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Separation of Gases by Enhanced Upstream Diffusion

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Abstract

Small amplitude oscillations have been shown to raise the diffusional flux in cylindrical tubes by orders of magnitude. The flux is especially high when the oscillation frequency is tuned to the size of the capillaries and to the properties of the gases involved. The process has been shown to permit separation of molecules of different molecular weight. The separation factor approaches, but is not equal to, the square root of the ratio of the molecular weight of the molecules involved. Hertz showed the separation can be enhanced by diffusion in a convective counterflow; it may then exceed the ratio of the square roots. We have combined oscillations and counterflow to obtain high yield and high separation. The results are encouraging. The separation is 20 to 40 times better than our past results. When applied to a simulated cascade, the savings in equipment and operational costs would be substantial.

INTRODUCTION

This is the second of a planned three papers on diffusional separation. It is a sequel to the paper entitled, "Diffusional Separation of Gases and Solutes in Oscillatory Flow" (*1*). The present paper summarizes new results found in the separation of gases via diffusion using counterflow.

In the first paper we presented data showing that enhanced diffusion by tuned oscillations allows one to raise the diffusional flux by 3 orders of magnitude in the gaseous phase and 6 orders of magnitude in the liquid phase. Despite this high flux, the transport is purely diffusional, setting up the possibility of separation with high yield. The separation factor obtained experimentally was adequate, but usually not as good as predicted by the

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theory. We present in this paper data that are substantially improved over those in the first paper. The separation factor is 20 to 40 times higher than found there. Restrictions as to the composition of the inlet gas mixture have been lifted. The experimental results match the derived theoretical predictions. These improved results are due mostly to the introduction of a counterflow.

The theory of diffusional enhancement by small amplitude oscillations was worked out quite early by Harris and Goren (*2*), and refined by Rice and Eagleton (*3*), Chatwin (*4*), and Watson (*5*). The theory has the familiar Taylor diffusion mechanism (*6*) as its limiting form as the oscillation frequency becomes quite small. The first experimental confirmation of such an enhanced diffusion process in gases was our own work (*7*) and that of Joshi and coworkers (*8*). Our first success in using the process for the purpose of separation came in 1986 (*9*). The theory indicates that under tuned conditions the effective diffusion coefficient D is equal to $\lambda\omega\Delta x^2$, where ω is the angular velocity of the oscillations in r/s, Δx is the oscillation amplitude in cm, and λ is a nondimensional coefficient (depending on Wormersley number and the Schmidt number) with a maximal value under tuned conditions near 10^{-2} (*1*). Tuned conditions are achieved when capillary diameter $2a$ and oscillation frequency ω are matched to the molecular diffusion coefficients D_m of the gases one wishes to separate and to the kinematic viscosity of the carrier gas. Tuning typically occurs when $a^2\omega = \pi D_m$. The factor λ is, in gases, under most practically important conditions, inversely proportional to D_m. This forms the basis of the separation process. Note that we use the symbol D to denote the effective diffusion coefficient and the symbol D_m for molecular diffusivity.

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MATHEMATICAL FORMULATION

The use of diffusion against a steady convective current goes back to Hertz (*10*) and Lange (*11*), who showed that the resulting logarithmic concentration profile along the diffusion path leads to far better separation than diffusion in a steady medium. In Hertz' setup however, the yield was very low because of the small numerical value of D_m. One can remedy this disadvantage by enhancing the upstream diffusion with small-amplitude oscillations. The separation process than takes place with the gas mixture undergoing two simultaneous convective flows: a small-amplitude, high-frequency reciprocal motion and a steady current. The small amplitude oscillations serve the purpose of raising the diffusional flux, the counterflow that of increasing the separation. The experimental configuration is shown in Fig. 1. It consists in a bundle of open-ended glass capillaries which are connected to end reservoirs as indicated. The feed mixture of heavy (H) and light (L) gas components flows into the right chamber at a flow rate of Q_0. At the same time, a carrier gas flows into the left reservoir at a rate Q_3. By controlling the outflows Q_1 out of the right chamber and Q_2 out of the left chamber, one can produce a variety of steady counterflows Q_4 from Chamber 2 to Chamber 1. A piston located in the left reservoir sets the gas mixture into laminar axial oscillations within the connecting capillaries and produces turbulent mixing in the two end chambers. An enhanced diffusion takes place from the right chamber, toward the left chamber where the flushing with carrier gas maintains a low concentration of H and L. The heavy gas is enriched in Chamber 2 since its effective diffusion is typically greater than that of the light species. The light gas is enriched in Chamber 1. The degree of enrichment depends on a number of factors, such as the ratio D_H/D_L, the counterflow Q_4, the rate of flushing of the two reservoirs, and most importantly, the tidal displacement or oscillation amplitude Δx. The setup in Fig. 1 contains four pumps and four flowmeters which allow us to control independently inflow and outflow of each compartment so that $Q_4 = Q_1 - Q_0 = Q_3 - Q_2$.

