

The Concentration of Carbon 13 by Thermal Diffusion

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A thermal diffusion column employing methane gas has been constructed for the purpose of concentrating C^{13} . A determination of the separation factor of the column for various pressures indicated a quantitative agreement between experiment and the theory of Furry, Jones and Onsager. When a reservoir was attached to the top of the column it was possible to produce methane containing over four times the normal amount of $C^{13}H_4$.

THE recent experiments of Clusius and Dickel¹ and other investigators²⁻⁷ indicate that by confining a gas in the annular space between two long vertical concentric cylinders at different temperatures, the combination of the convection currents and the thermal diffusion effect gives rise to an appreciable isotopic separation in the gas. Waldmann,⁸ Furry, Jones and Onsager⁹ have published papers dealing with the theoretical aspects of the problem.

To the writer's knowledge, there is at present no published account of any quantitative correlation between theory and experiment. It was the purpose of the present research to construct a column employing methane gas for the purpose of separating C^{13} . In addition it was hoped that by studying the performance of the column under various conditions it would be possible to obtain a check of the theory.

DESCRIPTION OF APPARATUS

A cross-sectional view of the thermal diffusion column used in the present experiments is shown in Fig. 1. Along the axis of the column is a No. 8 Nichrome V heating wire. This is surrounded by porcelain insulators to separate it from the steel tube 0.75" O. D., wall thickness 0.035". Next

there is a steel tube 1.375" O. D., wall thickness 0.035". This tube constitutes the inner wall of the annular space confining the gas. For the outer wall of this space is used 2" O. D. brass tubing, wall thickness 0.032". The outermost tube is a water-cooling jacket made of brass tubing 2.50" O. D. with a wall thickness of 0.032". The dimensions are given in inches as these are stock sizes of tubing. The column was 24' long; in order to obtain tubing of this length two standard 12' lengths were butted together and surrounded by a short sleeve at the point of the butt. The sleeve connecting the two lengths of 1.375" steel tubing was inside rather than outside the tubes. Thus there was no obstruction in the annular gas space at this point to interfere with the streamline flow of the gas. At the upper end the 1.375" steel tube was brazed to a cover which in turn was soft soldered to the 2" brass tube. The 0.750" steel tube extended up through the cover and was free to move in a vertical direction relative to the cover to allow for differential expansion of the two steel tubes. The only purpose of the 0.75" steel tube was to insure centering of the heating element.

At the lower end, the 0.75" and 1.375" steel tubes were brazed concentrically to a circular steel plate 1.375" in diameter. A 0.375" rod was also brazed to this plate and served as a guide to center the steel tubing assembly. The Nichrome wire extended through this rod and was silver-soldered to it. The position of the end of the Nichrome wire thus measured directly the expansion of the 1.375" steel tube and could therefore be used as a temperature indicator.

Although the tubes were centered at the ends, it was felt necessary to introduce spacers to insure that the tubes were also concentric all

¹ K. Clusius and G. Dickel, *Naturwiss.* **26**, 546 (1938); **27**, 148 (1939).

² A. K. Brewer and A. Bramley, *Phys. Rev.* **55**, 590 (1939).

³ A. K. Brewer and A. Bramley, *J. Chem. Phys.* **7**, 553 (1939).

⁴ W. Groth, *Naturwiss.* **27**, 260 (1939).

⁵ H. S. Taylor, *Nature* **144**, 8 (1939).

⁶ T. I. Taylor and G. Glockler, *J. Chem. Phys.* **7**, 851 (1939).

⁷ W. W. Watson, *Phys. Rev.* **56**, 703 (1939).

⁸ L. Waldmann, *Naturwiss.* **27**, 230 (1939).

⁹ W. Furry, R. Jones and L. Onsager, *Phys. Rev.* **55**, 1083 (1939).

along the length. Tightly fitting lavite spacer rings placed at intervals of 3 ft. separated the two steel tubes. In the annular gas space, spacers were placed at 6-ft. intervals along the length. In this case the spacer at the end of one of these 6-ft. sections consisted of three small lavite cylinders about $\frac{1}{4}$ " in diameter, of height equal to the space between the tubes and placed at 120° intervals around the tube. To hold the spacers in place a hole was drilled along their axes and they were slipped over steel pins brazed to the 1.375" steel tube. These pins were shorter than the heights of the cylinders so that there was no metallic connection between the two walls of the annular space. This prevented any appreciable loss of heat at these points.

