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## CARBON ISOTOPE SEPARATION BY ABSORPTIVE DISTILLATION

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### ABSTRACT

The feasibility of separating carbon isotopes by absorptive distillation has been studied for CO absorption by cryogenic solvents. Phase equilibrium, isotopic separation, and mass transfer data were taken between 77.4 and 114.3 K for the following solvents: propane, propylene, 1:1 propane-propylene, 1-butene, isobutane and nitrogen.

Carbon monoxide solubility followed Henry's Law, with a maximum experimental solubility of 6.5 mole per cent. Isotopic separation between CO in the gas and liquid phases using hydrocarbon solvents was several times that for pure CO vapor-liquid equilibrium. The maximum observed isotopic separation factor was 1.029 at 77.4 K with the propane-propylene solvent mixture. Mass transfer measurements yielded calculated HTU's of 2 to 5 cm for a possible separation system.

An attempt has been made to correlate isotopic separation data using Hildebrand's theory of solutions. The differential absorption of isotopic CO species is expressed as a difference in solubility of the isotopic CO molecules. Data for propane, propylene, and 1-butene show approximately the same behavior at varying temperatures.

### INTRODUCTION

The use of the isotope  $^{13}\text{C}$  as a tracer in organic reactions and biological systems has risen sharply in recent years. In addition to the mass difference from the most abundant carbon iso-

tope ( $^{12}\text{C}$ ),  $^{13}\text{C}$  has the highly desirable properties of nonradioactivity and a nuclear magnetic moment. These properties permit use of  $^{13}\text{C}$  as a tracer in human subjects and also allow nuclear magnetic resonance (NMR) studies.

Presently  $^{13}\text{C}$  is enriched from 1% to 99% at a rate of 6 to 20 kg per year by distillation of CO (1), and thermal diffusion (2) has been used in the past for smaller production rates. Chemical exchange systems which have been investigated for possible  $^{13}\text{C}$  enrichment include a cyanide system (3), a CO-complex system (4), a carbamate system (5), and a cyanohydrin system (6).

Absorptive separation of isotopes has received little attention. Augood (7) has investigated the separation of  $\text{H}_2$  and HD in a number of common solvents and reported sizeable separation factors at temperatures up to ambient. Because an absorptive process is more reversible (thus less costly to operate) than some other possible processes for separating isotopes, this approach was attempted for  $^{13}\text{C}$  separation.

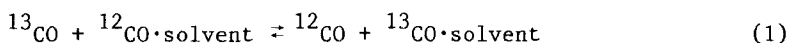
#### EXPERIMENTAL SYSTEM

Carbon monoxide was chosen as solute for several reasons. CO is the material used for  $^{13}\text{C}$  separation by distillation, thus direct comparison of isotopic separation may be made. One also expects to find the highest isotopic separation for a given element when operating at the lowest possible temperatures; CO is the lowest boiling carbon compound. Experimental pressures were kept below the CO vapor pressure at the temperatures studied because it was expected that the isotope separation becomes the same as for pure CO at the saturation pressure.

Initial choice of solvents was dictated by freezing points and vapor pressures; the solvent must remain liquid at the operating temperature and is desired to be nonvolatile to permit stripping of the solute from solution for sampling. Since most of the useful solvents are hydrocarbons, this second criterion is quite important to avoid analyzing any carbon other than that of

CO. Propane, propylene, a 1:1 propane-propylene mixture, isobutane, 1-butene, and nitrogen were used as solvents. Only the liquid nitrogen had an appreciable vapor pressure at the temperatures studied.

The isotopic separation for the absorption system is that attained in the equilibrium:



The isotopic separation factor is given by the ratio of the isotopic concentration ratios in the two phases.

$$\alpha = \frac{^{13}\text{CO}/^{12}\text{CO} \text{ (liquid)}}{^{13}\text{CO}/^{12}\text{CO} \text{ (gas)}} \quad (2)$$

As expressed here,  $\alpha$  is greater than 1.0 if  $^{13}\text{CO}$  concentrates in the liquid. Although it is likely that oxygen isotopic fractionation also occurs, no attempt was made to measure this effect.

