpha\, \partial C_R}{\partial t} \quad (15)$$

one can follow the procedures presented in Crank (5) to develop an expression for C_R at any position and any time within the spherical particle, assuming no angular concentration dependence. If Equation (15) is substituted in Equation (7), one can write (in spherical coordinates):

$$\frac{\partial C_R}{\partial t} = \frac{D}{\alpha + 1}\nabla^2 C_R = D'\left[\frac{\partial^2 C_R}{\partial r^2} + \frac{2}{r}\,\frac{\partial C_R}{\partial r}\right] \quad (16)$$

If a new variable

$$U = rC_R \quad (17)$$

is defined, Equation (16) becomes

$$\frac{\partial U}{\partial t} = D'\frac{\partial^2 U}{\partial r^2} \quad (18)$$

with boundary conditions

$$@\ t = 0, \quad U = r(C_R)_{r=a} \quad (19)$$

$$@\ r = 0, \quad U = 0 \quad (20)$$

$$@\ r = a, \quad U = a\,[(C_R)_{r=a} + (C_{\text{eq}} - (C_R)_{r=a})\,(1 - \exp(-\beta t))] \quad (21)$$

By use of Laplace transforms, Equation (18) may be integrated over r to yield an expression for $(C_R)_{r=a}$. Integration of this expression over time from $t = 0$ to some time t yields an expression for the cumulative uptake by the particle vs. time:

$$\frac{M_t}{M_\infty} = 1 - \frac{3D'}{\beta a^2} \exp(-\beta t) \left[1 - \sqrt{\frac{\beta a^2}{D'}} \cot \sqrt{\frac{\beta a^2}{D'}} \right] + \left(\frac{6\beta a^2}{\pi^2 D'} \right) \sum_{n=1}^{\infty} \frac{\exp(-D' n^2 \pi^2 t/a^2)}{n^2(n^2\pi^2 - \beta a^2/D')} \Bigg] \qquad (22)$$

where

$$D' = \frac{D}{1+\alpha} \qquad (23)$$

and

$$\beta = \frac{\eta}{2\xi} = \frac{3k_G k_L}{k_G ad + k_L ads} \text{ (approx)} \qquad (24)$$

which can be rewritten as

$$\frac{1}{\beta} = \frac{ad}{3} \left(\frac{1}{k_L} + \frac{s}{k_G} \right) = \frac{ad}{3K_L} \qquad (25)$$

so that

$$\beta = (K_L)\,(d)\,(3/a) \qquad (26)$$

The exponential function $\exp(-\beta t)$ thus reflects three important aspects of carbon dioxide transfer from the gas to the solid, namely, the overall mass transfer coefficient K_L across the gas and liquid films, the distribution coefficient d at the liquid-solid interface, and the surface to volume ratio $3/a$ of the particles.

Equation (15) which gives

$$M_t/M_\infty = \phi\,(\beta a^2/D',\ D't/a^2) \qquad (27)$$

can be compared by trial with experimental values of cumulative uptake of carbon dioxide vs. time as a function of temperature and gas composition. D' and β can then be calculated from the values of D'/a^2 and $\beta a^2/D'$ which characterize the calculated curve which most closely matches the experimental data. D' is, of course, assumed independent of concentration. The results obtained are shown in Figure 5.

To determine the value of α, one can make use of the fact, shown by Robins (*1*), that absorption of carbon dioxide by the resin is entirely in the bicarbonate form, while absorption by the water is almost completely in the carbon dioxide form.

Thus

$$\alpha = d \qquad (28)$$

By using the methods described by Robins, values of d may be calculated, which then can be used to determine D. The values of D determined in this way are shown in Figure 6. The best correlation for D, obtained by least squares, is given by

$$\frac{D}{a^2} = 3.78 \times 10^6 \exp(-8{,}610/RT) \text{ min.}^{-1} \qquad (29)$$

For this equation, the correlation coefficient obtained was 0.985.

The results of the regeneration runs are consistent with this model as well. It was found that a temperature of 70°C. was sufficient to regenerate the resin completely, usually within a matter of minutes.

DISCUSSION

The postulated model is seen to give a reasonable agreement with experiment. The calculated activation energy for diffusion of about 9 kcal./g.-mole is much higher than values reported in the literature for ion exchange reactions; the processes are not the same, however. The values of D obtained from Equation (29), independent of concentration, are of the order that the literature (*6*) would lead one to expect for such systems.

