The Separation of Isotopes by Countercurrent Gaseous Exchange Column. II. Experimental Tests of the Theory

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In order to test the theory developed in part 1, the isotope separation of carbon by the countercurrent gaseous exchange column was carried out by hot wire type thermal diffusion column. The isotopes used for this experiments are C^{12} and C^{14}, and the gaseous species for the exchange reaction are carbon dioxide and carbon monoxide. Taylor and Bernstein[1] had performed similar experiments on the separation of C^{13} and C^{12} but we need thorough investigation of this experiment and reliable data on the over-all separation factors for various filament temperatures.

Equilibrium constants for many isotopic exchanges have been studied by Urey and his co-workers[2]. The results of their calculation and the theory on the gaseous exchange column enable us to predict the possibilities of the high efficient isotope separations by the gaseous chemical exchange method.

(1) R. B. Bernstein and T. I. Taylor, *J. Chem. Phys.*, **16**, 903 (1948).

(2) H. C. Urey, *J. Chem. Soc.*, 562 (1947); H. C. Urey and L. J. Greiff, *J. Am. Chem. Soc.*, **57**, 321 (1935).

Experimental Apparatus

Figure 1 is an illustration of the apparatus arrangement. The exchange column was constructed by a water jacketed glass tube of 12.7 mm. in diameter and 150 cm. long. The filament used in the experiments was a platinum wire of 0.7 mm. diameter and it was hung from the top of the column. The centering of the filament was made by five spacers of a small piece of nichrome wire. At the bottom of the column a 70 g. weight was attached to the end of the filament to keep the filament taut. Electrical contact was made by a steel rod (13 cm. long) which was attached to the weight keeping the contact to the mercury pool at the bottom of the column. Constant electric power supply for filament heating was obtained using a ballast tube which has a plateau of characteristic curve between 28~40 volt with 8.5 amp. Power regulation was made by two autotransformers F. T and S. T in Figure 1. When the voltage applied to the ballast tube was adjusted to proper value we could obtain an almost constant power supply for filament heating within the input voltage variations between 90~100 volt.

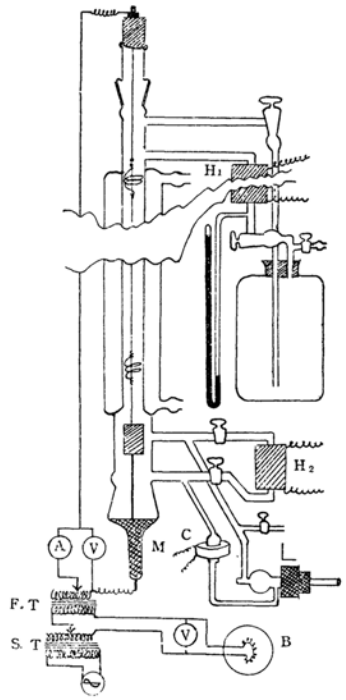

Fig. 1.—Experimental apparatus, H_1; electric furnace for circulation, H_2; Zn-reducer, C; gas circulation pump, M; mercury pool, L; Lauritsen electroscope, B; ballast tube, F. T. and S. T; autotransformers, A; ammeter, V; voltmeter

A top gas reservoir was a glass bottle of 22 l which was connected to the top of the column by two glass tubings. One of these was heated by an electric furnace in order let the gas in the reservoir flow to the top of the column. Flow velocity was measured in the preliminary experiments and we found that it was about 200 cc. per minute. To the bottom reservoir a zinc reducer was attached for reducing carbon dioxide to carbon monoxide. Temperature of the reducer was maintained to 400°C. by an electric furnace which was regulated by an automatic temperature regulator. The volume of the bottom gas reservoir was 250 cc. including the reducer and the ionization chamber of the Lauritsen type electrometer.