In anticipation of a practical separation system, one wishes some information on the rate of isotopic exchange between phases. Consider a small region of a packed absorptive distillation column where  $a$  is the specific area for gas-liquid contact ( $\text{cm}^2/\text{cm}^3$ ),  $A$  is the area, and  $Z$  is the height. During a period of time  $t_b - t_a$  the mass rate of  $^{12}\text{C}$  transferred to the gas phase,  $R_m$ , is (with no bulk CO transport):

$$R_m = m (y_b - y_a)/(t_b - t_a) \quad (3)$$

Using the definition of a mass transfer coefficient this can be related to the mean vapor phase driving force ( $\bar{y}^* - \bar{y}$ )

$$R_m = k_y a (\bar{y}^* - \bar{y}) AZ \quad (4)$$

By equating expressions one obtains the mass transfer coefficient and HTU (height of a transfer unit) in terms of experimental data. (m moles gas, G mole/ $\text{cm}^2$  sec gas flow.)

$$k_{y,a} = \frac{m (y_b - y_a)}{AZ (t_b - t_a)(\bar{y}^* - \bar{y})} \quad (5)$$

$$HTU = G/k_{y,a} \quad (6)$$

#### APPARATUS AND PROCEDURE

Phase equilibrium, isotopic separation, and mass transfer rate data were taken to evaluate the potential use of absorptive distillation for  $^{13}\text{C}$  separation.

Phase equilibrium and isotopic separations were measured during the same set of experiments. The apparatus is shown in Figures 1 and 2. A measured amount of solvent gas was condensed into the equilibrium absorption cell using a liquid nitrogen, liquid oxygen, or liquid nitrogen-natural gas mixture refrigerant bath. Any residual gas in the cell was evacuated except when nitrogen was used as solvent. A measured amount of enriched  $^{13}\text{CO}$  was then pumped into the system using a Toepler pump, and the  $\text{CO}$  was circulated continuously through the cell at constant pressure and temperature ( $\pm 0.2$  cm Hg and  $\pm 0.25$  K (LN<sub>2</sub>-LNG bath only)) for several hours using the Toepler pumps. The helical tube in the

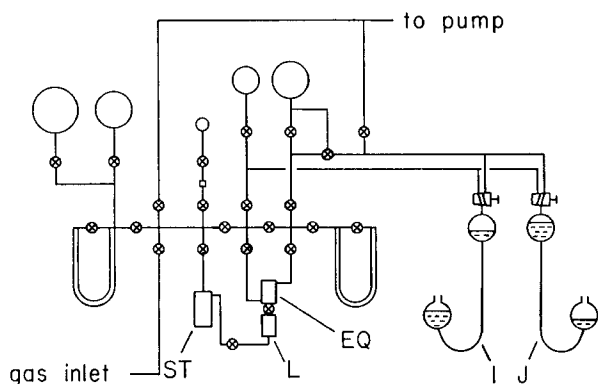


FIGURE 1. Gas Circulation Manifold. EQ - Equilibrium Cell; I, J - Toepler Pumps; L - Liquid Sampling Volume; ST - Stripping Trap

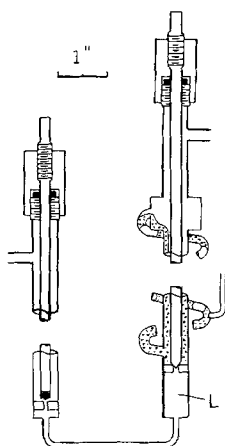


FIGURE 2. Equilibrium Absorption Cell and Valves used for Liquid Sampling.

absorption cell was designed to have large interfacial area via the gas bubbles and also to circulate the solvent for uniformity of concentrations.

Following the desired equilibration time, the system pressure was measured using a manometer, and CO solubility was calculated from a mass balance. Gas and liquid samples were then collected for mass spectrometric analyses of CO. The CO gas sample was collected in a small glass bulb, and the remaining gas was pumped into a holding volume. The liquid sample was taken by opening valve T to isolate a portion of the liquid. The CO was then desorbed from the solvent using a Toepler pump, and the gas obtained was mixed and expanded into a sample bulb.

A mass transfer cell (Figure 3) replaced the equilibrium absorption cell for rate measurements. The cell was filled to a height of 3.5 cm with a high efficiency random packing, Heli-Pak 3008 (Podbielniak, Inc.). First  $^{13}\text{CO}$  was equilibrated with the solvent in the manner described, and the gas was sampled. This gas was then isolated from the cell and was replaced by CO at the same pressure but at a different  $^{13}\text{C}$  isotopic concentration. The

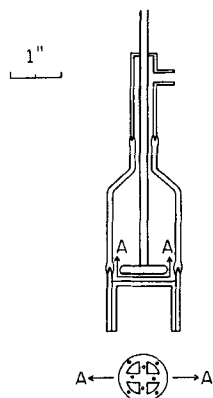


FIGURE 3. Mass Transfer Absorption Cell.

new gas was sampled and circulation was resumed. After varying circulation times the cell was isolated, the gas was mixed and sampled, and circulation would be resumed until another sample was desired. No samples of absorbed CO were taken.