From the conservation of mass and the application of Fick's diffusion equation, the total volume flow Q_4 of gas that moves as a time average through the cross-sectional area A_0 of the capillaries is

$$Q_4 = Q_4[C_{L(x)} + C_{H(x)} + C_{C(x)}] - A_0\left[D_L\frac{dC_{L(x)}}{dx} + D_H\frac{dC_{H(x)}}{dx} + D_C\frac{dC_{C(x)}}{dx}\right] \quad (1)$$

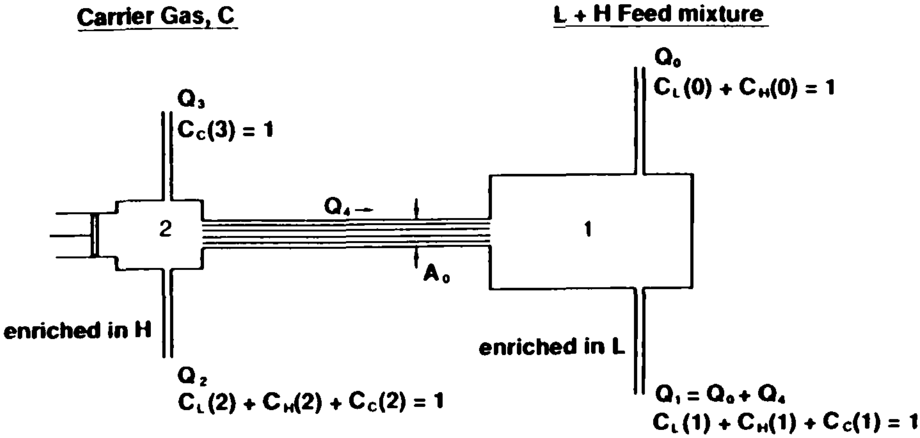

FIG. 1. Schematic of diffusional separation system.

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where the C's are the x-dependent concentrations of L and H. D_L and D_H are the effective diffusion coefficients which can be deduced from the work of Watson (*5*) and Demas (*12*) and which are proportional to $\lambda_L \omega \Delta x^2$ and to $\lambda_H \omega \Delta x^2$, as mentioned earlier. To avoid convective mixing of fluid between the two reservoirs, one generally requires that the tidal displacement $\Delta x < \frac{1}{2}$L. The separaton also requires that the oscillatory flow in the capillaries remain laminar (*5*). Looking only at the L component in Eq. (1) and applying the boundary conditions that at $x = 0$ $C_{L(0)} = C_{L1}$ and at $x = L$ $C_{L(x)} = C_{L2}$, one finds in solving the resulting first-order equation that

$$C_{L1} = C_{L2}e^{p} + (Q_{4L}/Q_4)(1 - e^{p}) \tag{2}$$

where $p = LQ_4/A_0D_L$ is a nondimensional parameter, A_0 is the cross-sectional area of the capillaries, and Q_{4L} is the diffusional flow of the L component through the capillaries. Next, using the fact that $Q_4 = Q_3 - Q_2 = Q_1 - Q_0$, and the experimental observation that, due to good mixing produced in the reservoirs by the oscillations, C_L at the reservoir exits equals essentially the time-averaged values at the end of the capillaries, one finds that Eq. (2) may be rewritten as

$$C_{L2} = (C_{L0}Q_0Q_4)/(Q_1Q_3e^{p} - Q_0Q_2) \tag{3}$$

where C_{L0} is the concentration of the L component in the feed mixture.