Carbon dioxide generated from sodium carbonate and sulfuric acid was introduced into the previously evacuated apparatus through two gas washing bottles with water. The active isotope C^{14} of two or three microcuries was previously mixed into the sodium carbonate used for the gas generation. It has been found by Brandner and Urey[3] that the water vapour or hydrogen is good catalysis for the isotopic exchange reaction between carbon dioxide and carbon monoxide. Increase of reaction velocity reduces the temperature T_b. Therefore we can expect the increase of separation factor by the presence of these gases. To saturate the water vapour in the bottom reservoir a little amount of water was introduced on the mercury pool. In all essential respects the details of operation of the separation column were the same as have been described by Bernstein and Taylor[1].

Measurements of Isotopic Ratio C^{14}/C^{12}

A concentration of C^{14} was measured by Lauritsen type electrometer having an ionization chamber of 160 cc. content. The gas of the bottom reservoir was circulated through the ionization chamber by a magnetically operated gas circulation pump with the flow velocity 30 cc. per minute. Ionization current produced by β-rays from C^{14} depends not only on the concentration of C^{14} but also the composition of gases in the ionization chamber. Therefore we have to know the relation between concentration of C^{14} and ionization current produced in the various mixtures of gases. Results on the measurements of ionization current of the Lauritsen electrometer at various compositions and pressure are represented in Figure 2. In these experiments the concentration of C^{14} was maintained constant (about 6 μc./mol.) and ionization current was expressed in div./sec. Pressure-ionization current curves for carbon dioxide and carbon monoxide showed similar variation. We obtained the similar curves for the mixtures of both gases although these were not represented in Figure 2. The linear dependences of ionization current on the composition of the mixture of two different gases are represented by curves 3 and 4 in Figure 2.

(3) J. D. Brandner and H. C. Urey, *J. Chem. Phys.*, **13**, 351 (1945).

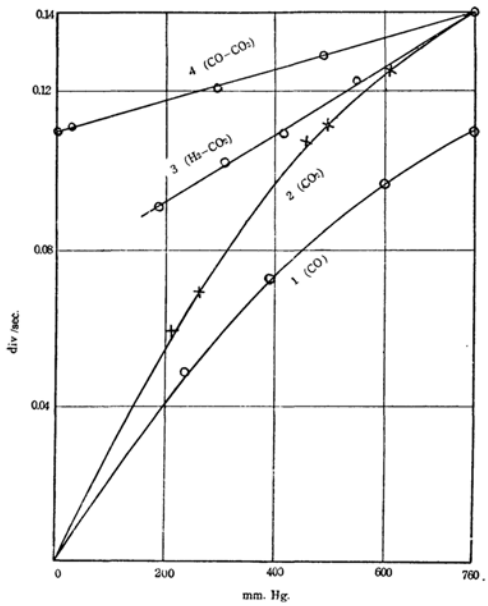

Fig. 2.—Pressure and composition dependence of ionization current with constant amount of C^{14}, Curve 1; pure CO, abscissa is total pressure. 2; pure CO_2, abscissa is total pressure. 3; H_2-CO_2 mixture, abscissa is partial pressure of CO_2 (total pressure is 760 mm. Hg.). 4; CO-CO_2 mixture, abscissa is partial pressure of CO_2 (total pressure is 760 mm. Hg.).

If we measure ionization current and pressure and composition of the samples using Figure 2 we can easily obtain the ionization current which would be observed if pure carbon dioxide is introduced under the standard pressure in the ionization chamber with the same amount of active isotope. The corrected ionization current thus obtained may be regarded to be proportional to C^{14} concentration, because a linear dependence of the ionization current on C^{14} concentration holds in a wide range of the concentration[4].

High content of hydrogen was observed in the bottom reservoir at the initial stage of the separation process. However after a few hours' operation, the hydrogen content in the bottom reservoir became less than 0.5 %, therefore the corrections to the measured activities were made only for carbon monoxide contents in the ionization chamber.

Results

Some of the typical changes of C^{14} concentration at the bottom reservoir are shown in Figure 3. We may see that the continuous operation of about fifty hours is ample time to obtain the equilibrium state. The estimation of the initial isotopic transport τ_0 was made by the initial increase of the heavy isotope in the bottom reservoir. The values of initial isotopic transport and over-all separation in the equilibrium states for various filament temperatures are tabulated in Table 1.