All samples were analyzed for isotopic composition using a CEC 21-130 cycloidal type mass spectrometer, which is well-suited for quantitative measurements on low molecular weight gases. It was necessary to use the  $^{12}\text{C}$  and  $^{13}\text{C}$  fragment ions at  $m/e$  12 and 13 for analyses due to a small air leak in the spectrometer. Although any isotopic discrimination would be very small using these peaks, the effect should be completely negligible for a gas-liquid pair of analyses. Up to twelve scans were made of these peaks for any given sample, and the average uncertainty in the isotopic separation factor due to the instrument was  $\pm 0.002$ .

For maximum measurement sensitivity, the  $^{13}\text{CO}$  used was enriched to the 60%  $^{13}\text{C}$  level. The isotope was purchased as barium carbonate (Bio-Rad Lab.) and converted to CO using a method in the literature (8) involving calcium carbonate as an intermediate. The solvents were C.P. or instrument grade compressed gases obtained from J. T. Baker and Matheson. The LNG used for cryogenic baths was liquified from laboratory gas jets using a

crude liquification apparatus cooled by liquid nitrogen. The bath temperature was maintained by periodic addition of LN<sub>2</sub>.

### RESULTS

Carbon monoxide solubility, as monitored by pressure, reached an equilibrium value within a few minutes of circulation for all solvents studied. Solubility data (Table 1.) followed Henry's Law over a significant pressure range as shown by Figure 4. The highest experimental solubility was 6.5 mole per cent CO in the propane-propylene solvent at 77.4 K.

Isotopic phase equilibrium required circulation times of one hour or more for the systems used. Isotopic separation factors (Table 1.) for a given solvent decreased with increasing temperature showed no effect due to pressure variation. The highest observed isotopic separation factor was 1.029 for CO in the propane-propylene solvent at 77.4 K. Figure 5 shows the separation factor as a function of temperature for this solvent; the vapor-liquid isotopic separation for pure CO as calculated by Johns (9) is shown for comparison. The data showed no tendency to correlate preferentially with either  $T^{-1}$  or  $T^{-2}$ , due partly to the sensitivity in measurements.

Mass transfer measurements using the C<sub>3</sub> solvents yielded HTU's between about 10 and 60 cm for low concentration driving force conditions (Table 2.). Visual observation during operation of the mass transfer cell indicated that bubbles were roughly the size of an individual piece of packing and that the residence time of a bubble was about 4 seconds. The resulting value of the specific mass transfer area,  $a$ , was about  $0.2 \text{ cm}^2/\text{cm}^3$ .

### THERMODYNAMIC ANALYSES

For gas-liquid equilibrium the concentrations of each component in the two phases may be related by equating the individual fugacities in each phase. The liquid fugacity may be expressed in terms of a pure liquid fugacity and an activity coefficient.



TABLE 1  
Equilibrium Data

Run	Solvent	Temp K	Pressure cm Hg	$x_{CO}$	$\alpha$
16	a	90.2	34	0.0168	1.019
17	a	90.2	34	0.0170	1.018
18	a	90.2	34	0.0170	1.016
19	a	90.2	57	0.0292	1.018
20	a	90.2	21	0.0102	1.018
22	a	110.7	60	0.0126	1.013
25	a	110.7	56	0.0121	1.012
26	a	100.9	41	0.0115	1.016
27	a	110.7	55	0.0112	1.011
31	a	90.2	57	0.0301	1.019
32	b	90.2	46	0.0261	1.018
33	b	90.2	30	0.0156	1.018
34	b	90.2	60	0.0337	1.021
36	b	107.9	55	0.0144	1.012
37	b	99.9	58	0.0194	1.017
38	b	107.9	35	0.0082	1.010
39	b	99.9	36	0.0121	1.013
42	c	90.2	43	0.0274	-
43	c	90.2	61	0.0390	-
44	c	77.4	41	0.0652	-
45	c	77.4	27	0.0405	-
46	c	90.2	57	0.0352	-
47	c	100.8	47	0.0172	-
49	c	90.2	33	0.0189	1.013
50	c	90.2	38	0.0246	1.014
51	c	77.4	33	0.0457	1.029
52	c	100.8	56	0.0208	1.011
53	c	77.4	24	0.0358	1.029
54	c	90.2	48	0.0295	1.015
55	c	100.8	44	0.0154	1.011
57	c	77.4	33	0.0508	1.028
58	c	90.2	42	0.0251	1.013
59	a	100.9	36	0.0122	1.013
61	d	77.4	80	-	1.007
64	d	77.4	80	-	1.005
66	e	90.2	44	0.0116	1.021
67	e	90.2	65	0.0201	1.020
69	f	114.3	70	0.0090	1.015
70	f	114.3	64	0.0086	1.019
71	f	114.3	66	0.0090	1.017