From this last result, one derives that the fraction of the species L that is transferred from the feed mixture to the left exit equals

$$f_{L2} = \frac{C_{L2}Q_2}{C_{L0}Q_0} = \frac{Q_2Q_4}{Q_1Q_3e^{p} - Q_0Q_2} \tag{4}$$

The heavy fraction is, in analogous manner, found to be

$$f_{H2} = \frac{C_{H2}Q_2}{C_{H0}Q_0} = \frac{Q_2Q_4}{Q_1Q_3e^{p\Gamma} - Q_0Q_2} \tag{5}$$

where $\Gamma = D_L/D_H$. The diffusional separation factor ρ_{H2} follows by taking the ratio of Eqs. (5) and (4) and is

$$\rho_{H2} = f_{H2}/f_{L2} = \frac{Q_1Q_3e^{p} - Q_0Q_2}{Q_1Q_3e^{p\Gamma} - Q_0Q_2} \tag{6}$$

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Note that ρ_{H2} can be made quite large by just increasing the counterflow rate Q_4. It may then exceed the ratio D_{mH}/D_{mL} by an order of magnitude or more. It is, of course, realized that the transfer fraction becomes smaller when ρ_{H2} increases.

For comparison, we list in the following equations that are equivalent to Eqs. (4)–(6), when no counterflow takes place.

$$f_{L2} = \frac{G_L Q_2}{G_L(Q_0 + Q_2) + Q_0 Q_2} \tag{7}$$

$$f_{H2} = \frac{G_H Q_2}{G_H(Q_0 + Q_2) + Q_0 Q_2} \tag{8}$$

$$\rho_{H2} = \frac{G_L/Q_0 + G_L/Q_2 + 1}{G_L/Q_0 + G_L/Q_2 + \Gamma} \tag{9}$$

with $G_L = A_0 D_L/L$ and $G_H = A_0 D_H/L$.

Since Eqs. (5) and (6) are fairly involved, it may be useful to illustrate the effect of the three variables, Q_0, Q_2, and Q_4, on ρ_{H2} and f_{H2}. All three

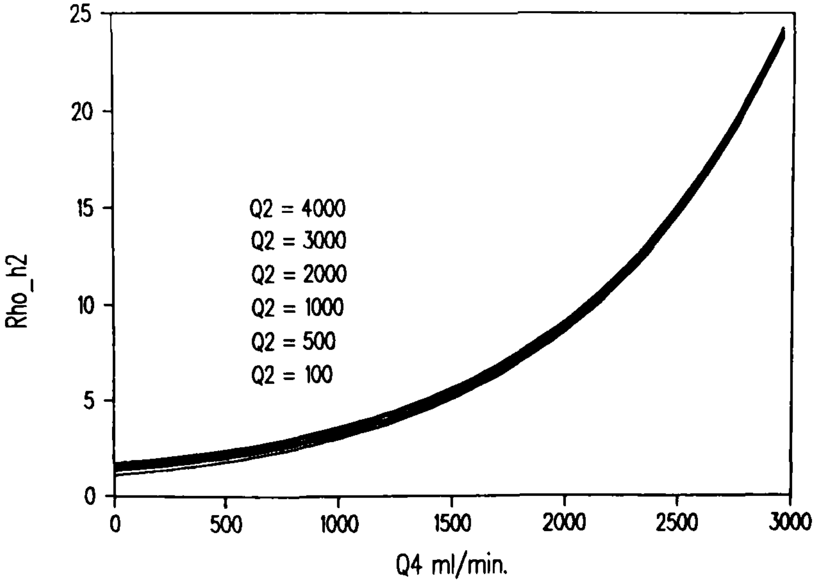

FIG. 2. Separation factor ρ_{H2} as a function of Q_4 at Q_0 = 2000 mL/min and Γ = .408. Different values of mixture input flow Q_2 are indicated.