PROCEDURE AND RESULTS

Prior to admitting the methane gas, the column was outgassed by heating the inner wall of the annular gas space (the 1.375" tube) to a temperature of approximately 375°C for several days while the column was attached to a Hyvac pump. The pressure at the end of this time as measured with a Pirani gauge was less than 10^{-3} mm. It was found that 1.22 kilowatts were necessary for heating the column under these conditions. Radiation was responsible for practically all of the heat transferred across the annular space in this case.

The methane used in the experiments was purified by distillation at liquid-air temperature by using a standard Podbielniak low temperature fractionating column.

In order to study the performance of the column itself runs were made at several pressures. No reservoirs were used at the ends of the column. Samples were removed periodically from the top and from the bottom so that the rate at which the column approached equilibrium could be determined. The average temperature of the inner wall of the annular gas space was approximately 300°C in each case. This was determined from the ratio of pressures in the column when hot and when cold as well as from the linear expansion of the steel tubing. Unfortunately a direct measurement of temperature was not possible as a result of an accident which destroyed thermocouple wires leading away from the hot

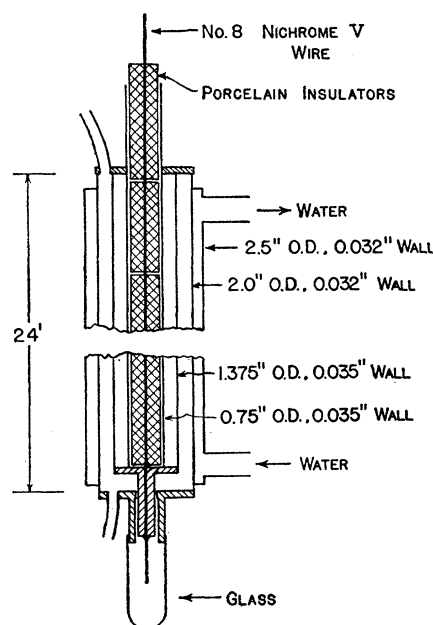


FIG. 1. Cross-sectional view of column. The column itself is used as a return lead for the current flowing through the Nichrome wire.

wall. However, as the performance of the column should not depend in any critical way upon the temperature⁹ this factor is not very important. The average temperature of the outer wall was approximately 27°C. Water was passed through the cooling jacket at such a rate that the rise in temperature from bottom to top was approximately 5°C. The power consumption under these circumstances was 2.75 kilowatts.

In Table I are recorded data obtained when the CH₄ pressure in the column was 65.6 cm Hg. The samples removed from the column were analyzed with a mass spectrometer similar to one already described.¹⁰ It differed mainly in that the slits *S*₁, *S*₂ and *S*₃ which appeared in Fig. 1 of reference 10 were 0.25, 0.23, and 0.90 mm wide. This type mass spectrometer uses a 180° magnetic analyzer. Positive ions are formed by electron impact of the gas at low pressure. The analyzed ion currents are measured with an electrometer tube amplifier. As the dissociation product (O¹⁶H)⁺ of water vapor, a residual impurity in a mass spectrometer, has the same mass as C¹³H₄⁺ one might expect some difficulty in accurately measuring the (C¹³H₄⁺)/C¹²H₄⁺ ratio. However, by employing

¹⁰ A. O. Nier, Phys. Rev. 52, 933 (1937).

TABLE I. $C^{13}H_4/C^{12}H_4$ ratio at top and at bottom of column as a function of time. Pressure = 65.6 cm.

Time (hours)	0	9	23.5	46	73
$C^{13}H_4/C^{12}H_4$ (bottom)	0.0112	0.0198	0.0215	0.0214	0.0213
$C^{13}H_4/C^{12}H_4$ (top)	0.0112	0.00611	0.0054	0.00505	0.00525
Ratio bottom/top	1.000	3.23	3.99	4.23	4.06

electrons having an energy of only about 15 volts for producing ions, no $(OH)^+$ ions were formed, whereas $(CH_4)^+$ ions were produced in sufficiently large numbers for the purpose of analysis. Although the ion $(C^{12}H_3D)^+$ contributes slightly to the mass 17 peak in the mass spectrometer, we will imply in what follows that this peak is due entirely to $(C^{13}H_4)^+$. That this is permissible follows immediately when we recall that we are interested principally in changes in the abundance ratio for mass 17/mass 16.