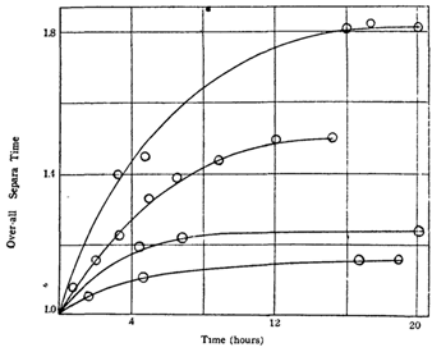

Fig. 3.—Dependence of over-all separation on time

Table 1

Run	$c_1(0)$	$c_1(Z)$	P mm.Hg.	T_2 °C.	S	τ_0/ν ×10⁷mol./sec. Obs.	Calc.
11	85.7	14.2	715	680	1.16	0.9~1.1	0.97
12	80.4	20.4	780	800	1.24	1.5~1.8	1.14
13	68.6	11.8	780	900	1.29		1.35
14	54.0	13.4	750	1100	1.64	2.2~2.5	1.90
15	93.0	30	755	650	1.19		0.95
16	75.0	24.2	746	1170	1.82	3.4~4.5	2.23
17	52	15	750	1130	1.68		2.05
18	85	21	772	1030	1.52	1.8~2.4	1.68
19	65.7	17.5	756	715	1.18	1.0~1.6	0.99
20	52.9	10.6	755	510	1.15		0.92

Values of isotopic transport, over-all separation and experimental conditions at final equilibrium states
$c_1(0)$ = CO% in the bottom reservoir,
$c_1(Z)$ = CO% in the top reservoir,
P = total pressure in the column,
T_2 = filament temperature,
S = over-all separation,
τ_0 = initial transport of C^{14} along the column,
ν = C^{14} concentration at the initial state

The filament temperature was measured by the thermal expansion of the filament. A linear expansion coefficient of 1.00×10^{-5} cm./cm., deg. for platinum wire was used for this measurement. This expansion coefficient was obtained from the measurements on the expansion of our platinum filament without any spacers. A platinum wire with 50~100g. weight at the end was hung outside the column and the temperature of electrically heated platinum wire was measured with optical pyrometer. The observed linear expansion coefficient was independent of the amount of weight

(4) F. C. Henriques, Jr., and C. Margnetti, *Ind. Eng. Chem.*, Anal. Ed., **18**, 417 (1946).

and was in accordance to other observations[5]. The uniformity of the temperature along the column was examined by optical pyrometer and we found almost uniform heating except the small regions (about 10 cm.) near the spacers at which the temperature was lower than other parts, but it did not exceed 100°C. Therefore the difference between measured temperature and maximum temperature of filament was ignored in our experiments.

Occasionally compositions of gases in the bottom and the top reservoirs were examined by ordinary gas analysis using few cc. of the samples. The bottom gas always contained 50~90 percent carbon monoxide and the required corrections on the activity measurements were made according to the measured gas compositions as described in the preceding section. Since the samples were small compared with the amount of gases in reservoirs, we ignored their effects on the time variation of isotopic concentration.

From the change of composition of the top reservoir we could obtain the net transport τ_1 of carbon monoxide along the tube. Observed value was $\tau_1=2.9\pm0.5$ cc./min. The results were insufficient in accuracy for the determination of τ_1. Perhaps the errors of the measurements were derived from the non-uniformity of gases in the top reservoir. Then in order to obtain an accurate value of transport we undertook the preliminary experiments. A well stirred bottom gas reservoir of two liters was filled by carbon monoxide at the initial states. The variations of the composition in this reservoir were measured during two or three hours' operations with the filament temperatures between 700 and 1000°C. We obtained $\tau_1=3.3\pm0.2$ cc./min. for these filament temperatures. The results were also not accurate enongh to obtain a dependence of τ_1 on the filament temperature, but rather good compared with the results from the top gas analysis; therefore we used $\tau_1=3.3$ cc./min. in our latter treatment.