There are certain assumptions implicit in the model which should be emphasized:

1. The particle interior is completely saturated with liquid. This is reasonable for the high humidity runs but becomes less reasonable as the gas humidity decreases. The fact that the rate of absorption appears to be linear with gas humidity indicates that, perhaps, as the humidity decreases, portions of the particle surface dry out and form islands of no activity, while the rest of the particle remains saturated. Or, the density of the material varies inversely with the humidity.
2. The gas temperature and composition are constant in time and space. The validity of these assumptions depends on a small heat of reaction and high enough gas flow rates to produce small gas composition changes. Although Equation (4) is not a true thermodynamic equilibrium constant, the temperature dependence of K does indicate a relatively small heat of reaction. As for composition changes, in all cases the maximum concentration difference across the bed was 20% of the inlet concentration, due to the maintenance of high gas flow rates (< 6 sec. residence time), so that it could be assumed that the model applied to the whole bed, for even that 20% maximum difference decayed in less than 5% of the total reaction time to less than 10% of the inlet value. The ratio M_t/M_∞ for every individual particle should therefore be well represented by the M_t/M_∞ value for the entire bed.
3. $\eta << \xi^2$. This assumption is crucial to the mathematical development. However, it is easy to show that

$$\frac{\eta}{\xi^2} < \frac{6\delta}{ad} \qquad (30)$$

Since δ/a was calculated to be less than 0.08, and since d is of the order of 10^3, this assumption is seen to be valid.

4. k_G, k_L, d, and s are functions of temperature only.

CONCLUSIONS

Estimates based on the results obtained in this study indicate that an atmospheric control system based on polyethylenimine could compete very successfully with atmospheric control systems now in use, provided that the regeneration procedure makes use of the space vacuum to remove the carbon dioxide released upon heating the bed while the simultaneously generated water vapor is condensed prior to venting. Since the rate of absorption is apparently diffusion controlled, an attempt is now being made to increase the surface-to-volume ratio of the resin phase by casting the resin in the form of porous membranes. In this way, it is hoped that the rate of absorption of carbon dioxide by the resin will be increased and the cycle time of the system correspondingly decreased.

ACKNOWLEDGMENT

Financial support of this work was provided by the NASA

Manned Spacecraft Center, under contract No. NAS 9-2792.

The work is based on a thesis submitted by Oscar W. Weber in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn

NOTATION

a = radius of resin particle, cm.
C = equilibrium capacity of resin for carbon dioxide, meq./dry g. (as HCO_3^-)
C_{imm} = immobilized carbon dioxide within resin particle, moles CO_2/1,000 g. resin
C_L = concentration of carbon dioxide in liquid, moles CO_2/1,000 g. solution
C_R = concentration of carbon dioxide in resin phase, moles CO_2/1,000 g. resin
C_{R_0} = concentration of carbon dioxide in resin phase at time = 0, moles CO_2/1,000 g. resin
C_{R_∞} = concentration of carbon dioxide in resin phase at time = ∞, moles CO_2/1,000 g. resin
d = distribution coefficient, defined as the ratio of carbon dioxide absorbed by the solid phase to that by the associated salt solution, dimensionless
D = diffusion coefficient, sq.cm./min.
D' = $D/(1+\alpha)$
K = equilibrium constant, defined by Equation (1)
k_G = gas phase mass transfer coefficient, g. moles/(min.) (atm.) (sq.cm.)
k_L = liquid phase mass transfer coefficient, cm./min.
K_L = overall liquid phase mass transfer coefficient, cm./min.
M_t = total amount of carbon dioxide absorbed by resin at time t, moles CO_2/1,000 g. resin
M_∞ = total amount of carbon dioxide absorbed by resin at time ∞, moles CO_2/1,000 g. resin
P_{CO_2} = partial pressure of carbon dioxide in gas phase, atm.
R = gas constant
r = distance from particle center, cm.
RH = relative humidity, fraction
s = equilibrium solubility of carbon dioxide in solution surrounding resin beads, moles CO_2/1,000 g. solution − atm. carbon dioxide partial pressure
t = time, min.
Z = thickness of gas boundary layer, cm.

Greek Letters

α = C_{imm}/C_R
β = $\eta/2\xi$
δ = thickness of solution film, cm.
ξ = $\frac{1}{2}\left(\frac{k_G}{s\delta}+\frac{k_L}{\delta}+\frac{3k_L}{ad}\right)$
∇^2 = Laplacian
η = $3k_Gk_L/a\delta ds$

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Manuscript received December 13, 1967; revision received January 15, 1969; paper accepted January 20, 1969.

Momentum, Heat, and Mass Transfer to a Continuous Cylindrical Surface in Axial Motion

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The transport equations for the region exterior to a cylindrical jet issuing continuously from an orifice are solved through the introduction of a similarity transform. The possibility of mass transfer normal to the jet is allowed. Of particular interest are the local transport coefficients (c_f, N_{Nu}, N_{Sh}) and their dependence on the rate of transfer from the jet.

In two areas of technological importance, namely, fiber spinning and liquid fuel injection, it is necessary to have estimates for the transport coefficients that characterize heat, mass, and momentum transfer between the cylindrical jet and the ambient fluid. Little attention has been given to this problem as regards fuel injection systems, primarily because these systems are designed so that the jet is unstable and rapidly transforms from a cylinder to

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