In Tables II and III are recorded the data obtained for pressures of 40.0 and 21.7 cm, respectively.

In addition to studying the variation of the $C^{13}H_4/C^{12}H_4$ ratio it seemed worth while to investigate what effect the separating effect of the column had on the impurities present in the methane. The principal impurities which appeared to be present had masses 28 and 44. The 28 ion was probably due to CO whereas the 44 ion was definitely shown to be associated with CO_2 . In Table IV are recorded the CO/CH_4 and CO_2/CH_4 ratios as found for the 40.0-cm run. In computing these values allowance was made for the difference in ionization efficiency of CH_4 , CO and CO_2 by calibration of the mass spectrometer with mixtures of gases of known proportions.

As the mass spectrometer itself contained traces of CO and CO_2 as residual impurities, some difficulty was encountered in measuring accurately the CO and CO_2 content for the samples removed from the top of the column. Although the data in Table IV can thus only be regarded as rough, they do show that the column is very effective in separating heavier molecules from CH_4 . The concentration of these heavy impurities is so low in all but the very lowest part of the column that one should expect the presence of the impurities would have little effect upon the performance of the column.

COMPARISON OF THEORY AND EXPERIMENT

According to Furry, Jones and Onsager⁹ the equilibrium separation factor for a column of the sort employed here may be written in the form

$$(C_1^L/C_1^U)(1-C_1^U)/(1-C_1^L) = \epsilon^{2AdL}, \quad (1)$$

where C_1^L and C_1^U represent the equilibrium concentrations of $C^{13}H_4$ in the lower and upper ends of the column, respectively. The length of the column is L and

$$A_d = A/(1+K_d/K), \quad (2)$$

where

$$A = H/2K = 252(\alpha\eta D/\rho g d^4)f(\Delta T/T) \quad (3)$$

and

$$K_d/K = 1890(T_1^2 + T_1T_2 + T_2^2) \times (8D\eta/d^3\rho g\Delta T)^2 \quad (4)$$

η = coefficient of viscosity; D = coefficient of diffusion; ρ = density of gas; g = acceleration of gravity; d = thickness of annular gas space; T_1, T_2 = absolute temperature outer, inner tube, $\Delta T = T_2 - T_1$; α is given by the equation $D_T/D = \alpha C_1 C_2$ where D_T = coefficient of thermal diffusion and C_1, C_2 represent concentrations of heavy, light components of gas mixture.

As $D \propto 1/\rho$ and $p \propto \rho$ we see from an inspection of Eqs. (2), (3), and (4), that we may write

$$2A_dL = (a/p^2)/(1+(b/p^4)) = x, \quad (5)$$

where a and b are constants independent of pressure and p = pressure measured in atmospheres. Also, as the concentration of $C^{13}H_4$ is always small, we can drop the $(1-C_1^U)$ and $(1-C_1^L)$ terms. Thus, we have

$$C_1^L/C_1^U = \epsilon^{(a/p^2)/(1+(b/p^4))} = \epsilon^x. \quad (6)$$

TABLE II. $C^{13}H_4/C^{12}H_4$ ratio at top and at bottom of column as a function of time. Pressure = 40.0 cm.

Time (hours)	0	12	23	47	71
$C^{13}H_4/C^{12}H_4$ (bottom)	0.0111	0.0202	0.0233	0.0248	0.0255
$C^{13}H_4/C^{12}H_4$ (top)	0.0111	0.00615	0.00486	0.00404	0.00414
Ratio bottom/top	1.000	3.29	4.78	6.14	6.16

TABLE III. $C^{13}H_4/C^{12}H_4$ ratio at top and at bottom of column as a function of time. Pressure = 21.7 cm.