Discussion of Results

In the theoretical consideration, the over-all separation of our experiments was given by the formula (51) in part 1. In this formula H_b/H was estimated by equation (54) which was valid only in the extreme case $r_2/r_1\to0$, but this approximation did not yield good results in the cases of our experiments. Therefore we had to use the original form of γ instead of the expression of γ described in equations (41). An exact expression of γ had been given by Furry and Jones[6] and the results of numerical calculation of γ for $r_1/r_2=18.2$, $T_2/T_1=10/3$, 11/3, 4, 13/3, 14/3 and 5 are illustrated in Figure 4. We can estimate H_a and H_b by the numerical integrations of the following expressions.

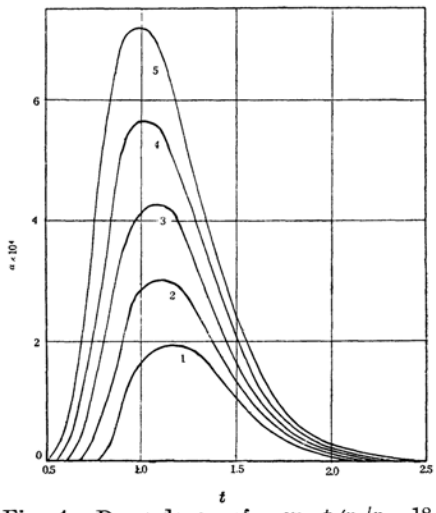

Fig. 4.—Dependence of γ on t ($r_1/r_2=18.2$). Curve 1; $T_2/T_1=10/3$, 2; $T_2/T_1=11/3$, 3; $T_2/T_1=4$, 4; $T_2/T_1=13/3$, 5; $T_2/T_1=5$

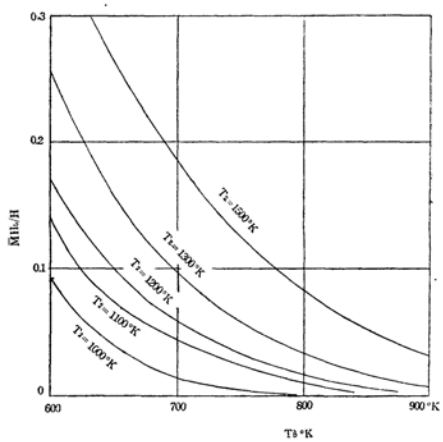

Fig. 5.—Dependence of $\bar{M}H_b/H$ on T_b

$$H/\bar{M}=a\int_{t_a}^{t_2}\alpha_t\frac{\gamma}{t}dt \qquad (1)$$

$$H_b=a\int_{t_b}^{t_2}\gamma\frac{d\alpha}{dt}dt \qquad (2)$$

where $a=2\pi(\rho^2g/\eta)_1\cdot r_1^4t_1^3\exp(2t_1^3)$, and α_t is thermal diffusion constant for the mixture of carbon dioxide and carbon monoxide. We used $\alpha_t=0.10$ which was obtained from the experimental data of Kitagawa and Wakao[7]. Expression (1) had been derived by Furry and Jones and expression (2) was obtained from equations (41) and (43) in part 1.

The results of numerical calculation of $\bar{M}H_b/H$ are graphically represented in Figure 5. Where

(5) Randolt and Börnstein, "Physik.-Chem. Tab. Eg III c" p. 2212.

(6) W. H. Furry and R. C. Jones, *Phys. Rev.*, **69**, 459 (1946).

(7) H. Kitagawa and M. Wakao, *J. Chem. Soc. Japan*, **62**, 100 (1941).

we assumed $T_1 = 300°K$, we neglected the temperature dependence of α_t. The equilibrium constant α for the isotopic exchange reaction

$$C^{14}O + C^{12}O_2 \rightleftarrows C^{12}O + C^{14}O_2 \qquad (3)$$

was calculated following the method adoped by Urey[2]. The results of numerical calculation of equilibrium constant

$$\alpha^{14} = \alpha = \frac{[C^{12}O][C^{14}O_2]}{[C^{14}O][C^{12}O_2]}$$

are shown in Figure 6 with the same constant α^{13} for the equilibrium between C^{12} and C^{13}.