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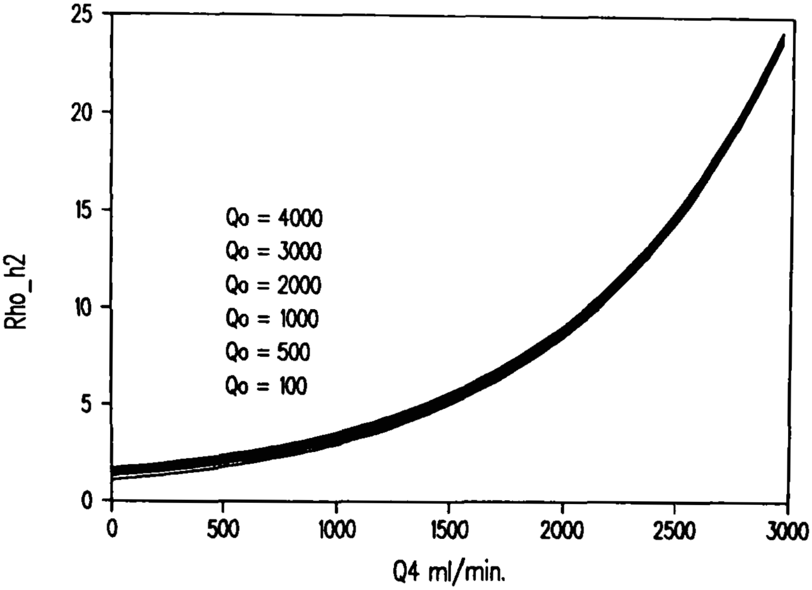

FIG. 3. Separation factor ρ_{H2} as a function of Q_4 at Q_2 = 2000 mL/min and Γ = .408. Different values of carrier gas flow Q_0 are indicated.

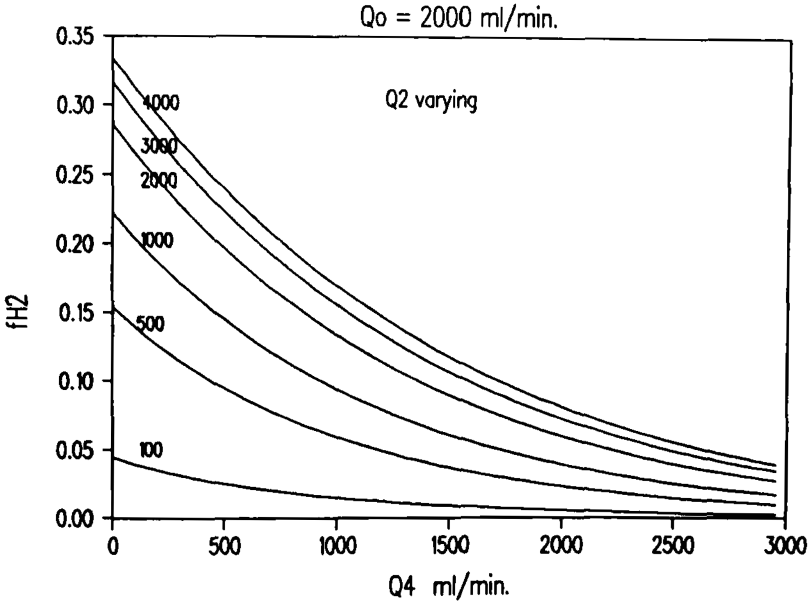

FIG. 4. Fraction of the heavy species (H) having diffused to the left reservoir (2) as a function of counterflow for different values of left reservoir outflow Q_2. Γ = .408.

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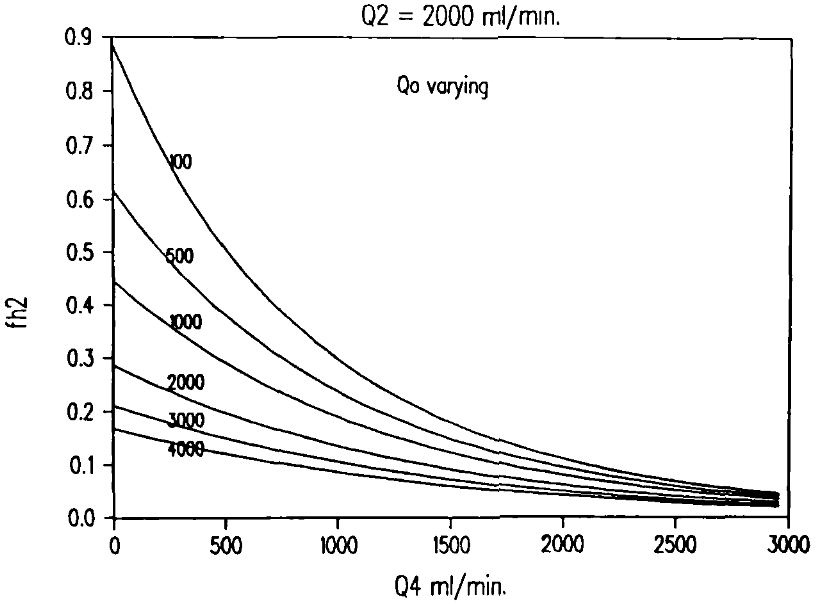