solvents: a - propylene; b - propane; c - 1:1 propane-propylene;  
d - nitrogen; e - 1-butene; f - isobutane

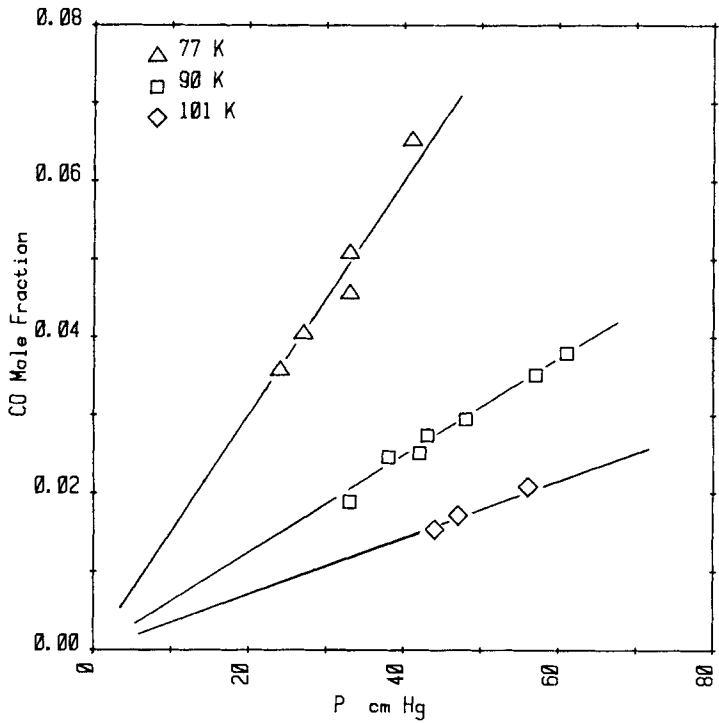


FIGURE 4. Solubility of CO in a 1:1 Propane-Propylene Liquid Mixture.

The gas phase fugacity is the partial pressure times a fugacity coefficient.

$$y_i \phi_i P = f_i^g = f_i^{\ell} = \gamma_i x_i f_i^{\ell, \text{pure}} \tag{7}$$

If the pressure is not the saturation pressure of the pure liquid a Poynting correction is added. (In the following equations, ° refers to saturation conditions)

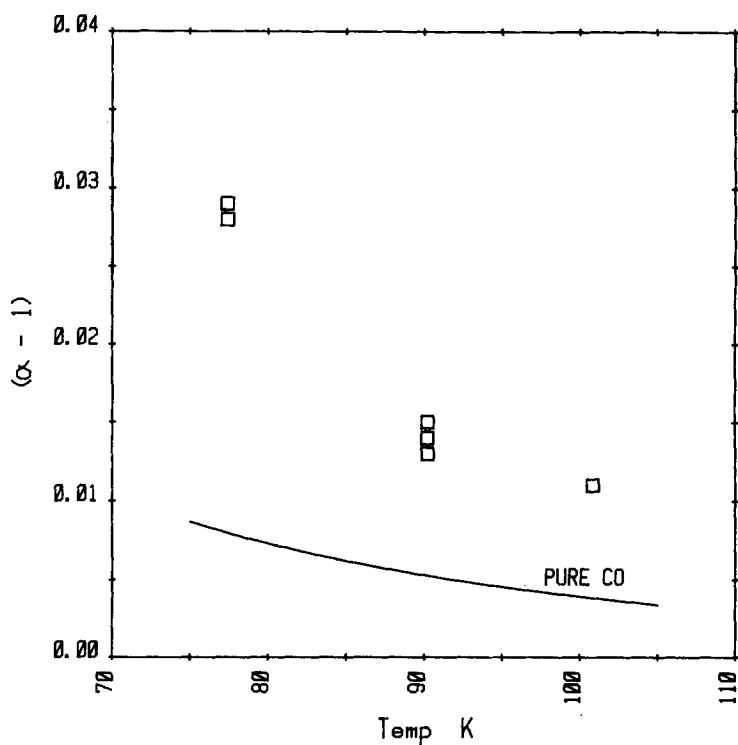


FIGURE 5. Isotopic Separation Factor for CO Gas-CO Dissolved in a Propane-Propylene Liquid Compared to Pure CO Isotopic Separation.