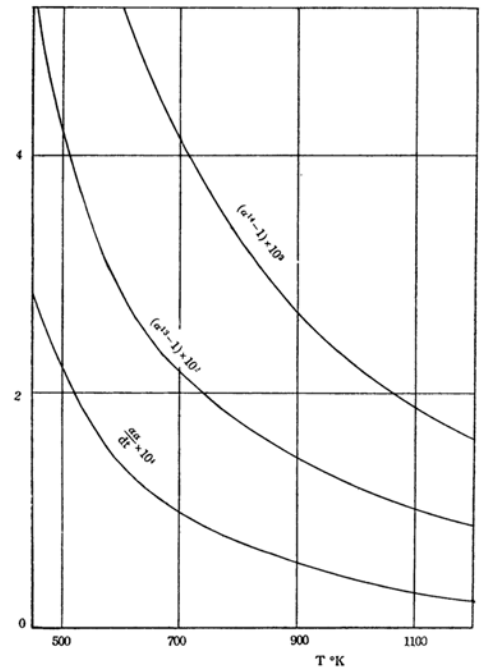

Fig. 6.—Temperature dependences of equilibrium constants $\alpha(=\alpha^{14})$, α^{13}, and $d\alpha/dT$

Our experiments were performed with the isotopic mixture which contains minute quantity of the heavy isotope C^{14} in the natural isotopes of carbon. Therefore the equilibrium constant α may be regarded as an isotopic ratio $\alpha = [C^{14}O_2]/[C^{14}O]$ at the equilibrium (3).

The over-all separation S was estimated by the following expression derived in part 1.

$$-\ln S = \ln \frac{\nu(Z)}{\nu(0)} = \left[1 - \alpha(T_b) + \frac{D_2 - D_1}{\bar{D}} \frac{\bar{M}H_b}{H}\right] \times \frac{\tau_1 Z}{B_c + B_d} + \frac{D_2 - D_1}{\bar{D}} \frac{\bar{M}H_b}{H} (c_1(Z) - c_1(0)) \qquad (4)$$

where $\nu(Z), \nu(0) =$ fractional molar concentration of C^{14} at the top and the bottom of the column, $D_1, D_2 =$ self diffusion coefficient of carbon monoxide and carbon dioxide, $\bar{D} =$ mean value of D_1 and D_2, $Z =$ column length, and $c_1(Z)$, $c_1(0) =$ fractional molar concentration of carbon monoxide at the top and the bottom of the column. A value of $(D_1 - D_2)/\bar{D} = 0.461$ was obtained from the self diffusion coefficients of carbon dioxide and carbon monoxide[8]. If an appropriate value of T_b is assumed, we may obtain over-all separation S using the experimental data on the value of transport (τ_1) of carbon monoxide along the tube and the concentrations of carbon monoxide in the top and the bottom reservoirs at a final equilibrium state. Assuming $T_b = 600$, 700, 750, 800, 850, and 900°K., the numerical evaluation of expression (4) was performed, and obtained the values of $\ln S$ as functions of filament temperature T_2 are illustrated in Figure 7. In these calculations B_c and B were obtained by substituting into equations (40) and (47) the following numerical data,

$\rho = 1.46 \times 10^{-3}$	$T_1 = 300°K.$
$\eta = 165 \times 10^{-6}$	$r_1 = 0.635$
$\bar{D} = 0.141$	$r_2 = 0.035$
$\bar{M} = 36$	$c_1(0) - c_1(Z) = 0.7$

In practice, $c_1(0) - c_1(Z)$ changed in each experimental case, but the second term of equation (4) did not exceed 5 % of the total value; therefore the variation of $c_1(0) - c_1(Z)$ was ignored in our treatment.