Time (Hours)	0	12	24	48	72	9*	23*
$C^{13}H_4/C^{12}H_4$ (bottom)	0.0109	0.0143	0.0158	0.0161	0.0161	0.0141	0.0155
$C^{13}H_4/C^{12}H_4$ (top)	0.0109		0.0076	0.0075	0.0074	0.0089	0.0079
Ratio, bottom/top	1.000		2.09	2.15	2.17	1.59	1.95

* Obtained in a second run. Pressure = 21.3 cm.

From our data in Tables I, II and III we can determine the numerical values of a and b . To do so we will assume that for $p=21.7$ cm = 0.285 atmos., $C_1^L/C_1^U=2.25$; for $p=40$ cm = 0.527 atmos., $C_1^L/C_1^U=6.25$; and for $p=65.6$ cm = 0.863 atmos., $C_1^L/C_1^U=4.25$. As there are only two unknowns, a and b , in Eq. (6), two of these three sets of data are sufficient to determine them. The third set of data may thus be regarded as a check upon the theory. In Fig. 2 is shown a plot of $x = (a/p^2)/[1 + (b/p^4)]$ versus p for $a=1.34$ and $b=0.126$. The fact that all three experimental points fall on the curve indicates an excellent check of the theory, at least as far as variation of separation factor with pressure is concerned.

The next question that arises is whether or not these experimentally determined values of a and b are in numerical agreement with the theoretical predictions given in Eqs. (2), (3) and (4). As the column used in the present experiments operated over the same temperature range as the one proposed by Furry, Jones and Onsager, we may use some of the same numerical data as were employed by these authors, namely: $\eta = 1.60 \times 10^{-4}$ poise; $\rho = 0.433 \times 10^{-3}$ g/cm³ at atmospheric pressure; $D = 1.4\eta/\rho = 0.52$ cm²/sec.; $\lambda = 1.20 \times 10^{-4}$ cal./cm sec. deg.; and $f(\Delta T/T) = 1.016$. However, we will use the experimentally determined value¹¹ of $\alpha (=0.0077)$ rather than the value 0.0106 assumed by Furry, Jones and Onsager. That α is somewhat smaller than was assumed by these authors accounts for the fact that the separation factor found in the present experiments is materially lower than for the hypothetical column designed by them.

The dimensions given earlier in this paper, when converted to metric units, give L (the length of the column) = 730 cm and d (the thickness of the annular space) = 0.712 cm. If now we

TABLE IV. CO/CH₄ and CO₂/CH₄ ratios at top and bottom of column as a function of time for the same run as the data in Table II were obtained.

Time (hours)	0	12	23	47	71
CO/CH ₄ (bottom)	0.012	0.183	0.176	0.192	0.203
CO/CH ₄ (top)	0.012	0.00099	0.00118	0.003	0.0021
Ratio, bottom/top	1.000	185	150	64	97
CO ₂ /CH ₄ (bottom)	0.00010	0.090	0.092	0.114	0.12
CO ₂ /CH ₄ (top)	0.00010	0.00006	0.0001	.00006	.00006
Ratio, bottom/top	1.000	1500	920	1900	2000

¹¹ A. O. Nier, Phys. Rev. **56**, 1009 (1939).

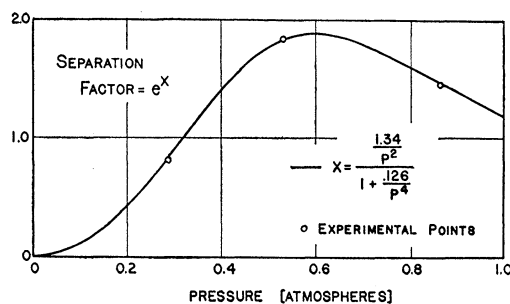


FIG. 2. Graph showing how the separation factor of the column depends upon pressure of methane. Note that separation factor is e^x , where x is the ordinate.

substitute in (2), (3) and (4), remembering that $D \propto 1/p$ and $p \propto \rho$, we find that

$$2A_aL = 2AL/(1 + K_d/K) = (2.19/p^2)/(1 + 0.25/p^4), \quad (7)$$

where p is in atmospheres pressure.