$$\begin{aligned}
 f_i^{\ell, \text{pure}} &= f_i^{\circ \ell, \text{pure}} \exp \int_{P_i}^P v_i^{\ell} dP/RT \\
 &= \phi_i^{\circ} P_i^{\circ} \exp \int_{P_i}^P v_i^{\ell} dP/RT \quad (8)
 \end{aligned}$$

Assuming the liquid molar volume to be pressure independent, we obtain

$$y_i/x_i = y_i \phi_i^{\circ} P_i^{\circ} / \phi_i P \exp [v_i^{\ell} (P - P_i^{\circ})/RT] \quad (9)$$

The isotopic separation factor may now be written for the gas-solvent system (1 =  $^{12}\text{CO}$  ; 2 =  $^{13}\text{CO}$  ; 3 = solvent).

TABLE 2  
 Mass Transfer Data

Run	Solvent	Temp K	t sec	$\bar{y}^* - \bar{y}$	HTU cm
74	propylene	90.2	0		
			90	0.307	13
			180	0.160	13
			360	0.078	18
			540	0.031	18
			720	0.013	16
			900	0.005	14
75	propane	90.2	0		
			90	-0.189	14
			180	-0.097	14
			360	-0.050	18
			540	-0.023	28
			720	-0.014	41
			900	-0.011	62
76	propane- propylene	77.4	0		
			90	-0.153	10
			180	-0.091	12
			360	-0.039	16
			540	-0.020	27
77	propane- propylene	77.4	0		
			90	0.293	10
			180	0.147	15
			360	0.073	10
			540	0.023	23
			720	0.022	17
			900	0.006	34

$$\alpha = (y_1/x_1)/(y_2/x_2) \\
 = \frac{P_1^o}{P_2^o} \frac{\gamma_1}{\gamma_2} \frac{\phi_1^o \phi_2}{\phi_2^o \phi_1} \exp [(v_2^L P_2^o - v_1^L P_1^o)/RT] \quad (10)$$

The liquid molar volumes of the isotopically differing molecules will be assumed equal for lack of data otherwise. The isotopic separation may be expressed in terms of the pure CO vapor-liquid system and a solvent contribution.

$$\alpha = \frac{P_1^o}{P_2} \beta = \alpha^o \beta \quad (11)$$

$$\beta = \frac{\gamma_1}{\gamma_2} \frac{\phi_1^o \phi_2}{\phi_2^o \phi_1} \exp [-v_1^L \frac{P_1^o}{P_1} (\alpha^o - 1)/RT] \quad (12)$$

For the experimental conditions studied, the numerical value of the produce of fugacity coefficient ratios and the exponential term was between 0.999 and 1.000 for all cases. Since the accuracy of isotopic analyses was roughly  $\pm 0.2\%$ , the solvent contribution to isotopic separation may be expressed solely in terms of the activity coefficient ratio.

$$\beta = \gamma_1/\gamma_2 \quad (13)$$

The Hildebrand theory of liquid solutions (10) is accepted as a good means of predicting activity coefficients in nonpolar solutions. (CO has a very small dipole moment and is assumed to be sufficiently nonpolar for treatment by this theory.) Hildebrand uses a quantity called a solubility parameter,  $\delta$ , to relate the activity coefficient in a binary solution to cohesive energy density and molar volume of the solution.

$$\delta = (\Delta E_{\text{ideal}}^V/v^L)^{0.5} \quad (14)$$

$$\ln \gamma_1 = \frac{v_1^L \phi_2^2}{RT} [(\delta_2 - \delta_1)^2 + 2\ell_{12}\delta_1\delta_1] \quad (15)$$

In a ternary solution, in general all possible pairs of interacting species in the liquid must be considered. For the special case of isotopic solutes in dilute solution, the isotopic solubility parameters are nearly equal, and a simplified equation results.

$$\ln \frac{y_1}{y_2} = \frac{2v_1 \ell_{\phi_3}^2}{RT} [\delta_3(1 - \ell_{13}) - \delta_1] (\delta_2 - \delta_1) \quad (16)$$

This expression relates the solvent effect on the isotopic separation to the difference in solubility parameters of the  $^{12}\text{CO}$  and  $^{13}\text{CO}$  as well as to some properties of the solvent itself. ( $\Phi$  is a volume fraction and  $\ell_{13}$  is a binary constant typical of a given solvent-solute pair.)