FIG. 5. Fraction of the heavy species (H) having diffused to the left reservoir (2) as a function of counterflow for the different values of right reservoir inflow Q_0.

variables can be freely adjusted for best efficiency. Figure 2 shows that ρ_{H2} rises sharply with increasing counterflow Q_4 and that the flushing of Container 2 (Q_2) has a negligible effect on that relationship. It can be shown that the flushing of Container 1 (Q_0) is also without major effect on ρ_{H2} (see Fig. 3). The fractional transport f_{H2} falls, however, as ρ_{H2} increases; this fall is modulated by Q_2 (Fig. 4) and Q_0 (Fig. 5). The last two figures show that optimization would, presumably, include using relatively high levels of Q_2 and low levels of Q_0 to obtain a high yield. In addition, optimization would include raising Q_4 to the most appropriate level.

METHODS

The experimental setup shown in Fig. 1 consists of 76 glass capillaries with an i.d. of .38 cm and a length of 120 cm. The total cross-section A_0 equals 8.63 cm^2. Container 2 on the left has a volume of 0.4L and is connected to a reciprocating pump (oscillator). The small volume is designed to keep the compression and decompression of gas minimal. The pressure in that container varies by ±0.1 ata. Container 1 on the right has a volume of 20 L. This volume is designed to keep the pressure variation at that end of the capillaries small (±0.01 ata). The oscillations are set at an angular frequency of 62.8 r/s and a tidal displacement of $\Delta x = 23$ cm. These conditions have been found to offer optimal separation when no counterflow is used (*1*). With N_2 as the carrier gas and O_2 and He as the two gases to be separated, $\Gamma = D_L/D_H = .408$ for these conditions as determined by experiment.

The feed into Container 1 consists of either a 50/50% O_2/He mix or a mixture of 95/5% of the same gases. The carrier gas (N_2) is fed into Container 2. In our earlier experiments, the feed mixture was diluted with a large proportion (80%) of carrier gas to comply with constraints of the theory which requires that the gas properties do not change along the diffusing path. These constraints have been relaxed in the present experiments. No rigorous analytical justification for this change of assumptions is available. Before starting an experiment, we check for leaks by pressurizing the system; the system is then flushed with the feed mix for approximately 3/4 h. After starting the pumps we wait another 45 min for steady state to become established. The adiabatic pressure changes in Container 1 are used to determine the volume of gas entering and leaving this container with each stroke; the oscillations amplitude Δx is derived from this reading and used to predict D_H and D_L. The linear amplitude, however, varies along the length of the capillaries because of compression effects. Its exact value is not known.

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The gases are analyzed with commonly available testing equipment. The accuracy of the measurement is better than 0.5% gas concentration. All testing equipment is calibrated at least once before and once after each experiment. The same equipment is used to measure inflow and outflow gas concentrations. The separation factors ρ^*_{H2} shown in the results are computed as $C_{H2}C_{L0}/C_{H0}C_{L2}$ (Eq. 6), and are independent of any assumptions or errors made in flow measurement (Q_0, Q_1, Q_2, Q_3, 4_4), as well as errors made in determining Δx.

RESULTS

The experimental results are summarized in Fig. 6 and Table 1. Represented in Fig. 6 are four of the thirteen experimental runs listed in the table. They were obtained when familiarity with the complex setup had allowed us to achieve close agreement between experiment and theory. Earlier experiments were not as good, as may be seen in Table 1. The table lists the conditions of the experiment (Q_0, Q_2); in each experiment Q_4 was varied between zero and 3000 mL/min in 4–6 steps (N). The column marked $(\rho^*_{H2} - \rho_{H2})/N$ lists the average deviation of the measured separation ratio (ρ^*_{H2}) from the expected one(ρ_{H2}); δ_N is the standard deviation from the predicted value. The last column $\rho_{H2\max}$ is the maximal separation