The experimentally determined expression for this quantity is:

$$2A_aL = (1.34/p^2)/(1 + 0.126/p^4). \quad (8)$$

To bring the numerators of (7) and (8) into numerical agreement we can multiply numerator and denominator of (8) by 2.19/1.34. Eq. (8) then becomes

$$2A_aL = (2.19/p^2)/(1.63 + 0.208/p^4). \quad (8a)$$

One sees immediately that except for the factor 1.63 in (8a) rather than 1.0 as in (7) the experimental and theoretical values for $2A_aL$ are in remarkable agreement. The slight difference in the coefficients of the $1/p^4$ term is not serious when one considers that the values of this term depend upon d^6 and p^4 .

The difference between 1 and 1.63 can readily be attributed to imperfections in the column. Furry, Jones and Onsager showed if there was an azimuthal variation of temperature around the column the denominator of Eq. (7) would contain an extra term which for an azimuthal temperature variation of as little as 5°C had a numerical value of one. Whether or not one should associate the extra 0.63 with such an effect cannot be told from the present data. However, it seems quite reasonable to attribute it to some sort of a remixing effect due to asymmetry or some other imperfections in the column. As alternating current heated the Nichrome wire, there was

TABLE V. $C^{13}H_4/C^{12}H_4$ ratio at bottom of column as a function of time when a 20-liter reservoir is attached to the top. Pressure = 46 cm.

Time (hours)	0	16	23.5	41	63	87	111	157.5	183	208
$C^{13}H_4/C^{12}H_4$	0.0113	0.0227	0.0245	0.0278	0.0314	0.0342	0.0376	0.0428	0.044	0.0457
Rel. Concentration	1.000	2.01	2.17	2.46	2.78	3.03	3.33	3.78	3.90	4.05

some vibration present which may possibly have introduced some remixing.

The power expended because of the conduction of the gas was shown by Furry, Jones, and Onsager to be

$$P_c = 4.18\lambda LB\Delta T/d \text{ watts,} \quad (9)$$

where λ = thermal conductivity of methane = 1.20×10^{-4} cal./cm-sec.-deg. and B the average circumference of the annular space. If we substitute numerical quantities in (9) we find $P_c = 2030$ watts. Experimentally it is found that the column consumes 2750 watts, of which approximately 750 watts (determined from vacuum conditions) may be attributed to radiation. The difference, 2000 watts, is seen to be in agreement with theory and may be taken as evidence that there is no appreciable turbulence of the gas.¹²

OPERATION OF COLUMN WITH A RESERVOIR ATTACHED TO TOP

If one plans to use the column to produce methane containing a maximum concentration of $C^{13}H_4$ one should maintain a normal concentration at the top; this may be achieved by attaching a large reservoir.

To test the column under these conditions a run was made for a pressure of 46 cm (=0.6 atmos.), the pressure for which one should expect the largest separation factor (see Fig. 2). Under these circumstances one should expect by Eq. (1) to obtain a concentration factor of approximately 6.2 provided that the reservoir at the top was infinite. Actually, however, the reservoir used

had a volume of 20 liters, whereas the column has a volume of approximately 7 liters. The depletion of $C^{13}H_4$ in the reservoir thus prevents one from attaining the full concentration at the bottom. If one assumes an exponential variation of concentration with length in the column and a total conservation of methane, one can readily show that the maximum attainable concentration of $C^{13}H_4$ would be 4.84 times.

In Table V are tabulated values for the concentration at the bottom of the column for various times after admitting the gas. From this it appears that, had the column been in operation for a long enough time, the full predicted concentration would have been reached.

Although no attempt has as yet been made to use the column for producing heavy methane on a practical scale, preliminary calculations based upon Eqs. (30) and (45) of the Furry, Jones and Onsager paper indicate that the column, if operated at a pressure of 46 cm, could produce every 24 hours, 148 mg of methane containing 4.5 percent of $C^{13}H_4$. If operated at a pressure of 61 cm the column could produce 376 mg of methane containing 3.4 percent of $C^{13}H_4$ every 24 hours.

In the paper that follows, additional correlations between experiment and theory will be presented.

The writer wishes to express his appreciation to Professor John Bardeen for many valuable discussions of the problem. The purified methane used in these experiments was very kindly supplied by Dr. T. I. Taylor and Professor George Glockler of the Chemistry Department. This research was aided by a grant from the Graduate School.

¹² L. Onsager and W. W. Watson, Phys. Rev. **56**, 474 (1939).