Solubility parameters for CO and the solvents were calculated at the appropriate temperatures using data from the literature (11), (12). The binary constants for solute-solvent interactions are necessary for quantitative calculations, and these quantities were evaluated using equation (15) and activity coefficients for the CO considered as a single species. Activity coefficients were calculated using experimental data, equation (9), and the corresponding states treatment of Pitzer (13) for evaluation of fugacity coefficients.

Figure 6 shows the variation of  $\delta_2 - \delta_1$  with temperature for the pure hydrocarbon solvents. To a rough approximation, the difference in isotopic solubility parameters is the same function for the straight-chain hydrocarbons; results for isobutane do not fall on this curve, possibly due to the branching of isobutane.

### DISCUSSION

The solubility data for CO in liquid propane are in basic agreement with low pressure data of Cheung and Wang (14). No other previous data were available for comparison of either isotopic separation or solubility for the systems studied.

Because of the many similarities in properties of CO and nitrogen, it was suspected that use of nitrogen as a solvent for CO would produce essentially the same isotopic separation as for pure CO vapor-liquid equilibrium. Within experimental error this suspicion has been verified.

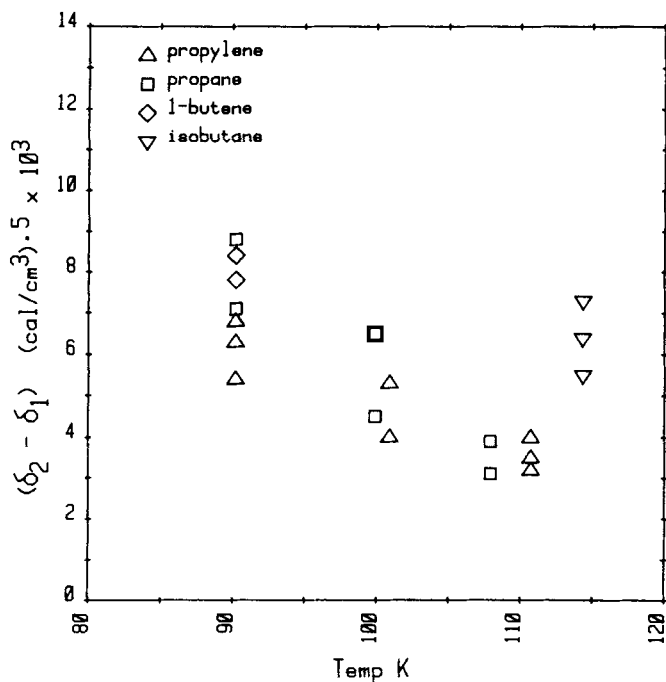


FIGURE 6. Difference in Solubility Parameters of  $^{13}\text{CO}$  and  $^{12}\text{CO}$  Dissolved in Hydrocarbon Solvents.

The HTU's obtained from mass transfer data were rather discouraging; however, the mass transfer cell used had poor mass transfer characteristics due to the low volume fraction of gas in it at any time. Since the gas bubbles in the cell were of uniform size, the mass transfer area per unit volume of packing,  $a$ , was proportional to the number of bubbles, i.e., the volume fraction of gas. Experimentally the gas volume fraction was 1.5%.

For an absorptive fractionation column using propane at 90 K and operating with equimolar holdup of CO in liquid and gas phases, the gas phase volume fraction would be 15%. If flow characteristics remained the same as for the experimental cell, the value of " $a$ " would be increased 10 times, and HTU's of 2 to 5 cm could be attained.

### CONCLUSIONS

The absorptive separation of carbon isotopes in CO gives greater isotopic separation factors than do most other  $^{13}\text{C}$  enrichment methods (in particular, CO distillation), while still promising a good rate of mass transfer. The observed separations show some correlation with difference in the Hildebrand solubility parameter for the isotopic species.

This larger separation factor has several implications which are important in designing a possible separation system: 1) smaller size equipment (less separating stages); 2) lower refrigeration requirement (lower reflux ratio); 3) less time to reach steady-state operation. Since construction of a cryogenic absorptive separating system is not beyond present technology, absorptive distillation appears to hold promise as an economically feasible method for enriching  $^{13}\text{C}$ .

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