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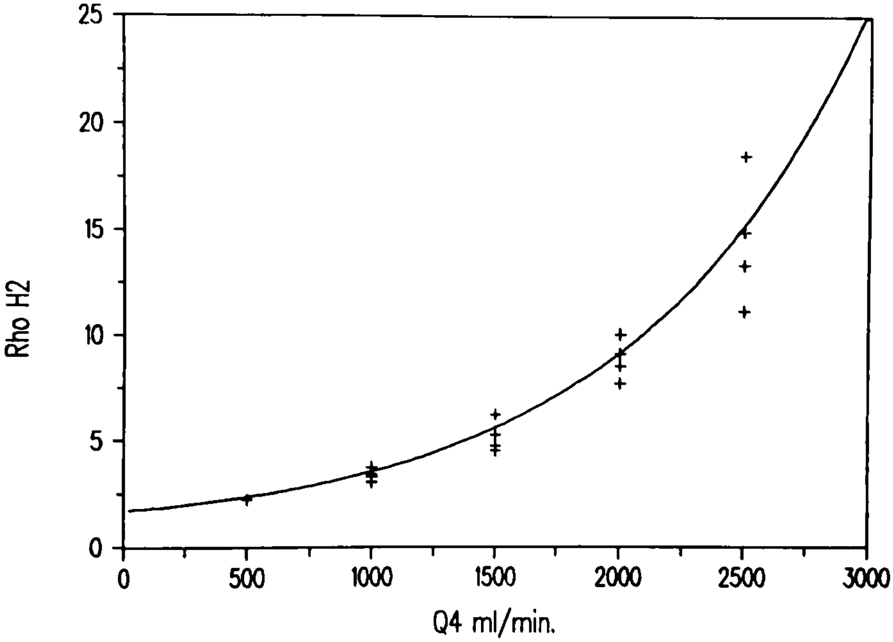

FIG. 6. Experimentally measured separation factor ρ_{H2} (crosses) as a function of counterflow Q_4. The continuous line is the theoretical prediction. Q_0 and Q_2 were constant for the duration of one experiment; Q_4, however, was varied between 500 and 2500 mL/min. The experiments are the last four in Table 1.

TABLE 1
Experimental Results of ρ_{H2} in He–O_2 Mixtures Diffusing into an N_2 Carrier Gas

Date	Q_0 (mL/min)	Q_2 (mL/min)	$(\rho^*_{H2} - \rho_{H2})/N$	σ_n	N	ρ^*_{H2} max
02:23:90	4000	2500	−1.1497	1.3604	4	5.7778
03:09:90	4000	1500	−5.8649	7.1639	6	5.7576
03:30:90	4000	2500	−1.3657	1.3544	4	5.6364
04:04:90	4000	1500	−6.8725	7.0644	6	7.8652
05:17:90	4040	2000	6.2177	11.8618	4	72.8033
06:12:90	4320	200	−1.2720	3.3542	5	17.5347
06:13:90	4120	200	−2.8681	51590	5	12.3850
06:13:90	4120	200	−0.4586	1.8468	4	11.1465
10:23:90	4000	2000	2.4462	2.5959	5	22.0000
10:24:90	4020	2000	0.4869	1.6523	4	18.4756
10:25:90	3920	2000	−0.9124	0.6685	5	13.3333
10:26:90	4020	1500	−1.4304	1.1069	5	11.7241
10:29:90	4020	200	0.4360	0.5521	4	14.9091

measured. The average deviation from the expected value and the standard deviation from the expected value are small in all cases. The errors increase with increasing values of Q_4; this stems from the fact that C_{H2} and C_{L2} are very small when Q_4 is large, nearing the limit of resolution of our equipment.

DISCUSSION

Upstream diffusion has the potential of separating gases with a separation factor exceeding the ratio of square roots of the molecular weights (i.e., Graham's law). This was recognized long ago by Hertz (*10*). The separation ratio increases exponentially with the rate of counterflow and can theoretically reach very high values. Our experimental results approximate 10 × the ratio of the molecular diffusion coefficients. In Hertz' description, the diffusional flux was too small to be of technical interest. This shortcoming has been overcome by combining the counterflow with small amplitude oscillations which increase the flux by several orders of magnitude. A more detailed description of the various factors that determine the yield is given below.