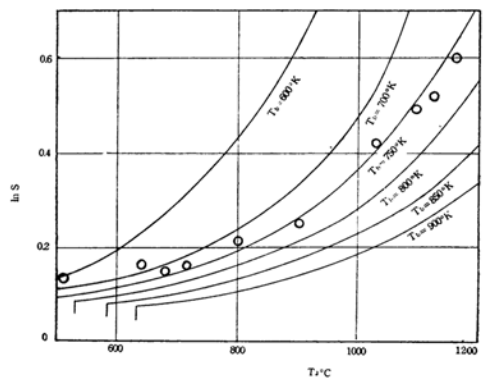

Fig. 7.—Dependence of calculated and observed over-all separation on the filament temperature

In Figure 7 we plotted $\ln S$ obtained from the experimental values of Table 1. Perhaps an appreciable error would be introduced concerning the temperature measurements of the filament. However within limits of error, observed over-all separations coincide with the calculated values for $T_b = 750°K$ as illustrated in Figure 7. The observed over-all separations in the cases of low filament temperatures were rather large compared with the expected values. These discrepancies between experimental values and theoretical values may be attributed to the neglect of isotopic

(8) J. H. Jeans, "The Dynamical Theory of Gases" (1925) p. 321.

enrichment by the ordinary thermal diffusion in the theoretical treatment of this report.

The theoretical estimation on the isotopic transport is made by equation (45) in part 1. Since there is no isotopic concentration gradient along the column at the initial state, an initial transport can be obtained putting $d\nu_1/dz=0$, then we have,

$$-\tau_0=(\tau_1)_{t=0}=\left[(1-\alpha(T_b))\tau_1+c_1c_2H_b\frac{D_2-D_1}{\bar{D}}\right]\nu_1$$

Using equation (2) in part 1, it becomes

$$-\tau_0=\left[1-\alpha(T_b)+\frac{D_2-D_1}{\bar{D}}\frac{\bar{M}H_b}{H}\left(1+\frac{B_c+B_d}{\tau_1}\frac{dc_1}{dz}\right)\right]\nu_1\tau_1. \qquad (5)$$

The substitutions of the values of $\bar{M}H_b/H$ for $T_b=750$°K. and of other constants corresponding to the experimental conditions in equation (5) yielded calculated initial isotopic transports tabulated in Table 1. On account of the difficulties in the determination of the initial slopes of curves such as in Figure 3, we can not draw any detailed conclusion from the small discrepancies between calculated and observed values in Table 1, but these experimental evidences support our theoretical interpretation.

At the cylindrical region of the column at T_b°K., we assumed that both variations of the isotopic composition by exchange reaction and by diffusion process maintain balance. Therefore it will be possible to estimate a parameter T_b from the data on the diffusion coefficients and reaction velocity of the exchange reaction. Unfortunately we have no satisfactory knowledge on the kinetics of isotope exchange reaction between carbon monoxide and carbon dioxide, although there have been detailed studies[3][9]. However we may construct a most efficient apparatus using the obtained theoretical results, because T_b takes a constant value for an isotopic exchange reaction employed for the experiments.

The high efficiency of the isotope separation in our experiments at the elevated filament temperatures was caused by the high value of $\bar{M}H_b/H$ in expression (4). On the similar base it is supposed that the rise of cold wall temperature brings high over-all separation factor. The elevation of the temperature in the whole tube results in decreasing of t_b—the lower limit of integral (2)—with respect to the curves of γ. A steep increase of γ with the decrease of t also yields a steep increase of $\bar{M}H_b/H$ by the elevation of the tube temperature, because a range of integration of H_b depends on t_b as was shown by expression (2).

Summary

The separation of carbon isotope C^{14} by the countercurrent gaseous exchange method has been studied using a hot wire type thermal diffusion column. The isotopic exchange reaction employed for the experiments was a reaction between carbon dioxide and carbon monoxide. The separation column was constructed with a water-jacketed glass tube of 150 cm. long and 12.7 mm. in diameter. An electrically heated platinum wire was placed at the center of the tube, and its temperature was measured by thermal expansion of the wire. The column was filled with carbon dioxide. A converter was put at the bottom of the column in order to reduce carbon dioxide to carbon monoxide. The concentration of C^{14} at the bottom of the column was measured by a Lauritsen type electrometer. The over-all separations at the equilibrium states were observed for the various filament temperatures between 570 and 1170°C. The dependence of over-all separation on the filament temperature and initial isotopic transports were in reasonable agneement witd theoretical estimates.

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(9) T. H. Norris and S. Ruben, *J. Chem. Phys.*, **18**, 1595 (1950).