The data are in excellent agreement with the theory based on an 1D analysis of diffusion in counterflow with superimposed oscillations (Eqs. 4–6). A more rigorous analysis is in the making, but is quite involved. The present theory makes several simplifications: It does not account for the distortion of the time-dependent velocity profile by the counterflow. This distortion is, however, small since the linear velocity of the counterflow is only about 1/100 of the root-mean-square of the oscillation velocity. The theory also neglects, at present, effects of compressibility within the capillaries and variations of the kinematic viscosity and of the molecular diffusion coefficients along the capillaries. These variations are quite substantial and may have an effect on the velocity profile and on the effective diffusion.

The acquisition of the experimental data is independent of these unresolved questions. The experimental ρ^*_{H2} is determined as the ratio of measured gas concentrations $(C_{H2}C_{L0}/C_{L2}C_{H0})$ and depends on one assumption only; namely, that there is good mixing within the reservoirs. Inadequate mixing would result in lack of agreement with the theory. Since we have good agreement, we can infer good mixing. The exact mixing process, however, is somewhat complicated, especially in Container 2. That small container (400 mL) undergoes large gas volume exchanges with the capillaries (200 mL); mixing has to take place despite these geometrical changes between the influx of carrier fluid (30 mL/s) and the influx of L and H from the capillaries (1–3 mL/s). In Container 1 (20,000 mL), the

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mixing is promoted by the oscillatory jet-like influx of the gas from the capillaries; one of the present authors has analyzed this mixing process in some detail (*13*).

The counterflow offers a number of advantages such as the possiblity to raise the separation ratio and to dramatically reduce the number the number of units needed in a cascade. It, however, has the disadvantage of reducing the fraction transferred. For technical use to be justified, these advantages and disadvantages need to be carefully weighed. A detailed analysis of such an optimization attempt is beyond the scope of the present paper; however, we try with the help of a numerical example to provide some estimate of these advantages and disadvantages. The example is based on our experimental data with the simple separation device described above. It assumes that, as measured, the values for $G_H = A_0D_H/L = 1341$ mL/min and $G_L = A_0D_L/L = 550$ mL/min. The tuning process required to obtain these values was described earlier (*1*).

Table 2 summarizes the result of these computations. They assume initial concentrations of $C_{H0} = C_{L0} = .5$ and a required purification at the end of a cascade of $C_{HN}/C_{LN} = 100$. It also assumes $Q_0 = 100$ and $Q_2 = 2000$ mL/min as suggested for an optimum with counterflow by Fig. 2–5. Different conditions ($Q_0 = 2000$; $Q_2 = 2000$ mL/min) are assumed when there is no counterflow, since Eqs. (7)–(9) predict different optima than Eqs. (4)–(6). The table indicates that ρ_{H2} increases from 1.61 to 10.6 when counterflow is raised from $p = 0$ to $p = 4$; however, f_{H2} falls from .18 to .09. This results in a decrease of the final yield. This yield is computd as C_H in the end-stage times Q_2 and is listed in Table 2. This table also lists an estimate of the number of units needed if one assumes simple cascading without the usual feedback. The number of stages is computed as log (C_{LN}/C_{HN})/log (ρ_{H2}), and the number of units needed in each stage is based on

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TABLE 2
Advantages and Disadvantages of Upstream Diffusion

	For single unit		For cascading			
$p = LQ_4/A_0D_L$	ρ_{H2}	f_{H2}	Yield (mL/min)	Number of stages	Number of unit/branch	Total number of units
0	1.61	.18	355	10	7	4.7×10^7
1	1.87	.48	47	8	3	3280
2	3.30	.27	26	4	6	259
3	5.92	.15	15	3	12	157
4	10.63	.09	8	2	21	22

the premise that Q_0 in a given stage is made up of the sum of the partially enriched gases from the previous stage so that $(Q_{H4} + Q_{L4}) \geq Q_0$. The total number of units required to achieve a given purification is seen to fall dramatically from 4.7 × to 10^7 to 22 when counterflow is raised. The yield of a cascade with $p = 4$ is, indeed, reduced to 8 mL/min as compared to the yield of 355 mL/min given by the cascade with $p = 0$. However, this decline is outweighed by far by the saving in terms of number of units required for the desired enrichment. At equal yield, the saving in number of units required equals four orders of magnitude.

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